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Chiral Phosphapalladacycles as Efficient Catalysts for the Asymmetric Hydrophosphination of Substituted Methylidenemalonate Esters: Direct Access to Functionalized Tertiary Chiral Phosphines

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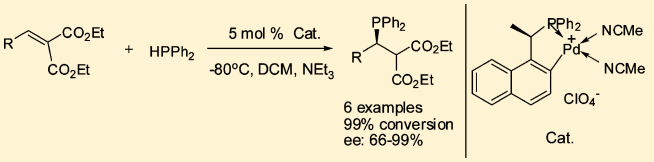
Supporting Information

ABSTRACT: A chiral palladacycle-promoted enantioselective asymmetric hydrophosphination of substituted methylidenemalonate esters using diphenylphosphine that provides direct access to chiral tertiary phosphines is reported. Screening of three easily accessible C,N and C,P palladacycles as catalysts for this synthetic scenario provided insights into critical factors in catalyst design that influence the activation and stereochemistry in Pd(II)-catalyzed asymmetric P−H addition reactions involving such activated substrates.



INTRODUCTION

Functionalized enantiopure phosphines are widely utilized as efficacious ligands toward a range of metal-catalyzed industrially relevant asymmetric transformations such as hydrogenations,[1] cross-coupling reactions,[2] and hydroformylations.[3] However the employment of stoichiometric promoters and resolving agents has been the dominant approach in their synthesis.[4] Metal-catalyzed asymmetric addition of the P−H moiety to unsaturated functionalized substrates offers an alternative atom-efficient protocol for accessing these compounds. Among the few reports in the literature of such a protocol are the pioneering work by Glueck et al. involving the Pt^0-(Me-Duphos)- and Pt^0-(diphos)-catalyzed hydrophosphination of activated olefins,[5] organocatalyst-catalyzed hydrophosphination of nitroalkenes[6] and α,β-unsaturated aldehydes,[7] and chiral P,C,P and P,C,N pincer complex catalyzed hydrophosphination of enones and α,β-*N*-acylpyrroles, generating phosphine oxides.[8] We have previously disclosed the extensive utilization of *stoichiometric* amounts of the chiral palladacycle (*R*/*S*)-$\{[Pd[Me_2NCH(Me)C_{10}H_6]](\mu\text{-Cl})\}_2$ and its derivatives toward the synthesis of a wide range of chiral tertiary phosphine ligand motifs.[9] Recently, we had also extended their use to the catalytic asymmetric hydrophosphination of aromatic enones, thus directly generating chiral keto-functionalized tertiary phosphines in good yields and enantioselectivities.[10a−c] However, catalytic asymmetric hydrophosphination of substrates other than those carrying cyano, keto, nitro, aldehyde, and pyrrole functionalities has been conspicuously absent in the literature except for the few instances wherein ester-functionalized phosphine products were obtained in low ee's.[5] This is indeed a drawback when considering the vast range of functionalities tolerated in traditional methods.

Herein we report the investigations into the palladacycle-promoted asymmetric P−H bond addition of ester to functionalized unsaturated moieties and present the results from our studies, which involve the first instance in the literature of catalytic addition of secondary phosphines to esters leading to the efficient generation of the corresponding chiral tertiary phosphines in good yields and high enantioselectivities. The analysis of three P,C- and N,C-based palladacycles in their role as catalysts gave us crucial insights into factors that influence the design of efficient catalysts in such synthetic scenarios.

RESULTS AND DISCUSSION

The three palladacycles employed in this study (Figure 1) were prepared by treating the corresponding chloro-bridged dimeric palladium compounds[11a−c] with silver perchlorate in acetonitrile via a procedure reported previously for (*R*)-**1**[10a] and (*R*)-**3**.[11d] In our hands, these complexes and their derivatives have repeatedly proven their efficacy in asymmetric C−C,[12a] C−N,[13c] C−P,[9a−e,12c] and C−As[12b,13a,b] bond formation scenarios.

