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Cymantrene-based iminodiamidophosphites: the first phosphite-type ligands with planar chirality

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Abstract—Optically active phosphite-type ligands with planar chirality have been synthesized for the first time. The new cymantrene-based *P*,*N*-iminodiamidophosphites demonstrated high enantioselectivity in the Pd-catalyzed allylic substitution of 1,3-diphenylallyl acetate with dimethyl malonate (up to 94% ee), pyrrolidine (up to 78% ee) and sodium *para*-toluene sulfinate (up to 84% ee).

1. Introduction

Phosphine ligands with planar chirality represent one of the largest classes of optically active *P*-containing compounds.[1–3] An outstanding place among them belongs to heterobifunctional ligands particularly *P*,*N*-bidentate ones.[4–8] Moreover, planar chiral compounds were historically the first group of optically active *P*,*N*-bidentate ligands.[9] *P*,*N*-Bidentate systems derived from ferrocene, cymantrene, chromium and rhenium tricarbonyl complexes have been actively investigated recently (see Refs. [10–18] and references cited therein). But, to the best of our knowledge, all known compounds represent phosphine-type ligands, and no examples of phosphite ligands with planar chirality have been described, to date. This situation is rather surprising, since many recent dramatic breakthroughs in asymmetric catalysis have been achieved with phosphites with central and axial chirality.[5–8,19,20] Herein, we report planar chiral diamidophosphite ligands and their application in Pd-catalyzed asymmetric allylations.

2. Results and discussion

Synthetic routes for **4a** and **4b**, and **5a** and **5b** are depicted in Schemes 1–3. Metallation of (2*S*,4*S*,5*R*)-3,4-dimethyl-5-phenyl-2-cymantrenyloxazolidine with BuLi followed by treatment with DMF and water gave its 2-formyl derivative. Further reduction with $NaBH_4$ into the corresponding alcohol followed by acidic hydrolysis afforded (R_p)-(hydroxymethyl)cymantrenecarbaldehyde **1** (90% ee).

Further reactions between this compound and amines proceeded smoothly and gave iminoalcohols **2** and **3** in high yields. Although (R_p)-(hydroxymethyl)cymantrenecarbaldehyde **1** was not enantiomerically pure, the NMR spectra of iminoalcohol **3**, and ligands **4b** and **5b** contained no additional signals of the minor (R_p)-epimers (see Experimental part and Table 1). Most probably, the reason is accidental identity of NMR signals of major (S_p) and minor (R_p) epimers. Indeed, the ^1H NMR spectrum of iminoalcohol **3**, specifically prepared by us from racemic (hydroxymethyl)cymantrenecarbaldehyde, is absolutely identical to the spectrum of **3** obtained from the 90% enantiomerically pure aldehyde. The structure of iminoalcohol **3** also has been confirmed by X-ray analysis (Fig. 1).

In **4a** and **4b**, **5a** and **5b** range, one can see a successive complication of the steric aspects of the ligands: **4a** has

