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Palladium catalyzed asymmetric hydrophosphination of α,β- and α,β,γ,δ-unsaturated malonate esters-efficient control of reactivity, stereo- and regio-selectivity

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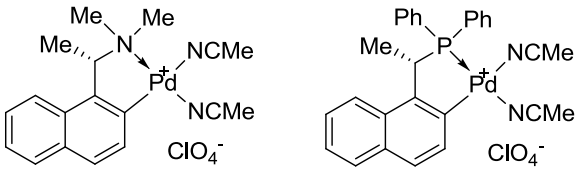
Abstract

The impact of catalyst design on the asymmetric addition of diphenylphosphine to *α,β*-alkylidenemalonate esters was examined. Both PC-cyclometalated and PCP-pincer palladium catalysts proved to be robust and efficacious, yielding the chiral phosphines in high isolated yields and enantiomeric excess. However, the two types of catalysts adopted different reaction mechanisms. When extended to a more challenging *α,β,γ,δ*-alkylidenemalonate ester, the two catalysts showed significantly contrasting regioselectivities (1,4- *vs* 1,6-addition). This study provides insights into the impact of catalyst design on the regioselectivity of such reaction.

Introduction

The conjugated addition of nucleophiles to electron-deficient olefins leading to the formation of C-C or C-heteroatom bonds is an important synthetic method in organic synthesis. The asymmetric variant of such reactions, especially those promoted by transition metal complexes, is an efficient tool towards the formation of optically active compounds that are of relevance in catalysis or biology.[1] However, existing reports are mostly focused on the 1,4-addition of carbon nucleophiles to *α*,*β*-unsaturated olefins.[2] In contrast, the 1,6-addition to *α*,*β*,γ,*δ*-diunsaturated olefins is relatively less developed[3] due to inherent challenge in controlling the regioselectivity while ensuring good stereoselectivity. This can be attributed to the presence of two reactive sites at the *β*- and *δ*-positions which are susceptible to nucleophilic attack. Although significant progress in this field has been achieved by Yamamoto, Krause, Feringa, Fillion and Hayashi with rhodium, iridium,[4] copper,[5] iron[6] and organocatalysts[7] leading to regio- and stereo-selective formation of C-C bonds, 1,6-additions in formation of C-heteroatom bonds are rare. This is attributed to the fact that the aforementioned regioselectivity issue becomes more significant due to the inherent preference for attack at *β*- position especially in the case of highly reactive nucleophiles.

Chiral phosphines have contributed significantly to the area of asymmetric transformations such as hydrogenation[8] and hydroformylation.[9] As demonstrated by the pioneering work of Glueck[10] and Togni,[11] the asymmetric formation of P-C bonds *via* substitution or addition reactions is an attractive strategy to access chiral phosphine motifs.[12] Our group has been involved in the direct synthesis of chiral phosphines *via* metal catalyzed asymmetric hydrophosphination reactions.[12a,13] We have recently reported the use of the chiral palladacycle (*R*/*S*)-**1** and its phosphapalladacycle analogue (*R*/*S*)-**2** (Figure 1) in catalytic hydrophosphination of enones,[14] dienones,[15] bis(enones),[16] *α*,*β*-unsaturated imines,[17] methylidenemalonate esters[18] and substituted isoxazoles.[19] Song, Gong and Duan also reported on the application of PCP/PCN pincer complexes[20] and N-heterocyclic carbene based palladacycles[21] in asymmetric hydrophosphination. One synthetic scenario which has been reported using both palladacycle and PCP pincer catalyst is the asymmetric hydrophosphination of alkylidenemalonate esters,[18,20b] which therefore provides an avenue to understand the critical impact of catalyst design on regio- and stereo-selectivities as well as reactivity in this useful synthetic protocol.



