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Iridafurans from the Reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ with Carbonyl Conjugated Terminal Alkynes: Dependence of Product on Polarity of Reaction Medium

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Abstract: Reaction of the dimeric species $[\text{Cp}^\text{IrCl}_2]_2$ with terminal alkynes containing a conjugated carbonyl group results in C-C bond formation between two or three alkyne molecules, depending on the polarity of the reaction medium. The reaction pathway has been studied experimentally and computationally.*

Key words: Iridium; iridafuran; terminal alkyne; conjugated carbonyl; C-C coupling

1. Introduction

The chemistry of half-sandwich iridium complexes with terminal alkynes that has been reported include hydration,¹ hydrosilylation,² $\text{C}\equiv\text{C}$ bond cleavage in the presence of water,³ and insertion into a metal-hydride/halide bond.⁴ In particular, we have found that the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$, **1**, with terminal alkynes in the presence of water, alcohols or anilines afforded carbonyl alkyl complexes $[\text{Cp}^*\text{IrCl}(\text{CO})(\text{CH}_2\text{R})]$ via $\text{C}\equiv\text{C}$ bond cleavage, alkoxycarbene complexes $[\text{Cp}^*\text{IrCl}_2(=\text{C}(\text{OR}')\text{CH}_2\text{R})]$,^{3c} or aminocarbene complexes $[\text{Cp}^*\text{Ir}(\text{Cl})\{\text{C}(\text{CH}_2\text{R}')\text{NHC}_6\text{H}_3\text{R}\}]$ via a hydroamination and an orthometallation,⁵ respectively. When the $\text{C}\equiv\text{C}$ bond of the alkyne was conjugated to a carbonyl functional group, however, the product obtained was an O-containing five membered metallacycle of iridium (iridafuran) resulting from C-C bond coupling. While there have been many documented methods to

synthesize iridacycles and iridafurans,⁶ that for the latter have mostly been accomplished via multistep reactions with dicarboxylates such as dimethylacetylenedicarboxylate,⁷ di-tert-butylacetylenedicarboxylate,⁸ and diethyl maleate,⁹ or unsaturated ketones.¹⁰ We wish to report here the formation of iridafurans from the direct reaction of carbonyl conjugated alkynes with **1**.

2. Results and Discussion

The reaction of **1** with terminal alkynes containing a conjugated carbonyl group (carboxylic acid, ester or ketone) afforded the iridafuran complexes $\text{Cp}^*\text{IrCl}(\text{ClC}=\text{C}(\text{COR})\text{CH}=\text{CHCOR})$, **2**, through C-C bond coupling between two units of the alkyne, in good yields (Scheme 1). The products have been characterized spectroscopically and analytically, and for **2a** and **2b**, also by single crystal X-ray crystallographic studies. No analogous product was observed if the carbonyl group was not conjugated to the alkyne, for example, with 4-pentynoic acid or propargyl glycine. This C-C bond coupling reaction was in contrast to that with terminal alkynes, in which the $\text{C}\equiv\text{C}$ bond was cleaved in the presence of water.⁴

<Insert scheme 1 here>

In the presence of Et_4NCl , the reaction afforded a mixture of **2b** and a new compound $\text{Cp}^*\text{IrCl}[\text{C}(\text{C}\{\text{COOEt}\}=\text{CHCl})=\text{C}(\text{COOEt})\text{CH}=\text{CHCOOEt}]$, **3**, which was clearly the result of C-C coupling of three units of alkyne, was obtained (Scheme 2). Complex **3** did not result from further reaction of **2b** with EtO_2CCCH ; its formation from the reaction of **1** and EtO_2CCCH was also found to occur in the presence of Et_4NBr , $[\text{PPN}]\text{Cl}$ or $[\text{PPN}]_2\text{SO}_4$, suggesting that the C-C coupling of three alkyne units was favoured by a polar environment. Indeed, when the reaction was carried out in a polar aprotic solvent, the conversion of **1** to **3** increased with solvent polarity.

