Structurally characterized normal and abnormal N-heterocyclic carbene based palladium and gold complexes and their catalysis

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Structurally Characterized Normal and
Abnormal *N*-Heterocyclic Carbene Based
Palladium and Gold Complexes and Their
Catalysis**

**XU XIANGYA
SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES
2011**

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Abnormal *N*-Heterocyclic Carbene Based
Palladium and Gold Complexes and Their
Catalysis**

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**A thesis submitted to the Nanyang Technological University
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Abbreviations and Symbols

Me	methyl
Ph	phenyl
<i>i</i> Pr	isopropyl
cm ⁻¹	inverse centimeter
tol	toluene
THF	tetrahydrofuran
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DMF	<i>N,N</i> -dimethylformamide
DCM	dichloromethane
CDCl ₃	deuterated chloroform
min	minute(s)
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
Ru	Ruthenium
Au	Gold
NHCs	<i>N</i> -heterocyclic carbenes
aNHC	abnormal <i>N</i> -heterocyclic carbenes
equiv.	equivalent(s)
ESI	electrospray ionization
Et	ethyl
Et ₃ N	triethylamine
EtOAc or EA	ethyl acetate
TLC	thin layer chromatography
g	gram(s)
h or hrs	hour(s)
HRMS	high resolution mass spectrometry
Hz	hertz
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
M	metal
MS	mass spectrometry

m/z	mass per charge ratio
M ⁺	parent ion peak (mass spectrum)
mL	milliliters
mmol	mill mole
mol%	mole percent
MeOH	methanol
ACN	acetonitrile
Rh	Rhodium
rt	room temperature
Å	angstrom(s)
et al.	and others (Latin alii)
δ	NMR chemical shift in ppm
ppm	parts per million
q	quartet
d	doublet, day(s)
s	singlet
m	multiplet
t	triplet
°C	degrees
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
<i>J</i>	coupling constant
cod	1,5-cyclooctadiene
Mes	mesithyl
GC	Gas Chromatography

Summary

N-heterocyclic carbenes (NHCs) have been extensively investigated and widely used as more efficient ligands. The experimental and theoretical evidences showed that C4 or C5-bound NHCs (aNHCs) are stronger donor ligands than C2-bound NHCs (nNHCs). It is expected that the outstanding strong donor abilities of aNHCs have a great influence on catalysis. However the synthesis and catalytic activity of M-aNHC complexes have not been thoroughly investigated till now compared to those of M-nNHC complexes.

In chapter 1 we gave an introduction of nNHC and aNHC including characteristics, synthesis, metalation and applications.

In chapters 2 and 3, considering the enormous possibilities of ligand tuning and hopeful achievements in activating unreactive bonds, several aNHC-based Pd and Au complexes were developed. The catalytic activity comparison study between two sterically similar nNHC and aNHC was explored. In chapter 2, the Pd-aNHC complexes were applied to cross-coupling reactions. In chapter 3, novel Au-aNHC complexes were synthesized and applied for alkyne hydration and cyclization reactions.

In chapter 4, we synthesized a series of *trans* and *cis* (NHC)₂PdX₂ (X= Cl, Br, I) complexes and the complexes were structurally characterized. Crystal structures analysis on the CH/π interactions in the group of (NHC)₂PdX₂ complexes were performed. It was indicated that CH/π interactions did play an important role in structural stability of these *cis* complexes. A comparison of Suzuki-Miyaura reaction progress with complexes *trans*-(NHC)₂PdX₂ and *cis*-(NHC)₂PdX₂ was also explored.

CHAPTER 1

Introduction

1.1 Classical normal *N*-heterocyclic carbenes (nNHC)

1.1.1 Historical development

The history of *N*-heterocyclic carbenes (NHCs) started in 1968. Wanzlick, Schonherr and Ofele had reported the preparation of NHC independently.^{1,2} In 1991, Arduengo reported the first solid crystalline NHC which was stable in the absence of oxygen and moisture.³ Its melting point was about 240-241°C (Fig. 1.1).

Figure 1.1 First stable crystalline free NHC.

In 1995, Herrmann recognized the potential of NHCs as ligands in transition-metal complexes.⁴ Compared to phosphine ligands, NHCs ligands act as excellent σ -donors and to generate rather stable-carbon bonds. For example an NHC-based Ru olefin metathesis catalyst^{5,6} (Fig. 1.2) exhibits higher activity and stability than the phosphine-based analog.

Figure 1.2 Grubbs' Catalysts.

NHCs have been used as ligands to transition metals in many research areas. The high donor ability of NHC ligands leads the NHC-metal complexes to show high performance in catalysis in many cases.^{1,7-10}

1.1.2 General characteristics of NHCs

Many kinds of NHCs such as imidazole³, triazole^{11,12}, thiazole¹³, pyrazole¹⁴ type of ylidenes have been reported (Fig. 1.3). Classical and widely used NHCs are five-membered rings such as imidazolin-ylidenes **1.1** (Fig.1.3) and imidazolidin-ylidenes **1.2** (Fig.1.3) with two nitrogen substituents next to C2 atom (Fig. 1.4). The steric and electronic effect of two nitrogen substituents can contribute to the stabilization of NHC.¹⁵

Figure 1.3 Isolated *N*-heterocyclic carbenes (NHCs).

In an NHC molecule, electronic property is regulated by both the π and σ effect. Two nitrogen substituents play an important role of push-pull effect to increase the singlet–triplet gap and stabilize the singlet state (two paired electrons in the σ -orbital).¹⁶⁻¹⁸ Firstly, π -electron-donation goes into the carbene from the p-orbitals which are out-of-plane of electron-rich system (N-C=C-N). The π -donation effect moderates typical electrophilic reactivity of a carbene; Secondly, σ -electron-withdrawal effect of the carbene carbon center (C2) offers additional stability of the carbene through electronegative nitrogen. The σ -withdrawal effect stabilizes typical nucleophilic reactivity of a carbene (Fig 1.4).¹⁶

Figure 1.4 Stabilization of NHC through σ and π Electronic Effects.

NHCs are the strong σ -donors but only weak π -acceptors due to their electronic structures. They bind more strongly to many transition metals than phosphines. These two features in the transition metal complex can lead to a stable metal ligand bond and high electron density on the metal centre and make NHCs popular ligands in many catalytic reactions.

1.1.3 Synthesis of imidazolium salts

Imidazolium salts can be prepared by two different routes: 1) nucleophilic

substitution at the nitrogen atoms of the imidazole;^{19,20} 2) multicomponent reactions for building the *N,N'*-substituted heterocycle. The direct alkylation of the nitrogen atoms of imidazole is initiated with the deprotonation of the nitrogen atom of imidazole. The product reacts with various alkyl halides under high temperature (eq. 1). However, this method is limited to the preparation of primary alkyl substituted NHCs.

1) Alkylation of existing imidazoles:

2) Preparation of the imidazolium ring:

a) Synthesis of symmetrical imidazolium ring

b) Synthesis of unsymmetrical imidazolium ring

Imidazolium salts (eq. 2 and 3)^{21,22} have been widely synthesized from primary amines, glyoxal and formaldehyde in the presence of a Brønsted acid.

This flexible route gives access to various kinds of symmetrical *N,N'*-substituted imidazolium salts even with unusual or very bulky substituents.²³⁻²⁵ Unsymmetrical *N,N'*-substituted derivative of imidazolium salts can be obtained through a multicomponent cyclization followed by an *N*-alkylation reaction (eq. 4).²⁶

1.1.4 Metalation of *N*-heterocyclic carbene

NHC coordinate to metal center via C-H activation or deprotonation of an imidazolium salt precursor. The activation strategies that have been reported to prepare NHC–metal complexes can be summarized as follows: 1) deprotonation of imidazolium precursor with a strong base to generate free carbene and reaction to the metal fragment;²⁷⁻³⁰ 2) transmetalation from a M1–NHC (M1=Ag, Hg) complex to form M2–NHC (M2=Rh, Ru, Au, Pd);³¹⁻³⁴ 3) insertion a metal into the C=C bond of bis (imidazolidin-2-ylidene);³⁵⁻³⁷ and 4) activation of an imidazolium precursor C2-X (X=Me, I, H) bond by oxidative addition.³⁸⁻⁴⁴ Methods 1 and 2 with very mild reaction conditions are most popular and they have been applied in industry (for example the synthesis of the 2nd generation Grubbs catalyst).

1.2 Significance of abnormal *N*-heterocyclic carbenes

1.2.1 Definition of abnormal *N*-heterocyclic carbenes

A normal NHC ligand coordinates to a metal center via the C2 carbon of the imidazolium ring. Recently, a new type of NHC ligand which coordinates to the metal center via the C4 or C5 carbon was reported by Crabtree and co-workers (Scheme 1.1).⁴⁵ Scheme 1.2 shows the resonance structures of both C2 and C4

carbenes.

Scheme 1.1 C5-bound carbenes.

C2-bound carbene

C4-bound carbene

Scheme 1.2 Resonance structures of C2 and C4 carbenes.

In C4 carbene, all the canonical form carries additional charge, whereas C2 Carbene has a neutral structure. These C4-NHCs are referred as ‘abnormal’ *N*-heterocyclic carbenes (aNHC) or ‘mesoionic’ carbenes.^{46,47} Since then, Bertrand and co-workers developed an aNHC with a bulky substituent and obtained an Au-aNHC complex successfully.⁴⁸

1.2.2 General characteristics of aNHC compared to nNHCs

The different arrangement of the carbene center makes aNHC less stable and stronger donor than nNHC.³ Energy decomposition analyses have shown that energy-gap between A and B is about 19 kcal.mol⁻¹, which means that the

nNHC **A** is more stable than the aNHC **B**.^{49,50} (Scheme 1.3)

Scheme 1.3

In 2004, Yates calculated the acid dissociation constant of imidazole aqueous pK_a value.⁵¹ The aqueous pK_a value of the C2-bound hydrogen of imidazole was 24.9 and the C4 or C5-bound hydrogen was 33.0, which indicated a higher barrier for C4 or C5 than C2 metallation of the imidazolium salts via C-H bond activation. Many experimental methods have been used to evaluate the electronic nature of the C4 or C5-carbene and they consistently indicated that aNHCs are more electron-donating than their nNHC analogues.⁵²⁻⁵⁴ C4 or C5-bound carbenes in Ir complexes (Fig. 1.5) could induce a considerably lower stretching frequency [$\nu(\text{CO})$ 1999–2015 cm^{-1}] than sterically similar C2-bound carbenes [$\nu(\text{CO})$ 2017–2020 cm^{-1}], suggesting that aNHCs are stronger electron donors.

Figure 1.5 Reported $\nu(\text{CO})$ value.

Albrecht prepared two related sterically identical NHC palladium complexes

1.9 and **1.10** (Fig 1.6), containing *cis* chelating carbenes bound via C2 and C5 respectively, to firmly explore the influence of the electronic factors of the carbene bonding mode.⁵⁵ They noted the differences of metal-halide bond lengths: the Pd-chloride bond [average Pd-Cl 2.404(4) Å] in the abnormal *N*-heterocyclic dicarbene complex **1.9** was longer than the complex **1.10** containing C2-bound carbene ligands [average Pd-Cl 2.357(2) Å]. These results indicated a higher trans influence of aNHCs compared to nNHCs.

Figure 1.6 Isostructural complexes **1.9** and **1.10**.

Figure 1.7 Electron effect comparisons of NHCs.

In 2010, Glorius summarized the electron effects of NHCs (Fig. 1.7). In the heterocycle of NHCs, the electronic properties of the NHCs were most influenced by the heteroatoms position. Obviously, from the electron donating trend of free carbenes, aNHCs are more electron rich than most kinds of nNHCs.

Among the nNHCs, the electron richness increases along with the ring size of carbenes increasing from five to six (Fig. 1.7 **1.12**)⁵⁶ and seven-membered (Fig. 1.7 **1.13**)^{57,58}. In 2005, Lassaletta et al. synthesized dicarbonyl Rh complexes **1.15a** and **1.17a** (Fig. 1.8) from **1.15** and **1.17**, and their $\nu(\text{CO})$ stretching frequencies 2079 cm^{-1} , 2000 cm^{-1} vs. 2072 cm^{-1} , 1992 cm^{-1} indicated that abnormal pyridylannulated carbene **1.17** was more electron donating than the corresponding nNHC **1.15**.^{59,60}

Figure 1.8

Moreover, the abnormal pyridylannulated carbene **1.17** is more electron rich than the abnormal 1,2,3-triazolylidene carbene **1.16**⁴⁷, whereas aNHC **1.18** reported by Crabtree and co-workers in 2004, is significantly more electron rich (Fig. 1.7).⁶¹

1.2.3 Impact on catalytic reactivity and application

The aNHCs metal complexes can be synthesized by various reliable methods, such as metallation via C4-H or C5-H bond activation and transmetalation.⁶² It is expected that the outstanding strong donor abilities of C4 or C5-bound carbenes have a big influence on catalysis. Following by the report of Crabtree and

co-workers (Scheme 1.4, cod = 1,5-cyclooctadiene),^{61,63} several research groups have used the similar strategy to prepare aNHC-M complexes.⁵⁹

Scheme 1.4 Synthesis of aNHC-Ir complex.

The stronger donor ability of aNHC showed up in a complex **1.19** (Scheme 1.5). The palladium dicarbene complex **1.19** reacted with silver ions (Scheme 1.5) to undergo halide ion exchange. Single-crystal x-ray analysis of the adduct **1.20** revealed that the distance of Pd-Ag was 2.8701(6) Å, which is the shortest distance known to date, suggesting a strong Pd···Ag interaction. It implied the higher electron density of the palladium center in an abnormal *N*-heterocyclic dicarbene ligand environment.⁶⁴ It is assumed that providing the required electron density is a crucial function of the abnormal *N*-heterocyclic dicarbene ligand.⁶⁵

Scheme 1.5

Because the metal center coordinated by aNHC is given high electron density, reactions involving oxidative addition sequences as key steps are most likely to benefit from these strongly donating aNHC ligands. The complex **1.21** showed a good catalytic activity in the hydrogenation of terminal olefins and *cis*-olefins

(Scheme 1.6).⁶⁴ Notably, aNHC complexes showed substantially better performances than their nNHC analogues and catalyzed the hydrogenation under mild conditions.

Scheme 1.6 Catalytic hydrogenation of alkene with complex **1.21**.

Rh-(aNHC)₂ **1.22** effectively catalyzed the transfer hydrogenation of ketones using *i*PrOH as hydrogen source (Scheme 1.7).⁶⁵ In contrast, the nNHC complex **1.23** failed to catalyze the transfer hydrogenation.

Scheme 1.7 Rh-NHC catalyzed transfer hydrogenation of ketones.

In 2004, Nolan reported a Pd-NHC complex **1.24** containing one nNHC ligand

and one aNHC ligand.⁶⁶ They explored the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions using the complex **1.24** and its bis-nNHC analogue **1.25**. The catalytic activity of the complex **1.24** was much better than the complex **1.25**, 44% vs. 5% for Suzuki-Miyaura reaction and 77% vs. 5% for Heck-Mizoroki reaction respectively (Scheme 1.8). But the yields of the reactions catalyzed by **1.24** were not as good as in situ generated catalyst. It was verified that the complex **1.25** was formed during the in situ reaction and the activity was not good as complex **1.24**.

Scheme 1.8 Pd-NHC-catalyzed Suzuki and Heck reactions using **1.24** and **1.25**.

Scheme 1.9 Synthesis of free aNHC and its gold(I) complex **1.28**, CO₂-adduct **1.29**.

In 2009, Bertrand and co-workers synthesized a novel aNHC precursor **1.26** (Scheme 1.9). The aNHC **1.27** was 14.1 kcal/mol less stable than its isomeric nNHC with phenyl group located to C5 instead of C2.⁴⁸ Free carbene **1.27** was stable both in the solid state and in solution at room temperature for a few days. They also obtained the Au(I)-aNHC **1.28** (Scheme 1.9) successfully.⁴⁸

Although many M-aNHC complexes have been reported, their applications in catalysis have not been investigated thoroughly. The objectives of the work described in this dissertation were to investigate the activity of aNHCs ligands in catalysis using either in situ-generated catalytic systems or well-defined M-aNHC complexes. Several aNHCs coordinated Pd (chapter 2) and Au (chapter 3) complexes have been synthesized in this study.⁶³ We focused on comparison in catalysis between sterically similar normal and abnormal NHCs based transition-metal complexes. In chapter 2 we found catalytic activities of aNHC-Pd complexes than their NHC-Pd analogs in the cross-coupling reactions.⁶³ During this study, we obtained *cis*-(NHC)₂PdX₂ complexes and found CH/π interactions (chapter 4). The good catalytic activities of Au-aNHC in alkyne hydration and cyclization reactions were demonstrated in chapter 3.

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CHAPTER 2

Abnormal N-Heterocyclic Carbene Promoted Suzuki- Miyaura Coupling Reaction: A Comparative Study

2.1 ABSTRACT

A C2 protected imidazolium salt that generates an aNHC was applied to the palladium-catalyzed Suzuki-Miyaura coupling reactions. The aNHC precursor promoted the reactions with suppression of homo-coupling of aryl boronic acids, which was pronounced with the corresponding nNHC precursor. The related well-defined abnormal NHC-based palladium complexes also showed better activity than the normal NHC-based analogs, exhibiting faster reaction rates especially at the initial stage of the reaction.

2.2 Introduction

NHCs have been intensively studied in organometallic chemistry and homogeneous catalysis for the past decade.¹⁻⁴ The NHCs are stronger neutral electron donors and less sensitive of oxidation than tertiary phosphines, so as to be excellent ligands for transition metals. Most of the NHCs are derived from imidazolium or 4,5-dihydroimidazolium salts and bind a metal at the C2 position. However, it has been reported that metalation of imidazolium salts can take place at the C4 or the C5 carbon since Crabtree and co-workers discovered it for the first time.⁵ These “abnormal” *N*-heterocyclic carbenes (aNHCs) are

reported as even stronger donors than C2 binding “normal” *N*-heterocyclic carbenes (nNHCs), which may provide new opportunities in catalysis.^{1-4,6-10}

It has been reported that the binding mode of NHC to a metal such as Pd could make a substantial effect on the catalytic behavior.¹¹ When normally bound [Pd(IMes)₂Cl₂] complex **2.1** and mixed bound complex **2.2** (Fig. 2.1) were screened for the Suzuki-Miyaura and the Heck cross-coupling reactions, interestingly, the complex **2.1** was inactive for the cross-coupling reactions while the complex **2.2** was active. This study suggested that a catalytically active NHC-Pd species cannot be the complex **2.1** in the Suzuki and the Heck coupling reactions under in situ catalytic conditions using IMes·HCl and a Pd precursor, and abnormal binding of carbene might play a role during the catalysis. Albrecht and co-workers also reported that the catalytic activity of cationic C4-bound Pd(dicarbene) complex **2.3** shows a significantly higher catalytic activity in alkene hydrogenation than its C2-bound analogue **2.4** (Fig. 2.1).^{12,13}

Figure 2.1. Normal and abnormal NHC-based Pd complexes.

However, most examples including those shown above have different steric environment near the Pd center, which makes it difficult to conclude whether the observed activity is from the steric difference or from the different electronic environment of aNHC.^{14,15,16-19} In addition, in contrast to extensive

use of imidazolium salts for in situ generation of NHC based catalytic species in Pd catalysis,²⁰⁻²⁵ to the best of our knowledge, there is no example of using abnormal binding carbene precursors for similar in situ generation of catalytic species. During our recent research focused on the NHC-based transition metal complexes for efficient organic transformations,²⁶⁻³⁰ we became interested in abnormal NHC as a new ligand scaffold in homogeneous catalysis. Herein, we report the first example of using a C2 protected imidazolium salt as an aNHC precursor in a Pd catalyzed cross-coupling reaction. To confirm the observation from in situ catalysis, we also screened the activity of the related well-defined aNHC and nNHC Pd complexes.

2.3 Results and discussion

2.3.1 NHC precursor.

Two imidazolium salts, **2.5** and **2.6**, were chosen as NHC precursors to investigate the activity between the normal and the abnormal carbenes (Fig. 2.2). Both precursors have isopropyl and phenyl groups as wingtip groups providing similar steric effect of NHC ligands. Percent buried volumes ($\%V_{\text{bur}}$) of the chosen nNHC and aNHC, calculated on the basis of X-ray crystal structures of **2.7** and **2.9** using SambVca software, are 29.5 for nNHC of **2.5** and 30.0 for aNHC of **2.6** (radius of the sphere $R = 3.5 \text{ \AA}$; M–NHC length at $2.1 \text{ \AA}$; Bondi radii scaled by 1.17).³¹⁻³³

Figure 2.2. Normal and abnormal NHC precursors.

For the compound **2.6**, the C2 and C4 carbons are functionalized by phenyl groups, leaving the C5 position only available for the binding to Pd.^{34,35} The phenyl group was chosen to avoid possible C–C cleavage observed when a methyl or an isopropyl group was used as the C2 protecting group.³⁶⁻³⁸ The precursor **2.5** is a stereotype of NHC precursors used in in situ generated transition metal catalysis. While the most acidic C2 position is the most favorable binding site, there is possibility for palladium to bind to the C4 or the C5 position as such case of **2.2**.¹¹

Electronic properties of the corresponding carbenes of **2.5** and **2.6** were examined by Crabtree and co-workers by measuring carbonyl stretching frequencies of Ir(CO)₂Cl(NHC) complexes.³⁹ While the nNHC from **2.5** showed slightly higher electron donating property ($\nu(\text{CO})$ 2061, 1976 cm⁻¹) than PCy₃ ($\nu(\text{CO})$ 2072, 1984 cm⁻¹), aNHC from **2.6** exhibited much better electron donating ability as reported by significantly decreased CO frequency ($\nu(\text{CO})$ 2045, 1961 cm⁻¹) of Ir(CO)₂Cl(aNHC). In addition, recent calculations performed aNHC showed that the aNHC is more basic than its nNHC isomer.⁴⁰

In summary, the NHC precursors **2.5** and **2.6** were chosen to rationally investigate the effect of aNHC: (1) they have similar steric effect near the Pd center; (2) **2.6** will only show the effect of aNHC in catalysis while it is possible for **2.5** to bind normally or abnormally although it is logically believed that normal NHC binding is more favored; and (3) aNHC from **2.6** is a better electron donor than nNHC from **2.5**.

2.3.2 In situ generated NHC promoted Pd catalyzed reactions.

With the chosen NHC precursors **2.5** and **2.6**, we compared the activity in the Suzuki-Miyaura coupling reactions using Pd(OAc)₂ (Table 2.1).⁴¹⁻⁴⁵ Based on

extensive screening, Cs₂CO₃ and dioxane were chosen as the optimal base and solvent, respectively. A mixture of Pd(OAc)₂, an NHC precursor, and Cs₂CO₃ in dioxane was stirred at 80 °C for 30 min before the addition of the substrates to generate a catalyst precursor. The reactions were promoted by both ligands.⁴⁶ The abnormal NHC precursor **2.6** gave slightly better yields in most cases whether it was used as 2 equiv. or 1 equiv. vs. Pd. Interestingly, undesirable deboronation homo-coupling of the aryl boronic acid was not observed with **2.6**, unlike with **2.5**. The symmetrical biaryl compound generated from the homo-coupling of the aryl boronic acid has often been observed in the Suzuki-Miyaura reactions.⁴⁷

Table 2.1. NHC Promoted Suzuki-Miyaura Cross-Coupling Reactions (NHC : Pd = 1 : 1)^{a,b}

entry	R ¹	R ²	2.5		2.6	
			A	B	A	B
1	OMe	Me	58 (55)	35	67 (64)	< 0.1
2	H	Me	77 (75)	15	88 (84)	< 0.1
3	F	Me	72 (67)	19	76 (69)	< 0.1
4	Me	OMe	40 (33)	10	49 (42)	< 0.1
5	Me	H	51 (43)	5	44 (35)	2
6	Me	F	20 (16)	2	14 (9)	0.6
7	H	OMe	62 (57)	11	75 (64)	< 0.1
8	H	F	12 (10)	2	44 (38)	< 0.1

^a GC yields using dodecane as an internal standard. ^b Isolated yields were shown in parenthesis, average of at least two runs.

Table 2.2. NHC Promoted Suzuki-Miyaura Cross Coupling Reactions (NHC : Pd = 2 : 1)^{a,b}

entry	R ¹	R ²	2.5		2.6	
			A	B	A	B
1	OMe	Me	60 (57)	23	76 (73)	< 0.1
2	H	Me	79 (76)	14	90 (89)	< 0.1
3	F	Me	75 (72)	28	84 (76)	< 0.1
4	Me	OMe	41 (34)	10	64 (61)	< 0.1
5	Me	H	30 (25)	4	66 (62)	2
6	Me	F	6 (4)	4	29 (24)	1.3
7	H	OMe	67 (63)	7	78 (70)	< 0.1
8	H	F	30 (25)	3	50 (41)	< 0.1

^a GC yields using dodecane as an internal standard. ^b Isolated yields were shown in parenthesis, average of at least two runs.

Substrate scope of Suzuki-Miyaura coupling reactions promoted by the abnormal carbene precursor **2.6** promoted was explored (Table 2.3). It showed excellent activity with electron deficient aryl bromides with good functional group tolerance. However, reduced yields or no activity were observed with unactivated electron rich aryl bromide (entries 13–14), aryl chloride (entry 17), and sterically bulky substrates (entry 18). It has been reported that Pd complexes of sterically demanding phosphines or NHC ligands were more efficient in the Suzuki-Miyaura coupling reactions by stabilizing a putative monoligated Pd complex and facilitating the reductive elimination.^{44,48-51} Therefore, development of more sterically bulky abnormal carbene precursors will be required for further improvement of aNHC as a supporting ligand in the Pd catalyzed cross-coupling reactions.