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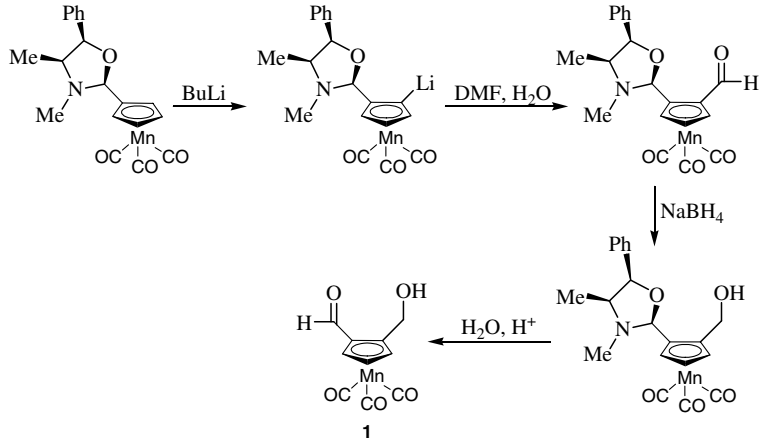
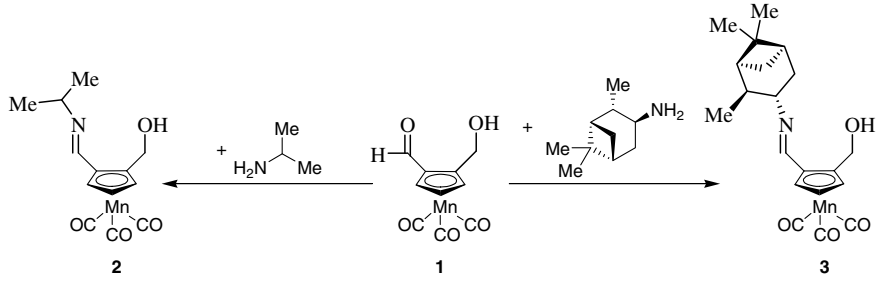
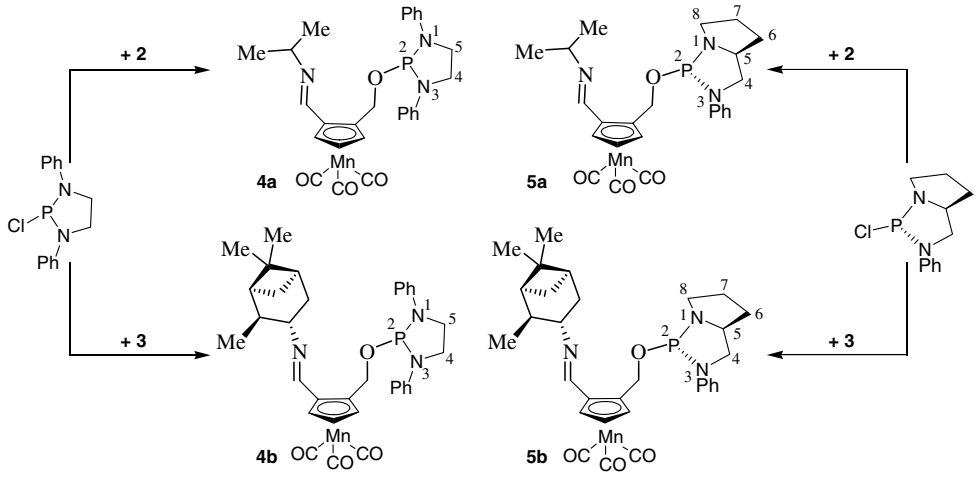


Scheme 1.



Scheme 2.



Scheme 3.

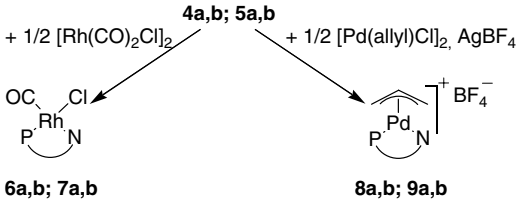
only a stereoplane, **4b** and **5a** bear additional *P*- also and (or) *C*-stereocenters, and finally **5b** has a maximal set of all the listed elements of chirality.

Due to the presence of the *P*-stereocenter, **5a** and **5b** consist of two stereoisomers (Table 1). In both cases, the major stereoisomer (δ_P 122.4 for **5a** and 122.0 for **5b**) is characterized by pseudoequatorial orientation of the exocyclic substituent at the phosphorus atom (i.e., *R* configuration at the *P*-stereocenter). This was concluded from the characteristic ^2J(C(8),P) values (38.2 and 38.3 Hz) in ^{13}C NMR spectra of **5a** and **5b**.[21] Accordingly, the minor epimers (δ_P 120.7 for **5a** and 120.0 for **5b**) have an (*S*)-configuration at the *P*-stereocenter. It is notable that signals of the minor (R_p)-stereoisomers are also visible in the ^{31}P NMR spectrum of **5a** (δ_P 121.9 and 120.3, Table 1). Neutral and cationic *cis*-chelate metal complexes were obtained using **4a** and **4b**, and **5a** and **5b** (Scheme 4).

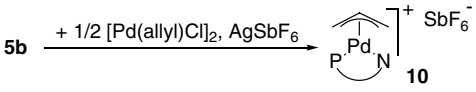
Table 1. Selected spectroscopic data for compounds **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **7a**, and **7b** (in $CHCl_3$)

Compound	^{31}P NMR		IR, ν(CO), cm^{-1}
	δ_P	^1J(P,Rh), Hz	
4a	102.9	—	2028, 1948
4b	103.0	—	2028, 1949
5a	122.4 (79%), 121.9 (7%), 120.7 (12%), 120.3 (2%)	—	2027, 1944
5b	122.0 (86%), 120.0 (14%)	—	2029, 1948
6a	115.9	237.8	2036, 1996,[a] 1948
6b	115.6	241.6	2032, 1997,[a] 1954
7a	130.8 (br)	227.5	2033, 2001,[a] 1952
7b	129.3	228.6	2032, 2000,[a] 1952

[a] For Rh-CO fragment.