<Insert scheme 2 here>

The use of Et₄NBr in the reaction gave a mixture of **2b**, **3** and **2b'**, an analogue of **2b** in which the chloride attached to the iridium was replaced with a bromide; the reaction of **2b** with Et₄NBr gave **2b'**, demonstrating that the latter was the result of halide substitution in **2b**. That the formation of **2b** and **3** were not hindered by the addition of free chloride, and bromine was not incorporated into the organic moiety of **2b** or **3**, thus suggested that the chloride transfer was probably intramolecular. Reaction of **1** with EtO₂CCCD showed incorporation of two deuterium atoms into the alkene moiety *exo* to the metallacycle, while the analogous reaction with EtO₂CCCH in the presence of D₂O showed no deuterium incorporation in **2b**. These results demonstrated that the alkenic hydrogens were both from the alkynes, and that there was intramolecular hydrogen transfer in the coupling of the alkynes. Similar deuterium labeling experiments on the reaction leading to the formation of **3** suggested that the hydrogen transfer in its formation was also intramolecular.

The above results put rather severe restrictions on the possible pathways to **2b** and **3**; that for **2b** are illustrated in Figure 1: (a) The alkynes must couple head-to-tail, (b) the R1 alkyne must cleave the C-H bond, and the H must be transferred to the R2 alkyne, and (c) the R1 alkyne must be bound to the Ir.

<Insert figure 1 here>

We have examined a number of possible pathways and feel that that depicted in Scheme 3 is consistent with the requirements above. We have also carried out computations using DFT in order to obtain estimates of the free energy changes (ΔG° in kJ mol⁻¹) for the reaction steps; these are also given in Scheme 3. The formation of the Ir-bound alkyne complex **A** is associated with a modest positive ΔG° (+44.5 kJ mol⁻¹).¹¹ The step from **A** to **C** involves formation of an alkynyl and an alkenyl ligand from the alkynes, and we propose that it could involve a σ -bond

metathesis-type reaction between **A** and a second alkyne molecule, via a transition state **B**. This process could possibly be assisted by the electron withdrawing properties of the conjugated C=O group on the initially coordinated alkyne, which would favour iridium to alkyne back-donation and thus a metallocyclopropene structure, as shown in transition state **B**.

<Insert scheme 3 here>

A formal 1,3-vinyl shift gives the vinylidene species **D**; this is similar to an electrophilic attack on the β -carbon of an alkynyl ligand.¹² Subsequent transfer of a nucleophilic chloride ligand to the electrophilic α -carbon of the vinylidene species gives the 16-electron species **E**. Coordination of the C=O group to the iridium center would then result in **2a**. This final coordination step can be reversed, as we have found that stirring a solution of **2b** in CO gave rise to **4**; standing a solution of **4** for a few days resulted in a mixture of **2b** and **4** (Scheme 4).

<Insert scheme 4 here>

The formation of **3** in a polar reaction environment, on the other hand, may have involved an initial 2,*I*-insertion of the alkyne into the Ir-Cl bond of **A** to form **G**; the geometry of the proposed intermediates have been optimized and the free energy (ΔG° in kJ mol⁻¹) for each step is given (Scheme 5). The divergence in the initial step is in agreement with the above observation that **2b** is not the precursor of **3**. The insertion could proceed via an ionic mechanism, i.e., dissociation of a chloride from **A** to give a tight ion pair **F**, followed by nucleophilic attack of the chloride on the terminal carbon of the alkyne; formation of the ion pair would be favoured by a polar environment and may account for the change in reaction pathway. This step is analogous to the well-studied 2,*I*-insertion of methyl acrylate into a Pd-C bond,¹³ the terminal carbon of the alkyne carries a δ^+ charge due to the electron withdrawing carbonyl group attached

to the α -carbon, thus facilitating nucleophilic attack there. Admittedly, insertion into an M-X bond is very rare in comparison to insertions into M-H and M-C bonds.¹⁴

<Insert scheme 5 here>

The next step involves a *cis-trans* isomerization to **H**, which could possibly be assisted by the conjugated carbonyl group via a zwitterionic intermediate; a similar experimentally observed isomerization process has previously been reported.¹⁵ Coordination of a second alkyne molecule gives **J**, an analogue of **A** in which one Cl ligand has been replaced by the alkenyl moiety X. The subsequent steps follow those in scheme 3.