Table 2.3. Scope of aNHC Promoted Suzuki-Miyaura Cross Coupling Reactions (**2.6** : Pd = 2 : 1).^a

entry	aryl bromide	boronic acid	yield (%) ^b
1			95 (84)
2			66 (59)
3			100 (93)
4			63 (55)
5			83 (71)
6			62 (52)
7			79 (70)
8			93 (87)
9			77 (63)
10			94 (82)
11			80 (71)
12			83 (67)
13			63 (55)
14			25 (9)

15			71 (67)
16			97 (92)
17			8(4)
18			0

^a Pd(OAc)₂ (2.5 mol%), **2.6** (5 mol%), Cs₂CO₃ (2 equiv), aryl halide (1.0 equiv), boronic acid (1.5 equiv), dioxane, 80 °C, 24 h. ^b GC yield (isolated yield), average of at least two runs.

The aNHC precursor **2.6** was probed in Pd catalyzed cross coupling reactions of aryl halide with phenyltrimethoxysilane, too (Table 2.4). It showed quite good activity either aryl bromide with electron donating or withdrawing group. No activity was observed when phenyltrimethoxysilane was reacted with aryl chloride.

Table 2.4. Scope of aNHC Catalyzed Cross Coupling of Aryl Halides with Phenyltrimethoxysilane (**2.6** : Pd = 1 : 1).

entry	R(Aryl halides)	X	Yield(%) ^a
1	H	Br	69
2	OMe	Br	78
3	F	Br	81
4	Me	Br	83
5	H	Cl	5

^a Isolated yield

A clear difference in the reaction rate for the nNHC and the aNHC systems was not observed when the progress of the reaction of *p*-tolylboronic acid and bromobenzene was monitored by GC (Fig. 2.3). To our surprise, the aNHC based catalyst exhibited much faster reaction rate than the nNHC based system, especially at the initial stage, although we postulated that **2.5** which has more acidic C-2 proton might generate (NHC)Pd species faster, which could affect the reaction rate.⁵² We think that the more electron donating aNHC promotes oxidative addition faster which is known as the rate determining step in many cases of the cross-coupling reaction.⁵³⁻⁵⁵

Figure 2.3. Comparison of reaction progress in the in situ catalytic systems.

2.3.3 Abnormal and normal *N*-heterocyclic carbene-based Pd complexes.

As different efficiency of formation of NHC–Pd bond from **2.5** and **2.6** might affect on the catalytic activity, C2 (**2.5**) or C5 (**2.6**) proton was monitored by ¹H NMR spectroscopy in a mixture of **2.5** or **2.6** (0.025mmol), Pd(OAc)₂

(0.025 mmol), Cs₂CO₃ (1 mmol) in THF-D₆ (1 mL) at 80 °C. The result indicated that **2.5** reacts faster with Pd (100% of C2 proton of **2.5** disappeared, vs. 82% of C5 proton of **2.6**, after 30 min). We synthesized well-defined NHC Pd complexes **2.7–2.11** following the reported conditions to investigate the effect of NHC and aNHC on the Pd catalyzed reaction further (Schemes 2.1 and 2.2).^{11,56-60} Interestingly, we could not observe any mixed (NHC)(aNHC)PdI₂ complexes **2.7a** or **2.7b** under the same condition of generation of **2.2** formed from Pd(OAc)₂ and an imidazolium salt without Cs₂CO₃.¹¹ Even in the presence of Cs₂CO₃, only **2.7** was obtained. With aNHC precursor **2.6**, a dimer complex **2.8** was obtained even though we used 2 equiv of **2.6**. Complex **2.9** was synthesized from **2.8** by the addition of an aNHC–Ag complex.

Scheme 2.1. Synthesis of NHC-Pd Complexes.

Figure 2.4. Crystal structures of **2.7–2.9** with thermal ellipsoids drawn at the 50% probability level.

Pd-PEPPSI-NHC (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization and initiation) complexes **2.10** and **2.11** have been prepared to compare reactivity and structural difference between aNHC and nNHC.^{56,57,59,60} The structures of complexes **2.7–2.11** were all characterized by X-ray crystallography (Fig. 2.4 and 2.5). The bond lengths between Pd–C(Carbene) were 2.017(5) Å in **2.7** and 2.021(5) Å in **2.9**, indicating similar bond lengths in contrast to our expectation of shorter bond length in **2.9** reflecting more electron donating property of aNHC. Similar bond lengths between Pd and carbene carbons of aNHC and nNHC were also reported in complex **2.2**.¹¹ It has been reported that M–C_{carbene} bond distances are not very sensitive to small changes in bond order.⁷ Similarly, the Pd–N_{pyridine} distances in **2.10** and **2.11** (Scheme 2.2) were also comparable as observed with other PEPPSI type NHC-based Pd precatalysts.^{56–60} nNHC based complex **2.10** could be synthesized by following the reported method. For the aNHC case, we did not obtain **2.11** by using the same method. When we added 2-chloro-pyridine to the DCM solution of the

complex **2.8**, the complex **2.11** was obtained near quantitatively.

Scheme 2.2. Synthesis of PEPPSI Complexes.

Figure 2.5. Crystal structures of **2.10** and **2.11**

Table 2.7. Suzuki-Miyaura Coupling with NHC-Pd Complexes^{a,b}

2.5 mol % Pd complex
Cs₂CO₃, Dioxane, 80 °C

A **B**

entry	precatalyst	A	B
1	2.7	40	13
2	2.8	52	< 0.1
3	2.9	84	< 0.1
4	2.10	35	7
5	2.11	62	< 0.1

^a Pd complex (2.5 mol %), Cs₂CO₃ (2 equiv), aryl halide (1.0 equiv), boronic acid (1.5 equiv), dioxane, 80 °C, 24 h. ^b GC yield (isolated yield), average of at least two runs.

Table 2.5. Selected Bond Lengths and Angles

	2.7	2.9	2.10	2.11	2.8
Pd-C _(carbene)	2.017(5)	2.021(5)	1.965(11)	1.9680(12)	1.971(5)
Pd-N _(pyridine)			2.121(9)	2.1376(11)	
Pd-I(1)	2.6189(4)	2.6244(4)	2.6021(10)	2.60993(16)	2.6672(5)
Pd-I(2)	2.6189(4)	2.6244(4)	2.6053(10)	2.60175(16)	2.6055(5)
C-Pd-C/N/I	180.00(1)	180.0(3)	176.8(4)	179.06(5)	174.66(13)

Table 2.6. X-ray Crystallographic Data for **2.7–2.11**

	2.7	2.9	2.10	2.11	2.8
Empirical formula	C ₂₄ H ₂₈ I ₂ N ₄ Pd	C ₃₈ H ₄₀ I ₂ N ₄ Pd	C ₁₇ H ₁₈ ClI ₂ N ₃ Pd	C ₂₄ H ₂₄ ClI ₂ N ₃ Pd	C ₂₀ H ₂₂ Cl ₂ I ₂ N ₂ Pd
Formula weight	732.70	912.94	659.99	750.11	721.50
Temperature (K)	173(2)	173(2)	103(2)	103(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/c	P2(1)/c	P2(1)/n	P2(1)/c
Unit cell dimensions (Å)	a = 8.6567(4) b = 8.7067(4) c = 10.3222(8)	a = 9.6490(5) b = 14.2995(7) c = 13.2073(6)	a = 14.9614(9) b = 8.8691(6) c = 16.6518(11)	a = 11.6209(5) b = 10.1227(4) c = 21.8342(10)	a = 9.6740(3) b = 19.8592(6) c = 12.6490(4)
Volume (Å ³)	657.40(7)	1772.47(15)	2090.8(2)	2567.99(19)	2390.57(13)
Z	1	2	4	4	4
D _{calcd} (Mg/m ³)	1.851	1.711	2.097	1.940	2.005
Absorption coefficient (mm ⁻¹)	3.071	2.297	3.972	3.247	3.591
F(000)	352	896	1240	1432	1368
Crystal size (mm ³)	0.38 x 0.12 x 0.10	0.30 x 0.24 x 0.22	0.40 x 0.32 x 0.30	0.40 x 0.24 x 0.20	0.20 x 0.12 x 0.10
θ range (deg)	2.71 - 31.32	2.13 - 26.50	2.52 - 27.00	1.87 - 41.55	1.93 - 26.59
Reflections collected	11966	20870	16087	114126	28870
Independent reflections / R _{int}	4170 / 0.0454	3635 / 0.0399	4511 / 0.0438	17349 / 0.0273	4922 / 0.0307
Data / restraints / parameters	4170 / 0 / 144	3635 / 14 / 208	4511 / 0 / 219	17349 / 0 / 283	4922 / 0 / 247
GOF on F ²	1.116	1.141	1.124	1.149	1.211
R1/wR2 (I > 2σ(I))	0.0592 / 0.1771	0.0415 / 0.1353	0.0702 / 0.1708	0.0252 / 0.0533	0.0288 / 0.0835
R1/wR2 (all data)	0.0663 / 0.1900	0.0483 / 0.1554	0.0835 / 0.1807	0.0318 / 0.0566	0.0437 / 0.1076
Largest diff. peak / hole (e Å ⁻³)	4.553 / -1.989	1.312 / -1.952	8.016 / -2.005	1.471 / -1.427	1.510 / -1.226

Activities of complexes **2.7–2.11** were compared in the coupling reaction of *p*-tolylboronic acid and bromobenzene (Fig. 2.6 and Table 2.7). Abnormal NHC based complexes **2.9** and **2.11** showed much better activity than **2.7** and **2.10**, indicating that aNHC better promoted the Pd coupling reaction than nNHC. Abnormal NHC-based complexes **2.8**, **2.9** and **2.10** exhibited faster reaction rate as observed with the in situ catalysts, without the induction period as observed with **2.7** (Fig. 2.5).⁶¹⁻⁶³ The significantly reduced activity of **2.7** compared with the in situ system (40 % vs. 76 %) might indicate the effect of C4 or C5 binding of NHC during in situ generation of Pd catalyst using nNHC precursor **2.5** as suggested by the previous report of complexes **2.1** and **2.2**.¹¹ However, unlike the complex **2.1**, the complex **2.7** showed moderate activity in the coupling reaction. We think that the reported inactivity of the complex **2.1** is presumably due to the steric effect of the four bulky mesityl hanging groups of the two IMes ligand, which would prevent by preventing the approach of boronic acids to the Pd center to be required for the generation of active Pd(0) species. Surprisingly, bis-aNHC Pd complex **2.9** exhibited comparably fast reaction rate with the PEPPSI mono-NHC complex **2.11**, presumably reflecting the promoted oxidative addition step by aNHC. Bis-aNHC Pd complexes **2.9** and **2.11** exhibited equally high reaction rates, consistent with the in situ results. The bis-nNHC Pd complex **2.7** showed much slower rate than the corresponding PEPPSI **2.10** as previously reported with the similar type Pd complexes.⁵⁶⁻⁶⁰

Figure 2.6. Comparison of reaction progress with complexes **2.7–11**.

We also explored the activity of **2.11** in the Sonogashira reaction. Compound **2.12** was developed by Organ as one of PEPPSI catalysts (Scheme 2.2 **2.12**).^{43,64}

Scheme 2.2 Synthesis of PEPPSI complexes.

The aNHC supported **2.11** only gave a comparable result with **2.12** [89% (GC) vs 87.6% (isolated)]. We changed the base as $t\text{BuNH}_2$ which was also used as solvent and the yield was not as good as the **2.12** which reported in 2009. The conditions need to be screened further.

Table 2.8 Sonogashira reaction catalyzed by PEPPSI **2.11**

entry	catalyst	solvent	base	T (°C)	Yield(%) ^a
1	2.12 (3.0 mol%)	DMF/H ₂ O(3:1)	Cs ₂ CO ₃ (4 eq)	90	89 ^b
2	2.11 (3.0 mol%)	DMF/H ₂ O(3:1)	Cs ₂ CO ₃ (4 eq)	90	87.6
3	2.11 (2.0 mol%)	$t\text{BuNH}_2$ /H ₂ O(1:1)	NO	25	36.3
4	2.11 (2.0 mol%)	$t\text{BuNH}_2$ /H ₂ O(1:1)	NO	50	77.0

^a Isolated yield ^b Reported GC yield

2.4 Conclusion

In conclusion, we have shown that an abnormal NHC is a better ligand than a normal NHC in the Pd catalyzed Suzuki-Miyaura reactions with suppressing homo-couplings of arylboronic acids when sterically similar NHC precursors are used. The corresponding well-defined abnormal and normal NHC-based Pd complexes were synthesized and structurally characterized. The aNHC based Pd precatalyst systems exhibit consistently faster reaction progress. Further ligand design by adjusting steric bulkiness of an aNHC precursor will be necessary for improved and practical usage of aNHCs in the cross-coupling reaction.

2.5 Experimental Section

General procedure for Suzuki-Miyaura coupling reactions (2.5 mol% catalyst loading): Pd(OAc)₂ (2.8 mg, 0.0125 mmol), NHC precursor (0.025 mmol), Cs₂CO₃ (326 mg, 1 mmol), and dioxane (2 mL) were placed in an oven dried Schlenk flask under an argon atmosphere. The Schlenk tube was heated to 80 °C in an oil bath. After 30 min of heating, boronic acid (0.75 mmol) and aryl halide (0.5 mmol) in 2 mL dioxane were added into the flask at room temperature. The reaction mixture was heated to 80 °C under an argon atmosphere for 24 h. After cooled down to room temperature, volatiles were removed *in vacuo*. The residue was purified by silica gel flash column chromatography. All the products were identified by spectral comparison with literature data or with analogous literature data.

Complex 2.7. Under Ar atmosphere, a Schlenk flask was charged with Pd(OAc)₂ (22.5 mg, 0.1 mmol), **2.5** (62.8 mg, 0.2 mmol), and dioxane (3 mL). The reaction mixture was heated to 80 °C for 6 h. After cooled down to room temperature, the product was purified by column chromatography with CH₂Cl₂ as an eluent. Complex **2.7** (light yellow powder, 51.2 mg, 0.070 mmol, 70.1%) was obtained by recrystallization with CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (m, 4H, CH_{arom}), 7.50 (m, 4H, CH_{arom}), 7.41(m, 2H, CH_{arom}), 7.15 (d, *J* = 1.8 Hz, 2H, CH_{imid}), 7.02 (d, *J* = 1.8 Hz, 2H, CH_{imid}), 5.18 (m, 2H, CH_{iPr}), 1.40 (d, *J* = 6.8 Hz, 12H, CH_{3-iPr}). ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 140.5, 128.4, 127.8, 126.5, 122.5, 117.1, 52.6, 22.4. HRMS–ESI (*m/z*) [M + Na]⁺ calcd for C₂₄H₂₈N₄I₂PdNa, 754.9336; found, 754.9329. Anal. Calcd for C₂₄H₂₈N₄I₂Pd: C, 39.34; H, 3.85; N, 7.65. Found: C, 39.28; H, 3.56; N, 7.92.

Complex 2.8. Under Ar atmosphere, a Schlenk flask was charged with Pd(OAc)₂ (22.5 mg, 0.1 mmol), **2.6** (80.8 mg, 0.2 mmol), and dioxane (3 mL). The reaction mixture was heated to 80 °C for 7 h. After cooled down to room temperature, all volatiles were removed. The product was isolated by column chromatography using CH₂Cl₂ as an eluent. Complex **2.8** (orange powder, 59.7 mg, 0.047 mmol, 46.9%) was obtained by recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, DMSO): δ 7.90 (d, *J* = 7.36 Hz, 4H, CH_{arom}), 7.67 (m, 10H, CH_{arom}), 7.50 (m, 4H, CH_{imid}), 7.41 (m, 2H, CH_{arom}), 5.58 (m, 2H, CH_{iPr}), 3.24 (s, 6H, NCH₃), 1.35 (d, *J* = 6.8 Hz, 12H, CH_{3-iPr}). ¹³C NMR (100 MHz, DMSO): δ 143.4, 131.7, 131.3, 130.4, 129.1, 127.9, 124.9, 57.2, 54.9, 33.3, 21.8. HRMS–ESI (*m/z*) [M + H]⁺ calcd for C₃₈H₄₁N₄Pd₂I₄, 1272.7584; found, 1272.7588. Anal. Calcd for C₃₈H₄₀N₄I₄Pd₂: C, 35.85; H, 3.17; N, 4.40. Found: C, 35.89; H, 2.95; N, 4.56.

Complex 2.9. Ag₂O (3.6 mg, 0.016 mmol) and **2.6** (13 mg, 0.032 mmol) were combined in a Schlenk flask with CH₂Cl₂ (1 ml) under Ar. The mixture was stirred at room temperature for 4 h. The solution filtrated through Celite and mixed with complex **2.8** (20 mg, 0.016 mmol). After stirred for 5 h at room temperature, the product was separated by column chromatography using CH₂Cl₂ as an eluent. Complex **2.9** (light yellow powder, 19.2 mg, 0.021 mmol, 65.8 %) was obtained by recrystallization from CH₂Cl₂/Et₂O. ¹H NMR (400 MHz, CDCl₃): δ 7.97 (m, 4H, CH_{arom}), 7.54 (m, 6H, CH_{arom}), 7.42 (m, 8H, CH_{arom}), 7.31 (m, 2H, CH_{arom}), 5.38 (m, 2H, CH_{iPr}), 3.19 (s, 6H, CH₃), 1.35 (d, *J* = 6.8 Hz, 12H, CH_{3-iPr}). ¹³C NMR (100 MHz, CDCl₃): δ 145.2, 141.9, 134.2, 132.2, 131.5, 131.0, 130.9, 128.9, 127.6, 126.9, 55.8, 32.8, 23.2. HRMS–ESI

(*m/z*) [*M* + Na]⁺ calcd for C₃₈H₄₀N₄I₂PdNa, 935.0275; found: 935.0303. Anal. Calcd for C₄₀H₄₄N₄Cl₄I₂Pd (**2.9**·2CH₂Cl₂) C, 44.37; H, 4.10; N, 5.17. Found: C, 44.29; H, 4.17; N, 5.21.

Complex 2.10. A Schlenk flask was charged with Pd(OAc)₂ (90.0 mg, 0.4 mmol), **2.5** (125.6 mg, 0.4 mmol), K₂CO₃, (276.0 mg, 2.0 mmol), and KI (66.4 mg, 0.4 mmol) and 3-chloropyridine (2 mL) under Ar. The reaction mixture was heated to 80 °C for 16 h. After cooled down to room temperature, 3-chloropyridine was evaporated under vacuum. The residue was washed with pentane and complex **2.10** was obtained (yellow solid, 263 mg, 0.4 mmol, 100%). ¹H NMR (400 MHz, CDCl₃): δ 8.80 (d, *J* = 1.2 Hz, 1H), 8.78 (d, *J* = 1.2 Hz, 1H), 8.02 (m, 2H), 7.70 (m, 1H), 7.67 (m, 2H), 7.52 (m, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.22 (m, 2H), 5.71 (m, *J* = 6.8 Hz, 1H), 1.64 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 152.7, 151.7, 143.8, 139.9, 137.5, 132.2, 129.0, 128.8, 126.5, 124.6, 124.1, 118.1, 53.8, 22.4. HRMS–ESI (*m/z*) [*M* + H]⁺ calcd for C₁₇H₁₉ClI₂N₃Pd, 659.8392; found: 659.8446. Anal. Calcd for C₁₇H₁₈ClI₂N₃Pd: C, 30.94; H, 2.75; N, 6.37. Found: C, 31.25; H, 2.94; N, 6.27.

Complex 2.11. A Schlenk flask was charged with complex **2.8** (95.0 mg, 0.075 mmol) in dichloromethane (2 mL) under Ar, and then 3-chloropyridine (17.0 mg, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. All volatiles were removed in vacuo. The residue was washed with pentane and complex **2.11** was obtained (yellow solid, 112.2 mg, 0.15 mmol, 100%). ¹H NMR (400 MHz, CDCl₃): δ 8.96 (d, *J* = 2.3 Hz, 1H), 8.87 (m, 1H), 7.93 (m, 2H), 7.61 (m, 4H), 7.49 (m, 5H), 7.17 (m, 1H), 5.97 (m,

$J = 8.2$ Hz, 1H), 3.20 (s, 3H), 1.49 (d, $J = 7.3$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 151.9, 143.0, 137.2, 133.2, 132.0, 131.8, 131.5, 130.8, 129.4, 128.6, 128.5, 126.1, 124.5, 117.3, 58.2, 33.4, 22.7. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{ClI}_2\text{N}_3\text{Pd}$, 753.8878; found: 753.8945. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{ClI}_2\text{N}_3\text{Pd}$ C, 38.43; H, 3.22; N, 5.60. Found: C, 38.24; H, 3.25; N, 5.24.

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CHAPTER 3^a

Structurally Characterized Abnormal N-Heterocyclic Carbene Gold(I) Complexes and Their Catalytic Activity

3.1 ABSTRACT

Herein we demonstrate the synthesis of two abnormally bound *N*-heterocyclic carbene gold(I) complexes [(aNHC)AuCl] from C2-blocked imidazolium salts. The air stable complexes [1-isopropyl-3-methyl-2,4-diphenylimidazolin-5-ylidene]chlorogold(I)(**3.1a**) and [1,4-diisopropyl-3-methyl-2-phenylimidazolin-5-ylidene]chlorogold(I) (**3.2a**) have been synthesized via transmetalation using (SMe₂)AuCl, characterized spectroscopically and structurally by X-ray diffraction. The catalytic activity of these two new complexes for the alkyne hydration reaction has been studied. To investigate the reactivity difference, the [(NHC)AuCl] complexes **3.3a** and **3.4a** bearing normal NHCs have also been synthesized. Better catalytic activities of abnormally bound complexes **3.1a** and **3.2a** were observed in comparison with the normal NHC complexes.

3.2 Introduction

The use of *N*-heterocyclic carbene ligands (NHCs) for the preparation of homogeneous catalysts has now become one of the most productive fields in

^a The research work described in this chapter was done in collaboration with Dr. Atanu Kumar Das.

organometallic chemistry.¹⁻⁴ The real breakthrough came after the first isolation of the stable free carbene by Arduengo⁵ formed at the C2 position. Most examples have shown the C2 metal binding. However C4 and C5 binding⁶⁻¹⁰ can also be possible since Crabtree and co-workers discovered it for the first time.⁶ It is considered that NHCs behave like tertiary phosphine in many aspects while NHCs exhibit stronger σ -donor properties.¹¹ This electronic feature leads to several advantages; stronger binding, greater thermal stability and increased basicity.^{12,13} These C4 or C5 bound carbenes³ are considered as even stronger donors^{6,14} than C2 bound normal carbenes, which may provide new opportunities in catalysis.¹

Recently, especially since 2004, great progress has been made in the development of efficient and selective Au-catalyzed organic transformations, as evidenced by the great number of review articles available on the various aspects of this growing field.¹⁵⁻²⁰ Among various gold complexes, normal NHC–Au(I) complexes have emerged as effective catalysts,²¹ for many transformations including C–H activation,²¹ olefin hydrogenation²² and cross coupling reactions²³ with high yield and selectivity. Recently, Bertrand and co-workers reported an elegant method for making abnormal carbenes, crystal structures of which allowed for a detailed structural study.²⁴ Our interest lies in advancing the abnormal *N*-heterocyclic carbene gold(I) chemistry with emphasis on designing highly efficient precatalysts for gold(I) mediated organic transformations.

We now report the preparation of two structurally characterized Au(I)-aNHC complexes (aNHC = 1-isopropyl-3-methyl-2,4-diphenylimidazolin-5-ylidene

and 1,4-diisopropyl-3-methyl-2-phenylimidazolin-5-ylidene, Fig. 3.1-3.2) not only aiming to fulfill the gap in the chemistry of aNHCs but also study their catalytic reactivity. For this purpose we have studied the catalytic activity in the hydration of terminal alkynes and cycloisomerization reactions, which are benchmark test for the evaluation of the catalytic activity of the Au(I)–NHC complexes. To investigate the activity difference, we used two normal NHC precursors **3.3** and **3.4**, which have similar steric effect near the Au center in comparison to the abnormal NHC precursors **3.1** and **3.2**, respectively (Fig. 3.1).

Figure 3.1. Molecular structures of normal and abnormal NHC precursors.

Figure 3.2. Molecular structures of normal and abnormal NHC Au complexes.

3.3 Results and discussions

A straightforward reaction between 1 equiv AuCl and free aNHC was initially attempted as the potentially most direct route to Au(aNHC)Cl. This route gave unsatisfactory results, as it led to poor yields and metallic gold

(Scheme 3.1). Similar byproducts have been observed in the attempted preparation of (I^tBu)Au(X) (I^tBu = 1,3-di-*tert*-butylimidazol-2-ylidene; X = BF₄, ClO₄).²⁵

Scheme 3.1

Then we examined an alternative approach, namely transmetalation from silver, where an equimolar amount of (SMe₂)AuCl is reacted with the respective in situ generated Ag(I)–aNHC salt giving rise to the complexes **3.1a** and **3.2a** in moderate yield. We attempted to prepare a C4 binding gold complex using a ligand precursor 1,3-diisopropyl-2-phenylimidazolium iodide under the same conditions. However, it was not successful. Instead, we obtained a Au(III) salt, which could be formed via protonolysis (Scheme 3.2).

Scheme 3.2

A similar result was reported by Crabtree for the attempted preparation of (COD)Ir(IPr)Cl (IPr = 1,3-diisopropyl-2-phenylimidazolin).¹⁴ The off-white solid obtained by reacting **3.1** and **3.2** (Fig. 3.1) with Ag₂O in dichloromethane, followed by transmetalation with (Me₂S)AuCl, gave pure **3.1a** and **3.2a** (Fig. 3.2) in 48% and 45% yields, respectively, after recrystallization from DCM/pentane solution. The complexes **3.1a** and **3.2a** were air stable both in solid state and in solution. The diastereotopic isopropyl methyl resonances observed in the ¹H NMR spectrum indicate hindered rotation about the gold–carbon bond. The bond lengths and angles are given in Table 3.2. A similar synthetic procedure was applied to obtain the complex **3.3a**. A dicarbene–Au(I) complex [**3.3a'**](PF₆) (Fig. 3.4(right)) was obtained using 0.5 equivalent of (Me₂S)AuCl instead of 1 equivalent (Fig. 3.6) (Scheme 3.3). The method could not be applied to obtain abnormal dicarbene–Au(I) complexes using one equivalent of (Me₂S)AuCl. The complex **3.4a** was synthesized by a modified method from the reported procedure.²⁶ The structures of the complexes **3.1a**, **3.2a** and **3.3a** were confirmed by X-ray crystallography (Fig. 3.3-3.4).