A key structural feature in these palladacyles is that the organometallic ring is locked into the static δ conformation in solution (for the *R* isomer).[14] This in turn fixes the position of

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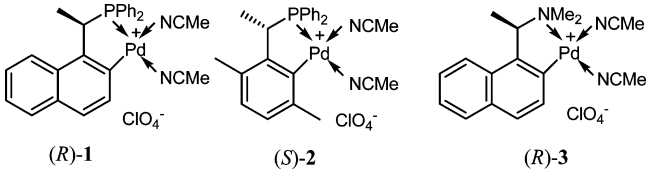


Figure 1. Palladacycles used in the study.

the prochiral NMe/PPh groups into nonequivalent axial and equatorial positions, whereby they can control the stereochemistry at the neighboring coordination sites. The electronic properties of the N and P heteroatoms and the comparatively stronger π-accepting aromatic carbon of the organopalladium ring allow the complex to possess unique molecular recognition ability with respect to incoming substrates.[15]

The three chosen complexes thus provided us an opportunity to evaluate the effect of variation in key electronic factors (N vs P), steric tuning of substituents on the heteroatom (Me_2 vs Ph_2), and different moieties at the site adjacent to the Pd−C bond on the aromatic ring (H vs Me) while retaining the key features that have made them highly effective chiral auxiliaries. With these catalysts in hand we proceeded to test their efficacy in the asymmetric P−H addition to unsaturated esters (Table 1).

Our preliminary investigation started with the P−H addition of diphenylphosphine to ethyl cinnamate. The reactions were performed in the presence of 5 mol % of (*R*)-**1**, (*S*)-**2**, and (*R*)-**3**, respectively, under conditions that have been established from our previous studies on enones.[10a−c] However all three complexes failed to generate any monophosphine product even after 2 weeks at room temperature. The reaction of diethyl allylmalonate with diphenylphosphine also did not proceed under similar conditions.

The adequate activation of the C═C bond by adjacent electron-withdrawing moieties has been established to be a key factor that aids such P−H addition protocols using metal complexes. It was evident from our initial results that the activation in these two instances does not meet the requirements for a metal-catalyzed P−H addition across the C═C bond. We have previously reported that this class of cyclopalladated complexes can indeed recognize the subtle electronic differences between the keto and ester functional groups. For instance, they activate the C═C bonds in vinyl ketones efficiently toward cycloaddition reactions[16] but provide only poor activation to the C═C bonds in acrylates.[17] We therefore proceeded to examine the addition of diphenylphosphine to diethyl benzylidenemalonate. With this diester-substituted substrate, the hydrophosphination proceeded in a facile manner, requiring only 1.5 h for full product conversion at room temperature (RT). The $^{31}P\{^1H\}$ NMR spectrum of the product in $CDCl_3$ displayed a singlet at δ 2.7, indicating a highly regioselective addition.

An efficient and reliable procedure for the analysis of ee of such tertiary phosphines has been previously reported by us[10] and is shown in Scheme 1.

Scheme 1. Protocol Adopted for the Determination of ee by Coordination of the Tertiary Phosphine to (*R*)-{[Pd[Me_2NCH(Me)$C_{10}H_6$](*μ*-Cl)}$_2$

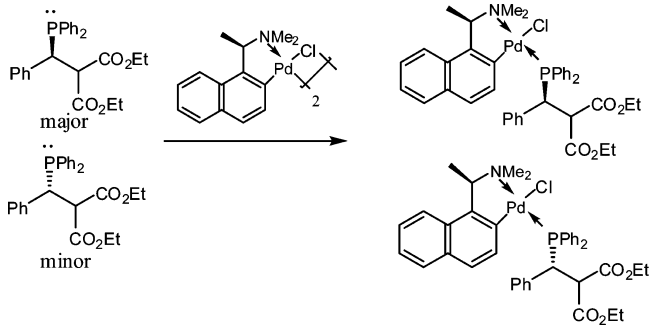
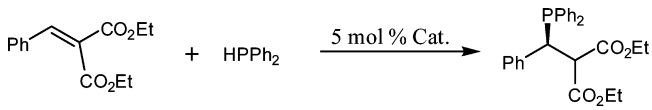


Table 1. Screening of Reaction Conditions[a]