Crystallographic studies

The molecular structures of **2a**, **2b** and **3** have been determined by single-crystal X-ray diffraction studies; the ORTEP plots for **2b** and **3** are shown in Figure 2. Compound **3** is structurally very similar to **2**, and hence a common atomic numbering scheme, together with selected bond parameters, for all four compounds is given in Table 1. The structure for **2a** exhibited disorder of the Cp* ring and the C-C coupled alkynes over each other, while that for the others refined satisfactorily. The bond parameters for **2a** are thus given for completeness but will not be further discussed.

All three structures show a 5-membered iridacycle. The bond lengths about this iridacycle suggest some delocalization of the π electrons. Thus the C(1)-C(2) (1.376(5) Å and 1.361(7) Å for **2b** and **3**, respectively) and C(2)-C(3) bond lengths (1.452(5) Å and 1.437(7) Å for **2b** and **3**, respectively) are between those for a C(sp²)-C(sp²) single and double bond (1.48 and 1.32 Å, respectively), and likewise the C(3)-O(3) bond lengths (1.242 Å) are also in between those for a C(sp²)-O(sp²) single and double bond (1.34 and 1.21 Å, respectively).¹⁶ The Ir-C(1)

bond length (1.996(4) Å and 2.022(5) Å for **2b** and **3**, respectively) is also very similar to the Ir=C bond lengths (~1.992 Å) which we have reported earlier for some aminocarbenes of iridium.⁵

<Insert figure 2 here>

<Insert table 1 here>

3. Concluding remarks

We have reported here that the reaction of carbonyl conjugated terminal alkynes with the iridium dimer **1** afforded iridafurans **2** and **3** resulting from C-C coupling of the alkynes. Experimental and computational studies into the reaction pathways have also been carried out and proposed for the formation of **2** and **3**. The carboxylate moiety has also been demonstrated to be labile, at least for **2b**, in which it can be displaced with CO. Given the recent intense interests in iridium-catalysed reactions,¹⁷ this reaction represents a straightforward route to a class of iridium complexes that should have catalytic potential; exploratory work on this is currently underway.

4. Experimental

4.1. General Procedures. All reactions and manipulations were performed under argon using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under argon prior to use, except for 1,2-dichloroethane, which was used as supplied. IR spectra were acquired as CH₂Cl₂ solutions. ¹H NMR spectra were recorded on a Bruker ACF300 or AV300 NMR spectrometer as CDCl₃ solutions; chemical shifts reported were referenced against the residual signals of the solvent. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB) or a Finnigan MAT LCQ spectrometer with MeOH as solvent (ESI). All

elemental analyses were performed by the microanalytical laboratory at NUS. $[\text{Cp}^*\text{IrCl}_2]_2$, **1**, was prepared according to the published method.¹⁸ $[\text{PPN}]_2\text{SO}_4$ was prepared from $[\text{PPN}]\text{Cl}$ and sodium sulphate following a literature procedure.¹⁹ All other reagents were from commercial sources and used without further purification.

4.2. Deuteration of ethyl propiolate.²⁰ Ethyl propiolate (0.6 ml, 5.9 mmol) in dichloromethane (3 ml) was treated under phase transfer conditions using tetrabutylammonium iodide (50 mg, 0.136 mmol), with deuterium oxide (0.6 ml, 33.6 mmol) containing catalytic quantity of sodium deuterioxide. After stirring for 1 h, the aqueous phase was replaced with fresh deuterium oxide and this deuterium exchange process was repeated twice to give deuterated ethyl propiolate, $\text{DC}\equiv\text{CCO}_2\text{Et}$. ^1H NMR: δ 1.32 (t, 3H, CH_3), 4.26 (q, 2H, CH_2), 2.86 (s, 1H, <0.05).