Scheme 3.3 Synthesis of **3.3a** and **3.3a'**.

Figure 3.3. X-ray crystal structures of **3.1a** and **3.2a**.

Layering a dichloromethane solution with pentane grew X-ray quality crystals of **3.1a**, **3.2a** and **3.3a**. The crystal structure analysis confirms abnormal ligand binding through C5 labeled as C1 (Fig. 3.3-3.4) in both **3.1a** and **3.2a**.

The complexes commonly feature a linear two-coordinate, C–Au–Cl geometry. The bond lengths between Au–C_{carbene} in these abnormal carbene complexes, **3.1a** [2.002(6) Å] and **3.2a** [2.020(8) Å] (Table 3.6) are comparable to what is observed in normally bound Au–NHC complexes **3.3a** [1.989(6) Å] and **3.4a** [1.964(6) Å]. The distances suggest a single-bond character, and are in good agreement with their strong σ -donor characteristics. Similarly, the Au–Cl distances in these abnormal carbene complexes, **3.1a** [2.310(2) Å], **3.2a** [2.289(3) Å] are comparable with the distances observed in **3.3a** [2.301(2) Å] and **3.4a** [2.262(2) Å].

Figure 3.4. X-ray crystal structures of **3.3a** and **[3.3a']⁺**.

Complexes **3.1a**, **3.2a**, **3.3a** and **3.4a** contain four different types of NHCs with similar topological framework but different electron-donor ability. To investigate the activity difference, we have chosen the well-known gold-catalyzed reaction of hydration of alkyne^{27,28} (Table 3.1), as a benchmark test for the evaluation of the catalytic activity. The alkyne hydration reaction²⁹ has long been known dating back to 1881 and more recent interest lies in the use of transition-metal based catalytic systems. Among these, gold complexes

have taken a dominant figure, replacing toxic mercury(II) salts. In particular, gold shows a high affinity for alkynes as a Lewis acid. The alkynophilicity of gold is similar to that of mercury, and this behavior has been attributed to the common electronic properties for these two elements in the valence shell, in part due to relativistic effects. Therefore use of gold instead of toxic mercury, as catalyst for the hydration of alkynes deserves effort to study. Thus, Utimoto³⁰ and Teles³¹ applied gold salts and complexes as catalyst for the hydration of alkynes. Hayashi and Tanaka³² reported the use of a $[(\text{Ph}_3\text{P})\text{AuMe}]/\text{H}^+$ catalytic systems which showed a high turnover frequency (TOF) in the hydration of alkynes. More recently, Nolan reported a general catalytic system for alkyne hydration, using $[(\text{NHC})\text{AuCl}]/\text{AgSbF}_6$ as the catalyst, that displays high efficiency at parts-per-million catalyst loading. To the best of our knowledge, it is the only report to date on the use of *N*-heterocyclic carbene gold(I) complexes as the catalyst for alkyne hydration reaction. Further interest for our study came from the fact that there is no report about the catalytic activity of abnormal *N*-heterocyclic carbene gold complex though normal *N*-heterocyclic carbene gold complexes have been remarkably successful in homogeneous catalysis. Herein, we report the results obtained for hydration of phenylacetylene using the catalytic system $(\text{aNHC})\text{AuCl}$ and $(\text{NHC})\text{AuCl}$ -Ag-salt in MeOH.

Table 3.1. Hydration of Phenylacetylene with different Ag(I)-salt using (aNHC)AuCl.

Entry	Ag-salt	H ₂ O (equiv)	GC-yield ^a	
			3.1a	3.2a
1	AgSbF ₆	4	94	95
2	AgSbF ₆	8	69	70
3	AgOTf	4	63	80
4	AgOTf	8	71	82
5	AgPF ₆	4	48	43
6	Ag(CF ₃ COO)	4	62	54

^a GC yields are average of at least two runs using dodecane as an internal standard.

Table 3.2. Hydration of Phenylacetylene.

entry	[Au]	GC yield(%) ^a
1	3.1a	94
2	3.2a	96
3	3.3a	86
4	3.4a	71

^a GC yields are average of at least two runs using dodecane as an internal standard.

The results obtained for different catalysts, water/alkyne ratio and different Ag(I)-salt are shown in Table 3.1-3.2. The equimolar combination of

3.2a/AgSbF₆ (5 mol %) in MeOH/H₂O was found to be most effective combination resulting in 96% GC conversion. The phenyl-substituted (C4 position) aNHC complex **3.1a** shows a slightly lower efficiency than **3.2a**, probably because of the higher steric crowding around the metal center. Addition of more water resulted in a decreased yield in case of AgSbF₆ salt, however significant increase in yield was observed in AgOTf (Table 3.1). Slightly reduced final yields of **3.3a** compared with **3.1a** (86% vs. 94%) and **3.4a** compared to **3.2a** (71% vs. 96%) were observed.

Cycloisomerization reactions catalyzed by Au-NHC complexes were also explored. Fürstner and co-workers³² compared Au(I) catalytic activity supported by different σ -donor and π -acceptor properties of NHCs. In the case of cycloisomerization of eneallene **3.6**, they reported that the electron-rich NHC-Au(I) would favor the [3+2] products **3.8** and **3.9**; the electron-deficient and better π -acceptor NHC-Au (I) preferred to going through [2+2] pathway to form **3.7** (Scheme 3.4). The best π -acceptor NHC-Au(I) (**3.15a**) gave the [2+2] product **3.7** only. In addition, they also reported that the stronger electron donor NHCs-supported Au(I) complexes preferred to catalyzing allene-diene **3.12** to form seven-member ring **3.13** via 1,2-alkyl shift; better π acidic ligands coordinated Au(I) complexes favored the 1,2-H shift pathway to produce compound **3.13** (Scheme 3.6).³²

Scheme 3.4. Au catalyzed cycloisomerization reaction of eneallene **3.6**.³²

Scheme 3.5. Au catalyzed cycloisomerization reaction of eneallene **3.10**.

Scheme 3.6. Au catalyzed cycloisomerization reaction of allene-diene **3.12**.³²

We explored the reactions mentioned above using our Au(I)-NHC complexes. We discovered the Au(I)-aNHCs (**3.1a**, **3.2a**) catalyzed reactions giving better yields than their Au(I)-NHCs analogues (**3.3a**, **3.4a**) (Table 3.3 and 3.4). A commercially available Au(I)-NHC **3.5a** was also examined. The yield obtained with **3.5a** was a slightly lower than with **3.1a** and **3.2a**, and the selectivity was same in our tested cases of cycloisomerization reaction of eneallenes **3.6**, **3.10** [We selected eneallene **3.10**³³ as substrate to get rid of [3+2] products using the cyclohexyl instead of isopropyl group (Scheme 3.5)]. Compounds **3.8** and **3.9** were not observed in any case. According to the Fürstner's report, better π -acceptor NHC supported Au(I) complexes would prefer giving **3.7** by [2+2] cycloaddition (Table 3.3), indicating aNHCs **3.1** and **3.2** may be good π -acceptor carbenes.

Table 3.3. Cycloisomerization reaction of eneallene **3.6**.

Catalyst	Yield (%)
3.1a	95 ^a
3.2a	73 ^b
3.3a	35 ^b
3.4a	37 ^b
 (3.5a)	68 ^a

^a Isolated yield; ^b Determined by ¹H NMR. None of the compounds **3.8** and **3.9** was observed.

Table 3.4. Cycloisomerization reaction

Catalyst	Yield (%)
3.1a	79 ^a
3.2a	68 ^a
3.3a	17 ^a
3.4a	16 ^a

^a Determined by ¹H NMR.³³

Table 3.5. Cycloisomerization reaction of allene-diene **3.12**.

Catalyst	Yield (%)	Ratio (3.13 : 3.14)
3.1a	97 ^a	69 : 31 ^b
3.2a	72 ^a	60 : 40 ^b
3.3a	69 ^a	72 : 28 ^b
3.4a	27 ^b	55 : 45 ^b
3.17a	47 ^c	Only 3.14 was obtained
3.15a	92 ^c	72 : 28 ^c

^a Isolated yield; ^d Determined by ¹H NMR. ^c Reported results.³²

In the case of cycloisomerization reaction of allene-diene **3.12** in Table 3.5, the yields of **3.1a** and **3.2a** were not only better than **3.3a** and **3.4a** but also better than reported **3.17a** and **3.15a**. Although the selectivity was comparable between aNHC and NHC gold complexes, **3.1a** and **3.2a** showed a slightly better selectivity in catalysis of allene-diene **3.12** than **3.3a** and **3.4a** to form 1,2-alkyl shift product **3.13** (**3.13** : **3.14** ratio = 68.7 : 31.3 and 71.8 : 28.2 vs. 17.9 : 12.1 and 23.5 : 19.5). According to the Fürstner results, the π -acidic ligands would prefer to give the compound **3.13**, while electron donating

ligands favor the 1,2-H shift pathway to give the product **3.14**.

3.4 Conclusion

We have prepared two novel air stable (aNHC)AuCl complexes by the transmetallation from the corresponding silver–carbene preformed complexes. The X-ray analysis showed similar Au–Cl bond lengths in comparison to the normally bound complex **3.3a**. Complexes **3.1a** and **3.2a** were screened to test the catalytic reactivity of abnormal (aNHC)AuCl complexes. Abnormal gold complexes **3.1a** and **3.2a** showed higher catalytic activities in hydration of phenylacetylene and cycloisomerization reactions than their normal analogue complexes **3.3a** and **3.4a**, respectively. In the present contribution we have developed clean synthetic route leading to two well-defined (aNHC)AuCl complexes which will serve as very useful starting point for the development of new abnormally bound catalytic system for different Au–mediated transformations.

Table 3.6. Selected bond lengths (Å) for **3.1a**, **3.2a**, **3.3a** and **3.4a**.

	3.1a	3.2a	3.3a		3.4a
Au–Cl	2.310(2)	2.289(3)	2.301(2)	Au–Cl	2.3124(12)
C1–Au	2.002(6)	2.020(8)	1.989(8)	C1–Au	1.986(6)
C1–C2	1.375(8)	1.337(12)	-----	C2–C3	1.345(9)
C2–N1	1.399(8)	1.384(11)	1.391(10)	C2–N1	1.392(8)
N1–C3	1.342(8)	1.327(12)	-----	N1–C1	1.348(8)
C3–N2	1.346(8)	1.353(11)	1.386(10)	C1–N2	1.338(9)
N2–C1	1.393(8)	1.394(11)	1.352(10)	N2–C3	1.386(8)
C3–C4	1.472(9)	1.464(12)	-----	-----	-----
C2–C14	1.471(9)	1.505(16)	-----	-----	-----
N1–C10	1.469(8)	1.477(11)	-----	-----	-----
N2–C11	1.477(8)	1.467(11)	-----	-----	-----
C2–C3	-----	-----	1.364(11)	-----	-----
N1–C1	-----	-----	1.346(10)		

Table 3.7. Selected bond angles (°) for **3.1a**, **3.2a**, **3.3a** and **3.4a**.

	3.1a	3.2a	3.3a		3.4a	
Au–C1–C2	128.0(5)	124.4(6)	N1–C1–N2	105.5(7)	Au–C1–N1	128.6(5)
Au–C1–N2	126.4(5)	124.4(7)	C1–N1–C2	110.7(6)	Au–C1–N2	125.3(5)
C1–N2–C3	110.2(5)	108.6(7)	N1–C2–C3	106.6(7)	C3–N2–C1	110.8(5)
N2–C3–N1	108.0(5)	107.5(8)	C2–C3–N2	106.2(7)	N2–C1–N1	105.8(5)
N1–C2–C1	107.8(5)	107.7(8)	C3–N2–C1	111.0(7)	C2–N1–C1	110.0(5)
C1–Au–Cl	178.4(2)	177.7(3)	C1–Au–Cl	176.2(2)	C1–Au–Cl	175.2(2)

Table 3.8. Crystallographic table.

	3.1a	3.2a	3.3a	3.4a
Empirical formula	C ₂₀ H ₂₂ AuCl ₃ N ₂	C ₁₆ H ₂₂ AuClN ₂	C ₁₃ H ₁₆ AuCl ₃ N ₂	C ₉ H ₁₆ AuClN ₂
Formula weight	593.71	474.77	503.59	384.65
Temperature	296(2) K	296(2) K	103(2)	103(2)K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	P2(1)/n	P-1	P2(1)/c
Unit cell dimensions	a = 9.4462(19) Å b = 9.778(2) Å c = 12.372(3) Å	a = 8.8970(5) Å b = 14.3233(7) Å c = 13.8846(7) Å	a = 8.0203(7) Å b = 9.4539(5) Å c = 10.6332(7) Å	a = 10.3769(4) Å b = 9.8216(3) Å c = 12.3357(4) Å
Volume	1036.0(4) Å ³	1748.22(16) Å ³	762.65(7) Å ³	1192.58(7) Å ³
Z	2	4	2	4
Density (calculated)	1.903 Mg/m ³	1.804 Mg/m ³	2.193 Mg/m ³	2.142 Mg/m ³
Absorption coefficient	7.493 mm ⁻¹	8.561 mm ⁻¹	10.157 mm ⁻¹	12.521 mm ⁻¹
F(000)	572	912	476	720
Crystal size	0.30x0.08x0.06 mm ³	0.24x0.20x0.10 mm ³	0.10x0.10x0.04 mm ³	0.40x0.40x0.10 mm ³
Theta range for data collection	2.80–27.00°	2.06–30.42°	2.96–29.00°	2.07–31.13°
Reflections collected	21303	18540	17617	11262
Independent reflections	4115 [R(int) = 0.0335]	2733 [R(int) = 0.0521]	3447 [R(int)=0.0521]	3816 [R(int) = 0.0423]
Data / restraints / parameters	4394 / 51 / 248	5221 / 110 / 216	3974 / 0 / 174	3816 / 0 / 122
Goodness-of-fit on F ²	1.100	1.034	1.204	1.103
Final R indices [I>2sigma(I)]	R1=0.0353, wR2=0.0920	R1=0.0522, wR2=0.1299	R1=0.0450, wR2=0.1140	R1=0.0443, wR2=0.1235
R indices (all data)	R1 = 0.0389, wR2 = 0.0945	R1 = 0.1442, wR2 = 0.1731	R1=0.0554, wR2=0.1190	R1=0.0525, wR2=0.1299
Largest diff. peak and hole	3.899 and -2.164 e.Å ⁻³	1.025 and -2.480 e.Å ⁻³	3.621 and -3.042 e.Å ⁻³	5.047 and -4.606 e.Å ⁻³

3.5 Experimental Section

Synthesis of complexes

(1-Isopropyl-3-methyl-2,4-diphenylimidazolin-5-ylidene)chlorogold(I)

(3.1a). A mixture of 1-isopropyl-3-methyl-2,4-diphenylimidazolium iodide (100 mg, 0.25 mmol) and silver(I) oxide (34.5 mg, 0.15 mmol) in dichloromethane (30 mL) was stirred for 4 h under an argon atmosphere at room temperature in dark. The mixture was filtered through celite and (dimethylsulphide) gold(I) chloride (73.5 mg, 0.25 mmol) and excess NaCl (2.5 mmol, 146 mg) were added. The resulting mixture was stirred for 4 h and filtered through celite. Activated carbon was added to the filtrate and stirred for another 30 min. The mixture was filtered through celite, the solvent was removed in vacuo, and then dichloromethane (5 mL) was added. Pentane (10 mL) was added to the solution, resulting in an immediate precipitation of an off white solid. The solid was further washed with pentane (3 × 5 mL) and recrystallized from dichloromethane/pentane (1 : 3) at -20 °C to obtain the analytically pure compound (88 mg, 70%). Crystals suitable for X-ray analysis studies were grown by diffusion of concentrated solution of complex **3.1a** layered with pentane. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.66 (m, 5H, CH_{arom}), 7.55 (m, 5H, CH_{arom}), 4.52 (sept, *J* = 6.8 Hz, 1H, CH_{iPr}), 2.94 (s, 3H, NCH₃), 1.75 (d, *J* = 6.8, 6H, CH_{3-iPr}). ¹³C NMR (100 MHz, CD₂Cl₂): δ 144.7, 136.8, 133.2, 131.1, 130.9, 130.5, 130.4, 129.7, 126.1, 122.2, 116.8 (C_{arom}), 53.7 (CH_{iPr}), 35.0 (NCH₃), 23.4 (CH_{3-iPr}). Anal. Calcd for C₁₉H₂₀AuClN₂ (508.80): C, 44.85; H, 03.96; N, 5.51. Found: C, 44.67; H, 3.89; N, 5.24.

(1,4-Diisopropyl-3-methyl-2-phenylimidazolin-5-ylidene)chlorogold(I)

(3.2a)

A mixture of 1,4-diisopropyl-3-methyl-2-phenylimidazolium iodide (100 mg, 0.27 mmol) and silver(I) oxide (36.9 mg, 0.16 mmol) in dichloromethane (30 ml) was stirred for 4 h under an argon atmosphere at room temperature in dark. The mixture was filtered through celite and (dimethylsulphide) gold(I) chloride (79.4 mg, 0.27 mmol). The resulting mixture was stirred for 4 h and filtered through celite. Activated carbon was added to the filtrate and stirred for another 30 min. The solvent was removed in vacuo, and then dichloromethane (5 mL) was added. Pentane (10 mL) was added to the solution, resulting in an immediate precipitation of a bright white solid. The solid was further washed with pentane (3 × 5 mL) and recrystallized from dichloromethane/pentane (1 : 3) to obtain analytically pure compound (57.5 mg, 45%). Crystals suitable for X-ray analysis studies were grown by diffusion of concentrated solution of complex **3.2a** layered with pentane. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.69 (m, 5H, CH_{arom}), 4.32 (sept, *J* = 6.8 Hz, 1H, CH_{*i*Pr}), 3.25 (s, 3H, NCH₃), 3.18 (sept, *J* = 6.8 Hz, 1H, CH_{*i*Pr}), 1.50 (d, *J* = 6.8 Hz, 6H, CH_{3-*i*Pr}), 1.38 (d, *J* = 6.8 Hz, 6H, CH_{3-*i*Pr}). ¹³C NMR (100 MHz, CD₂Cl₂): δ 143.5, 142.3, 132.9, 130.4, 130.1, 121.5, 114.1 (C_{arom}), 51.7 (CH_{*i*Pr}), 33.2 (NCH₃), 24.8, 22.8, 21.5 (CH_{3-*i*Pr}). Anal. Calcd for C₁₆H₂₂AuClN₂ (474.11): C, 40.48; H, 04.67; N, 5.90. Found: C, 40.72; H, 04.42; N, 05.72.

(3-Isopropyl-1-phenylimidazolin-2-ylidene)chlorogold(I) (3.3a)

A mixture of 1-phenyl-3-isopropylimidazolium iodide (100 mg, 0.32 mmol) and silver(I) oxide (44.5 mg, 0.19 mmol) in dichloromethane (30 mL) was

stirred for 1 h under an argon atmosphere at room temperature in dark. The mixture was filtered through celite and (dimethylsulphide)gold(I) chloride (94.2 mg, 0.32 mmol) was added. The resulting mixture was stirred for 3h and filtered through celite. The solvent was removed in vacuo and then dichloromethane (5 mL) was added. Pentane (10 mL) was added to the solution, resulting in an immediate precipitation of a bright white solid. The solid was further washed with pentane (3×5 mL) and recrystallized from dichloromethane/pentane (1 : 3) to obtain analytically pure compound (85.3 mg, 64%). Crystals suitable for X-ray analysis studies were grown by slow diffusion of concentrated solution of complex **3.3a** layered with pentane. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.64-7.47 (m, 5H, CH_{arom}), 7.22-7.17 (m, 2H, $\text{CH}_{\text{imidazole}}$), 5.16 (sept, $J = 6.8$ Hz, 1H, $\text{CH}_{i\text{Pr}}$), 2.09, 1.53 (d, $J = 6.8$ Hz, 6H, $\text{CH}_{3-i\text{Pr}}$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 169.2, 129.6, 129.0, 125.0, 122.1, 117.2 (C_{arom}), 30.6 ($\text{CH}_{i\text{Pr}}$), 23.1 ($\text{CH}_{3-i\text{Pr}}$). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{AuClN}_2$: 419.0589. Found: 419.0594 [MH^+].

**Bis(3-isopropyl-1-phenylimidazolin-2-ylidene)chlorogold(I)
hexafluorophosphate [3.3a'](PF_6)**

A mixture of 1-phenyl-3-isopropylimidazolium iodide (100 mg, 0.32 mmol) and silver(I) oxide (44.5 mg, 0.19 mmol) in dichloromethane (30 mL) was stirred for 4 h under an argon atmosphere at room temperature in dark. The mixture was filtered through celite and (dimethylsulphide) gold(I) chloride (47.0 mg, 0.16 mmol) was added. The resulting mixture was stirred for 3 h and filtered through celite. The solvent was removed in vacuum yielding a white solid. The solid was collected and then dissolved in dichloromethane and then

excess AgPF₆ (76 mg, 0.30 mmol) was added into it. The resultant precipitate was collected and washed with pentane and recrystallized from dichloromethane/pentane (1 : 3) to obtain analytically pure compound (104.6 mg, 46%). Crystals suitable for X-ray analysis studies were grown by slow diffusion of concentrated solution of complex **[3.3a']**(PF₆) layered with pentane. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.54-7.42 (m, 10H, CH_{arom}), 7.31-7.27 (m, 4H, CH_{imidazole}), 4.72 (sept, *J* = 6.8 Hz, 2H, CH_{*i*Pr}), 1.48 (d, *J* = 6.8 Hz, 6H, CH_{3-*i*Pr}). ¹³C NMR (100 MHz, CDCl₃): δ 181.3, 155.8, 139.3, 129.6, 129.3, 125.2, 122.8, 118.8 (C_{arom}), 54.1 (CH_{*i*Pr}), 23.6 (CH_{3-*i*Pr}). HRMS (ESI) calcd for C₂₄H₂₈AuN₄: 569.1980. Found: 569.1985 [M⁺].

(1, 3-diisopropylimidazolin-2-ylidene)chlorogold(I) (3.4a)

A mixture of 1, 3-diisopropylimidazolium iodide (100 mg, 0.36 mmol) and silver(I) oxide (49.2 mg, 0.21 mmol) in dichloromethane (20 mL) was stirred for 1 h under an argon atmosphere at room temperature in dark. The mixture was filtered through celite and (dimethylsulphide) gold(I) chloride (105.9 mg, 0.36 mmol) was added. The resulting mixture was stirred for 3 h and filtered through celite. The solvent was removed in vacuum, and then dichloromethane (5 mL) was added. Pentane (15 mL) was added to the solution. The resulting white crystalline solid was collected, washed with pentane (3 × 5 mL) and recrystallized from dichloromethane/pentane (1 : 3) to yield **3.4a** (57.5 mg, 42%). Crystals Suitable for X-ray analysis studies were grown by slow diffusion of concentrated solution of complex **3.4a** layered with pentane. ¹H NMR (400 MHz, CD₂Cl₂): δ 6.99 (s, 2H, CH_{imidazole}), 4.98 (sept, *J* = 6.8 Hz, 2H, CH_{*i*Pr}), 1.48 (d, *J* = 6.8 Hz, 6H, CH_{3-*i*Pr}).

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CHAPTER 4

CH/ π Interaction Study based on cis Isomers of Pd-NHC Complexes

4.1 ABSTRACT

CH/ π interaction was observed in the *cis*-(NHC)₂PdX₂ complexes. It was suggested as one of the driving forces for *trans* to *cis* conversion of square planar *bis*-NHC-Pd complexes. We synthesized a series of *trans* and *cis*-(NHC)₂PdX₂ complexes and explored their structural properties and catalytic activities.

4.2 Introduction

N-heterocyclic carbenes (NHCs) have been used as ligands in Pd complexes and investigated for organometallic chemistry and homogeneous catalysis in the past decade.¹⁻⁷ NHC-Pd complexes have been proven to be excellent catalysts especially for cross-coupling reactions. So far, most reported well-defined Pd-NHC complexes have *trans* configurations and only a few *cis* ones⁸⁻¹¹ have been reported except chelating NHC.^{10,12-16} In 1995, Herrmann and co-workers prepared *cis*-(NHC)₂PdX₂ complexes¹⁷ and explored their physical properties and catalytic activities in the Heck reaction. They failed to monitor the rearrangement by ¹H NMR due to the different solubility of two isomers. Huynh group¹⁸ did comparative study on the catalytic activity in the Heck-type reaction (Fig. 4.1) and found that **4.1-trans** isomer need induction time in the

catalysis process. Our group explored the activity of abnormal *N*-heterocyclic carbene-based Pd complexes in the Suzuki-Miyaura reactions.¹⁹ During the study, we obtained **4.3-cis-anti** complex (Scheme 4.1) and its ¹H NMR showed high up field shift of a methyl group of isopropyl hanging group. Driven by curiosity, we extended the research work on the formation of the *cis*-isomers. Herein we reported CH/ π interaction in *cis*-(NHC)₂PdX₂ type complexes.

Figure 4.1. **4.1-cis** and **4.1-trans** catalyzed Heck-type reaction (x [%]: conversion).

CH/ π interaction, a weak hydrogen-bond-like force, is occurring between CH (soft acid) and π -group (soft base). In 1957, Reeves and Schneider showed that this interaction was a type of H-bond.²⁰ It plays an important role in the crystal packing of compounds, and the stacking of peptide, organic compound, polymer molecule etc. π -Interactions or π -effects are a type of non-covalent interaction that involves π systems. Benzene (π system) has no dipole moment, but it does have a large permanent quadrupole moment. The sp^2 carbon is more electronegative than hydrogen, and the six $C^{\delta-}-H^{\delta+}$ bond dipoles form an electronegative centre under the symmetry of benzene added up to a

quadrupole moment (Fig. 4.2).

Figure 4.2. Quadrupole moment of benzene.