entry	cat	solvent	base	temp (°C)	reactivity (h)	conversion[b] (%)	ee[c] (%)
1	(*R*)-**1**	DCM	NEt_3	RT	1.5	99	63
2	(*R*)-**1**	DCM	NEt_3	−80	3.5	99	96
3	(*S*)-**2**	DCM	NEt_3	−80	24	99	65
4	(*R*)-**3**	DCM	NEt_3	−80	7	99	86
5	(*S*)-**1**	DCM	NEt_3	−80	3.5	99	96
6	(*R*)-**1**	DCM	NEt_3	−40	2.5	99	93
7	(*R*)-**1**	acetone	NEt_3	−80	>6	99	95
8	(*R*)-**1**	MeCN	NEt_3	−40	4	99	81
9	(*R*)-**1**	chloroform	NEt_3	−40	24	99	85
10	(*R*)-**1**	THF	NEt_3	−80	NIL	NIL	NIL
11	(*R*)-**1**	1,4-dioxane/water, 10:1	NEt_3	RT	10	83	18
12	(*R*)-**1**	toluene	NEt_3	−80	>24	NIL	NIL
13	(*R*)-**1**	DCM	DBU	−80	24	35	NIL
14	(*R*)-**1**	DCM	*t*-BuONa[d]	−40	5.5	99	36

[a]Conditions: $HPPh_2$ (50.0 mg, 2.69×10^{-4} mol), 5 mol % cat, 1.2 equiv of diethyl benzylidenemalonate (80.2 mg, 3.23×10^{-4} mol), 1 equiv of base (2.69×10^{-4} mol), and 6 mL of degassed dichloromethane were reacted at the indicated temperature. [b]Conversion was calculated from $^{31}P\{^1H\}$ NMR. [c]ee was determined from $^{31}P\{^1H\}$ NMR integration of the respective signals via the use of a chiral derivatizing agent. The detailed procedure is described in S5. [d]Solid ^{t}BuONa was used.

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This procedure was used to determine the ee of 63% by $^{31}P\{^{1}H\}$ NMR spectroscopy for the asymmetric P−H bond addition to diethyl benzylmalonate at RT (Table 1, entry 1). It needs to be noted that the use of this procedure usually allows us to obtain single crystals of the adducts of the tertiary phosphine on the palladacycle directly, thus allowing the assignment of absolute stereochemistry from X-ray diffraction data. Interestingly, for the current diester-substituted phosphine complexes, it is necessary to replace the chloro ligand with iodo in order to generate single crystals that are suitable for structural investigations (Figure 2).

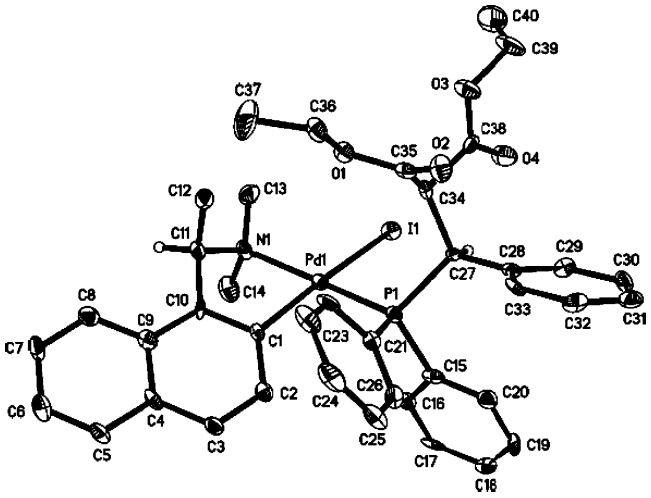


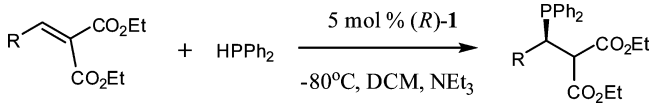
Figure 2. Molecular structure and absolute stereochemistry of the tertiary phosphine (major isomer) coordinated to the palladacycle complex (Scheme 1) with 50% probability thermal ellipsoids shown (Cl atom on Pd replaced with I to aid in crystallization).

The asymmetric hydrophosphination reaction of diethyl benzylidenemalonate was then screened as a model reaction in order to examine the effect of the palladacycles as catalysts. The palladacycle complex **1** is the most effective among the three (Table 1, entries 2 to 5) and was selected as the catalyst. The reaction, when performed in the presence of 5 mol % **1**, generated the desired product in 99% yield with 96% ee (Table 1, entries 2 and 5) within 3.5 h and at −80 °C. It was seen that the change of catalyst from (*R*)-**1** to its equally accessible enantiomeric counterpart (*S*)-**1** resulted in the generation of the opposite enantiomeric form of the tertiary phosphine product in exactly the same ee (Table 1, entries 2 and 5). Besides providing definitive evidence of the influence of the chiral catalyst on stereocontrol, this experiment also provides access to both enantiomers of the product in high optical purity.