Scheme 4.



Scheme 5.

Besides, for catalytic purposes, we synthesized a cationic complex **10** having a bulky SbF_6^- anion (Scheme 5).

The ^1J(P,Rh) and ν(CO) data of complexes **6a** and **6b**, and **7a** and **7b** (Table 1) are in a good agreement with the suggested structures with a cis-orientation of the donor phosphorus and nitrogen atoms bound to the metal atom.[22] According to the ^1J(P,Rh) and ν(CO) parameters of **6a** and **6b** and **7a** and **7b**, diamidophosphites **4a** and **4b**, and **5a** and **5b** occupy an intermediate position between phosphines and phosphoramidites in a spectrochemical range of organophosphorus ligands.[23,24] Besides, **4a** and **4b**, and **5a** and **5b** have practically identical π-acceptor and σ-donor properties, for ^1J(P,Rh) and ν(CO) parameters of their chlorocarbonyl rhodium complexes are rather close.

The suggested chelate structure of the cationic palladium complexes **8a** and **8b**, **9a** and **9b** and **10** is supported by ^{31}P NMR and ESI MS data. Duplication of peaks in ^{31}P NMR spectra of complexes **8a** and **9a** indicates the existence of *exo*- and *endo*-isomers of the compounds. This is not observed for complexes **8a**, **9b** and **10** either because of the fast interconversion of the isomers or due to the absence of one of the isomers.[22] It should be mentioned that compounds **8a** and **8b**, **9a** and **9b** and **10** are photosensitive. Thus, even a short-term exposure to light of their chloroform solutions resulted in precipitation of a black solid and in the appearance of additional signals in the δ_P 110–130 and 7–33 ppm regions of their ^{31}P NMR spectra. Therefore, catalytic experiments with participation of ligands **4a**, **4b**, **5a** and **5b** and complexes **8a**, **8b**, **9a**, **9b** and **10** were protected from light.

Catalytic properties of iminodiamidophosphites **4a**, **4b**, **5a** and **5b** and their palladium complexes were tested in several model reactions such as allylic alkylation, allylic sulfonylation and allylic amination (Scheme 6).

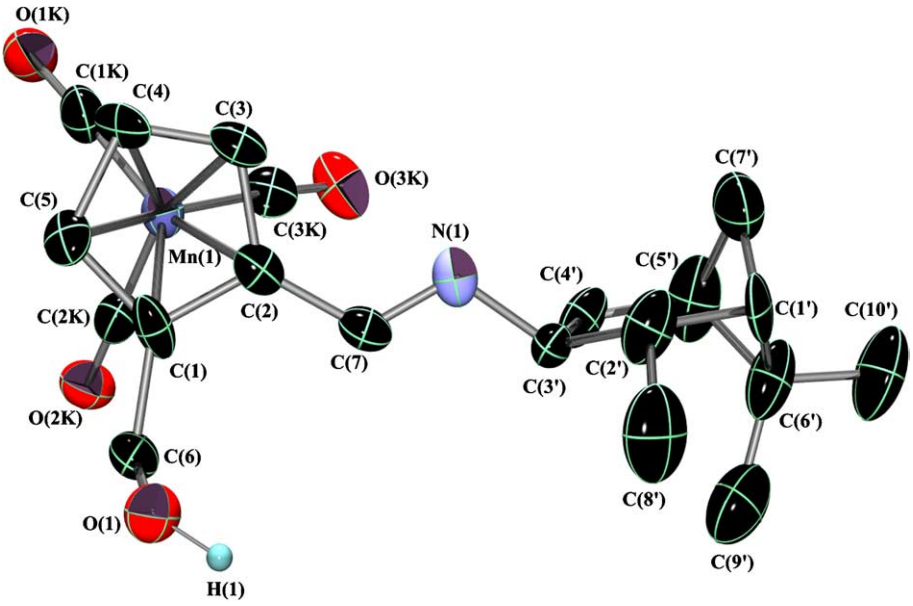
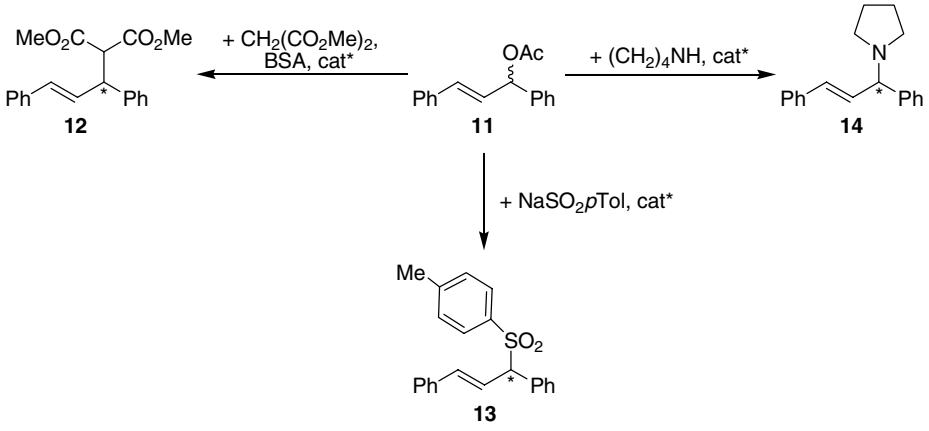