The electron rich π system can interact with a metal (cationic or neutral), another molecule and even another π system. There are four types of π binding forces: 1) Cation- π interaction which involves interaction of a cation and the face of a π -plane; 2) Polar- π interaction which is interaction of a polar molecule and a π system; 3) Aromatic-aromatic interaction concerns interactions of aromatic molecules with each other; 4) π donor-acceptor interaction is an interaction between two molecules or two regions of a molecule, where one with a low energy empty orbital (acceptor) interacts with the other bearing a high energy filled orbital (donor). CH/ π interaction is one kind of polar- π interaction through which the positive hydrogen region ($C^{\delta-}-H^{\delta+}$) interacts with an in front π -system.

Nishio and co-workers have done database studies in the field of CH/ π interaction since 1970s.²¹⁻²⁸ They summarized a set of methods to distinguish the existence of CH/ π interaction shown in Figure 4.3: (i) O: centre of the π -system plane; C^1-C^2 : the nearest line in aromatic ring to C^x ; α : dihedral angle between plane C^1OC^2 and plane H C^1C^2 ; β : $\angle HC^x C^1$; d_p : distance of H/ π -plane; d_l : distance of H/line C^1-C^2 ; d_a : distance of HC^1 (C^1 is the nearest carbon to C^x); (ii) *Ra* 1: the area H is above the π -system plane; *Ra* 2 and 3: the area H interact with

the π -system plane but it is out of *Ra* 1. d_m : the maximum distance H interact with π -system plane. *Ra* 1: $d_p < d_m$, $\beta < 60^\circ$, $|\alpha| < 90^\circ$; *Ra* 2: $d_p < d_m$, $\beta < 60^\circ$, $90^\circ < |\alpha| < 130^\circ$; *Ra* 3: $d_p < d_m$, $\beta < 60^\circ$, $50^\circ < |\alpha| < 90^\circ$. ($d_m = 2.9 \text{ \AA}$ ²⁹). A CH group would strongly interact with the π -orbital in *Ra* 1, *Ra* 2 and *Ra* 3 of the π -plane, where the H atom is not exactly above the π -plane. The software Mercury was used to calculate the related data.

Figure 4.3. Surveying method for CH/ π interaction.

4.3 Results and discussion

Herrmann¹⁷, Hahn¹¹ and Huynh¹⁸ observed only *cis* isomers under the condition of heating Pd(OAc)₂ and NHC precursor in THF, for example **4.2-cis** (Scheme 4.1). In case of NHC precursor **4.3**, *cis* isomers were not obtained under these reaction conditions. In the X-ray crystallography, only Pd-NHC complex **4.3-trans** was observed (Scheme 4.1). In the ¹H NMR spectra, the methyl doublet peaks of isopropyl group appeared at 1.40 ppm.

Scheme 4.1. Synthesis of Pd-NHC complexes.

4.3-trans-anti ($R^1=Ph$; $R^2=iPr$; $X=I$) **4.3-cis-anti**

Figure 4.4. X-ray structures of **4.3-trans-anti** and **4.3-cis-anti** complexes.

Only the *trans* isomer **4.3-trans** was observed by heating $PdCl_2$, NHC precursor **4.3** and Cs_2CO_3 in dioxane at 80 °C. **4.3-trans** was transformed to the cis-anti configuration in the $CDCl_3$ completely in 12 days at 55 °C (Fig. 4.4). The transformation took place even at room temperature. The solubility of **4.3-cis-anti** was not as good as **4.3-trans** isomer, and it was crystallized out from $CDCl_3$. **4.3-cis-anti** was easily distinguished by 1H NMR and the structure was confirmed by X-ray crystallographic analysis (Fig. 4.4). Methyl doublet peaks of isopropyl group appeared at 0.54 ppm and 1.40 ppm. NOE measurements indicated that the methyl group responsible for the doublet signal at 0.54 ppm is close to the phenyl ring of the other NHC.

Figure 4.5. 4.3-trans transferred to 4.3-cis-anti in CDCl₃ at 55 °C.

We heated the solution of the *trans* isomer at 55 °C for 12 days (Fig. 4.5) in CDCl₃, and observed that all of the **4.3-*trans*** were transformed to the *cis* complexes which suggested that the *cis* isomer is thermodynamically more stable. **4.3-*cis-anti*** was stable over the temperature range 23-60 °C in CDCl₃, 23-65 °C in D₆-THF, 23-80 °C in CDCl₂CDCl₂ and 23-90 °C in dioxane-D₈. When it was cooled down from high temperature, the *cis* isomer was collected again without any decomposition.

Scheme 4.2. Synthesis of **4.4**.

Figure 4.6. X-ray structures of **4.4-*trans-anti*** and **4.4-*cis-anti*** complexes.

We synthesized **4.4-*trans*** and **4.4-*cis-anti*** with bromide as X-type ligands to reduce the steric sized of X (Scheme 4.2, Fig. 4.6). The same result with **4.3-*cis-anti*** was obtained. The methyl doublet peaks of the isopropyl groups appeared at 0.66 ppm and 1.39 ppm. **4.4-*cis-anti*** is also stable in CDCl₃ even at

55 °C. The two methyl peaks of **4.4-cis-anti** were not coalesced even at 90 °C in dioxane-D₈ similarly as **4.3-cis-anti**. There should be another driving force to control the formation of cis-anti isomer.

Figure 4.7. X-ray structures of **4.5-trans** and **4.5-cis** complexes.

4.5-trans (Fig. 4.7) with only isopropyl groups was also transformed to **4.5-cis** in CDCl₃, but ¹H NMR showed that the doublet peaks of the methyl groups were not so much different. They appeared at 1.53 ppm and 1.26 ppm in CDCl₃. The *trans* to *cis* isomerization rate was slower than that of **4.3-trans** in CDCl₃. The final transfer conversion rate was 70% vs. 90% of **4.3-trans** (Fig. 4.9). It is suggested that **4.3-cis-anti** is more stable than **4.5-cis** (Fig. 4.7). **4.5-cis** was heated in CDCl₂CDCl₂ from 25 °C to 80 °C, the two methyl peaks were not coalesced. However, it transformed back to **4.5-trans** starting from 30 °C. The ratio of **4.5-trans** to **4.5-cis** increased with the increasing of temperature. We also found that if we dissolved **4.5-cis** in CDCl₃, it isomerized to **4.5-trans** slowly. Eventually, the system reached an equilibrium at *trans* : *cis* ratio of 3 : 7. There was no change in the ratio even with prolonged heating at 55 °C in CDCl₃.

Therefore, we propose that the interaction of CH/π between methyl of *iPr* and

phenyl (belong to anti NHC) plays a role in the stability of *cis*-isomers and the different chemical shifts of the methyl groups in the ^1H NMR. According to Nishio's method²⁹, we used the software Mercury to calculate the dihedral angle and distance data $d_a(\text{\AA})$, $d_p(\text{\AA})$, $d_l(\text{\AA})$, $\beta(^{\circ})$ and $\alpha(^{\circ})$ (Table 4.1).

Table 4.1. Dihedral angle and distance of **4.3-cis-anti** crystal structure

	CH/ π	$d_a(\text{\AA})$	$d_p(\text{\AA})$	$d_l(\text{\AA})$	$\beta(^{\circ})$	$\alpha(^{\circ})$
4.3-cis-anti	$\text{C}^4\text{H}/\text{PIC}^{19,20,21}$	2.812	2.755	2.787	30.3	81.3
	$\text{C}^{15}\text{H}/\text{PIC}^{7,8,9}$	2.861	2.814	2.854	33.5	80.4

In the X-ray structure of **4.3-cis-anti**: C^4 is the labeled carbon, $\text{PIC}^{19,20,21}$ is the plane formed by C^{19} , C^{20} and C^{21} ; α : dihedral angle between plane C^1OC^2 and plane $\text{H C}^1\text{C}^2$; β : $\angle \text{HC}^x\text{C}^1$; d_p : distance of H of $\text{C}^4\text{H}/\pi$ -plane of $\text{C}^{19,20,21}$; d_l : distance of H/line $\text{C}^{21}-\text{C}^{20}$; d_a : distance of H and C^{21} (C^{21} is the nearest carbon to C^4).

The dihedral angle and distance data of **4.3-cis-anti** (Table 4.1) was consistent with our conjecture ' $d_p = 2.755 \text{ \AA}$, $2.814 \text{ \AA} < d_m$, $\beta = 30.3^{\circ}$, $33.5^{\circ} < 60^{\circ}$, $|\alpha| = 81.3^{\circ}$, $80.4^{\circ} < 90^{\circ}$ '. It showed that C^4H and C^{15}H belonged to CH_3 of *iPr* group were exactly in the *Ra* 1 of $\text{C}^{19,20,21}$ and $\text{C}^{7,8,9}$ π -system planes. There were CH/π interactions between C^4H , C^{15}H (methyl of *iPr*) and $\text{C}^{19,20,21}$, $\text{C}^{7,8,9}$ phenyl planes (anti-NHC) in the **4.3-cis-anti** molecule. Dihedral angle and distance data (Table 4.2) of **4.4-cis-anti** (Fig. 4.5) was ' $d_p = 2.748 \text{ \AA}$, $2.720 \text{ \AA} < d_m$, $\beta = 35.2^{\circ}$, $52.1^{\circ} < 60^{\circ}$, $|\alpha| = 86.0^{\circ}$, $69.8^{\circ} < 90^{\circ}$ '. The locations of the C^{12}H and C^{24}H were also in *Ra* 1s above the aromatic planes of $\text{C}^{16,17,18}$ and $\text{C}^{4,5,6}$ which suggested that interactions between CHs and phenyl groups.

4.6-trans-anti ($R^1 = p\text{-F-Ph}$; $R^2 = i\text{Pr}$; $X = \text{I}$) **4.6-cis-anti**

4.7-trans-anti ($R^1 = p\text{-MeO-Ph}$; $R^2 = i\text{Pr}$; $X = \text{I}$) **4.7-cis-anti**

4.8-trans-anti ($R^1 = p\text{-Me-Ph}$; $R^2 = i\text{Pr}$; $X = \text{I}$)

Figure 4.8. X-ray structures of **4.6**, **4.7**, **4.8-trans-anti** and **4.6**, **4.7-cis-anti** complexes.

To extend our conclusion we also synthesized **4.6-trans**, **4.7-trans** and **4.8-trans**, which isomerized to **4.6**, **4.7** and **4.8-cis-anti** at room temperature in CDCl_3 . The *trans* and *cis* isomers can be isolated by column chromatography in

the air. The dihedral angle and distance data (Table 4.2) ' $d_p = 2.701 \text{ \AA}$, $2.845 \text{ \AA}$; $2.635 \text{ \AA}$, $2.666 \text{ \AA} < d_m$, $\beta = 27.0^\circ$, 26.9° ; 42.8° , $31.1^\circ < 60^\circ$, $|\alpha| = 78.4^\circ$, 75.7° ; 68.6° , $73.5^\circ < 90^\circ$ ' showed that CH/ π interaction took place in complexes **4.6** and **4.7-cis-anti** configurations (Fig. 4.8). The locations of CHs were also *Ra* 1s of the π systems. The electron-donating methoxy group made the benzene ring a more electron rich centre than electron withdrawing fluoro, resulting in the shorter d_p data of **4.7-cis-anti** was $2.635 \text{ \AA}$, $2.666 \text{ \AA}$ than the d_p data of **4.6-cis-anti** $2.701 \text{ \AA}$, $2.845 \text{ \AA}$. The interaction between CH and π -system in **4.7-cis-anti** would be stronger than that in **4.6-cis-anti**.

Table 4.2. dihedral angles and distances of *cis*-(NHC)₂PdX₂ complexes.

	CH/ π	$d_a(\text{\AA})$	$d_p(\text{\AA})$	$d_l(\text{\AA})$	$\beta(^{\circ})$	$\alpha(^{\circ})$
4.4-cis-anti	C ²⁴ H/PIC ^{4,5,6}	2.957	2.720	2.899	52.1	69.8
	C ¹⁵ H/PIC ^{16,17,18}	2.808	2.748	2.755	35.2	86.0
4.6-cis-anti	C ¹⁸ H/PIC ^{7,8,9}	2.827	2.701	2.757	27.0	78.4
	C ⁵ H/PIC ^{19,20,21}	2.920	2.757	2.845	26.9	75.7
4.7-cis-anti	C ²⁶ H/PIC ^{4,5,6}	2.911	2.635	2.829	42.8	68.6
	C ¹³ H/PIC ^{17,18,19}	2.849	2.666	2.780	31.1	73.5
4.9-cis	C ¹⁵ H/PIC ^{25,26,27}	2.714	2.617	2.651	22.6	80.1
	C ¹⁸ H/PIC ^{2,3,4}	2.683	2.529	2.626	16.0	74.4
4.10-cis-syn^a	C ²⁴ F ₁₀ /PIC ^{8,9,10}	2.784	2.681	2.739	4.1	78.2
4.13-cis-anti	C ¹³ H/PIC ^{6,7,8}	2.939	2.746	2.891	30.2	71.9
	C ² H/PIC ^{17,18,19}	2.943	2.744	2.915	32.1	70.3
4.11-trans-syn	C ¹⁵ H/PIC ^{7A,8A,10A}	3.359	3.213	3.290	31.0	77.6

α : dihedral angle between plane C¹OC² and plane H C¹C²; β : $\angle \text{HC}^x\text{C}^1$; d_p : distance of H/ π -plane; d_l : distance of H/line C¹-C²; d_a : distance of HC¹ (C¹ is the nearest carbon to C^x); ^a The calculation data was about CF similar to CH.

Figure 4.9. Conversion (cis/trans+cis) of trans-anti transfer to cis-anti complexes in CDCl_3 at 55°C .

Figure 4.10. X-ray structures of **4.9-trans** and **4.9-cis** complexes.

4.10-trans-anti ($R^1 = C_6F_5$; $R^2 = iPr$; $X=I$) **4.10-cis-syn**

Figure 4.11. X-ray structures of **4.10-trans-anti** and **4.10-cis-syn** complexes.

4.9-cis and **4.10-cis-syn** were synthesized and structurally characterized. The **4.9-cis** gave a twisted shape shown in Fig. 4.10 in which the sp^2 CH interacts with the in front aromatic. Dihedral angle and distance data (Table 4.2) ' $d_p = 2.617 \text{ \AA}$, $2.529 \text{ \AA} < d_m$, $\beta = 22.6^\circ$, $16.0^\circ < 60^\circ$, $|\alpha| = 80.1^\circ$, $74.4^\circ < 90^\circ$ ' indicated the $C^{15}H$ and $C^{18}H$ located at Ra 1 of aromatic rings of $C^{25,26,27}$ and $C^{2,3,4}$. **4.10-trans** was prepared using the same method to **4.3-trans** and converted to *cis* isomer, but **4.10-cis-syn** (Fig. 4.11) was observed. In **4.10-cis-syn** X-ray structure, the CF/π data was in the range of CH/π interaction. The dihedral angle and distance data ' $d_p = 2.681 \text{ \AA} < d_m$, $\beta = 4.1^\circ < 60^\circ$, $|\alpha| = 78.2^\circ < 90^\circ$ ' showed the location of $C^{24}F^{10}$ was in Ra 1 of $C^{7,8,9}$ plane. In the case of **4.9-cis**, the six $C^{\delta-} - H^{\delta+}$ developed a negative center and interacted with the sp^2 carbon bond $H^{\delta+}$ (Fig. 4.12 a). For **4.10-cis-syn**, due to the strong electronegativity of fluorine, the six $C^{\delta+} - F^{\delta-}$ bond dipoles could not form a strong negative centre like phenyl group. The $C^{\delta-} - H^{\delta+}$ bond dipoles disfavored the interaction with electron-deficient π -system C_6F_5 plane (**4.10-cis-syn**) (Fig. 4.12 b). In contrast, the $C^{\delta+} - F^{\delta-}$ bond dipole interacted with the C_6F_5 positive centre which shown in

Fig. 4.12 **c**. A different geometry of **4.10-cis-syn** was obtained instead of **4.10-cis-anti**. Alkorta et al. found an attractive interaction between electron-donating atoms and π cloud of C_6F_6 in 1997³⁰ and did a series of work with perfluoro aromatic compounds.^{31,32} They proved that the hexafluorobenzene played the part of a lone pair acceptor in the interaction. In 2004, Kawahara and co-workers first referred the theoretical definition of the CF/ π interaction similar to CH/ π interaction and performed computational studies.³³ Here, the CF/ π interaction plays a role in the formation and stability of **4.10-cis-syn** complex.

Figure 4.12. CH/ π and CF/ π interactions.

When mesityl and isopropyl group were chosen the ratio **4.11-trans-anti** and **4.11-trans-syn** (Fig. 4.13) were found to be 3 : 1. There was no exchange between the *syn* and the *anti* isomers when heated them in $CDCl_3$ at 55 °C even for 30 days. In addition, the dihedral angle and distance data of **4.11-trans-syn** ' $\beta = 31.0^\circ < 60^\circ$, $|\alpha| = 77.2^\circ < 90^\circ$ ' showed $C^{15}H$ (methyl of mesitylene) located above $C^{7A,8A,10A}$ mesitylene plane, but $d_p = 3.213 \text{ \AA} > d_m$ suggested there was a very weak CH/ π interaction between $C^{15}H$ and $C^{7A,8A,10A}$ π system. The distance of two mesityl group was too long in **4.11-trans-syn** due to the rigidity of two Pd-C2 bonds.

4.11-trans-syn ($R^1 = 2, 4, 6\text{-Me-Ph}$; $R^2 = i\text{Pr}$; $X = \text{I}$) **4.12-trans-anti**

Figure 4.13. X-ray structures of **4.11-trans-anti** and **4.12-trans-syn** complexes.

4.12-trans (Fig. 4.13) were transformed to both **4.12-cis-anti** and **4.12-cis-syn** at room temperature in CDCl_3 . **4.12-cis-anti** and **4.12-cis-syn** mixture could be identified by ^1H NMR. They were not isolated by recrystallization or column chromatography.

4.13-trans-anti

4.13-cis-anti

Figure 4.14. X-ray structures of **4.13-trans-anti** and **4.13-cis-anti**

The above analysis has shown the interaction of methyl proton and aromatic ring existing in the *cis*-(NHC) $_2$ PdX $_2$ complexes. We designed a new NHC ligand which includes an ethyl group instead of an isopropyl group (Fig. 4.14)

and expected the methyl group pointed to aromatic ring in **4.13-cis-anti** due to the CH/ π interaction between the CH group and the phenyl ring. However, the methyl group pointed at the opposite direction in contrast with our expectation. Interestingly, the ^1H NMR of **4.13-cis-anti** gave unusual behavior, the ^1H NMR multiplet of CH_2 (ethyl) appeared at 4.37 ppm and 2.36 ppm. The dihedral angle and distance data was ' $d_p = 2.771 \text{ \AA}$, $2.742 \text{ \AA} < d_m$, $\beta = 32.1^\circ$, $26.0^\circ < 60^\circ$, $|\alpha| = 73.0^\circ$, $71.7^\circ < 90^\circ$ ' showed CH/ π interaction between protons of C^2H , C^{13}H (CH_2) and aromatics $\text{C}^{6,7,8}$, $\text{C}^{17,18,19}$ rings instead of C^3H , C^{14}H (CH_3). NOE NMR experiment showed that the Para proton of the CH_2 (ethyl) group multiplet at 2.36 ppm was closer to the phenyl ring. We propose that the proton of the CH_2 group is more acidic than the proton of the CH_3 group due to the bonding of CH_2 to the nitrogen atom. Thus, the more positive proton of the CH_2 group would be more favorable to interact with the phenyl ring.

Scheme 4.3. Synthesis of 4.14-trans.

Figure 4.15. X-ray structure of **4.14-trans-anti**.

We also synthesized **4.14-trans-anti** that bears chloride ligands instead of iodide and bromide to decrease the steric effect in *cis*-(NHC)₂PdX₂ (Scheme 4.3, Fig. 4.15). **4.14-trans-anti** complex was heated in CDCl₃ at 55 °C for 20 days but did not isomerize to *cis*-anti like **4.3-trans** or **4.4-trans**. The result suggested that the CH/π interaction was not the unique reason for stability of the *cis* isomers. More efforts should be made to understand the geometrical change on the steric and electronic effects.

We compared Pd-C_{carbene} bond lengths in both isomers (Table 4.3). All the bond lengths for *cis*-Pd-NHC are shorter than the *trans*-Pd-NHC cases. The bond lengths are 2.007(4) Å, 2.015 (3) Å for **4.3-cis-anti** complex vs. 2.017(5) Å, 2.017(5) Å for **4.3-trans** complex; 2.012(2) Å, 2.014(2) Å for **4.5-cis-anti** vs. 2.0328(14) Å, 2.0329(14) Å for **4.5-trans** and revealed that bonds of Pd-C_{carbene} are stronger in *cis* isomers than in *trans* isomers. The longer Pd-I bonds (Table 4.3. 2.6640(4) Å, 2.6647(4) Å for **4.3-cis-anti** vs. 2.6189(4) Å, 2.6189(4) Å for **4.3-cis-anti**) reflects the stronger trans-effect in *cis* isomers.

Figure 4.16. Comparison of reaction progress with complexes **4.3-trans** and **4.3-cis-anti**.

The kinetics of the Suzuki-Miyaura cross-coupling reaction catalyzed by **4.3-trans** and **4.3-cis-anti** complexes were explored (Fig. 4.16). Induction time of **4.3-cis-anti** was around 9 hrs and the final yield 65% was observed whereas a slower rate was shown for **4.3-trans** and a lower yield of 45% was obtained. The reason need to be screened further.

Table 4.3. Selected bond lengths and angles.

complex	4.3-trans-anti	4.3-cis-anti	4.4-trans-anti	4.4-cis-anti
Pd-C _(carbene)	2.017(5) Å	2.007(4) Å	2.021(4) Å	1.988(3) Å
Pd-C _(carbene)	2.017(5) Å	2.015(3) Å	2.033(4) Å	1.991(3) Å
Pd-I(1)	2.6189(4) Å	2.6640(4) Å	2.4332(5) Å	2.4854(4) Å
Pd-I(2)	2.6189(4) Å	2.6647(4) Å	2.4461(5) Å	2.4894(4) Å
C(2) _(carbene) -N(1)	1.379(15) Å	1.397(5) Å	1.390(5) Å	1.392(4) Å
C(3) _(carbene) -N(2)	1.389(14) Å	1.391(5) Å	1.385(5) Å	1.388(3) Å
C(1) _(carbene) -N(1)	1.346(14) Å	1.376(5) Å	1.353(5) Å	1.371(3) Å
C(1) _(carbene) -N(2)	1.347(14) Å	1.354(5) Å	1.343(5) Å	1.354(4) Å
C-Pd-C	176.8(4) °	95.10(14) °	176.8(4) °	96.08(11) °
complex	4.5-trans-anti	4.5-cis-anti	4.6-trans-anti	4.6-cis-anti
Pd-C _(carbene)	2.0328(14) Å	2.012(2) Å	2.157(15) Å	2.014(2) Å
Pd-C _(carbene)	2.0329 (14) Å	2.014(2) Å	2.158(15) Å	2.017(2) Å
Pd-I(1)	2.60441(11) Å	2.6514(2) Å	2.61242(13) Å	2.6530(2) Å
Pd-I(2)	2.60441(11) Å	2.6682(2) Å	2.61241(13) Å	2.6584(2) Å
C(2) _(carbene) -N(1)	1.3889(19) Å	1.385(3) Å	1.392(2) Å	1.396(3) Å
C(3) _(carbene) -N(2)	1.3869(19) Å	1.384(3) Å	1.389(2) Å	1.388(3) Å
C(1) _(carbene) -N(1)	1.3505(18) Å	1.357(3) Å	1.359(2) Å	1.360(3) Å
C(1) _(carbene) -N(2)	1.3485(18) Å	1.353(3) Å	1.392(2) Å	1.355(3) Å
C-Pd-C	180.00(6) °	97.11(8) °	180.0 °	95.83(9) °
complex	4.7-trans-anti	4.7-cis-anti	4.9-trans-anti	4.9-cis-anti
Pd-C _(carbene)	2.0220(12) Å	2.009(4) Å	2.0248(13) Å	1.9871(19) Å
Pd-C _(carbene)	2.0220(12) Å	2.012(4) Å	2.0248(13) Å	2.002(2) Å
Pd-I(1)	2.6252 Å	2.6455(5) Å	2.63315(12) Å	2.6455(2) Å
Pd-I(2)	2.62519(10) Å	2.6518(4) Å	2.63316(12) Å	2.6562(2) Å
C(2) _(carbene) -N(1)	1.3958(16) Å	1.387(6) Å	1.394(2) Å	1.390(3) Å
C(3) _(carbene) -N(2)	1.3927(16) Å	1.394(6) Å	1.3942(19) Å	1.388(3) Å
C(1) _(carbene) -N(1)	1.3603(16) Å	1.369(6) Å	1.3569(18) Å	1.350(3) Å
C(1) _(carbene) -N(2)	1.3476(16) Å	1.343(6) Å	1.3609(18) Å	1.365(2) Å
C-Pd-C	180.0 °	96.65(17) °	180.0 °	91.75(8) °
complex	4.10-trans-anti	4.10-cis-anti	4.13-trans-anti	4.13-cis-anti
Pd-C _(carbene)	2.0194(16) Å	2.008(2) Å	2.0256(9) Å	1.989(3) Å
Pd-C _(carbene)	2.0195(16) Å	2.0176(19) Å	2.0256(9) Å	1.992(3) Å
Pd-Br(I)(1)	2.61856(11) Å	2.6407(4) Å	2.60532(12) Å	2.6566(3) Å
Pd-Br(I)(2)	2.61857(12) Å	2.6507(5) Å	2.60532(12) Å	2.6577(3) Å
C(2) _(carbene) -N(1)	1.398(2) Å	1.393(3) Å	1.3914(13) Å	1.394(3) Å
C(3) _(carbene) -N(2)	1.391(2) Å	1.386(3) Å	1.3914(13) Å	1.384(4) Å
C(1) _(carbene) -N(1)	1.366(2) Å	1.363(3) Å	1.3591(12) Å	1.354(3) Å
C(1) _(carbene) -N(2)	1.339(2) Å	1.353(2) Å	1.3512(13) Å	1.351(3) Å
C-Pd-C	180.0 °	92.94(8) °	180.0 °	87.51(10) °

4.4 Conclusion

A series of *cis*-(NHC)₂PdX₂ complexes have been synthesized, and CH/ π interactions involved therein have been studied by X-ray crystallographic and ¹H NMR analysis. Suzuki-Miyaura reaction progress was also investigated with complex **4.3-cis-anti** and **4.3-trans**. **4.3-cis-anti** needs longer induction time and higher yield than **4.3-trans** in catalysis.