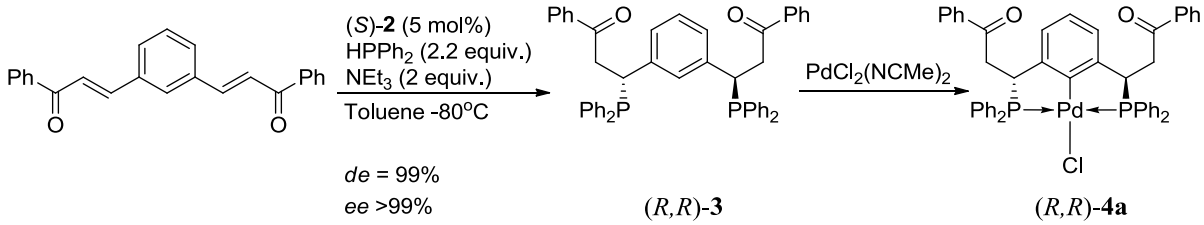
(*S*)-**1** (*S*)-**2**

Figure 1. Palladacycle Based Catalysts Used in Asymmetric Hydrophosphination .

Results And Discussion

Preparation of PCP Pd-Pincer

In an earlier communication, we reported the stepwise hydrophosphination of dienones catalyzed by catalyst (*S*)-**2** resulting in the formation of optically pure diphosphine (*R*,*R*)-**3** (*de* = 99%, *ee* >99%) and its subsequent metallation with $PdCl_2(NCMe)_2$ to yield pincer (*R*,*R*)-**4a** in 85% isolated yield (Scheme 1).[15] We now observed that the chloro ligand in (*R*,*R*)-**4a** could be readily converted to other potential leaving groups in (*R*,*R*)-**4b-c** (Table 1) by simple ligand exchange reactions. The molecular structure of pincer (*R*,*R*)-**4d** was confirmed crystallographically upon conversion of the chloro ligand to an iodo substituent (Figure 2).



(*R*,*R*)-**3** (*R*,*R*)-**4a**

Scheme 1. Synthesis of PCP Pd Pincer (*R,R*)-4

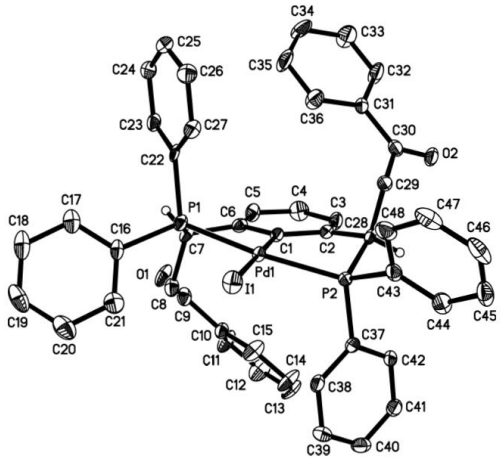


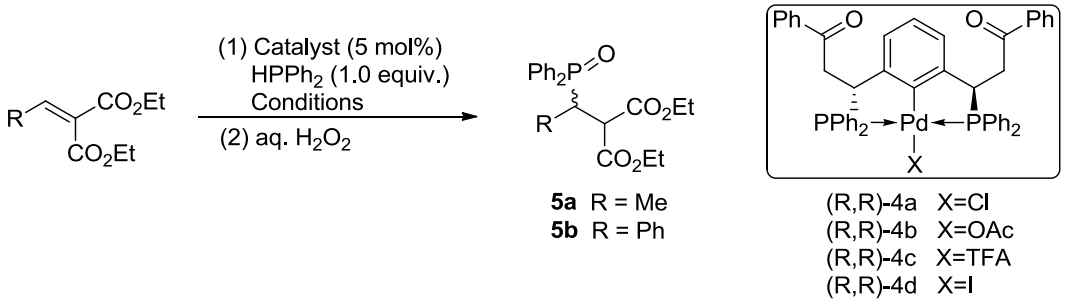
Figure 2. Single Crystal X-Ray Molecular Structure of (*R,R*)-4d

Hydrophosphination of Alkylidenemalonate Esters

In order to reveal the influence of ligand design on reactivity and stereo-selectivity, both catalysts (*S*)-**2** and (*R*,*R*)-**4b** were selected for the asymmetric hydrophosphination of the same alkylidenemalonate esters.