Figure 1. Molecular structure of **3**. Atoms are presented by thermal ellipsoids drawn at 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å): O(1)–C(6) 1.435(10), N(1)–C(3′) 1.464(10), N(1)–C(7) 1.242(10), Mn–C (averaged) 2.148(8); selected bond angles (deg): O(1)–C(6)–C(1) 108.1(7), C(7)–N(1)–C(3′) 118.5(8).



Scheme 6.

The results achieved in the allylic substitution of **11** with dimethyl malonate are shown in Table 2. Planar chiral ligand **4a** showed low enantioselectivity (up to 41% ee, entry 2). In this case, one can assume that a stereoplane as a sole element of chirality does not provide effective asymmetric induction. Considering 90% enantiomeric purity of **4a**, a negative nonlinear effect is also not excluded. Low enantioselectivity in the case of iminodiamidophosphite **4b**, which has additional *C*-stereocenters (Table 2, entries 5–8), was rather surprising. Probably, a mismatched combination of planar and central chirality is observed in this case. Multichiral ligands **5a** and **5b** were much more successful. In particular, up to 71% ee were achieved using **5a** (Table 2, entry 10), CH_2Cl_2 being a solvent of choice, **5b** demonstrated higher stereoselectivity. $[Pd(allyl)Cl]_2$ was found to be superior catalyst precursor for **5b** at the L/Pd = 1:1 molar ratio, while $[Pd_2(dba)_3 \times CHCl_3]$ was preferable at the L/Pd = 2:1 molar ratio (Table 2, entries 14–17). The cationic complex **9b** afforded product **12** with excellent enantioselectivity (94% ee, 90% conversion, Table 2, entry 18). Complex **10** with a bulky SbF_6^- anion showed somewhat inferior results (up to 83% ee, Table 2, entries 20 and 21).

Table 2. Enantioselective allylic alkylation of **11** with dimethyl malonate (L/Pd = 1:1)

Entry	Catalyst	Solvent	Conv. [%]	ee [%]
1	$[Pd(allyl)Cl]_2$/**4a**	THF	—	—
2	$[Pd(allyl)Cl]_2$/**4a**	CH_2Cl_2	82	41 (*S*)
3	**8a**	THF	34	9 (*S*)
4	**8a**	CH_2Cl_2	50	34 (*S*)
5	$[Pd(allyl)Cl]_2$/**4b**	THF	19	1 (*S*)
6	$[Pd(allyl)Cl]_2$/**4b**	CH_2Cl_2	95	15 (*S*)
7	**8b**	THF	25	5 (*S*)
8	**8b**	CH_2Cl_2	65	10 (*S*)
9	$[Pd(allyl)Cl]_2$/**5a**	THF	5	55 (*S*)
10	$[Pd(allyl)Cl]_2$/**5a**	CH_2Cl_2	87	71 (*S*)
11	**9a**	THF	8	31 (*S*)
12	**9a**	CH_2Cl_2	99	63 (*S*)
13	$[Pd(allyl)Cl]_2$/**5b**	THF	3	33 (*S*)
14	$[Pd(allyl)Cl]_2$/**5b**	CH_2Cl_2	62	81 (*S*)
15	$[Pd(allyl)Cl]_2$/**5b**[a]	CH_2Cl_2	33	74 (*S*)
16	$[Pd_2(dba)_3 \times CHCl_3]$/**5b**	CH_2Cl_2	99	67 (*S*)
17	$[Pd_2(dba)_3 \times CHCl_3]$/**5b**[a]	CH_2Cl_2	75	81 (*S*)
18	**9b**	THF	90	94 (*S*)
19	**9b**	CH_2Cl_2	70	76 (*S*)
20	**10**	THF	64	82 (*S*)
21	**10**	CH_2Cl_2	68	83 (*S*)