4.5 Experimental Section

NHC precursor prepared

Phenylboronic acid (16.0 mmol), imidazole (884 mg, 13.0 mmol), copper(I) iodide (116 mg, 0.6 mmol) and 100 mL methanol were mixed in 200 mL two necks RBF, then it was refluxed for 10 h with pumping air continuously. The solvent was evaporated, and extracted by Et₂O (3 x 100 mL). The Et₂O phase was concentrated to 50 mL and filtered through celite. The crude product was dissolved in 15 mL toluene, and added 2-iodopropane (2.6 mL, 26.0 mmol). It was kept refluxing for 46 hrs, then toluene was evaporated and the solid was washed by diethyl ether. Off-white solid was obtained.

Pentafluorophenyl-3-isopropylimidazolium iodide

Glyoxal (40% wt, 0.58 mL) and paraformaldehyde (140 mg) were dissolved in acetic acid (1 mL), and the mixture was heated to 70 °C. A slurry of 2,3,4,5,6-pentafluoroaniline (915.4 mg, 5 mmol), ammonium acetate (383 mg, 5 mmol) were added to the mixture. More acetic acid and water (1 mL + 1 mL) washed for transfer solid. The mixture was stirred at 70 °C overnight. It was poured to saturated NaHCO₃ 50 mL. KOH was added to adjust the PH to 8. The

aqueous layer was extracted by Et₂O, dried over Na₂SO₄ and concentrated. It was purified by column chromatography. White solid (507 mg, 43%) was obtained. It was dissolved in 15 mL toluene, and added 2-iodopropane (2.6 mL, 26.0 mmol) and refluxed for 46 hrs and toluene was evaporated, and then the solid was washed by diethyl ether, and off-white solid was obtained (875 mg, 61%). ¹H NMR (400 MHz, CDCl₃): δ 10.66 (s, 1H), 8.02 (s, 1H), 7.87 (s, 1H), 5.13 (sept, *J* = 6.9 Hz, 2H), 1.73 (d, *J* = 6.4 Hz, 6H, CH₃-iPr). ¹⁹F NMR (376 MHz, CDCl₃): δ -144.5, -147.4, -157.8. ¹³C NMR (100 MHz, CDCl₃): δ 144.7, 144.1, 142.1, 141.6, 139.7, 137.4, 124.6, 121.9, 110.1, 55.1, 23.2.

Complex 4.14-trans-anti

Under Ar, Pd(OAc)₂ (22.5 mg, 0.1 mmol) and imidazolium chloride salt (44.6 mg, 0.2 mmol) were mixed in 3 mL dioxane. The mixture was heated at 80 °C for 6 h. The mixture was filtered through a pat of celite and the solvent was evaporated. Then the product was separated by column chromatography (silica, DCM). Recrystallized by DCM and off-white powder was obtained. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (m, 4H), 7.55 (m, 4H), 7.49 (m, 2H), 7.11 (d, *J* = 1.8 Hz, 2H), 6.99 (d, *J* = 1.8 Hz, 2H), 5.51 (sept, *J* = 6.4 Hz, 2H), 1.48 (d, *J* = 6.9 Hz, 6H, CH₃-iPr). ¹³C NMR (100 MHz, CDCl₃): δ 169.7 (Pd-C), 140.5, 128.9, 127.9, 126.1, 121.9, 52.5, 23.4. HRMS–ESI (*m/z*) [*M* + *H*]⁺ calcd for C₂₄H₂₈Cl₂N₄Pd, 549.8319; found: 549.8326. Anal. Calcd for C₂₄H₂₈Cl₂N₄Pd: C, 52.43; H, 5.13; N, 10.19. Found: C, 52.34; H, 5.42; N, 10.63.

Pd-NHC *trans* complexes

Under Ar, PdCl₂ (17.7 mg, 0.1 mmol) and imidazolium salt (0.2 mmol) and Cs₂CO₃ (326 mg, 1 mmol) were mixed in 3 mL dioxane, and then heated to 80

°C and stirred for 6 h. The mixture product was filtered through a pat of celite and the solvent was evaporated. The product was separated by column chromatography (silica, dichloromethane). Recrystallized by DCM and light yellow powder was obtained.

Pd-NHC *cis* complexes

Pd-NHC *trans* complexes were dissolved in CDCl₃ for several days. Then they were isolated by silica chromatography. Light yellow solid was obtained.

Complex 4.3-cis-anti

¹H NMR (400 MHz, CDCl₃): δ 8.49 (m, 4H), 7.60 (m, 4H), 7.50 (m, 2H), 7.18 (s, 2H), 6.95 (s, 2H), 4.67 (sept, *J* = 1.8 Hz, 2H), 1.40 (d, *J* = 6.4 Hz, 6H, CH₃-iPr), 0.54 (d, *J* = 6.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 141.2 (Pd-C), 129.8, 128.7, 125.4, 124.8, 54.1, 23.2, 23.1. HRMS–ESI (*m/z*) [*M* + H]⁺ calcd for C₁₇H₁₉ClI₂N₃Pd, 659.8392; found: 659.8446. Anal. Calcd for C₁₇H₁₈ClI₂N₃Pd: C, 39.34; H, 3.85; N, 7.65. Found: C, 39.28; H, 3.59; N, 7.72.

Complex 4.5-trans-anti

¹H NMR (400 MHz, CDCl₃): δ 6.96 (d, 4H), 5.45 (sept, *J* = 6.9 Hz, 2H), 1.53 (d, *J* = 6.8 Hz, 12H). ¹³C NMR (100 MHz, CD₂Cl₂): δ 165.0, 117.2, 52.5, 23.0. HRMS–ESI (*m/z*) [*M* + H]⁺ calcd for C₁₈H₃₃N₄PdI₂, 663.9846; found: 663.9837. Anal. Calcd for C₁₈H₃₂I₂N₄Pd: C, 32.52; H, 4.85; N, 8.43. Found: C, 32.36; H, 4.80; N, 8.50.

Complex 4.5-cis-anti

¹H NMR (400 MHz, CDCl₃): δ 7.02 (d, *J* = 6.8 Hz, 4H), 5.35 (sept, *J* = 6.9 Hz,

2H), 1.53 (d, $J = 6.8$ Hz, 6H), 1.26 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.3, 118.0, 52.7, 24.0, 22.8. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{33}\text{N}_4\text{PdI}_2$, 666.9834; Found: 666.9861. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{I}_2\text{N}_4\text{Pd}$: C, 32.52; H, 4.85; N, 8.43. Found: C, 32.62; H, 4.51; N, 8.19.

Complex 4.6-trans-anti

^1H NMR (400 MHz, CDCl_3): δ 7.91 (m, 4H), 7.17 (m, 4H), 7.11 (d, $J = 1.8$ Hz, 2H), 7.03 (d, $J = 2.3$ Hz, 2H), 5.09 (sept, $J = 6.9$ Hz, 2H), 1.41 (d, $J = 6.8$ Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3): δ -113.5. ^{19}F NMR (376 MHz, CDCl_3): δ -112.3. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 167.5, 163.7, 137.3, 129.0, 128.9, 123.3, 117.9, 115.8, 115.5, 53.2, 22.6. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{N}_4\text{F}_2\text{PdI}_2$, 770.9332; Found: 770.9338. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{F}_2\text{I}_2\text{N}_4\text{Pd}$: C, 37.50; H, 3.41; N, 7.29. Found: C, 37.79; H, 3.15; N, 7.76.

Complex 4.6-cis-anti

^1H NMR (400 MHz, CDCl_3): δ 8.47 (m, 4H), 7.28 (m, 2H), 7.15 (d, $J = 1.8$ Hz, 2H), 6.98 (d, $J = 1.8$ Hz, 2H), 4.64 (sept, $J = 6.9$ Hz, 2H), 1.45 (d, $J = 6.4$ Hz, 6H), 0.64 (d, $J = 6.8$ Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3): δ -113.5. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 163.5, 161.6, 161.1, 136.6, 127.4, 127.3, 118.4, 115.9, 115.7, 53.6, 24.3, 24.1. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{N}_4\text{F}_2\text{PdI}_2$, 768.9328; Found: 768.9300. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{F}_2\text{I}_2\text{N}_4\text{Pd}$: C, 37.50; H, 3.41; N, 7.29. Found: C, 37.46; H, 3.45; N, 7.31.

Complex 4.7-trans-anti

^1H NMR (400MHz, CD_2Cl_2): δ 7.85 (m, 4H), 7.14 (d, $J = 1.8$ Hz, 2H), 7.04 (d, $J = 1.8$ Hz, 2H), 6.99 (m, 4H), 5.14 (sept, $J = 6.9$ Hz, 2H), 3.84 (s, 6H), 1.37 (d, J

= 6.9 Hz, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 166.7, 159.2, 133.7, 127.5, 122.7, 117.0, 113.4, 53.7, 52.9, 22.2. HRMS–ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_2\text{PdI}_2\text{Na}$, 814.9547; Found: 814.9559; Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{I}_2\text{N}_4\text{O}_2\text{Pd}$: C, 39.39; H, 4.07; N, 7.07. Found: C, 39.25; H, 4.09; N, 7.04.

Complex 4.7-cis-anti

^1H NMR (400MHz, CDCl_3): δ 8.38 (d, J = 9.0 Hz, 4H), 7.12 (d, J = 2.0 Hz, 2H), 7.09 (d, J = 9.0 Hz, 4H), 6.94 (d, J = 2.0 Hz, 2H), 4.64 (sept, J = 6.6 Hz, 2H), 3.89 (s, 6H), 1.42 (d, J = 6.6 Hz, 6H), 0.64 (d, J = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 127.2, 124.8, 118.4, 116.6, 116.4, 54.0, 23.0. HRMS–ESI (m/z) $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{32}\text{N}_4\text{O}_2\text{PdI}_2\text{Na}$, 814.9547; Found: 814.9555. Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{I}_2\text{N}_4\text{O}_2\text{Pd}$: C, 39.39; H, 4.07; N, 7.07. Found: C, 39.26; H, 3.84; N, 7.18.

Complex 4.9-trans-anti

^1H NMR (400MHz, CDCl_3): δ 7.63 (d, J = 7.8 Hz, 4H), 7.37 (t, J = 7.2 Hz, 4H), 7.23 (t, J = 7.6 Hz, 2H), 7.04 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.4 (Pd-C), 140.0, 129.1, 128.3, 127.0, 124.0. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{25}\text{I}_2\text{N}_4\text{Pd}$, 804.9220; Found: 804.9205. Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{I}_2\text{N}_4\text{Pd}$: C, 45.00; H, 3.02; N, 7.00. Found: C, 45.42; H, 3.19; N, 7.01.

Complex 4.9-cis-anti

^1H NMR (400MHz, CD_2Cl_2): δ 7.41-7.38 (m, 4H), 7.38-7.28(m, 8H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 163.3 (Pd-C), 139.9, 129.0, 128.8, 125.5, 123.3. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{25}\text{I}_2\text{N}_4\text{Pd}$, 799.9220; Found: 799.9265. Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{I}_2\text{N}_4\text{Pd}$: C, 45.00; H, 3.02; N, 7.00. Found: C, 45.45; H,

3.19; N, 7.05.

Complex 4.10-trans-anti

^1H NMR (400MHz, DMSO-D6): δ 7.10 (d, J = 2.3 Hz, 4H), 5.32 (sept, J = 5.5 Hz, 2H), 1.45 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, DMSO-D6): δ 169.7, 169.1, 145.2, 142.5, 125.6, 119.8, 119.7, 55.3, 53.6, 21.9, 21.7. ^{19}F NMR (376 MHz, CDCl_3): δ -150.6. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{19}\text{N}_4\text{F}_{10}\text{PdI}_2$, 912.8574; Found: 912.8540. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{F}_{10}\text{PdI}_2$: C, 31.58; H, 1.99; N, 6.14; found: C, 31.35; H, 2.06; N, 5.84.

Complex 4.10-cis-syn

^1H NMR (400MHz, DMSO-D6): δ 7.14 (d, J = 2.3 Hz, 4H), 5.75 (sept, J = 5.5 Hz, 2H), 1.60 (d, J = 6.8 Hz, 6H), 1.33 (d, J = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, CDCl_3): δ -151.6. ^{13}C NMR (100 MHz, DMSO-D6): δ 164.6, 127.1, 124.0, 123.0, 120.5, 54.0, 23.5, 20.9. HRMS–ESI (m/z) $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{19}\text{N}_4\text{F}_{10}\text{PdI}_2$, 912.8574; Found: 912.8573. Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{F}_{10}\text{PdI}_2$: C, 31.58; H, 1.99; N, 6.14; found: C, 31.43; H, 2.13; N, 6.03.

Complex 4.12-trans

^1H NMR (400MHz, CDCl_3): δ 7.02 (s, 2H), 7.54 (t, 4H), 7.45 (t, 2H), 7.10 (d, J = 6.8 Hz, 2H), 6.98 (d, J = 6.8 Hz, 2H), 5.50 (sept, J = 6.8 Hz, 2H), 1.46 (d, J = 6.8 Hz, 12H).

Complex 4.13-tran-anti

^1H NMR (400MHz, CDCl_3): δ 7.97 (d, J = 8.2 Hz, 4H), 7.49 (t, J = 8.0 Hz, 4H), 7.45 (m, 2H), 7.13 (d, J = 1.8 Hz, 2H), 7.00 (d, J = 1.84 Hz, 2H), 4.23 (q, J

= 7.3 Hz, 4H), 1.40 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.3, 128.7, 128.6, 128.6, 126.5, 122.4, 120.7, 46.2, 118.6, 15.4. HRMS–ESI (m/z) [$\text{M} + \text{Na}$] $^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{I}_2\text{N}_4\text{PdNa}$, 726.9023; Found: 726.9038. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{I}_2\text{N}_4\text{Pd}$: C, 37.50; H, 3.43; N, 7.95. Found: C, 37.45; H, 3.52; N, 7.87.

Complex 4.13-cis-anti

^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.6$ Hz, 4H), 7.57 (t, $J = 8.0$ Hz, 4H), 7.51 (m, 2H), 6.99 (d, $J = 2.0$ Hz, 2H), 6.85 (d, $J = 2.0$ Hz, 2H), 4.37 (sept, $J = 7.6$ Hz, 2H), 2.36 (m, $J = 7.2$ Hz, 2H), 1.15 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.7, 129.6, 128.9, 125.7, 123.1, 119.9, 45.2, 14.0. HRMS–ESI (m/z) [$\text{M} + \text{Na}$] $^+$ calcd for $\text{C}_{22}\text{H}_{24}\text{I}_2\text{N}_4\text{PdNa}$, 726.9023; Found: 726.9041. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{I}_2\text{N}_4\text{Pd}$: C, 37.50; H, 3.43; N, 7.95. Found: C, 37.47; H, 3.40; N, 8.02.

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Publications

- [1] “Direct amide synthesis from alcohols and amines by phosphine-free ruthenium catalysts system” Subhash Chandra Ghosh, Senthilkumar Muthaiah, Yao Zhang, Xiangya Xu and Soon Hyeok Hong, *Adv. Synth. Catal.* **2009**, 351, 2643-2649.
- [2] “Abnormal *N*-Heterocyclic Carbene Promoted Suzuki-Miyaura Coupling Reaction: A Comparative study” Xiangya Xu, Baochang Xu, Soon Hyeok Hong, Yongxin Li *Organometallics* **2010**, 29 (23), 6343–6349.
- [3] Ruthenium Catalysts for Direct Amide Synthesis from Alcohols and Amines U.S. Soon Hyeok Hong; Subhash Chandra Ghosh; Yao Zhang; Senthilkumar Muthaiah; Cheng Chen; Xiangya Xu Provisional Patent Application No 61/243,803. September 18, **2009**.
- [4] CH/ π Interaction Study Based on cis Isomers of Pd-NHC Complexes. Manuscript in preparation.
- [5] Structurally Characterized Abnormal *N*-Heterocyclic Carbene Gold(I) Complexes and Their Catalytic Activity. Manuscript in preparation

Appendix

1. ^1H and ^{13}C NMR spectra

x-1-94-cis-C 13C NMR
400 MHz

4.3-cis-anti

X-5-9-3 1H CD₂Cl₂, BBFO1

4.4-trans

X-5-9-3 13C CD2Cl2, BBFO1

x-3-B ^1H NMR, 400MHz (BBFO1), CDCl_3

X-3-B-CIS 1H NMR, 400MHz (BBFO1), CDCl3

X-3-B-CIS-C 13C NMR, 400MHz (BBFO1), CDCl3

x-3-E-F 19F NMR, 400MHz (BBFO1), CDCl₃

X-3-E-CIS-F 19F | NMR BBFO2 CD2Cl2

-113.31
-113.32
-113.34
-113.34

4.6-cis-anti

X-4-54-H 1H NMR, 400MHz (BBFO1), CDCl3

X-4-54-C ¹³C NMR, 400MHz(BBFO1), CDCl₃

X-4-54-Cis ¹H |NMR BBFO2 CDCl₃

x-3-132-trans-2 1H BBFO1 D-DMSO

x-3-132-trans-2 13C BBFO1 D-DMSO

4.10-trans

X-3-132-F 1F NMR, 400MHz (BBFO1), CDCl₃

4.10-trans

x-3-132 13C BBFO2 DMSO

x-4-66 cdcl3 1H nmr

x-5-74-cis 1H BBFO1 CD2Cl2

x-5-74-cis 13C BBF01 CD2Cl2

4.13-cis-anti

X-ray Crystallographic Data

Table A1. Crystal data and structure refinement for Complex **2.7**.

Identification code	Complex 2.7	
Empirical formula	C ₂₄ H ₂₈ I ₂ N ₄ Pd	
Formula weight	732.70	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.6567(4) Å	α = 102.880(3)°.
	b = 8.7067(4) Å	β = 92.338(3)°.
	c = 10.3222(8) Å	γ = 118.385(2)°.
Volume	657.40(7) Å ³	
Z	1	
Density (calculated)	1.851 Mg/m ³	
Absorption coefficient	3.071 mm ⁻¹	
F(000)	352	
Crystal size	0.38 x 0.12 x 0.10 mm ³	
Theta range for data collection	2.71 to 31.32°.	
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15	
Reflections collected	11966	
Independent reflections	4170 [R(int) = 0.0454]	
Completeness to theta = 31.32°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7487 and 0.3882	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4170 / 0 / 144	
Goodness-of-fit on F ²	1.116	
Final R indices [I > 2σ(I)]	R1 = 0.0592, wR2 = 0.1771	
R indices (all data)	R1 = 0.0663, wR2 = 0.1900	
Largest diff. peak and hole	4.553 and -1.989 e.Å ⁻³	

Table A2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **2.7**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	10000	10000	5000	17(1)
C(1)	9052(7)	7403(7)	5041(5)	21(1)
C(2)	8281(8)	4882(7)	5752(6)	26(1)
C(3)	7407(7)	4366(7)	4482(6)	25(1)
C(4)	10447(7)	7887(8)	7348(5)	24(1)
C(5)	12154(8)	9211(9)	7377(7)	30(1)
C(6)	13193(11)	10258(9)	8594(7)	38(1)
C(7)	12646(10)	9947(11)	9820(7)	42(2)
C(8)	10923(11)	8583(13)	9763(7)	44(2)
C(9)	9793(9)	7546(10)	8523(6)	32(1)
C(10)	7229(8)	5952(8)	2743(6)	26(1)
C(11)	5271(10)	5351(13)	2635(9)	46(2)
C(12)	7629(12)	4823(12)	1597(7)	43(2)
I(1)	12474(1)	9889(1)	3670(1)	27(1)
N(1)	9300(6)	6774(6)	6078(5)	22(1)
N(2)	7902(6)	5906(6)	4064(5)	21(1)

Table A3. Crystal data and structure refinement for Complex **2.8**.

Identification code	Complex 2.8	
Empirical formula	C ₂₀ H ₂₂ Cl ₂ I ₂ N ₂ Pd	
Formula weight	721.50	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.6740(3) Å	α = 90°.
	b = 19.8592(6) Å	β = 100.348(2)°.
	c = 12.6490(4) Å	γ = 90°.
Volume	2390.57(13) Å ³	
Z	4	
Density (calculated)	2.005 Mg/m ³	
Absorption coefficient	3.591 mm ⁻¹	
F(000)	1368	
Crystal size	0.20 x 0.12 x 0.10 mm ³	
Theta range for data collection	1.93 to 26.59°.	
Index ranges	-11 ≤ h ≤ 12, -24 ≤ k ≤ 21, -15 ≤ l ≤ 15	
Reflections collected	28870	
Independent reflections	4922 [R(int) = 0.0307]	
Completeness to theta = 26.59°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7153 and 0.5337	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4922 / 0 / 247	
Goodness-of-fit on F ²	1.211	
Final R indices [I > 2σ(I)]	R1 = 0.0288, wR2 = 0.0835	
R indices (all data)	R1 = 0.0437, wR2 = 0.1076	
Largest diff. peak and hole	1.510 and -1.226 e.Å ⁻³	

Table A4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **2.8**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	10233(1)	4287(1)	6025(1)	25(1)
C(1)	8945(5)	3582(2)	6358(4)	26(1)
C(2)	7847(5)	3655(2)	6901(4)	27(1)
C(3)	7471(5)	4261(2)	7461(4)	32(1)
C(4)	8528(6)	4605(3)	8152(5)	41(1)
C(5)	8222(7)	5212(3)	8616(5)	56(2)
C(6)	6918(7)	5477(3)	8410(5)	57(2)
C(7)	5852(7)	5133(3)	7744(5)	51(2)
C(8)	6122(6)	4533(3)	7265(4)	40(1)
C(9)	5870(5)	2890(3)	7307(4)	37(1)
C(10)	7753(5)	2608(2)	6272(4)	27(1)
C(11)	7302(5)	1907(2)	6044(4)	30(1)
C(12)	6121(6)	1771(3)	5284(4)	39(1)
C(13)	5750(6)	1109(3)	5044(5)	47(2)
C(14)	6517(7)	595(3)	5577(5)	51(2)
C(15)	7665(7)	721(3)	6365(5)	45(1)
C(16)	8058(6)	1385(3)	6596(4)	36(1)
C(17)	9794(5)	2670(2)	5233(4)	30(1)
C(18)	10782(6)	2127(3)	5739(5)	51(2)
C(19)	8968(6)	2469(3)	4165(4)	46(1)
C(20)	3200(7)	3706(4)	4291(5)	60(2)
Cl(1)	5018(2)	3736(1)	4559(2)	87(1)
Cl(2)	2651(2)	2940(1)	3651(2)	92(1)
I(1)	11765(1)	5313(1)	5512(1)	37(1)
I(2)	12200(1)	3802(1)	7508(1)	39(1)
N(1)	7130(4)	3048(2)	6837(3)	28(1)
N(2)	8863(4)	2929(2)	5974(3)	25(1)

Table A5. Crystal data and structure refinement for Complex **2.9**.

Identification code	Complex 2.9	
Empirical formula	C ₃₈ H ₄₀ I ₂ N ₄ Pd	
Formula weight	912.94	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.6490(5) Å	α = 90°.
	b = 14.2995(7) Å	β = 103.428(2)°.
	c = 13.2073(6) Å	γ = 90°.
Volume	1772.47(15) Å ³	
Z	2	
Density (calculated)	1.711 Mg/m ³	
Absorption coefficient	2.297 mm ⁻¹	
F(000)	896	
Crystal size	0.30 x 0.24 x 0.22 mm ³	
Theta range for data collection	2.13 to 26.50°.	
Index ranges	-11 ≤ h ≤ 9, -17 ≤ k ≤ 17, -16 ≤ l ≤ 16	
Reflections collected	20870	
Independent reflections	3635 [R(int) = 0.0399]	
Completeness to theta = 26.50°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6319 and 0.5457	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3635 / 14 / 208	
Goodness-of-fit on F ²	1.141	
Final R indices [I > 2σ(I)]	R1 = 0.0415, wR2 = 0.1353	
R indices (all data)	R1 = 0.0483, wR2 = 0.1554	
Largest diff. peak and hole	1.312 and -1.952 e.Å ⁻³	

Table A6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **2.9**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5000	0	10000	20(1)
C(1)	6831(7)	-509(4)	8126(5)	31(1)
C(2)	7109(7)	-1340(5)	7670(5)	34(1)
C(3)	8490(7)	-1620(4)	7735(5)	35(1)
C(4)	9595(6)	-1061(4)	8252(5)	31(1)
C(5)	9333(6)	-232(4)	8733(4)	27(1)
C(6)	7932(6)	53(4)	8685(4)	22(1)
C(7)	7543(6)	875(4)	9237(4)	23(1)
C(8)	9481(7)	1990(4)	8900(5)	33(1)
C(9)	7600(6)	2326(4)	9852(4)	25(1)
C(10)	7964(7)	3325(4)	10049(4)	27(1)
C(11)	9049(7)	3600(5)	10874(5)	36(1)
C(12)	9291(9)	4548(5)	11093(6)	46(2)
C(13)	8464(8)	5203(5)	10474(6)	44(2)
C(14)	7417(10)	4941(5)	9627(7)	50(2)
C(15)	7175(8)	3998(5)	9418(6)	38(1)
C(16)	5602(6)	2190(4)	10806(5)	31(1)
C(17)	6469(9)	2492(7)	11866(6)	55(2)
C(18)	4508(9)	2905(6)	10254(8)	62(2)
C(19)	6453(5)	935(4)	9744(4)	22(1)
I(1)	3111(1)	689(1)	8418(1)	36(1)
N(1)	8241(5)	1739(3)	9319(4)	22(1)
N(2)	6526(5)	1852(3)	10121(4)	25(1)

Table A7. Crystal data and structure refinement for Complex **2.10**.