From Table 1, catalyst (*S*)-2 proved to be more efficacious and robust in terms of both reactivity and stereoselectivity (Table 1, entries 5, 17), achieveing a high *ee* of 67% for product 5a and 94% for product 5b. Interestingly, a previous report indicated that a PCP Pd pincer catalyzed hydrophosphination of diethyl benzylidenemalonate could not proceed in THF at room temperature.[20b] However, when pincer (*R*,*R*)-4b was employed, the reaction proceeded smoothly to form product 5b in yields of up to 78% albeit with low enantioselectivity. It needs to be noted that the addition of an external base (NEt_3) was necessary with catalyst (*S*)-2[13a] but not with (*R*,*R*)-4b[20g] due to the presence of an internal base (AcO^-). When the acetate group was replaced by a chloride ion (Table 1, entry 9), the reaction rate decreased tremendously, but with the addition of NEt_3 (Table 1, entry 11), the reaction rate improved but enantioselectivity was poor. Substitution of the chloride ion (Table 1, entry 10) with a triflate group gave no observable product but when NEt_3 was added (Table 1, entry 12), the reaction proceeded to completion. This reactivity trend can be attributed to the fact that a Pd-O bond is more labile than a Pd-Cl bond and could easily be replaced by diphenylphosphine. However the pK_a of triflate is lower than that of an acetate group, thus the triflate anion is not sufficiently basic for the deprotonation of diphenylphosphine and the reaction is unable to proceed.

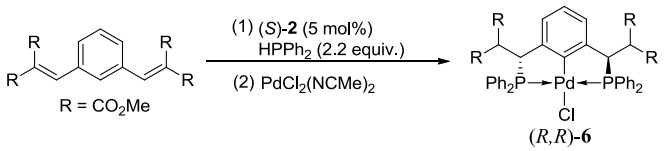
Table 1. Screening of Reaction Conditions for Substituted Alkylidenemalonate Esters



entry	Cat	R	solvent	base	duration (h)	temp (^oC)	Yield[a] (%)	*ee*[b] (%)
1	(*R*,*R*)-**4b**	Me	MeCN	-	0.5	RT	93	3
2	(*R*,*R*)-**4b**	Me	Acetone	-	0.5	RT	84	1
3	(*R*,*R*)-**4b**	Me	DCM	-	1	RT	88	5
4	(*R*,*R*)-**4b**	Me	DCM	-	1.5	-80	93	6
5	(*S*)-**2**	Me	DCM	NEt_3	1.5	-80	93	72
6	(*R*,*R*)-**4b**	Me	Toluene	-	1	RT	89	16
7	(*R*,*R*)-**4b**	Me	Toluene	-	3	-80	93	40
8	(*S*)-**2**	Me	Toluene	NEt_3	2	-80	81	7
9	(*R*,*R*)-**4a**	Me	Toluene	-	24	RT	2	ND[c]
10[d]	(*R*,*R*)-**4c**	Me	Toluene	-	4	RT	Nil	Nil
11	(*R*,*R*)-**4a**	Me	Toluene	NEt_3	24	RT	50	1
12	(*R*,*R*)-**4c**	Me	Toluene	NEt_3	3	RT	71	5
13	(*R*,*R*)-**4b**	Ph	Toluene	-	5	RT	78	1
14	(*S*)-**2**	Ph	Toluene	NEt_3	24	-80	70	28
15	(*R*,*R*)-**4b**	Ph	DCM	-	5	RT	76	3
16	(*R*,*R*)-**4b**	Ph	DCM	-	24	0	52	18
17	(*S*)-**2**	Ph	DCM	NEt_3	4	-80	81	94

[a] For entries 1-12, R = Me and for entries 13-17, R = Ph. [b] Unless otherwise stated, the absolute configurations of the pincer catalyst is (*R*,*R*). [c] Isolated yields. [d] Determined by chiral HPLC with hexane-2-propanol. [e] Not determined

Based on the promising results, we then extended the hydrophosphination reaction to tetramethyl 2,2'-(1,3-phenylenebis(methanylylidene))dimalonate and synthesized pincer (*R*,*R*)-**6** in an isolated yield of 85% with a *de* and *ee* of 99%. The single crystal molecular structure of (*R*,*R*)-**6** is depicted in Figure 3.



Scheme 2. Synthesis of Pincer (*R*,*R*)-**6**.