[a] L/Pd = 2:1.

Table 3. Enantioselective allylic sulfonylation of **11** with $NaSO_2pTol$ (in THF)

Entry	Catalyst	L/[Pd]	Isolated yield [%]	ee [%]
1	$[Pd(allyl)Cl]_2$/**4a**	1:1	41	15 (*S*)
2	$[Pd(allyl)Cl]_2$/**4a**	2:1	55	28 (*S*)
3	$[Pd(allyl)Cl]_2$/**4b**	1:1	39	11 (*S*)
4	$[Pd(allyl)Cl]_2$/**4b**	2:1	45	12 (*S*)
5	$[Pd(allyl)Cl]_2$/**5a**	1:1	66	55 (*S*)
6	$[Pd(allyl)Cl]_2$/**5a**	2:1	71	74 (*S*)
7	**9a**	1:1	40	80 (*S*)
8	$[Pd(allyl)Cl]_2$/**5b**	1:1	48	61 (*S*)
9	$[Pd(allyl)Cl]_2$/**5b**	2:1	51	67 (*S*)
10	**9b**	1:1	42	84 (*S*)

Similar dependence of asymmetric induction on the nature of ligands was observed in Pd-catalyzed allylic sulfonylation and allylic amination (Scheme 6). Iminodiamidophosphites **4a** and **4b** were again ineffective (up to 28% ee for product **13**, Table 3, entries 1–4; and up to 12% ee for product **14**, Table 4, entries 1–4). On the contrary, ligands **5a** and **5b** having *P*-stereocenters gave high enantiomeric excesses, the results being slightly better in the case of **5b**. In allylic sulfonylation, complexes **9a** and **9b** were the most efficient providing correspondingly 80% and 84% ee at similar conversion (Table 3, entries 7 and 10). In the synthesis of amine **14**, the highest enantioselectivity was observed for catalytic systems $[Pd(allyl)Cl]_2$/**5a** and $[Pd(allyl)Cl]_2$/**5b** (Table 4, entries 6 and 9, L/Pd = 1:1, CH_2Cl_2, up to 75% and 78% ee, respectively).

3. Conclusions

In summary, we have designed and synthesized a number of previously unknown planar chiral *P*,*N*-bidentate

Table 4. Enantioselective allylic amination of **11** with pyrrolidine (L/Pd = 1:1)

Entry	Catalyst	Solvent	Isolated yield [%]	ee [%]
1	$[Pd(allyl)Cl]_2$/**4a**	THF	41	7 (*R*)
2	$[Pd(allyl)Cl]_2$/**4a**	CH_2Cl_2	36	12 (*R*)
3	$[Pd(allyl)Cl]_2$/**4b**	THF	47	5 (*R*)
4	$[Pd(allyl)Cl]_2$/**4b**	CH_2Cl_2	52	10 (*R*)
5	$[Pd(allyl)Cl]_2$/**5a**	THF	67	55 (*R*)
6	$[Pd(allyl)Cl]_2$/**5a**	CH_2Cl_2	82	75 (*R*)
7	**9a**	CH_2Cl_2	99	68 (*S*)
8	$[Pd(allyl)Cl]_2$/**5b**	THF	67	55 (*R*)
9	$[Pd(allyl)Cl]_2$/**5b**	CH_2Cl_2	89	78 (*R*)
10	$[Pd(allyl)Cl]_2$/**5b**[a]	CH_2Cl_2	81	63 (*R*)
11	**9b**	CH_2Cl_2	99	75 (*R*)

[a] L/Pd = 2:1.

phosphite-type compounds and applied them as ligands in asymmetric Pd-catalyzed allylation. These iminodiamidophosphites represent a new family of optically active ligands with planar chirality. Their modular construction makes possible an extensive and independent variation of the phosphite part, $Mn(CO)_3$ backbone (for example, CO could be substituted by phosphine), and the imine part (by use of various starting amines). We hope that, due to their electronic and steric variability, planar chiral phosphites will find further fruitful applications in asymmetric catalysis. Such experiments are currently in progress in our laboratories.