4.3. Reaction of 1 with methyl propiolate. A dichloroethane solution (3 ml) of $[\text{Cp}^*\text{IrCl}_2]_2$, **1** (36.0 mg, 45.2 μmol) and methyl propiolate (16 μL , 0.18 mmol) was stirred at room temperature for 0.5 h. The solvent was then removed under reduced pressure and the residue obtained was dissolved in a minimum of dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/ CH_2Cl_2 (1/1, v/v) yielded **2a** as an orange yellow solid. Yield = 47 mg, 92%. ν_{CO} : 1710 (br), 1620 (br) cm^{-1} . ^1H NMR: δ 1.72 (s, 15H, Cp^*), 3.75 (s, 3H, OMe), 4.03 (s, 3H, OMe), 6.40 (d, 1H, $=\text{CH}$), 7.71 (d, 1H, $=\text{CH}$). ^{13}C NMR: δ 203.2 (Ir-C=), 183.5 ($\text{C}=\text{O}$), 168.8 ($\text{C}=\text{O}$), 135.7 ($=\text{C}$), 128.0 ($=\text{C}$), 115.2 ($=\text{C}$), 90.5 (C_5 ring), 54.8 (OCH_3), 51.7 (OCH_3), 9.2 ($\text{Cp}-\text{CH}_3$). FAB-MS: 566 $[\text{M}]^+$, 531 $[\text{M} - \text{Cl}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{Cl}_2\text{IrO}_4$: C, 38.16; H, 4.09. Found: C, 37.86; H, 4.27.

A similar procedure employing the same amount of **1** afforded the corresponding species **2** with the other alkynes.

Data for **2b**: Yield = 48 mg, 89%. ν_{CO} : 1700 (br), 1624 (br) cm^{-1} . ^1H NMR: δ 1.30 (t, 3H, CH_3), 1.41 (t, 3H, CH_3), 1.71 (s, 15H, Cp^*), 4.21 (q, 2H, CH_2), 4.50 (q, 2H, CH_2), 6.40 (d, 1H, $=\text{CH}$), 7.71 (d, 1H, $=\text{CH}$). ^{13}C NMR: δ 202.6 (Ir-C=), 183.0 (C=O), 168.4 (C=O), 135.6 ($=\text{C}$), 128.1 ($=\text{C}$), 115.7 ($=\text{C}$), 90.3 (C_5 ring), 64.6 (OCH_2), 60.4 (OCH_2), 14.6 (CH_2CH_3), 14.4 (CH_2CH_3), 9.2 (Cp-CH_3). FAB-MS: 594 $[\text{M}]^+$, 559 $[\text{M} - \text{Cl}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{Cl}_2\text{IrO}_4 \cdot \text{CH}_2\text{Cl}_2$: C, 37.12; H, 4.30. Found: C, 37.26; H, 4.07. Presence of dichloromethane in analytical sample confirmed by ^1H spectroscopy.

Data for *d*-**2b**: ^1H NMR: δ 1.30 (t, 3H, CH_3), 1.41 (t, 3H, CH_3), 1.71 (s, 15H, Cp^*), 4.21 (q, 2H, CH_2), 4.50 (q, 2H, CH_2).

Data for **2c**: Yield = 46 mg, 94%. ν_{CO} : 1699 (br), 1621 (br) cm^{-1} . ^1H NMR: δ 1.70 (s, 15H, Cp^*), 6.52 (d, 1H, $=\text{CH}$), 7.83 (d, 1H, $=\text{CH}$), 11.97 (br, s, 1H, COOH). FAB-MS: 538 $[\text{M}]^+$, 503 $[\text{M} - \text{Cl}]^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{Cl}_2\text{IrO}_4$: C, 35.69; H, 3.56. Found: C, 36.08; H, 3.73.

Data for **2d**: Yield = 21 mg, 87%. ν_{CO} : 1601 (br) cm^{-1} . ^1H NMR: δ 1.75 (s, 15H, Cp^*), 2.32 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 6.51 (d, 1H, $=\text{CH}$), 7.53 (d, 1H, $=\text{CH}$). FAB-MS: 499 $[\text{M} - \text{Cl}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{Cl}_2\text{IrO}_2 \cdot \frac{1}{2}\text{C}_6\text{H}_{14}$: C, 43.67; H, 5.24. Found: C, 44.12; H, 5.47. Presence of hexane in the analytical sample confirmed by ^1H spectroscopy.