Under the optimum conditions mentioned above, with (*R*)-**1** as the catalyst, various solvents, temperatures, and bases were also subsequently examined (Table 1, entries 6−14). Dichloromethane uniformly gave the highest conversions (99%) and ee values (63−96%) (Table 1, entries 1, 2, 5, 6). Although similar selectivity was observed with acetone as solvent (Table 1, entry 7), it was accompanied by a concommitent decrease of reactivity. Appreciable selectivities were also recorded with acetonitrile and chloroform, but these were not comparable with those obtained using dicloromethane as solvent (Table 1, entries 8, 9). No desired phosphine product was obtained when the hydrophosphination was carried out in THF (Table 1, entry 10), extremely poor reactivity was observed with toluene (Table 1, entry 12), and poor selectivity was attained with 1,4-dioxane/water = 10:1 (Table 1, entry 11). The results of screening of bases showed that Et_3N offered the most appropriate basicity, compared with ^{t}BuONa, which was associated with a low ee (36%) and DBU, which caused lowering of reactivity (Table 1, entries 13, 14). In the absence of base, no product formation was observed even after 1 week at room temperature. A variety of temperatures were also examined using dichlormethane as solvent. The analysis (Table 1, entries 1, 2, 6) revealed a general trend: an increase in temperature leads to an increase in reactivity, coinciding with a decrease in enantioselectivity. When the temperature was increased from −80 to −40 °C, the reaction time decreased by 1 h with a slight decrease of ee (3%). When the temperature was raised from −40 °C to room temperature, the reaction time again decreased by 1 h, but a marked 30% drop in ee was observed.

With the optimized conditions established, i.e., (*R*)-**1** as the catalyst, dichloromethane as solvent, and NEt_3 as base at −80 °C, various substituted methylidenemalonate esters were screened, and the results are summarized in Table 2. The results show that the catalyst is highly efficient for the P−H

Table 2. Substrate Scope for the Phospalladacycle-Catalyzed P−H Addition of Diphenylphosphine to Substituted Methylidenemalonate Esters[a]



entry	R	conversion[b] (%)	ee[c] (%)
1	Ph	99	96
2	OEt	99	74
3	Me	99	ca. 66
4	2-furan	99	94
5	4-$MeOC_6H_4$	99	ca. 99
6	(*E*)-PhCH=CH	99	>99
7	NH_2	NIL	NIL

[a]Conditions: $HPPh_2$ (50.0 mg, 2.69 × 10^{-4} mol), 5 mol % cat (*R*)-**1** (8.4 mg, 1.34 × 10^{-5} mol, 5 mol % of $HPPh_2$), 1.2 equiv of substituted methylidenemalonate ester (3.23 × 10^{-4} mol), 1 equiv of NEt_3 (27.1 mg, 2.69 × 10^{-4} mol), and 6 mL of degassed DCM were reacted at −80 °C. [b]Conversion was calculated from $^{31}P\{^{1}H\}$ NMR. [c]ee was determined from $^{31}P\{^{1}H\}$ NMR integration of the respective signals via the use of a chiral derivatizing agent. The detailed procedure is described in S5.

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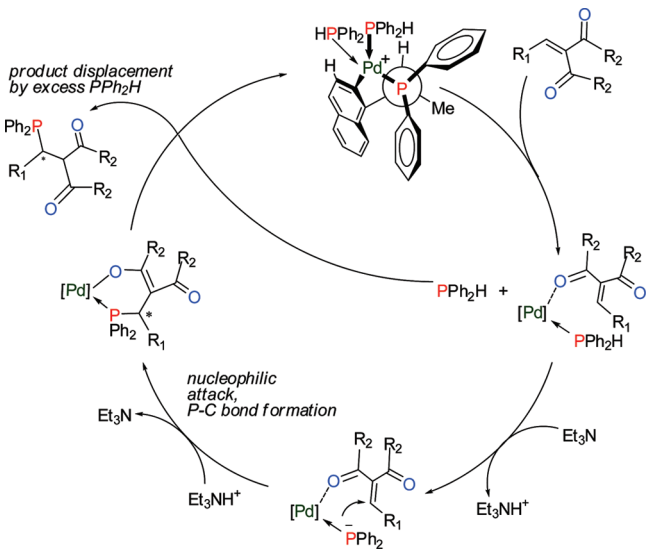
addition process (99% conversion; Table 2, entries 1−6), allowing the transformation of substrates to the corresponding C-chiral monophosphine adducts (ee value 66−99%; Table 2, entries 1−6). The substituents at the β-position of the substituted methylidenemalonate esters also had a large influence on the ee value of the products. Substrates bearing an aromatic phenyl group and a substituted phenyl group showed higher stereoselectivities (ee: 96, 99%; Table 2, entries 1, 5) than their aliphatic counterparts (ee: 74, 66% ; Table 2, entries 2, 3).