Identification code	Complex 2.10	
Empirical formula	C ₁₇ H ₁₈ Cl I ₂ N ₃ Pd	
Formula weight	659.99	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.9614(9) Å	α = 90°.
	b = 8.8691(6) Å	β = 108.870(3)°.
	c = 16.6518(11) Å	γ = 90°.
Volume	2090.8(2) Å ³	
Z	4	
Density (calculated)	2.097 Mg/m ³	
Absorption coefficient	3.972 mm ⁻¹	
F(000)	1240	
Crystal size	0.40 x 0.32 x 0.30 mm ³	
Theta range for data collection	2.52 to 27.00°.	
Index ranges	-19 ≤ h ≤ 18, -8 ≤ k ≤ 11, -20 ≤ l ≤ 21	
Reflections collected	16087	
Independent reflections	4511 [R(int) = 0.0438]	
Completeness to theta = 27.00°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3820 and 0.2995	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4511 / 0 / 219	
Goodness-of-fit on F ²	1.124	
Final R indices [I > 2σ(I)]	R1 = 0.0702, wR2 = 0.1708	
R indices (all data)	R1 = 0.0835, wR2 = 0.1807	
Largest diff. peak and hole	8.016 and -2.005 e.Å ⁻³	

Table A8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **2.10**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2350(1)	2070(1)	53(1)	12(1)
C(1)	1128(7)	4700(14)	-775(7)	19(2)
C(2)	613(8)	6004(14)	-840(7)	23(2)
C(3)	638(9)	6803(14)	-119(8)	24(3)
C(4)	1182(8)	6227(13)	657(8)	22(2)
C(5)	1676(8)	4894(13)	686(8)	20(2)
C(6)	2978(8)	98(12)	170(7)	17(2)
C(7)	3620(9)	-2073(14)	-56(8)	28(3)
C(8)	3601(8)	-2097(13)	733(7)	19(2)
C(9)	3147(9)	-140(15)	-1257(7)	26(3)
C(10)	4085(10)	350(20)	-1304(10)	43(4)
C(11)	2681(13)	-1376(18)	-1914(8)	44(4)
C(12)	3067(8)	-308(13)	1659(7)	17(2)
C(13)	3843(8)	-154(15)	2389(8)	23(2)
C(14)	3714(9)	384(15)	3122(8)	27(3)
C(15)	2813(9)	715(14)	3142(7)	24(3)
C(16)	2043(9)	517(16)	2403(8)	29(3)
C(17)	2151(8)	13(14)	1667(7)	22(2)
Cl(1)	-65(3)	6599(4)	-1837(2)	39(1)
I(1)	811(1)	746(1)	-884(1)	21(1)
I(2)	3974(1)	3303(1)	847(1)	23(1)
N(1)	1647(6)	4166(10)	-16(5)	14(2)
N(2)	3226(6)	-720(10)	-405(6)	16(2)
N(3)	3201(6)	-753(10)	878(6)	16(2)

Table A9. Crystal data and structure refinement for Complex **2.11**.

Identification code	Complex 2.11	
Empirical formula	C ₂₄ H ₂₄ Cl I ₂ N ₃ Pd	
Formula weight	750.11	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.6209(5) Å	α = 90°.
	b = 10.1227(4) Å	β = 91.097(2)°.
	c = 21.8342(10) Å	γ = 90°.
Volume	2567.99(19) Å ³	
Z	4	
Density (calculated)	1.940 Mg/m ³	
Absorption coefficient	3.247 mm ⁻¹	
F(000)	1432	
Crystal size	0.40 x 0.24 x 0.20 mm ³	
Theta range for data collection	1.87 to 41.55°.	
Index ranges	-21 ≤ h ≤ 21, -18 ≤ k ≤ 18, -39 ≤ l ≤ 40	
Reflections collected	114126	
Independent reflections	17349 [R(int) = 0.0273]	
Completeness to theta = 41.55°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5628 and 0.3566	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17349 / 0 / 283	
Goodness-of-fit on F ²	1.149	
Final R indices [I > 2σ(I)]	R1 = 0.0252, wR2 = 0.0533	
R indices (all data)	R1 = 0.0318, wR2 = 0.0566	
Largest diff. peak and hole	1.471 and -1.427 e.Å ⁻³	

Table A10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **2.11**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2363(1)	7340(1)	911(1)	12(1)
C(1)	2464(1)	8197(1)	105(1)	13(1)
C(2)	2760(1)	9464(1)	-44(1)	12(1)
C(3)	2323(1)	8422(1)	-918(1)	13(1)
C(4)	3117(1)	10575(1)	348(1)	14(1)
C(5)	2494(2)	11749(2)	356(1)	27(1)
C(6)	2857(2)	12797(2)	722(1)	33(1)
C(7)	3843(2)	12683(2)	1084(1)	28(1)
C(8)	4464(2)	11512(2)	1081(1)	28(1)
C(9)	4110(1)	10464(2)	710(1)	22(1)
C(10)	2967(1)	10755(1)	-1028(1)	16(1)
C(11)	2178(1)	8232(1)	-1585(1)	14(1)
C(12)	1336(1)	8962(1)	-1899(1)	18(1)
C(13)	1272(1)	8934(1)	-2536(1)	21(1)
C(14)	2046(2)	8184(1)	-2862(1)	22(1)
C(15)	2884(1)	7448(2)	-2551(1)	21(1)
C(16)	2949(1)	7466(1)	-1914(1)	17(1)
C(17)	1666(1)	6236(1)	-470(1)	19(1)
C(18)	443(2)	6296(2)	-721(1)	32(1)
C(19)	2412(2)	5230(2)	-786(1)	36(1)
C(20)	1280(1)	5715(1)	1913(1)	18(1)
C(21)	1182(1)	5008(2)	2451(1)	20(1)
C(22)	2078(2)	4966(2)	2875(1)	26(1)
C(23)	3058(2)	5676(2)	2741(1)	27(1)
C(24)	3114(1)	6366(2)	2193(1)	22(1)
Cl(1)	-96(1)	4185(1)	2579(1)	28(1)
I(1)	280(1)	8297(1)	956(1)	19(1)
I(2)	4445(1)	6486(1)	744(1)	19(1)
N(1)	2188(1)	7572(1)	-448(1)	13(1)
N(2)	2667(1)	9580(1)	-677(1)	13(1)
N(3)	2242(1)	6381(1)	1780(1)	17(1)

Table A11. Crystal data and structure refinement for Complex **3.1a**.

Identification code	Complex 3.1a	
Empirical formula	C ₂₀ H ₂₂ Au Cl ₃ N ₂	
Formula weight	593.71	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4462(19) Å	α = 86.645(11)°.
	b = 9.778(2) Å	β = 69.053(9)°.
	c = 12.372(3) Å	γ = 76.210(9)°.
Volume	1036.0(4) Å ³	
Z	2	
Density (calculated)	1.903 Mg/m ³	
Absorption coefficient	7.493 mm ⁻¹	
F(000)	572	
Crystal size	0.30 x 0.08 x 0.06 mm ³	
Theta range for data collection	1.76 to 27.00°.	
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15	
Reflections collected	21315	
Independent reflections	4396 [R(int) = 0.0335]	
Completeness to theta = 27.00°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6620 and 0.2121	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4396 / 51 / 248	
Goodness-of-fit on F ²	1.204	
Final R indices [I > 2σ(I)]	R1 = 0.0355, wR2 = 0.1001	
R indices (all data)	R1 = 0.0403, wR2 = 0.1132	
Largest diff. peak and hole	3.602 and -1.798 e.Å ⁻³	

Table A12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **3.1a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Au(1)	6722(1)	5459(1)	3943(1)	16(1)
C(1)	7317(8)	4248(7)	5149(6)	16(1)
C(2)	7665(8)	2802(7)	5184(6)	16(1)
C(3)	7748(8)	1752(7)	4345(6)	19(1)
C(4)	8534(9)	1901(8)	3163(6)	22(2)
C(5)	8581(10)	953(9)	2353(7)	28(2)
C(6)	7875(10)	-180(8)	2714(8)	29(2)
C(7)	7094(10)	-332(8)	3882(8)	27(2)
C(8)	7017(9)	632(8)	4692(7)	22(2)
C(9)	8333(10)	1014(8)	6650(7)	24(2)
C(10)	7768(8)	3614(7)	6792(6)	16(1)
C(11)	7956(9)	3667(7)	7918(6)	19(1)
C(12)	9358(9)	3802(8)	7951(7)	26(2)
C(13)	9546(10)	3815(9)	9036(8)	31(2)
C(14)	8300(12)	3797(10)	10048(8)	37(2)
C(15)	6887(13)	3692(14)	9996(8)	52(3)
C(16)	6703(12)	3639(12)	8943(8)	42(2)
C(17)	7127(8)	6192(7)	6548(7)	19(1)
C(18)	8388(9)	6880(8)	5744(8)	27(2)
C(19)	5476(9)	7013(8)	6693(7)	24(2)
C(20)	6840(30)	8770(17)	10076(16)	127(7)
Cl(1)	6052(2)	6795(2)	2520(2)	22(1)
Cl(2)	6620(50)	8170(30)	8960(20)	155(9)
Cl(2A)	7546(18)	7657(15)	8935(8)	105(5)
Cl(3)	7391(7)	10287(5)	9891(3)	100(2)
N(1)	7933(7)	2432(6)	6215(5)	17(1)
N(2)	7402(7)	4720(6)	6161(5)	16(1)

Table A13. Crystal data and structure refinement for Complex **3.2a**.

Identification code	Complex 3.2a	
Empirical formula	C ₁₆ H ₂₂ Au Cl N ₂	
Formula weight	474.77	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.8970(5) Å	α = 90°.
	b = 14.3233(7) Å	β = 98.869(3)°.
	c = 13.8846(7) Å	γ = 90°.
Volume	1748.22(16) Å ³	
Z	4	
Density (calculated)	1.804 Mg/m ³	
Absorption coefficient	8.561 mm ⁻¹	
F(000)	912	
Crystal size	0.24 x 0.20 x 0.10 mm ³	
Theta range for data collection	2.06 to 30.42°.	
Index ranges	-12 ≤ h ≤ 10, -20 ≤ k ≤ 18, -17 ≤ l ≤ 19	
Reflections collected	18540	
Independent reflections	5221 [R(int) = 0.0521]	
Completeness to theta = 30.42°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4815 and 0.2331	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5221 / 110 / 216	
Goodness-of-fit on F ²	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0522, wR2 = 0.1299	
R indices (all data)	R1 = 0.1442, wR2 = 0.1731	
Largest diff. peak and hole	1.025 and -2.480 e.Å ⁻³	

Table A14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **3.2a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Au(1)	2408(1)	10241(1)	7023(1)	47(1)
C(1)	3912(9)	9297(6)	6662(6)	36(2)
C(2)	5243(10)	9033(6)	7170(7)	40(2)
C(3)	4921(10)	8209(6)	5805(7)	42(2)
C(4)	5187(10)	7578(5)	5019(7)	41(2)
C(5)	5844(15)	7922(9)	4263(11)	88(4)
C(6)	6082(15)	7335(10)	3496(10)	88(4)
C(7)	5779(15)	6410(9)	3534(10)	78(4)
C(8)	5183(17)	6082(8)	4260(10)	81(4)
C(9)	4833(13)	6644(6)	5019(8)	63(3)
C(10)	7342(10)	7890(9)	6899(8)	64(3)
C(11)	2387(10)	8758(6)	5024(7)	45(2)
C(12)	984(11)	8449(8)	5427(8)	64(3)
C(13)	2263(15)	9728(8)	4507(9)	69(3)
C(14)	6100(30)	9358(18)	8132(13)	57(5)
C(15)	5520(50)	8820(20)	8930(20)	81(8)
C(16)	6070(50)	10403(17)	8260(30)	71(8)
C(14A)	5980(40)	9290(30)	8185(15)	58(6)
C(15A)	4950(50)	9150(40)	8940(30)	74(9)
C(16A)	6650(60)	10260(30)	8200(40)	75(10)
Cl(1)	772(4)	11328(2)	7485(2)	74(1)
N(1)	5859(8)	8360(5)	6631(6)	44(2)
N(2)	3695(8)	8766(5)	5810(5)	37(2)

Table A15. Crystal data and structure refinement for Complex **3.3a**.

Identification code	Complex 3.3a	
Empirical formula	C ₁₃ H ₁₆ Au Cl ₃ N ₂	
Formula weight	503.59	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0203(4) Å	α = 105.110(3)°.
	b = 9.4539(5) Å	β = 100.168(4)°.
	c = 10.6332(7) Å	γ = 92.556(3)°.
Volume	762.65(7) Å ³	
Z	2	
Density (calculated)	2.193 Mg/m ³	
Absorption coefficient	10.157 mm ⁻¹	
F(000)	476	
Crystal size	0.10 x 0.10 x 0.04 mm ³	
Theta range for data collection	2.96 to 29.00°.	
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	
Reflections collected	17617	
Independent reflections	3974 [R(int) = 0.0440]	
Completeness to theta = 29.00°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6868 and 0.4299	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3974 / 0 / 174	
Goodness-of-fit on F ²	1.103	
Final R indices [I > 2σ(I)]	R ₁ = 0.0450, wR ₂ = 0.1140	
R indices (all data)	R ₁ = 0.0554, wR ₂ = 0.1190	
Largest diff. peak and hole	3.621 and -3.042 e.Å ⁻³	

Table A16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **3.3a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	1525(1)	5801(1)	6428(1)	19(1)
C(1)	872(10)	3929(8)	6819(8)	17(1)
C(2)	-358(10)	2170(9)	7525(8)	20(2)
C(3)	919(10)	1579(9)	6928(9)	21(2)
C(4)	3113(10)	2486(9)	5818(9)	22(2)
C(5)	4623(11)	2031(10)	6673(10)	27(2)
C(6)	2567(11)	1381(10)	4464(9)	26(2)
C(7)	-1593(9)	4575(9)	7924(9)	21(2)
C(8)	-1930(10)	4654(10)	9159(9)	23(2)
C(9)	-3118(11)	5551(10)	9640(10)	28(2)
C(10)	-3959(11)	6381(10)	8868(10)	30(2)
C(11)	-3655(11)	6267(9)	7609(10)	28(2)
C(12)	-2449(10)	5358(9)	7118(9)	24(2)
C(13)	2266(14)	9530(15)	9354(12)	47(3)
Cl(1)	2466(3)	7930(2)	5997(2)	25(1)
Cl(2)	349(4)	8384(4)	8941(3)	55(1)
Cl(3)	3507(3)	9430(3)	10881(3)	42(1)
N(1)	-369(8)	3609(7)	7432(7)	19(1)
N(2)	1668(8)	2689(7)	6522(7)	18(1)

Table A17. Crystal data and structure refinement for Complex **3.3a'**.

Identification code	Complex 3.3a'	
Empirical formula	C _{24.50} H ₂₉ Au Cl F ₆ N ₄ P	
Formula weight	756.90	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.3450(4) Å	$\alpha = 90^\circ$.
	b = 21.6251(14) Å	$\beta = 90.791(3)^\circ$.
	c = 40.383(3) Å	$\gamma = 90^\circ$.
Volume	5540.5(6) Å ³	
Z	8	
Density (calculated)	1.815 Mg/m ³	
Absorption coefficient	5.527 mm ⁻¹	
F(000)	2952	
Crystal size	0.40 x 0.08 x 0.06 mm ³	
Theta range for data collection	2.69 to 35.12°.	
Index ranges	-10 ≤ h ≤ 9, -34 ≤ k ≤ 34, -65 ≤ l ≤ 65	
Reflections collected	101937	
Independent reflections	24297 [R(int) = 0.0311]	
Completeness to theta = 35.12°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7327 and 0.2159	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	24297 / 0 / 687	
Goodness-of-fit on F ²	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0293, wR2 = 0.0535	
R indices (all data)	R1 = 0.0435, wR2 = 0.0584	
Largest diff. peak and hole	3.276 and -2.895 e.Å ⁻³	

Table A18. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **3.3a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Au(1)	7402(1)	5755(1)	7479(1)	14(1)
Au(2)	5000	10000	5000	12(1)
Au(3)	5000	5000	5000	12(1)
C(1)	6663(4)	5190(1)	7860(1)	17(1)
C(2)	6665(5)	4430(1)	8243(1)	29(1)
C(3)	5247(5)	4853(1)	8333(1)	27(1)
C(4)	9189(4)	4334(1)	7781(1)	25(1)
C(5)	10837(5)	4079(1)	7970(1)	36(1)
C(6)	12472(6)	3793(2)	7810(1)	48(1)
C(7)	12485(6)	3764(1)	7471(1)	48(1)
C(8)	10837(7)	4012(2)	7281(1)	46(1)
C(9)	9160(5)	4297(1)	7440(1)	31(1)
C(10)	4012(4)	5890(1)	8114(1)	20(1)
C(11)	1668(4)	5749(2)	8093(1)	33(1)
C(12)	4618(5)	6243(1)	8426(1)	28(1)
C(13)	8069(4)	6349(1)	7110(1)	16(1)
C(14)	7876(4)	7175(1)	6769(1)	20(1)
C(15)	9282(4)	6775(1)	6641(1)	22(1)
C(16)	5629(4)	7178(1)	7275(1)	17(1)
C(17)	6061(4)	7218(1)	7613(1)	20(1)
C(18)	4537(5)	7454(1)	7823(1)	24(1)
C(19)	2615(4)	7653(1)	7692(1)	26(1)
C(20)	2221(4)	7625(1)	7355(1)	24(1)
C(21)	3721(4)	7388(1)	7142(1)	21(1)
C(22)	10629(4)	5704(1)	6796(1)	21(1)
C(23)	12920(5)	5859(2)	6747(1)	54(1)
C(24)	9702(6)	5350(2)	6507(1)	41(1)
C(25)	5675(3)	9263(1)	4716(1)	14(1)
C(26)	5522(4)	8550(1)	4307(1)	18(1)
C(27)	6954(4)	8360(1)	4535(1)	18(1)
C(28)	3174(4)	9484(1)	4259(1)	15(1)
C(29)	1304(4)	9208(1)	4150(1)	20(1)

C(30)	-258(4)	9577(1)	4007(1)	25(1)
C(31)	40(4)	10211(1)	3978(1)	25(1)
C(32)	1928(4)	10478(1)	4079(1)	22(1)
C(33)	3516(4)	10113(1)	4218(1)	17(1)
C(34)	8338(4)	8766(1)	5088(1)	17(1)
C(35)	7924(5)	8170(1)	5275(1)	29(1)
C(36)	10648(5)	8845(2)	5009(1)	34(1)
C(37)	3005(3)	5455(1)	4695(1)	14(1)
C(38)	561(4)	5669(1)	4302(1)	19(1)
C(39)	1295(4)	6211(1)	4422(1)	18(1)
C(40)	1354(4)	4562(1)	4412(1)	15(1)
C(41)	-643(4)	4304(1)	4431(1)	20(1)
C(42)	-922(4)	3682(1)	4358(1)	23(1)
C(43)	781(4)	3320(1)	4271(1)	22(1)
C(44)	2780(4)	3579(1)	4253(1)	23(1)
C(45)	3075(4)	4202(1)	4323(1)	20(1)
C(46)	4050(4)	6525(1)	4855(1)	19(1)
C(47)	2839(5)	7124(1)	4902(1)	26(1)
C(48)	6155(5)	6619(2)	4690(1)	34(1)
C(49)	5505(5)	3835(1)	6338(1)	29(1)
Cl(1)	4647(1)	4472(1)	6095(1)	31(1)
Cl(2)	5590(3)	4023(1)	6753(1)	77(1)
F(1)	10379(4)	7467(1)	9080(1)	42(1)
F(2)	7116(3)	7519(1)	8849(1)	42(1)
F(3)	8539(4)	7667(1)	8347(1)	43(1)
F(4)	11797(3)	7621(1)	8577(1)	43(1)
F(5)	9421(3)	8302(1)	8769(1)	27(1)
F(6)	9495(3)	6836(1)	8657(1)	30(1)
F(7)	6151(3)	1332(1)	4044(1)	41(1)
F(8)	3975(3)	2157(1)	4000(1)	32(1)
F(9)	6644(3)	2736(1)	3807(1)	32(1)
F(10)	8818(3)	1914(1)	3853(1)	56(1)
F(11)	5776(4)	1841(1)	3556(1)	46(1)
F(12)	6985(4)	2239(1)	4297(1)	47(1)
N(1)	7530(4)	4638(1)	7949(1)	21(1)
N(2)	5260(3)	5315(1)	8097(1)	19(1)
N(3)	7157(3)	6910(1)	7060(1)	16(1)
N(4)	9382(3)	6273(1)	6853(1)	18(1)

N(5)	4752(3)	9113(1)	4420(1)	15(1)
N(6)	7023(3)	8798(1)	4783(1)	15(1)
N(7)	1623(3)	5208(1)	4473(1)	15(1)
N(8)	2775(3)	6072(1)	4664(1)	14(1)
P(1)	9457(1)	7567(1)	8710(1)	18(1)
P(2)	6395(1)	2033(1)	3928(1)	20(1)

Table A19. Crystal data and structure refinement for Complex **4.3-cis-anti**.

Identification code	Complex 4.3-cis-anti	
Empirical formula	C ₂₅ H ₂₉ Cl ₃ I ₂ N ₄ Pd	
Formula weight	852.07	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7358(3) Å	α = 82.259(2)°.
	b = 11.5479(4) Å	β = 77.309(2)°.
	c = 14.0782(4) Å	γ = 77.719(2)°.
Volume	1502.34(8) Å ³	
Z	2	
Density (calculated)	1.884 Mg/m ³	
Absorption coefficient	2.960 mm ⁻¹	
F(000)	820	
Crystal size	0.36 x 0.12 x 0.02 mm ³	
Theta range for data collection	2.64 to 33.81°.	
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 18, -21 ≤ l ≤ 22	
Reflections collected	61179	
Independent reflections	11979 [R(int) = 0.0507]	
Completeness to theta = 33.81°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9432 and 0.4154	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11979 / 7 / 357	
Goodness-of-fit on F ²	1.099	
Final R indices [I > 2σ(I)]	R1 = 0.0362, wR2 = 0.0707	
R indices (all data)	R1 = 0.0676, wR2 = 0.1007	
Largest diff. peak and hole	1.667 and -2.829 e.Å ⁻³	

Table A20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.3-cis-anti**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(25)	4178(14)	3570(9)	2703(11)	45(3)
Cl(1)	4060(5)	4926(4)	1974(7)	80(2)
Cl(2)	2668(9)	2956(8)	2755(7)	70(2)
Cl(3)	4386(6)	3765(5)	3875(5)	78(1)
C(25A)	4080(30)	3512(19)	2948(17)	64(11)
Cl(1A)	3829(13)	5017(10)	2533(19)	108(5)
Cl(2A)	2800(20)	2871(15)	2626(14)	66(4)
Cl(3A)	3880(20)	3270(20)	4221(11)	112(7)
Pd(1)	-1158(1)	1948(1)	2254(1)	19(1)
C(1)	-130(4)	1596(3)	3386(3)	22(1)
C(2)	-1747(5)	3137(4)	4435(3)	30(1)
C(3)	-2905(6)	2762(5)	5264(4)	41(1)
C(4)	-1178(7)	4170(4)	4676(4)	45(1)
C(5)	352(5)	1640(4)	4876(3)	33(1)
C(6)	1326(5)	779(4)	4458(3)	30(1)
C(7)	1903(4)	-120(3)	2903(3)	25(1)
C(8)	3377(4)	-332(4)	2818(3)	31(1)
C(9)	4231(5)	-1219(4)	2269(4)	38(1)
C(10)	3626(5)	-1891(4)	1801(3)	38(1)
C(11)	2152(5)	-1683(4)	1871(3)	33(1)
C(12)	1279(5)	-794(4)	2434(3)	28(1)
C(13)	181(4)	2963(3)	1434(3)	23(1)
C(14)	1670(5)	1373(4)	366(3)	35(1)
C(15)	3249(5)	906(5)	334(4)	48(1)
C(16)	1287(7)	1347(5)	-619(4)	52(1)
C(17)	1913(5)	3520(4)	209(3)	37(1)
C(18)	1250(5)	4491(4)	658(3)	35(1)
C(19)	-749(4)	5003(3)	2035(3)	26(1)
C(20)	-144(5)	5846(4)	2351(4)	36(1)
C(21)	-1016(6)	6730(4)	2889(4)	43(1)
C(22)	-2478(7)	6799(4)	3126(4)	44(1)
C(23)	-3078(5)	5957(4)	2814(4)	39(1)

C(24)	-2213(5)	5066(4)	2261(3)	30(1)
I(1)	-2630(1)	2468(1)	815(1)	34(1)
I(2)	-2921(1)	531(1)	3243(1)	30(1)
N(1)	-545(4)	2143(3)	4224(2)	26(1)
N(2)	1044(3)	741(3)	3533(2)	22(1)
N(3)	1257(4)	2587(3)	682(3)	29(1)
N(4)	178(3)	4159(3)	1415(2)	25(1)

Table A21. Crystal data and structure refinement for Complex **4.4-trans**.