4. Experimental

4.1. General

IR spectra were recorded with a Specord M80 instrument. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker AMX 400 instrument (400.13 MHz for ^1H, 100.6 MHz for ^{13}C and 162.0 MHz for ^{31}P). Complete assignment of all the resonances in ^{13}C NMR spectra was achieved by the use of DEPT techniques. Chemical shifts are given in ppm relative to Me_4Si (^1H), internal $CDCl_3$ (76.91 ppm for ^{13}C NMR) and external 85% aqueous H_3PO_4 solution (0 ppm for ^{31}P NMR). Mass spectra were recorded with a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI). Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Conversion of substrate **11** and enantiomeric excesses of product **12** were determined using HPLC (Daicel Chiralcel OD-H column) according to the literature.[25] Enantiomeric excesses of product **13** were determined using HPLC ((*R*,*R*)-WHELK-01 column) according to the literature.[26] Enantiomeric excesses of compound **14** were determined by HPLC (Daicel Chiralcel OD-H column) as described previously.[27]

All reactions were carried out under a dry argon in freshly dried and distilled solvents; Et_3N and pyrrolidine were twice distilled over KOH and then over a small amount of $LiAlH_4$ before use. (2*S*,4*S*,5*R*)-3,4-dimethyl-5-phenyl-2-cymantrenyloxazolidine was prepared as published.[28,29] Phosphorylating reagents 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine and (2*R*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane were prepared according to previously described methods.[21,30] Rhodium complexes **6a** and **6b**, and **7a** and **7b** were synthesized for ^{31}P NMR and IR experiments in chloroform analogously to the known procedures.[22] Syntheses of cationic palladium complexes **8a** and **8b**, **9a** and **9b** and **10** were performed by techniques similar to those reported earlier.[31]

Starting substrate **11** and complex $[Pd(allyl)Cl]_2$ for catalysis were synthesized as published.[32] (1*R*,2*R*,3*R*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-amine [(+)-isopinocampheylamine, dimethyl malonate, BSA *N*,*O*–bis(trimethylsilyl) acetamide] and sodium *para*-toluene sulfinate were commercially available.

Catalytic experiments: Allylic alkylation of substrate **11** with dimethyl malonate and allylic sulfonylation with sodium *para*-toluene sulfinate were performed according to appropriate procedures.[21]

4.2. Preparation of (R_p)-(hydroxymethyl)cymantrenecarbaldehyde 1

To a vigorously stirred solution of 1.14 g (0.003 mol) of (4*S*,5*R*)-3,4-dimethyl-5-phenyl-2-cymantrenyl-1,3-oxazolidine[28,29] in THF at −70 °C was added 1.6 M solution of BuLi in hexane, 4 ml (0.0075 mol) for 10 min. The resulted mixture was stirred for another 1 h and solution of 1.64 g (0.0225 mol) of DMF in THF (100 ml) was added for 0.5 h. The resulted mixture was slowly heated to rt and 20% solution of H_3PO_4 was added dropwise until pH = 7. The resulted mixture was extracted by ether, washed with water and dried over $MgSO_4$ and concentrated in vacuo (40 Torr); the residue was dissolved in ethanol (50 ml) and $NaBH_4$ (0.29 g, 0.0075 mol) was added in portions during 30 min at 15°C. Then 20% solution of H_3PO_4 was added dropwise until pH = 7 and the resulting solution was diluted with water and extracted with ether. The combined extracts were dried over $MgSO_4$ and the solvent was evaporated in vacuo (40 Torr). The residue was dissolved in a mixture of dioxane (10 ml), 20% H_3PO_4 (10 ml) and 10% HCl (5 ml), extracted with ether, washed with water, dried over $MgSO_4$, and concentrated in vacuo (40 Torr). The obtained oil was purified by flash chromatography ($CHCl_3$). Brown oil, solidified on standing. Yield 0.35 g (45%). $[\alpha]_D^{22} = -203.6$ (*c* 0.334, C_6H_6) (90% stereoselectivity at the lithiation step was previously determined by ^1H NMR, the product of quenching of the lithiated derivative with D_2O being investigated).[28] ^1H NMR ($CDCl_3$): δ 4.53 (m, 2H; CH_2O), 4.8 (m, 1H; CH_{Cp}), 5.09 (m, 1H; CH_{Cp}), 5.44 (m, 1H; CH_{Cp}), 9.66 (s, 2H; CHO). IR, (ν(CO)/cm^{-1}): 1700, 1960 and 2040. MS (ESI), *m*/*z* (I, %): 262 (100) $[M]^+$, 244 (87) $[M-H_2O]^+$, 178 (52) $[M-3CO]^+$, 160 (23) $[M-3CO-H_2O]^+$. Anal. Calcd for $C_{10}H_7MnO_5$: C, 45.82; H, 2.69. Found: C, 46.04; H, 2.68.