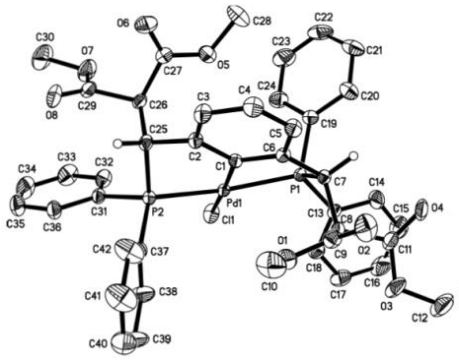
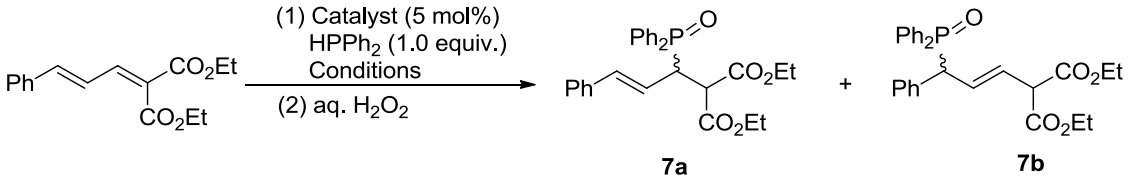


Figure 3. Molecular Structure of (*R*,*R*)-**6**. All hydrogen atoms except H(C7) and H(C25) were omitted for clarity.

Regioselectivity in Enantioselective Hydrophosphination

Having established the reactivity of both catalysts, we decided to evaluate their reactivity along with regio- and stereo-selectivity in the catalytic hydrophosphination of *α*,*β*,γ,*δ*-diunsaturated olefins. When catalyst (*S*)-**2** was used, two products **7a** and **7b** were observed (Table 2, entries 6,8). Under optimized conditions (Table 2, entry 7) it led to the exclusive formation of the 1,4-adduct **7a** with >99% *ee*. To our surprise, when the pincer (*R*,*R*)-**4b** was employed under similar conditions (Table 2, entry 2), the reaction proceeded over 24 hrs to yield the 1,6-adduct **7b** as the major product in 57% yield with an *ee* of 60%. A judicious choice of reaction conditions and catalyst afforded >99% regioselectivity with moderate to excellent enantioselectivity. The identities of both products **7a** and **7b** were confirmed crystallographically.[22]

Table 2. Screening of Reaction Conditions for Diethyl 2-Cinnamylidenemalonate



7a **7b**

entry	Cat	solvent	base	duration (h)	temp (°C)	Yield[a] (%)	Ratio of 7a:7b[b]	*ee*[c] (%)
1	(*R*,*R*)-**4b**	DCM	-	2	RT	79	0:100	38
2	(*R*,*R*)-**4b**	DCM	-	24	-80	57	6:94	60
3	(*R*,*R*)-**4b**	MTBE	-	1	RT	73	2:98	22
4	(*R*,*R*)-**4b**	Toluene	-	3	RT	64	3:97	29
5	(*R*,*R*)-**4b**	Toluene	-	24	-80	41	5:95	70
6	(*S*)-**2**	DCM	NEt_3	2	RT	70	97:3	55
7	(*S*)-**2**	DCM	NEt_3	4	-80	91	100:0	>99
8	(*S*)-**2**	DCM	NEt_3	0.5	50	80	62:38	24(35)[d]
9[e]	-	DCM	NEt_3	96	50	-	ND[f]	ND

10[e]	-	DCM	NaOAc	96	50	-	ND	ND

[a] Catalyst (*R*,*R*)-**4b** was used in entries 1-5 and (*S*)-**2** in entries 6-8 respectively. No catalyst was used for entries 9 and 10. [b] Combined isolated yields of **7a** and **7b**. [c] Ratio of **7a**:**7b** was determined by integration of their respective proton signals at 6.41 and 5.73 ppm. [d] *ee* of major product determined by chiral HPLC. [e] Absolute configuration was determined by X-ray analysis of the product. [f] *ee* in parentheses belongs to the minor product. [g] <5% conversion was calculated based on $^{31}P\{^{1}H\}$ NMR after 96 h. Only the 1,4-adduct **7a** was observed. [h] Not determined.