Identification code	Complex 4.4-trans	
Empirical formula	C ₂₄ H ₂₈ Br ₂ N ₄ Pd	
Formula weight	638.72	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 19.6103(8) Å	$\alpha = 90^\circ$.
	b = 8.4013(3) Å	$\beta = 90^\circ$.
	c = 15.1154(7) Å	$\gamma = 90^\circ$.
Volume	2490.29(18) Å ³	
Z	4	
Density (calculated)	1.704 Mg/m ³	
Absorption coefficient	3.973 mm ⁻¹	
F(000)	1264	
Crystal size	0.40 x 0.20 x 0.10 mm ³	
Theta range for data collection	2.96 to 31.18°.	
Index ranges	-28 ≤ h ≤ 28, -9 ≤ k ≤ 12, -17 ≤ l ≤ 21	
Reflections collected	21434	
Independent reflections	6339 [R(int) = 0.0342]	
Completeness to theta = 31.18°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6921 and 0.2995	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6339 / 1 / 285	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0343, wR2 = 0.0745	
R indices (all data)	R1 = 0.0424, wR2 = 0.0775	
Absolute structure parameter	0.218(7)	
Largest diff. peak and hole	3.822 and -0.938 e.Å ⁻³	

Table A22. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.4-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	8741(1)	175(1)	8603(1)	12(1)
Br(1)	9536(1)	1244(1)	7520(1)	18(1)
Br(2)	7951(1)	-833(1)	9724(1)	20(1)
C(1)	8870(2)	-2016(5)	8058(3)	14(1)
C(2)	7859(2)	-1856(5)	7076(3)	18(1)
C(3)	7243(2)	-2937(6)	7045(4)	35(1)
C(4)	8044(3)	-1221(7)	6172(3)	38(1)
C(5)	8701(2)	-4138(5)	7180(3)	19(1)
C(6)	9277(2)	-4410(5)	7627(3)	18(1)
C(7)	9966(2)	-2874(4)	8722(3)	16(1)
C(8)	10596(2)	-3456(5)	8438(3)	22(1)
C(9)	11166(2)	-3307(6)	8980(3)	26(1)
C(10)	11105(2)	-2581(5)	9800(4)	28(1)
C(11)	10477(2)	-2015(5)	10076(3)	25(1)
C(12)	9900(2)	-2162(5)	9538(3)	20(1)
C(13)	8623(2)	2381(5)	9114(3)	13(1)
C(14)	9662(2)	2261(5)	10071(3)	15(1)
C(15)	10297(2)	3294(6)	9917(4)	31(1)
C(16)	9548(2)	1879(7)	11033(3)	34(1)
C(17)	8831(2)	4579(5)	9925(3)	18(1)
C(18)	8252(2)	4851(5)	9473(3)	15(1)
C(19)	7549(2)	3270(5)	8415(3)	18(1)
C(20)	6917(2)	3841(5)	8706(3)	24(1)
C(21)	6356(2)	3711(6)	8153(3)	31(1)
C(22)	6415(2)	2988(6)	7335(3)	29(1)
C(23)	7052(2)	2436(6)	7057(3)	26(1)
C(24)	7615(2)	2578(5)	7594(3)	20(1)
N(1)	8454(2)	-2676(4)	7456(2)	15(1)
N(2)	9383(2)	-3079(4)	8156(2)	15(1)
N(3)	9052(2)	3059(4)	9699(2)	15(1)
N(4)	8128(2)	3468(4)	8982(2)	14(1)

Table A23. Crystal data and structure refinement for Complex **4.4-cis**.

Identification code	Complex 4.4-cis	
Empirical formula	C ₂₄ H ₂₈ Br ₂ N ₄ Pd	
Formula weight	638.72	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9083(3) Å	α = 65.464(2)°.
	b = 11.4015(4) Å	β = 76.392(2)°.
	c = 12.2913(4) Å	γ = 70.034(2)°.
Volume	1180.12(7) Å ³	
Z	2	
Density (calculated)	1.797 Mg/m ³	
Absorption coefficient	4.191 mm ⁻¹	
F(000)	632	
Crystal size	0.40 x 0.28 x 0.20 mm ³	
Theta range for data collection	1.83 to 35.24°.	
Index ranges	-16 ≤ h ≤ 15, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	
Reflections collected	28784	
Independent reflections	10484 [R(int) = 0.0330]	
Completeness to theta = 35.24°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4878 and 0.2849	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10484 / 0 / 284	
Goodness-of-fit on F ²	1.103	
Final R indices [I > 2σ(I)]	R1 = 0.0402, wR2 = 0.1195	
R indices (all data)	R1 = 0.0553, wR2 = 0.1337	
Largest diff. peak and hole	1.977 and -2.345 e.Å ⁻³	

Table A24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.4-cis**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2640(1)	2880(1)	3335(1)	6(1)
Br(1)	4554(1)	3834(1)	3331(1)	16(1)
Br(2)	2218(1)	1898(1)	5570(1)	18(1)
C(1)	3158(3)	3484(3)	1563(2)	9(1)
C(2)	3474(3)	4698(3)	-435(2)	13(1)
C(3)	4534(3)	3543(3)	-204(2)	14(1)
C(4)	1432(3)	5765(3)	734(2)	10(1)
C(5)	1281(3)	6280(3)	1616(2)	11(1)
C(6)	165(3)	7416(3)	1620(3)	16(1)
C(7)	-791(4)	8040(3)	742(3)	19(1)
C(8)	-636(4)	7513(3)	-126(3)	18(1)
C(9)	477(3)	6375(3)	-142(3)	14(1)
C(10)	5291(3)	1476(3)	1620(3)	11(1)
C(11)	6806(4)	1559(3)	1576(3)	18(1)
C(12)	5300(4)	521(3)	1043(3)	17(1)
C(13)	929(3)	2328(3)	3355(2)	9(1)
C(14)	-623(3)	1161(3)	3539(3)	13(1)
C(15)	-1408(3)	2329(3)	3664(3)	12(1)
C(16)	1968(3)	53(3)	3200(2)	9(1)
C(17)	1792(3)	-553(3)	2477(3)	12(1)
C(18)	2847(3)	-1696(3)	2392(3)	16(1)
C(19)	4059(3)	-2228(3)	3006(3)	18(1)
C(20)	4216(3)	-1613(3)	3718(3)	16(1)
C(21)	3171(3)	-474(3)	3829(3)	12(1)
C(22)	-909(3)	4321(3)	3732(2)	11(1)
C(23)	-1491(4)	4117(4)	5037(3)	20(1)
C(24)	-2025(4)	5349(3)	2885(3)	17(1)
N(1)	2623(3)	4657(2)	650(2)	9(1)
N(2)	4327(3)	2810(2)	1018(2)	10(1)
N(3)	823(3)	1168(2)	3345(2)	9(1)
N(4)	-447(3)	3032(2)	3543(2)	9(1)

Table A25. Crystal data and structure refinement for Complex **4.5-trans**.

Identification code	Complex 4.5-trans	
Empirical formula	C ₁₈ H ₃₂ I ₂ N ₄ Pd	
Formula weight	664.68	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.7933(3) Å	α = 90°.
	b = 9.8613(2) Å	β = 103.5080(10)°.
	c = 16.8320(3) Å	γ = 90°.
Volume	2387.55(8) Å ³	
Z	4	
Density (calculated)	1.849 Mg/m ³	
Absorption coefficient	3.372 mm ⁻¹	
F(000)	1280	
Crystal size	0.40 x 0.38 x 0.38 mm ³	
Theta range for data collection	2.50 to 36.44°.	
Index ranges	-24 ≤ h ≤ 24, -11 ≤ k ≤ 16, -27 ≤ l ≤ 28	
Reflections collected	24734	
Independent reflections	5809 [R(int) = 0.0249]	
Completeness to theta = 36.44°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3606 and 0.3457	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5809 / 0 / 119	
Goodness-of-fit on F ²	1.119	
Final R indices [I > 2σ(I)]	R1 = 0.0234, wR2 = 0.0518	
R indices (all data)	R1 = 0.0278, wR2 = 0.0532	
Largest diff. peak and hole	1.152 and -1.114 e.Å ⁻³	

Table A26. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.5-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2500	7500	5000	11(1)
C(1)	3193(1)	6771(2)	4180(1)	13(1)
C(2)	3559(1)	5700(2)	3115(1)	17(1)
C(3)	4334(1)	6318(2)	3536(1)	17(1)
C(4)	4746(1)	7758(2)	4817(1)	17(1)
C(5)	5327(1)	6803(2)	5448(1)	28(1)
C(6)	5340(2)	8676(2)	4427(1)	32(1)
C(7)	1895(1)	5535(2)	3248(1)	20(1)
C(8)	1395(1)	6428(2)	2543(1)	29(1)
C(9)	1850(2)	4041(2)	3016(1)	30(1)
I(1)	2204(1)	9793(1)	4214(1)	19(1)
N(1)	4098(1)	6977(1)	4188(1)	14(1)
N(2)	2867(1)	5979(1)	3523(1)	15(1)

Table A27. Crystal data and structure refinement for Complex **4.5-cis-anti**.

Identification code	Complex 4.5-cis-anti	
Empirical formula	C ₁₈ H ₃₂ I ₂ N ₄ Pd	
Formula weight	664.68	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.9093(6) Å	α = 90°.
	b = 13.4953(7) Å	β = 124.472(2)°.
	c = 17.4928(7) Å	γ = 90°.
Volume	2317.75(19) Å ³	
Z	4	
Density (calculated)	1.905 Mg/m ³	
Absorption coefficient	3.473 mm ⁻¹	
F(000)	1280	
Crystal size	0.30 x 0.22 x 0.18 mm ³	
Theta range for data collection	2.07 to 31.01°.	
Index ranges	-17 ≤ h ≤ 17, -19 ≤ k ≤ 17, -25 ≤ l ≤ 25	
Reflections collected	29525	
Independent reflections	7333 [R(int) = 0.0348]	
Completeness to theta = 31.01°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5737 and 0.4222	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7333 / 0 / 234	
Goodness-of-fit on F ²	1.074	
Final R indices [I > 2σ(I)]	R1 = 0.0240, wR2 = 0.0468	
R indices (all data)	R1 = 0.0288, wR2 = 0.0484	
Largest diff. peak and hole	0.561 and -0.875 e.Å ⁻³	

Table A28. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.5-cis-anti**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	2833(1)	7811(1)	7271(1)	8(1)
C(1)	1177(2)	7644(2)	5966(1)	11(1)
C(2)	-505(2)	8682(2)	6046(2)	16(1)
C(3)	-1440(2)	9484(2)	5377(2)	27(1)
C(4)	-1172(3)	8121(2)	6444(2)	29(1)
C(5)	-1003(2)	7564(2)	4726(2)	18(1)
C(6)	-267(2)	6959(2)	4565(2)	17(1)
C(7)	2187(2)	6427(2)	5422(2)	17(1)
C(8)	2388(3)	6706(2)	4665(2)	27(1)
C(9)	1932(2)	5326(2)	5427(2)	24(1)
C(10)	3432(2)	9130(2)	7083(1)	9(1)
C(11)	4845(2)	8595(2)	6494(1)	13(1)
C(12)	4663(3)	8922(2)	5600(2)	22(1)
C(13)	6352(2)	8457(2)	7274(2)	17(1)
C(14)	4578(2)	10327(2)	6899(1)	13(1)
C(15)	3953(2)	10754(2)	7258(1)	13(1)
C(16)	2518(2)	10181(2)	7806(1)	14(1)
C(17)	1332(2)	10899(2)	7222(2)	19(1)
C(18)	3487(2)	10549(2)	8798(2)	21(1)
I(1)	1971(1)	6179(1)	7651(1)	15(1)
I(2)	5122(1)	7901(1)	8955(1)	12(1)
N(1)	-103(2)	7993(1)	5584(1)	13(1)
N(2)	1071(2)	7015(1)	5325(1)	13(1)
N(3)	4240(2)	9331(1)	6788(1)	10(1)
N(4)	3251(2)	10015(1)	7369(1)	11(1)

Table A29. Crystal data and structure refinement for Complex **4.6-trans**.

Identification code	Complex 4.6-trans	
Empirical formula	C ₂₄ H ₂₆ F ₂ I ₂ N ₄ Pd	
Formula weight	768.69	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.5956(4) Å	α = 90°.
	b = 10.0821(4) Å	β = 116.962(2)°.
	c = 17.0428(7) Å	γ = 90°.
Volume	1316.42(10) Å ³	
Z	2	
Density (calculated)	1.939 Mg/m ³	
Absorption coefficient	3.083 mm ⁻¹	
F(000)	736	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	3.12 to 35.08°.	
Index ranges	-13 ≤ h ≤ 10, -16 ≤ k ≤ 16, -25 ≤ l ≤ 27	
Reflections collected	27935	
Independent reflections	5816 [R(int) = 0.0308]	
Completeness to theta = 35.08°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4582 and 0.3719	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5816 / 0 / 153	
Goodness-of-fit on F ²	1.154	
Final R indices [I > 2σ(I)]	R1 = 0.0242, wR2 = 0.0569	
R indices (all data)	R1 = 0.0273, wR2 = 0.0580	
Largest diff. peak and hole	0.569 and -1.569 e.Å ⁻³	

Table A30. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.6-trans**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	11815(1)	6985(1)	5968(1)	14(1)
Pd(1)	10000	5000	5000	8(1)
F(1)	5547(2)	10168(1)	2926(1)	23(1)
N(1)	7126(2)	6162(1)	5376(1)	11(1)
N(2)	8316(2)	4461(1)	6184(1)	11(1)
C(1)	8353(2)	5210(2)	5537(1)	10(1)
C(2)	6332(2)	6002(2)	5924(1)	13(1)
C(3)	7092(2)	4936(2)	6436(1)	14(1)
C(4)	9448(2)	3304(2)	6570(1)	13(1)
C(5)	8374(3)	2085(2)	6500(2)	25(1)
C(6)	10783(3)	3594(2)	7512(1)	23(1)
C(7)	6733(2)	7198(2)	4742(1)	11(1)
C(8)	6447(2)	6891(2)	3891(1)	12(1)
C(9)	6047(2)	7904(2)	3271(1)	15(1)
C(10)	5960(2)	9184(2)	3532(1)	15(1)
C(11)	6252(2)	9513(2)	4373(1)	16(1)
C(12)	6648(2)	8498(2)	4988(1)	15(1)

Table A31. Crystal data and structure refinement for Complex **4.6-cis-anti**.

Identification code	Complex 4.6-cis-anti	
Empirical formula	C ₂₅ H ₂₈ Cl ₂ F ₂ I ₂ N ₄ Pd	
Formula weight	853.61	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6311(3) Å	α = 83.513(2)°.
	b = 11.5508(4) Å	β = 78.0390(10)°.
	c = 13.8932(4) Å	γ = 77.4340(10)°.
Volume	1472.07(8) Å ³	
Z	2	
Density (calculated)	1.926 Mg/m ³	
Absorption coefficient	2.943 mm ⁻¹	
F(000)	820	
Crystal size	0.30 x 0.30 x 0.26 mm ³	
Theta range for data collection	2.68 to 27.00°.	
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	
Reflections collected	29133	
Independent reflections	6379 [R(int) = 0.0322]	
Completeness to theta = 27.00°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5150 and 0.4722	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6379 / 0 / 329	
Goodness-of-fit on F ²	1.071	
Final R indices [I > 2σ(I)]	R1 = 0.0208, wR2 = 0.0467	
R indices (all data)	R1 = 0.0234, wR2 = 0.0477	
Largest diff. peak and hole	0.984 and -0.839 e.Å ⁻³	

Table A32. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.6-cis-anti**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	6181(1)	7969(1)	2795(1)	12(1)
C(1)	4771(3)	7008(2)	3597(2)	15(1)
C(2)	3625(3)	5528(2)	4334(2)	22(1)
C(3)	2972(3)	6519(2)	4789(2)	21(1)
C(4)	3304(3)	8633(2)	4684(2)	20(1)
C(5)	1733(3)	9175(2)	4655(2)	26(1)
C(6)	3617(3)	8599(3)	5715(2)	29(1)
C(7)	5698(3)	4971(2)	2976(2)	16(1)
C(8)	5118(3)	4141(2)	2618(2)	22(1)
C(9)	6033(3)	3268(2)	2052(2)	24(1)
C(10)	7500(3)	3255(2)	1844(2)	21(1)
C(11)	8092(3)	4053(2)	2204(2)	20(1)
C(12)	7187(3)	4914(2)	2790(2)	17(1)
C(13)	5277(3)	8250(2)	1584(2)	15(1)
C(14)	3959(3)	9034(2)	405(2)	23(1)
C(15)	5023(3)	8174(2)	15(2)	23(1)
C(16)	7107(3)	6725(2)	559(2)	22(1)
C(17)	8317(3)	7147(3)	-190(2)	34(1)
C(18)	6686(4)	5662(3)	230(2)	31(1)
C(19)	3167(3)	9950(2)	1996(2)	17(1)
C(20)	1689(3)	10113(2)	2026(2)	20(1)
C(21)	746(3)	11005(2)	2559(2)	22(1)
C(22)	1320(3)	11705(2)	3041(2)	20(1)
C(23)	2782(3)	11560(2)	3030(2)	18(1)
C(24)	3724(3)	10665(2)	2490(2)	17(1)
C(25)	1105(3)	6604(3)	2608(2)	34(1)
Cl(1)	971(1)	5100(1)	2932(1)	42(1)
Cl(2)	2386(1)	6758(1)	1538(1)	55(1)
F(1)	8378(2)	2431(1)	1252(1)	30(1)
F(2)	397(2)	12583(1)	3574(1)	26(1)
I(1)	7968(1)	9346(1)	1831(1)	18(1)
I(2)	7553(1)	7543(1)	4312(1)	18(1)

N(1)	4736(2)	5837(2)	3597(2)	16(1)
N(2)	3676(2)	7422(2)	4335(2)	16(1)
N(3)	4116(2)	9079(2)	1370(2)	16(1)
N(4)	5819(2)	7697(2)	737(1)	17(1)

Table A33. Crystal data and structure refinement for Complex **4.7-trans**.

Identification code	Complex 4.7-trans	
Empirical formula	C ₂₆ H ₃₂ I ₂ N ₄ O ₂ Pd	
Formula weight	792.76	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.4235(3) Å	α = 90°.
	b = 9.5373(3) Å	β = 100.6170(10)°.
	c = 16.0536(5) Å	γ = 90°.
Volume	1418.11(8) Å ³	
Z	2	
Density (calculated)	1.857 Mg/m ³	
Absorption coefficient	2.860 mm ⁻¹	
F(000)	768	
Crystal size	0.24 x 0.16 x 0.14 mm ³	
Theta range for data collection	3.07 to 36.45°.	
Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 15, -26 ≤ l ≤ 26	
Reflections collected	33649	
Independent reflections	6913 [R(int) = 0.0358]	
Completeness to theta = 36.45°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6902 and 0.5468	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6913 / 0 / 163	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0216, wR2 = 0.0462	
R indices (all data)	R1 = 0.0286, wR2 = 0.0488	
Largest diff. peak and hole	0.727 and -1.074 e.Å ⁻³	

Table A34. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.7-trans**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	10000	10000	0	10(1)
C(1)	8674(1)	9968(1)	857(1)	12(1)
C(2)	7576(1)	10704(2)	1916(1)	17(1)
C(3)	6793(1)	9621(2)	1529(1)	17(1)
C(4)	9810(1)	12033(1)	1646(1)	16(1)
C(5)	9078(2)	13450(2)	1451(1)	25(1)
C(6)	10689(2)	11956(2)	2537(1)	24(1)
C(7)	7030(1)	8026(1)	312(1)	14(1)
C(8)	5591(1)	7888(2)	-64(1)	18(1)
C(9)	5150(1)	6793(2)	-630(1)	20(1)
C(10)	6168(1)	5843(2)	-825(1)	17(1)
C(11)	7613(1)	5971(2)	-431(1)	17(1)
C(12)	8047(1)	7050(2)	137(1)	16(1)
C(13)	4395(2)	4533(2)	-1766(1)	26(1)
I(1)	12072(1)	8672(1)	1013(1)	18(1)
N(1)	8727(1)	10896(1)	1495(1)	13(1)
N(2)	7489(1)	9165(1)	882(1)	14(1)
O(1)	5872(1)	4760(1)	-1388(1)	22(1)

Table A35. Crystal data and structure refinement for Complex **4.7-cis-anti**.

Identification code	Complex 4.7-cis-anti	
Empirical formula	C ₂₆ H ₃₂ I ₂ N ₄ O ₂ Pd	
Formula weight	792.76	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1751(3) Å	α = 65.0450(10)°.
	b = 12.5107(3) Å	β = 78.5960(10)°.
	c = 12.6110(3) Å	γ = 77.418(2)°.
Volume	1410.33(6) Å ³	
Z	2	
Density (calculated)	1.867 Mg/m ³	
Absorption coefficient	2.876 mm ⁻¹	
F(000)	768	
Crystal size	0.40 x 0.30 x 0.04 mm ³	
Theta range for data collection	2.57 to 26.00°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15	
Reflections collected	26951	
Independent reflections	5421 [R(int) = 0.0274]	
Completeness to theta = 26.00°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8936 and 0.3925	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5421 / 7 / 333	
Goodness-of-fit on F ²	1.235	
Final R indices [I > 2σ(I)]	R1 = 0.0310, wR2 = 0.0695	
R indices (all data)	R1 = 0.0388, wR2 = 0.0752	
Largest diff. peak and hole	1.333 and -1.245 e.Å ⁻³	

Table A36. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.7-cis-anti**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2839(1)	2751(1)	3356(1)	12(1)
C(1)	3372(5)	3368(4)	1602(4)	14(1)
C(2)	3729(5)	4493(5)	-348(4)	21(1)
C(3)	4596(5)	3489(5)	-138(4)	20(1)
C(4)	1940(5)	5388(4)	766(4)	14(1)
C(5)	1853(5)	5883(4)	1575(4)	19(1)
C(6)	884(5)	6879(5)	1518(4)	22(1)
C(7)	20(5)	7370(5)	648(5)	24(1)
C(8)	98(6)	6864(5)	-152(5)	25(1)
C(9)	1050(5)	5882(5)	-90(4)	22(1)
C(10)	-890(50)	9100(40)	1040(40)	32(7)
C(10A)	-1190(40)	8820(40)	1340(40)	51(7)
C(11)	5186(5)	1623(4)	1633(4)	20(1)
C(12)	6632(5)	1770(5)	1621(5)	24(1)
C(13)	5132(6)	817(5)	1023(5)	28(1)
C(14)	1089(5)	2253(4)	3359(4)	14(1)
C(15)	-548(5)	1223(5)	3485(4)	20(1)
C(16)	-1164(5)	2197(5)	3677(4)	20(1)
C(17)	1790(5)	337(4)	3046(4)	15(1)
C(18)	2862(5)	-282(4)	3699(4)	16(1)
C(19)	3707(5)	-1233(4)	3496(4)	18(1)
C(20)	3457(5)	-1561(4)	2639(4)	17(1)
C(21)	2374(5)	-941(4)	1987(4)	18(1)
C(22)	1541(5)	4(4)	2194(4)	17(1)
C(23)	5389(6)	-3082(5)	2942(5)	31(1)
C(24)	-438(5)	3922(4)	3838(4)	19(1)
C(25)	-1100(6)	3649(5)	5102(5)	32(1)
C(26)	-1330(5)	4893(5)	2958(5)	24(1)
I(1)	4878(1)	3677(1)	3492(1)	19(1)
I(2)	2434(1)	1650(1)	5676(1)	25(1)
N(1)	2964(4)	4426(4)	713(3)	16(1)
N(2)	4366(4)	2802(4)	1065(3)	16(1)

N(3)	839(4)	1261(3)	3290(3)	15(1)
N(4)	-153(4)	2825(3)	3602(3)	15(1)
O(1)	-960(4)	8345(4)	508(4)	35(1)
O(2)	4219(3)	-2462(3)	2350(3)	22(1)

Table A37. Crystal data and structure refinement for Complex **4.8-trans**.

Identification code	Complex 4.8-trans	
Empirical formula	C ₂₆ H ₃₂ I ₂ N ₄ Pd	
Formula weight	760.76	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.3595(3) Å	α = 90°.
	b = 9.5710(3) Å	β = 103.494(2)°.
	c = 16.2228(6) Å	γ = 90°.
Volume	1413.12(8) Å ³	
Z	2	
Density (calculated)	1.788 Mg/m ³	
Absorption coefficient	2.861 mm ⁻¹	
F(000)	736	
Crystal size	0.40 x 0.30 x 0.28 mm ³	
Theta range for data collection	3.09 to 42.43°.	
Index ranges	-17 ≤ h ≤ 17, -16 ≤ k ≤ 17, -29 ≤ l ≤ 30	
Reflections collected	38328	
Independent reflections	9916 [R(int) = 0.0329]	
Completeness to theta = 42.43°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5013 and 0.3940	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9916 / 0 / 154	
Goodness-of-fit on F ²	1.042	
Final R indices [I > 2σ(I)]	R1 = 0.0276, wR2 = 0.0565	
R indices (all data)	R1 = 0.0389, wR2 = 0.0600	
Largest diff. peak and hole	1.170 and -1.130 e.Å ⁻³	

Table A38. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.8-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	10000	0	0	10(1)
C(1)	8726(1)	-81(1)	846(1)	12(1)
C(2)	10064(1)	-2089(1)	1644(1)	16(1)
C(3)	9408(2)	-3539(2)	1461(1)	29(1)
C(4)	10991(2)	-1946(2)	2540(1)	28(1)
C(5)	7780(1)	-888(1)	1913(1)	17(1)
C(6)	6911(1)	165(1)	1541(1)	16(1)
C(7)	6906(1)	1792(1)	335(1)	13(1)
C(8)	5399(1)	1890(1)	39(1)	19(1)
C(9)	4810(2)	2970(1)	-506(1)	22(1)
C(10)	5703(2)	3957(1)	-774(1)	20(1)
C(11)	5032(2)	5087(2)	-1394(1)	29(1)
C(12)	7212(2)	3857(1)	-454(1)	18(1)
C(13)	7823(1)	2789(1)	104(1)	16(1)
I(1)	12038(1)	1373(1)	1075(1)	18(1)
N(1)	8888(1)	-1023(1)	1480(1)	14(1)
N(2)	7512(1)	667(1)	890(1)	13(1)

Table A39. Crystal data and structure refinement for Complex **4.9-trans**.