4.4. Reaction of 1 with ethyl propiolate in the presence of Et_4NCl . A dichloroethane solution (3 ml) of **1** (36 mg, 44 μmol) containing Et_4NCl (7.4 mg, 44 μmol) was stirred with ethyl propiolate (19 μL , 0.19 mmol) at room temperature for 0.5 h. All volatiles were removed under reduced pressure and a reddish-orange residue was obtained. ^1H NMR analysis showed that small amount of **2b** was formed along with an unknown product. The mixture was subsequently filtered using silica gel to remove Et_4NCl . Slow evaporation of the DCM/hexane solution gave **3** as dark orange crystals. Yield = 30 mg, 49%. ^1H NMR: δ 1.27 (t, 3H, CH_3), 1.31

(t, 3H, CH₃), 1.41 (t, 3H, CH₃), 1.63 (s, 15H, Cp*), 4.18 (q, 2H, CH₂), 4.26 (q, 2H, CH₂), 4.49 (q, 2H, CH₂), 6.23 (d, 1H, =CH), 6.78 (s, 1H, =CH) 7.26 (d, 1H, =CH). ¹³C NMR: δ 205.0 (Ir-C=), 184.3 (C=O), 167.8 (C=O), 163.9 (C=O), 141.7 (=C), 136.9 (=C), 128.4 (=C), 125.2 (=C), 116.0 (=C), 89.7 (C₅ ring), 64.4 (OCH₂), 61.3, (OCH₂), 60.0 (OCH₂), 14.3 (CH₂CH₃), 14.1 (CH₂CH₃), 14.0 (CH₂CH₃), 8.9 (Cp-CH₃). FAB-MS: 692 [M]⁺, 657 [M-Cl]⁺. Anal. Calcd for C₂₅H₃₃Cl₂IrO₆: C, 43.35; H, 4.80. Found: C, 43.27; H, 4.67.

A similar procedure was employed with [PPN]Cl and [PPN]₂SO₄, and both salts generated the same mixture as when Et₄NCl was used.

4.5. Reaction of 1 with ethyl propiolate in the presence of Et₄NBr. A dichloroethane solution (1.5 ml) of **1** (18 mg, 22.2 μmol) containing Et₄NBr (20 mg, 97 μmol) was stirred with ethyl propiolate (9.5 μL, 0.097 mmol) at room temperature for 0.5 h. All volatiles were then removed under reduced pressure and a reddish-orange residue was obtained. ¹H NMR spectroscopic analysis showed the presence of **2b**, **3** and an unknown with resonances similar to that of **2b**.

4.6. Reaction of 2b with Et₄NBr. An independent experiment was conducted by placing **2b** and Et₄NBr together in CDCl₃. The resultant mixture contained **2b** and the unknown, which was determined to be the bromo analogue **2b'**, on the basis of its spectroscopic data. ¹H NMR: δ 1.29 (t, 3H, CH₃), 1.41 (t, 3H, CH₃), 1.74 (s, 15H, Cp*), 4.21 (q, 2H, CH₂), 4.50 (q, 2H, CH₂), 6.38 (d, 1H, =CH), 7.72 (d, 1H, =CH). ESI-MS: 640 [⁸¹Br, M+H]⁺, 638 [⁷⁹Br, M+H]⁺, 559 [M-Br]⁺.

4.7. Attempted reaction of 2b with ethyl propiolate in the presence of [PPN]Cl. A dichloromethane solution (1 ml) of **2b** (7.5 mg, 12.5 μmol) containing [PPN]Cl (7.2 mg, 12.5 μmol) was stirred with excess ethyl propiolate at room temperature for 1 h. The solution was

then passed through silica gel before all volatiles were removed under reduced pressure to give an orange residue. ^1H NMR analysis showed only the presence of **2b**.

4.8. Reaction of 1 with ethyl propiolate in the presence of [PPN]Cl and D₂O. A dichloroethane solution (1 ml) of **1** (5 mg, 6.3 μmol) with [PPN]Cl (7.2 mg, 12.5 μmol), deuterium oxide (0.1 ml, 5.6 mmol) and ethyl propiolate (3.9 μL , 9.5 μmol) was stirred at room temperature for 1 h. The mixture was passed through silica gel before all volatiles were removed under reduced pressure to give an orange residue. ^1H NMR analysis showed only resonances due to **3** with no deuterium incorporation.