Mechanistic Considerations

Based on these results, we proposed the reaction mode for the 1,6-addition of diphenylphosphine to diethyl 2-cinnamylidenemalonate catalyzed by pincer (*R*,*R*)-**4b** (Figure 4).

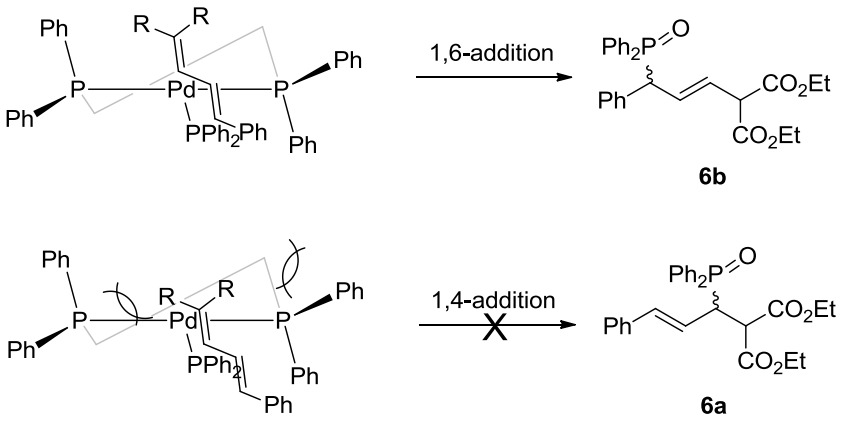
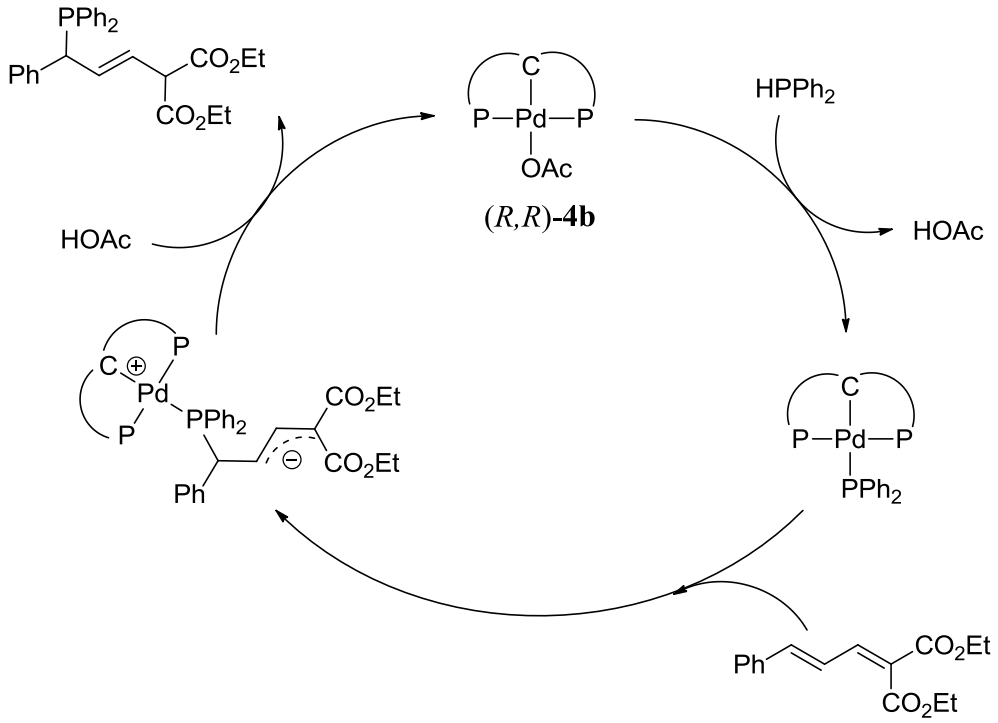


Figure 4. Reaction Mode for 1,6-Addition Catalyzed by (*R*,*R*)-**4b**.