Identification code	Complex 4.9-trans	
Empirical formula	C ₃₀ H ₂₄ I ₂ N ₄ Pd	
Formula weight	800.73	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.5320(3) Å	α = 90°.
	b = 20.0344(6) Å	β = 114.4590(10)°.
	c = 8.9173(3) Å	γ = 90°.
Volume	1387.47(8) Å ³	
Z	2	
Density (calculated)	1.917 Mg/m ³	
Absorption coefficient	2.920 mm ⁻¹	
F(000)	768	
Crystal size	0.40 x 0.30 x 0.30 mm ³	
Theta range for data collection	2.71 to 38.53°.	
Index ranges	-14 ≤ h ≤ 14, -35 ≤ k ≤ 34, -15 ≤ l ≤ 15	
Reflections collected	38030	
Independent reflections	7759 [R(int) = 0.0314]	
Completeness to theta = 38.53°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4745 and 0.3880	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7759 / 0 / 169	
Goodness-of-fit on F ²	1.096	
Final R indices [I > 2σ(I)]	R1 = 0.0262, wR2 = 0.0575	
R indices (all data)	R1 = 0.0327, wR2 = 0.0595	
Largest diff. peak and hole	1.110 and -1.586 e.Å ⁻³	

Table A40. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.9-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5000	0	5000	10(1)
C(1)	7551(2)	154(1)	5694(2)	12(1)
C(2)	10079(2)	698(1)	6340(2)	18(1)
C(3)	10444(2)	129(1)	7206(2)	18(1)
C(4)	7424(2)	1249(1)	4334(2)	15(1)
C(5)	6344(2)	1127(1)	2699(2)	18(1)
C(6)	5552(2)	1664(1)	1667(2)	21(1)
C(7)	5851(2)	2312(1)	2280(2)	20(1)
C(8)	6916(2)	2427(1)	3913(2)	21(1)
C(9)	7715(2)	1896(1)	4956(2)	18(1)
C(10)	8757(2)	-841(1)	7466(2)	16(1)
C(11)	9624(2)	-942(1)	9143(2)	23(1)
C(12)	9541(3)	-1563(1)	9804(2)	29(1)
C(13)	8608(2)	-2079(1)	8789(2)	24(1)
C(14)	7747(2)	-1974(1)	7111(2)	21(1)
C(15)	7817(2)	-1354(1)	6434(2)	17(1)
I(1)	5429(1)	643(1)	7717(1)	16(1)
N(1)	8303(2)	707(1)	5406(2)	14(1)
N(2)	8887(2)	-207(1)	6785(2)	14(1)

Table A41. Crystal data and structure refinement for Complex **4.9-cis**.

Identification code	Complex 4.9-cis	
Empirical formula	C ₃₀ H ₂₄ I ₂ N ₄ Pd	
Formula weight	800.73	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.1334(4) Å	α = 90°.
	b = 15.3484(6) Å	β = 94.548(2)°.
	c = 16.7306(7) Å	γ = 90°.
Volume	2849.92(19) Å ³	
Z	4	
Density (calculated)	1.866 Mg/m ³	
Absorption coefficient	2.843 mm ⁻¹	
F(000)	1536	
Crystal size	0.40 x 0.36 x 0.18 mm ³	
Theta range for data collection	1.80 to 31.06°.	
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 22, -24 ≤ l ≤ 23	
Reflections collected	42779	
Independent reflections	9096 [R(int) = 0.0346]	
Completeness to theta = 31.06°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6286 and 0.3959	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9096 / 0 / 334	
Goodness-of-fit on F ²	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0251, wR2 = 0.0575	
R indices (all data)	R1 = 0.0319, wR2 = 0.0599	
Largest diff. peak and hole	1.224 and -0.792 e.Å ⁻³	

Table A42. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.9-cis**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	7884(1)	3159(1)	2645(1)	11(1)
C(1)	8952(2)	4198(1)	2720(1)	14(1)
C(2)	8116(2)	5071(1)	3794(1)	16(1)
C(3)	8444(2)	4785(1)	4562(1)	20(1)
C(4)	7683(2)	4952(2)	5165(2)	24(1)
C(5)	6609(2)	5393(2)	4985(2)	26(1)
C(6)	6289(2)	5670(2)	4214(2)	24(1)
C(7)	7050(2)	5519(1)	3610(1)	19(1)
C(8)	9876(2)	5478(1)	3042(1)	20(1)
C(9)	10498(2)	5094(1)	2486(1)	19(1)
C(10)	10375(2)	3687(1)	1746(1)	16(1)
C(11)	11602(2)	3526(2)	1790(2)	23(1)
C(12)	12053(2)	2916(2)	1281(2)	29(1)
C(13)	11297(2)	2472(2)	735(2)	26(1)
C(14)	10067(2)	2640(2)	692(1)	23(1)
C(15)	9601(2)	3252(1)	1198(1)	18(1)
C(16)	6440(2)	3892(1)	2317(1)	14(1)
C(17)	5152(2)	3401(1)	3395(1)	16(1)
C(18)	5945(2)	3361(1)	4068(1)	18(1)
C(19)	5627(2)	2887(2)	4730(2)	23(1)
C(20)	4524(2)	2466(2)	4704(2)	26(1)
C(21)	3741(2)	2503(2)	4026(2)	27(1)
C(22)	4049(2)	2969(2)	3359(2)	22(1)
C(23)	4633(2)	4549(1)	2395(2)	21(1)
C(24)	5140(2)	4909(1)	1775(2)	22(1)
C(25)	6989(2)	4639(1)	1076(1)	16(1)
C(26)	6783(2)	4121(1)	405(1)	22(1)
C(27)	7465(2)	4244(2)	-248(2)	26(1)
C(28)	8334(2)	4892(2)	-217(2)	27(1)
C(29)	8522(2)	5421(2)	453(2)	25(1)
C(30)	7844(2)	5295(1)	1112(1)	19(1)
I(1)	9719(1)	2343(1)	3418(1)	18(1)

I(2)	6617(1)	1734(1)	2255(1)	20(1)
N(1)	8929(2)	4921(1)	3178(1)	15(1)
N(2)	9929(2)	4310(1)	2287(1)	14(1)
N(3)	5424(2)	3924(1)	2720(1)	15(1)
N(4)	6247(2)	4496(1)	1732(1)	16(1)

Table A43. Crystal data and structure refinement for Complex **4.10-trans**.

Identification code	Complex 4.10-trans	
Empirical formula	C ₂₄ H ₁₈ F ₁₀ I ₂ N ₄ Pd	
Formula weight	912.62	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 7.75440(10) Å	α = 90°.
	b = 16.6035(3) Å	β = 109.2170(10)°.
	c = 11.6572(2) Å	γ = 90°.
Volume	1417.24(4) Å ³	
Z	2	
Density (calculated)	2.139 Mg/m ³	
Absorption coefficient	2.921 mm ⁻¹	
F(000)	864	
Crystal size	0.40 x 0.32 x 0.26 mm ³	
Theta range for data collection	3.07 to 35.04°.	
Index ranges	-6 ≤ h ≤ 12, -26 ≤ k ≤ 26, -18 ≤ l ≤ 18	
Reflections collected	24429	
Independent reflections	6178 [R(int) = 0.0242]	
Completeness to theta = 35.04°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5172 and 0.3878	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6178 / 0 / 189	
Goodness-of-fit on F ²	1.076	
Final R indices [I > 2σ(I)]	R1 = 0.0237, wR2 = 0.0569	
R indices (all data)	R1 = 0.0299, wR2 = 0.0608	
Largest diff. peak and hole	2.055 and -0.998 e.Å ⁻³	

Table A44. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.10-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5000	5000	5000	13(1)
C(1)	3340(2)	5942(1)	4974(2)	16(1)
C(2)	981(3)	6830(1)	4446(2)	24(1)
C(3)	2313(3)	7141(1)	5383(2)	25(1)
C(4)	5538(3)	6725(1)	6631(2)	23(1)
C(5)	5339(3)	6932(1)	7851(2)	33(1)
C(6)	6576(4)	7361(2)	6182(2)	39(1)
C(7)	667(2)	5593(1)	3201(2)	18(1)
C(8)	300(2)	4785(1)	3331(2)	19(1)
C(9)	-647(3)	4323(1)	2337(2)	26(1)
C(10)	-1305(3)	4665(2)	1196(2)	31(1)
C(11)	-970(3)	5468(1)	1049(2)	30(1)
C(12)	33(3)	5916(1)	2036(2)	22(1)
F(1)	840(2)	4440(1)	4418(1)	24(1)
F(2)	-953(2)	3546(1)	2481(1)	36(1)
F(3)	-2241(2)	4216(1)	251(1)	47(1)
F(4)	-1566(2)	5802(1)	-54(1)	44(1)
F(5)	423(2)	6683(1)	1861(1)	29(1)
I(1)	4668(1)	4459(1)	7027(1)	20(1)
N(1)	1618(2)	6085(1)	4196(1)	18(1)
N(2)	3742(2)	6589(1)	5700(1)	19(1)

Table A45. Crystal data and structure refinement for Complex **4.10-cis-syn**.

Identification code	Complex 4.10-cis-syn	
Empirical formula	C ₂₅ H ₁₉ Cl ₃ F ₁₀ I ₂ N ₄ Pd	
Formula weight	1031.99	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.482(3) Å	α = 90°.
	b = 10.0686(17) Å	β = 118.440(6)°.
	c = 18.907(3) Å	γ = 90°.
Volume	3261.1(9) Å ³	
Z	4	
Density (calculated)	2.102 Mg/m ³	
Absorption coefficient	2.790 mm ⁻¹	
F(000)	1960	
Crystal size	0.40 x 0.40 x 0.26 mm ³	
Theta range for data collection	1.19 to 34.67°.	
Index ranges	-31 ≤ h ≤ 31, -16 ≤ k ≤ 16, -30 ≤ l ≤ 27	
Reflections collected	67706	
Independent reflections	13962 [R(int) = 0.0381]	
Completeness to theta = 34.67°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5307 and 0.4016	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13962 / 0 / 410	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0302, wR2 = 0.0678	
R indices (all data)	R1 = 0.0413, wR2 = 0.0723	
Largest diff. peak and hole	1.613 and -1.672 e.Å ⁻³	

Table A46. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.10-cis-syn**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	3203(1)	885(1)	2993(1)	10(1)
C(1)	3648(1)	2712(2)	3038(1)	11(1)
C(2)	5062(1)	2014(2)	3649(1)	15(1)
C(3)	5418(1)	1873(2)	3092(2)	20(1)
C(4)	5679(1)	2425(3)	4494(2)	22(1)
C(5)	4528(1)	4317(2)	3213(1)	16(1)
C(6)	3823(1)	4909(2)	2883(1)	15(1)
C(7)	2472(1)	4161(2)	2395(1)	13(1)
C(8)	2033(1)	4023(2)	1569(1)	16(1)
C(9)	1249(1)	4337(2)	1174(1)	19(1)
C(10)	905(1)	4827(2)	1609(2)	21(1)
C(11)	1332(1)	4984(2)	2429(2)	19(1)
C(12)	2116(1)	4646(2)	2823(1)	14(1)
C(13)	2811(1)	1374(2)	3766(1)	12(1)
C(14)	4026(1)	2271(2)	4927(1)	16(1)
C(15)	4172(1)	3759(2)	5018(2)	20(1)
C(16)	4383(2)	1569(3)	5738(2)	26(1)
C(17)	2678(1)	2269(2)	4793(1)	19(1)
C(18)	1976(1)	1794(2)	4265(2)	20(1)
C(19)	1444(1)	503(2)	3009(1)	15(1)
C(20)	1092(1)	-535(2)	3206(2)	20(1)
C(21)	491(1)	-1260(2)	2616(2)	26(1)
C(22)	244(1)	-986(3)	1819(2)	27(1)
C(23)	579(1)	32(3)	1606(2)	22(1)
C(24)	1171(1)	770(2)	2201(1)	17(1)
C(25)	1814(2)	6943(3)	5583(2)	28(1)
Cl(1)	1708(1)	6033(1)	4748(1)	45(1)
Cl(2)	2452(1)	8297(1)	5772(1)	33(1)
Cl(3)	899(1)	7516(1)	5431(1)	35(1)
F(1)	2369(1)	3573(2)	1146(1)	25(1)
F(2)	834(1)	4164(2)	382(1)	30(1)
F(3)	149(1)	5156(2)	1235(1)	32(1)

F(4)	993(1)	5460(2)	2847(1)	30(1)
F(5)	2521(1)	4810(2)	3616(1)	21(1)
F(6)	1338(1)	-833(2)	3974(1)	30(1)
F(7)	141(1)	-2212(2)	2822(1)	39(1)
F(8)	-337(1)	-1691(2)	1248(1)	43(1)
F(9)	337(1)	323(2)	835(1)	34(1)
F(10)	1475(1)	1764(1)	1977(1)	22(1)
I(1)	3441(1)	407(1)	1753(1)	17(1)
I(2)	2871(1)	-1640(1)	3086(1)	18(1)
N(1)	4414(1)	2986(2)	3312(1)	12(1)
N(2)	3289(1)	3911(2)	2783(1)	12(1)
N(3)	3180(1)	1997(2)	4481(1)	13(1)
N(4)	2056(1)	1242(2)	3630(1)	14(1)

Table A47. Crystal data and structure refinement for Complex **4.11-trans-syn**.

Identification code	Complex 4.11-trans-syn	
Empirical formula	C ₃₀ H ₄₀ I ₂ N ₄ Pd	
Formula weight	816.86	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.0466(17) Å	$\alpha = 90^\circ$.
	b = 13.4040(11) Å	$\beta = 105.056(4)^\circ$.
	c = 12.8231(12) Å	$\gamma = 90^\circ$.
Volume	3161.4(5) Å ³	
Z	4	
Density (calculated)	1.716 Mg/m ³	
Absorption coefficient	2.565 mm ⁻¹	
F(000)	1600	
Crystal size	0.34 x 0.30 x 0.26 mm ³	
Theta range for data collection	2.68 to 33.00°.	
Index ranges	-29 ≤ h ≤ 29, -20 ≤ k ≤ 20, -19 ≤ l ≤ 18	
Reflections collected	37003	
Independent reflections	5960 [R(int) = 0.0297]	
Completeness to theta = 33.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5553 and 0.4759	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5960 / 0 / 170	
Goodness-of-fit on F ²	1.112	
Final R indices [I > 2σ(I)]	R1 = 0.0192, wR2 = 0.0487	
R indices (all data)	R1 = 0.0238, wR2 = 0.0513	
Largest diff. peak and hole	0.500 and -1.170 e.Å ⁻³	

Table A48. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.11-trans-syn**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	5000	2380(1)	7500	10(1)
C(1)	3958(1)	2408(1)	7600(1)	12(1)
C(2)	2787(1)	2037(1)	7506(1)	19(1)
C(3)	2892(1)	3000(1)	7810(1)	18(1)
C(4)	3953(1)	4200(1)	8134(1)	17(1)
C(5)	3851(1)	4572(1)	9202(2)	28(1)
C(6)	3655(1)	4924(1)	7208(2)	32(1)
C(7)	3525(1)	687(1)	6992(1)	13(1)
C(8)	3147(1)	450(1)	5930(1)	16(1)
C(9)	2705(1)	1213(1)	5180(1)	23(1)
C(10)	3203(1)	-518(1)	5569(1)	17(1)
C(11)	3619(1)	-1244(1)	6225(1)	16(1)
C(12)	3668(1)	-2281(1)	5804(2)	25(1)
C(13)	3985(1)	-982(1)	7272(1)	16(1)
C(14)	3948(1)	-22(1)	7679(1)	14(1)
C(15)	4363(1)	203(1)	8816(1)	21(1)
I(1)	4500(1)	2561(1)	5400(1)	16(1)
N(1)	3443(1)	1676(1)	7378(1)	14(1)
N(2)	3615(1)	3211(1)	7870(1)	14(1)

Table A49. Crystal data and structure refinement for Complex **4.12-trans**.

Identification code	Complex 4.12-trans	
Empirical formula	C ₂₅ H ₂₄ Cl ₂ F ₆ I ₂ N ₄ Pd	
Formula weight	925.58	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9021(4) Å	α = 93.036(2)°.
	b = 9.3944(4) Å	β = 110.332(2)°.
	c = 10.2792(4) Å	γ = 101.987(2)°.
Volume	781.14(6) Å ³	
Z	1	
Density (calculated)	1.968 Mg/m ³	
Absorption coefficient	2.799 mm ⁻¹	
F(000)	442	
Crystal size	0.40 x 0.30 x 0.30 mm ³	
Theta range for data collection	2.87 to 31.25°.	
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 12	
Reflections collected	22807	
Independent reflections	5038 [R(int) = 0.0290]	
Completeness to theta = 31.25°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4872 and 0.4006	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5038 / 1 / 189	
Goodness-of-fit on F ²	1.072	
Final R indices [I > 2σ(I)]	R1 = 0.0269, wR2 = 0.0674	
R indices (all data)	R1 = 0.0310, wR2 = 0.0693	
Largest diff. peak and hole	1.176 and -1.735 e.Å ⁻³	

Table A50. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.12-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	2329(3)	5186(2)	1337(2)	16(1)
C(2)	4561(3)	4893(3)	3120(3)	22(1)
C(3)	5075(3)	6004(3)	2484(3)	23(1)
C(4)	3650(3)	7270(3)	414(3)	24(1)
C(5)	4905(5)	7232(4)	-258(4)	44(1)
C(6)	3848(6)	8769(3)	1153(5)	51(1)
C(7)	1793(3)	3264(3)	2744(2)	19(1)
C(8)	1258(3)	3510(3)	3838(2)	22(1)
C(9)	144(4)	2458(3)	4147(3)	28(1)
C(10)	-414(4)	1109(3)	3321(3)	30(1)
C(11)	88(4)	771(3)	2236(3)	31(1)
C(12)	1197(3)	1873(3)	1983(3)	24(1)
C(13)	3956(11)	-101(18)	4664(10)	129(7)
Cl(1)	5247(3)	1412(2)	4516(2)	131(1)
F(1)	1857(2)	4830(2)	4628(2)	27(1)
F(2)	-1508(3)	47(2)	3587(2)	45(1)
F(3)	1753(2)	1581(2)	966(2)	32(1)
I(1)	523(1)	3516(1)	-1942(1)	22(1)
N(1)	2868(2)	4397(2)	2404(2)	18(1)
N(2)	3689(2)	6162(2)	1391(2)	18(1)
Pd(1)	0	5000	0	13(1)

Table A51. Crystal data and structure refinement for Complex **4.13-trans**.

Identification code	Complex 4.13-trans	
Empirical formula	C ₂₂ H ₂₄ I ₂ N ₄ Pd	
Formula weight	704.65	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.9124(3) Å	α = 95.135(2)°.
	b = 8.2761(3) Å	β = 94.723(2)°.
	c = 10.5186(7) Å	γ = 115.8660(10)°.
Volume	611.62(5) Å ³	
Z	1	
Density (calculated)	1.913 Mg/m ³	
Absorption coefficient	3.297 mm ⁻¹	
F(000)	336	
Crystal size	0.40 x 0.20 x 0.08 mm ³	
Theta range for data collection	2.76 to 40.55°.	
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -18 ≤ l ≤ 19	
Reflections collected	33568	
Independent reflections	7753 [R(int) = 0.0257]	
Completeness to theta = 40.55°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7784 and 0.3522	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7753 / 0 / 134	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0182, wR2 = 0.0414	
R indices (all data)	R1 = 0.0216, wR2 = 0.0430	
Largest diff. peak and hole	1.141 and -1.178 e.Å ⁻³	

Table A52. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.13-trans**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	10000	10000	0	11(1)
C(1)	7292(1)	8393(1)	253(1)	13(1)
C(2)	4721(1)	6529(1)	1107(1)	17(1)
C(3)	4089(1)	6920(1)	5(1)	17(1)
C(4)	5608(2)	8866(2)	-1686(1)	19(1)
C(5)	4791(2)	7452(2)	-2878(1)	23(1)
C(6)	7892(2)	7423(1)	2334(1)	16(1)
C(7)	7446(2)	7696(2)	3562(1)	24(1)
C(8)	8578(2)	7646(2)	4624(1)	30(1)
C(9)	10133(2)	7334(2)	4462(1)	28(1)
C(10)	10576(2)	7079(2)	3234(1)	23(1)
C(11)	9445(2)	7110(1)	2158(1)	18(1)
I(1)	10076(1)	12486(1)	1741(1)	15(1)
N(1)	6691(1)	7444(1)	1250(1)	14(1)
N(2)	5682(1)	8064(1)	-506(1)	15(1)

Table A53. Crystal data and structure refinement for Complex **4.13-cis-anti**.

Identification code	Complex 4.13-cis-anti	
Empirical formula	C ₂₃ H ₂₆ Cl ₂ I ₂ N ₄ Pd	
Formula weight	789.58	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6869(4) Å	α = 105.486(2)°.
	b = 10.8204(4) Å	β = 101.573(2)°.
	c = 13.7285(8) Å	γ = 110.461(2)°.
Volume	1355.27(11) Å ³	
Z	2	
Density (calculated)	1.935 Mg/m ³	
Absorption coefficient	3.178 mm ⁻¹	
F(000)	756	
Crystal size	0.40 x 0.40 x 0.30 mm ³	
Theta range for data collection	1.63 to 31.02°.	
Index ranges	-14 ≤ h ≤ 15, -15 ≤ k ≤ 15, -15 ≤ l ≤ 19	
Reflections collected	15724	
Independent reflections	15724 [R(int) = 0.0000]	
Completeness to theta = 31.02°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4490 and 0.3629	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	15724 / 0 / 292	
Goodness-of-fit on F ²	1.083	
Final R indices [I > 2σ(I)]	R1 = 0.0316, wR2 = 0.0917	
R indices (all data)	R1 = 0.0389, wR2 = 0.1043	
Largest diff. peak and hole	1.620 and -1.362 e.Å ⁻³	

Table A54. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.13-cis-anti**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5895(1)	8332(1)	2500(1)	10(1)
C(1)	6300(3)	9217(3)	1432(2)	12(1)
C(2)	6513(3)	7226(3)	136(2)	18(1)
C(3)	5397(4)	6377(3)	-966(2)	23(1)
C(4)	6942(3)	9619(3)	41(2)	20(1)
C(5)	6845(3)	10797(3)	610(2)	20(1)
C(6)	6175(3)	11500(3)	2238(2)	16(1)
C(7)	7155(4)	12918(3)	2702(2)	22(1)
C(8)	6866(4)	13879(3)	3412(2)	26(1)
C(9)	5629(4)	13428(3)	3668(2)	25(1)
C(10)	4676(4)	12016(3)	3203(2)	22(1)
C(11)	4938(3)	11037(3)	2482(2)	17(1)
C(12)	7815(3)	9733(3)	3486(2)	12(1)
C(13)	7114(3)	11244(3)	4793(2)	18(1)
C(14)	7354(3)	11279(3)	5934(2)	22(1)
C(15)	9587(3)	11698(3)	4782(2)	18(1)
C(16)	10188(3)	11028(3)	4198(2)	19(1)
C(17)	9286(3)	8766(3)	2631(2)	15(1)
C(18)	10192(3)	9201(3)	2070(2)	20(1)
C(19)	10425(4)	8178(4)	1362(2)	27(1)
C(20)	9753(3)	6767(4)	1208(2)	25(1)
C(21)	8833(3)	6343(3)	1765(2)	21(1)
C(22)	8601(3)	7345(3)	2490(2)	16(1)
C(23)	1781(7)	4457(7)	2691(4)	102(3)
Cl(1)	652(2)	2830(2)	1662(1)	86(1)
Cl(2)	1085(2)	4782(2)	3766(1)	72(1)
I(1)	3292(1)	6706(1)	1138(1)	16(1)
I(2)	5622(1)	7139(1)	3950(1)	15(1)
N(1)	6446(3)	10524(2)	1465(2)	14(1)
N(2)	6608(3)	8668(3)	555(2)	16(1)
N(3)	8137(3)	10892(2)	4345(2)	14(1)

N(4)	9084(3)	9816(2)	3401(2)	16(1)
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Table A55. Crystal data and structure refinement for Complex **4.14-trans**.

Identification code	Complex 4.14-trans	
Empirical formula	C ₂₆ H ₃₂ Cl ₆ N ₄ Pd	
Formula weight	719.66	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.0456(7) Å	$\alpha = 90^\circ$.
	b = 11.2285(8) Å	$\beta = 108.070(4)^\circ$.
	c = 14.7537(10) Å	$\gamma = 90^\circ$.
Volume	1582.09(19) Å ³	
Z	2	
Density (calculated)	1.511 Mg/m ³	
Absorption coefficient	1.116 mm ⁻¹	
F(000)	728	
Crystal size	0.30 x 0.18 x 0.14 mm ³	
Theta range for data collection	2.32 to 31.19°.	
Index ranges	-14 ≤ h ≤ 13, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21	
Reflections collected	28127	
Independent reflections	5037 [R(int) = 0.0543]	
Completeness to theta = 31.19°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8595 and 0.7307	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5037 / 0 / 171	
Goodness-of-fit on F ²	1.085	
Final R indices [I > 2σ(I)]	R1 = 0.0407, wR2 = 0.1019	
R indices (all data)	R1 = 0.0571, wR2 = 0.1315	
Largest diff. peak and hole	1.364 and -1.858 e.Å ⁻³	

Table A56. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Complex **4.14-trans**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	0	5000	0	18(1)
C(1)	1105(3)	5560(3)	1326(2)	24(1)
C(2)	1735(4)	6536(4)	2726(2)	40(1)
C(3)	2878(4)	5985(4)	2650(2)	39(1)
C(4)	3384(3)	4672(3)	1435(2)	27(1)
C(5)	2977(4)	3549(3)	1073(2)	33(1)
C(6)	3893(4)	2868(3)	750(3)	39(1)
C(7)	5197(4)	3310(4)	790(3)	40(1)
C(8)	5594(4)	4438(4)	1153(3)	41(1)
C(9)	4697(4)	5121(3)	1477(3)	36(1)
C(10)	-797(3)	6712(3)	1708(2)	33(1)
C(11)	-1370(4)	6326(4)	2498(3)	50(1)
C(12)	-830(5)	8047(4)	1574(4)	58(1)
C(13)	2970(7)	8571(5)	1102(4)	72(2)
Cl(1)	-1165(1)	3610(1)	624(1)	35(1)
Cl(2)	1954(3)	9680(2)	402(2)	108(1)
Cl(3)	4732(2)	8636(2)	1171(2)	123(1)
N(1)	2475(3)	5382(3)	1785(2)	29(1)
N(2)	655(3)	6264(3)	1910(2)	29(1)