4.9. Reaction of 1 with ethyl propiolate in polar aprotic solvents. An acetone solution (1 ml) of **1** (5 mg, 6.3 μmol) and ethyl propiolate (2.6 μL , 25 μmol) was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure to give a residue. ^1H NMR analysis showed the presence of a mixture of **2b** and **3**. This was repeated using acetonitrile (ACN), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The amount of **1** converted to **3** increased with the polarity of the solvents: acetone < ACN < DMF. The ratio of **2b** to **3** based on integration of their Cp* signals were 3.5:1, 0.87:1 and 0.39:1, respectively. No reaction was observed when DMSO was used.

4.10. Reaction of 1 with DMSO in CDCl₃. DMSO (1 ml) was added to a CDCl₃ solution (0.5 ml) of **1** (5 mg, 6.3 μmol) and allowed to stand for 2 h. ^1H NMR analysis showed that both the peaks of **1** and DMSO have shifted considerably, possibly due to interaction.

^1H NMR: δ 1.75 (s, 15H, Cp*), 3.28 (s, 6H, CH₃ of DMSO).

Free **1** and DMSO in CDCl₃ has δ_{H} of 1.60 ppm and 2.62 ppm, respectively.

4.11. Reaction of 2b with CO. A DCM solution (3 ml) of **2b** (28 mg, 0.047 mmol) in a carius tube was subjected to three cycles of freeze-pump-thaw, and was subsequently charged with 1

atm of CO. The solution was then stirred overnight. The solvent was then removed under reduced pressure to give **4** as an orange oil. ν_{CO} : 2043 (vs) cm^{-1} . ^1H NMR: δ 1.29 (t, 3H, CH_3), 1.33 (t, 3H, CH_3), 1.90 (s, 15H, Cp^*), 4.20 (m, 4H, CH_2), 5.59 (d, 1H, $=\text{CH}$), 8.05 (d, 1H, $=\text{CH}$). FAB-MS: 587 $[\text{M}-\text{Cl}]^+$, 559 $[\text{M}-\text{Cl}-\text{CO}]^+$.

4.12. X-ray crystallographic studies. Crystals were grown from dichloromethane/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo $\text{K}\alpha$ radiation, at 223 K with the SMART suite of programs.²¹ Data were processed and corrected for Lorentz and polarization effects with SAINT²² and for adsorption effects using SADABS.²³ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. The crystal of **2a** exhibited disorder about a mirror, which was modelled with two alternative sites of equal occupancies. The crystal of **3** exhibited disorder of the outermost ethyl group, which was modeled with two sites of equal occupancies. Appropriate restraints on the bond and thermal parameters were placed on the disordered parts. All non-hydrogen atoms were given anisotropic displacement parameters in the final model. Crystal and refinement data are collected in Table 2.

<Insert table 2 here>

4.13. Computational studies

The computational studies were carried out using density function theory (DFT), utilising the Becke's three parameter hybrid function²⁴ and Lee-Yang-Parr's gradient-corrected correlation function²⁵ (B3LYP). The basis set used was the LANL2DZ (Los Alamos Effective Core Potential Double- ζ) augmented with an f polarization function,²⁶ for the iridium atom, and the 6-311G+(2d,p) for the light atoms. Spin-restricted calculations were used for structural

optimization, harmonic frequency calculations and to evaluate zero-point energy (ZPE) corrections. Optimized geometries were characterized as equilibrium structures with all real frequencies. All calculations were performed using the Gaussian 09 suite of program.²⁷

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Supporting Information Available: CCDC 935124-6 contain the supplementary crystallographic data for **2a**, **2b** and **3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Optimized geometry of computed structures. Ordering information is given on any current masthead page.

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Captions for figures

Figure 1. Mechanistic requirements for the formation of **2**. The dotted lines show the bonds to be formed, and the dotted arrows show the atoms to be transferred.

Figure 2. ORTEP plots for **2b** (left) and **3** (right). Thermal ellipsoids are drawn at 50% probability, and H atoms are omitted for clarity.

Captions for tables

Table 1. Common atomic numbering scheme and selected bond parameters for **2a**, **2b** and **3**.

Table 2. Crystal and refinement data for **2a**, **2b** and **3**.