Interestingly, the asymmetric hydrophosphination of diethyl cinnamylidenemalonate (Table 2, entry 6) also proceeded with excellent regio- and enantioselectivities. Diphenylphosphide addition occurred exclusively at the more electron-deficient C═C bond, yielding a vinyl phosphine adduct with an ee value of >99%. Addition of 2 equiv of diphenylphosphine to the substrate under similar conditions also resulted in the generation of the same monophosphine product with no trace of diphosphines observed in the crude $^{31}P\{^{1}H\}$ NMR spectrum. Substrates bearing a furan-2-yl heterocyclic beta-substituent also showed a rather high reactivity and stereoselectivity (ee, 94%, Table 2, entry 4). The lack of reactivity seen in the case of diethyl 2-(aminomethylene)malonate (Table 2, entry 7) is attributed to the potential chelation impeding the availability of catalyst vacant sites in the catalyst (*vide infra*).

We have previously discussed the possible mechanism in place for such metal-catalyzed hydrophosphination scenarios using palladacycles.[10a−c] We believe that a similar mechanism is in action for this particular synthetic scenario (Scheme 2).

Scheme 2. Proposed Mechanism for the Pd-Catalyzed Hydrophosphination of Substituted Methylidenemalonate Esters



However the screening of the three palladacycles in this study provided us further insights into the key catalyst design features that are of consequence in the catalytic cycle. For instance, the hindered reactivity of (*S*)-**2** when compared to (*R*/*S*)-**1** (Table 1, entries 2, 3, 5) is a clear indication that the presence of the Me group at the site adjacent to the Pd−C bond on the aromatic ring in (*S*)-**2** prevents the easy accessibility of the bulky phosphine moieties involved to the electronically preferred coordination site (*trans* to the P of the palladacycle).[15] It needs to be noted that the coordination of diphenylphoshine to palladium and the subsequent P−H activation are crucial in generating the nucleophile prior to the P−C bond formation, as shown in Scheme 2.

The enhanced reactivity of the phosphapalladacycle (*R*)-**1** when compared to the naphthylamine-based palladacycle (*R*)-**3** (Table 1, entries 2, 4, 5) can be also attributed to the fact that the phosphorus of the metallacycle ring (by virtue of its ability to accommodate extensive back-donation from the metal center) makes the activation of the diphenylphosphine moiety and its subsequent nucleophilic attack on the diester more facile. The relatively slower reactivity of the C,N complex (*R*)-**3** can also be attributed to the classic features that *trans* N−Pd−P bonds are more stable than *trans* P−Pd−P bonds. Thus the product elimination process will be slower when (*R*)-**3** is involved. The enhanced stereoselectivity exhibited by (*R*)-**1** and (*S*)-**1** can also be attributed to the fact that the conformational rigidity of the palladacycle fixes the positions of the phenyl groups on P (as compared to Me on (*R*)-**3**) into axial and equatorial positions, from wherein they can project their greater stereochemical influence on the adjacent reaction site.

On the basis of the same mechanism, it is also easy to understand why diethyl 2-(aminomethylene)malonate failed to undergo P−H addition (Table 2, entry 7). The product from the initial hydrophosphination reaction in this instance will be a P,N (N from the amino moiety) chelate on palladium, which can then potentially block the access of both catalytic sites on the metal to incoming substrates, thus effectively terminating the reaction once 5% of the catalyst is rendered inactive via chelation.

CONCLUSION

In summary, we have developed an efficient protocol for the palladacycle-catalyzed asymmetric P−H additions to substituted methylidenemalonate esters. This approach thus provides a practical direct route toward optical pure functionalized tertiary chiral phosphines in high yields and enantioselectivities, circumventing the need for elaborate protection and deprotection protocols as well as avoiding the need to deal with phosphine oxides, which can in some instances lead to complications.[18] This body of work has also provided insights into the factors that need to be considered when designing catalysts for such asymmetric P−H additions. Further studies are currently under way to explore the applicability of this protocol to other functionalized substrates.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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