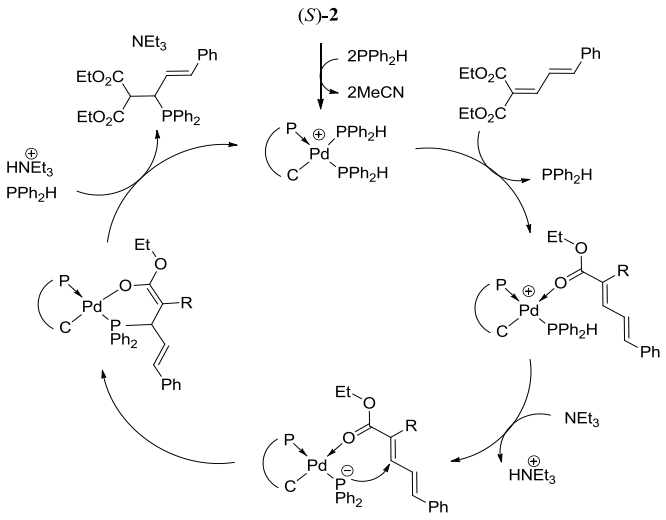
The presence of the bulky carboxylic ester groups prevents the Pd-phosphido intermediate from approaching the *β*-position, hence favoring the 1,6-addition of diphenylphosphine to the *δ*-position of the substrate. A simple NMR experiment[23] was conducted to elucidate the proposed reaction mechanism of catalyst (*R*,*R*)-4b (Scheme 3). In the absence of catalyst (Table 2, entries 9, 10), the reactivity was drastically reduced, which indicates that the addition of diphenylphosphine to the

catalyst acidifies the proton thus priming it for deprotonation.



Scheme 3. Proposed Catalytic Cycle for Catalyst (*R*,*R*)-4b

We proposed a catalytic cycle (Scheme 4) in which the substrate replaces the phosphine that is *trans* to the naphthalene carbon due to the lability of the Pd-P bond. The coordination of the phosphine to the Pd metal acidifies the P-H bond thus allowing for its deprotonation by a base. The nucleophilic phosphido species is then directed to attack the *β*-position of the substrate due to the formation of a favored 6-membered intermediate. This mechanism is similar to other P-H addition reactions catalysed by catalyst (*S*)-**2**.[13a]



Scheme 4. Proposed Catalytic Cycle for Catalyst (*S*)-**2.**

In Table 2, we observed that the regioselectivity afforded by (*R,R*)-**4b** decreased while that of (*S*)-**2** increased at lower temperatures. Based on the reaction mode of catalyst (*R,R*)-**4b**, it is likely that at lower temperatures, the formation of the 1,6-adduct **7b** slows down significantly. A competing pathway (Scheme 5) involving the dissociation of one of the labile trans Pd-P bonds in this pincer complex to form a bidentate complex 8 allowed the subsequent coordination of the substrate through

the carbonyl oxygen atom. The 6-membered intermediate directed the nucleophile to the *β*-position and resulted in the formation of the 1,4-adduct **7a**.

The lower regioselectivity of catalyst (*S*)-**2** at elevated temperature could be attributed to the competing pathway involving an external nucleophilic attack at the *δ*-position of the substrate, resulting in the formation of the kinetically favored product **7b**. At higher temperatures, **7b** will be favored over the thermodynamic product **7a**, hence a larger proportion of the 1,6-adduct **7b** was observed.

Conclusions

The growth of interest in the development of methodologies for 1,6-conjugate addition, especially those involving non-carbon nucleophiles, to *α*,*β*,γ,*δ*-diunsaturated systems emphasizes the significance of this type of reaction. However its development is inhibited by limitations concerning the control of steric and electronic factors. In summary, we have shown that the asymmetric addition of diphenylphosphine to *α*,*β*-unsaturated olefins could be achieved with both palladacycles as well as PCP pincer type catalysts in high yields. However, when the reaction was extended to *α*,*β*,γ,*δ*-diunsaturated malonate esters, the palladacycle (*S*)-**2** and pincer (*R*,*R*)-**4b** exhibited a dramatic difference in regioselectivity due to the influence of ligand design. Further studies are currently underway in our laboratory to extend the protocol to other conjugated substrates.

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