4.3. Preparation of iminoalcohols

4.3.1. General technique. (R_p)-(Hydroxymethyl)cymantrenecarbaldehyde **1** (0.928 g, 3.5×10^{-2} mol) was dissolved in 30 ml of dichloromethane. Isopropylamine (0.3 ml, 3.5×10^{-2} mol), for **2** or (+)-isopinocampheylamine (0.587 ml, 3.5×10^{-2} mol) for **3**, Na_2SO_4 (3 g) and 15 ml of dichloromethane were added to this solution with stirring, and the mixture was heated under reflux for 3 h. After the mixture had cooled to room temperature, Na_2SO_4 was filtered off and washed with dichloromethane. The solvent was removed and the resulting residue was dried under vacuum (1 Torr, 2 h).

4.3.2. (S_p)-(2-((*E*)-(Isopropylimino)methyl)cymantrenyl)-methanol 2. Red-brown oil, 1.02 g, (95% yield). $[\alpha]_D^{25}=-193.8$ (*c* 0.8, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 1.22 (d, 6H, $^3J_{H,H}=6.3$; $2CH_3$ (*i*-Pr)), 3.48 (septet, 1H, $^3J_{H,H}=6.3$; CH (*i*-Pr)), 4.31 (m, 2H; CH_2O), 4.55 (t, 1H, $^3J_{H,H}=2.7$; CH_{Cp}), 4.88 (br t, 1H, $^3J_{H,H}=1.9$; CH_{Cp}), 5.05 (br t, 1H, $^3J_{H,H}=1.9$; CH_{Cp}), 6.16 (br s 1H; OH), 7.93 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$): δ 23.8 and 23.4 (both s, Me (*i*-Pr)), 57.4 (s, OCH_2), 60.8 (s, NCH (*i*-Pr)), 77.8, 86.1 and 87.1 (all s, CH_{Cp}), 94.1 (s, C_{Cp}), 105.1 (s, C_{Cp}), 154.0 (s, C=N), 223.5 (s, CO). MS (ESI), *m*/*z* (I, %): 304 (100) $[M+H]^+$, 286 (38) $[C_3H_7N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 139 (19). Anal. Calcd for $C_{13}H_{14}MnNO_4$: C, 51.50; H, 4.65; N, 4.62. Found: C, 51.68; H, 4.71; N, 4.70.

4.3.3. (S_p)-(2-((*E*)-(1′*R*,2′*R*,3′*R*,5′*S*)-(2′,6′,6′-Trimethylbicyclo[3.1.1]heptan-3′-imino)methyl)cymantrenyl)methanol 3. Light-brown solid, 1.36 g, (97% yield). $[\alpha]_D^{25}=-124.1$ (*c* 1, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 1.02 (s, 3H; CCH_3), 1.03 (d, 3H, $^3J_{H,H}=7.2$; CH*C*H_3), 1.09 (d, 1H, $^3J_{H,H}=10.0$; CH), 1.23 (s, CCH_3), 1.86 (m, 2H; CH_2), 1.98 (m, 2H; 2CH), 2.31 (m 2H; CH_2), 2.40 (m, 2H; 2CH), 3.43 (quintet, 1H, $^3J_{H,H}=4.8$; CH), 4.34 (m, 2H; OCH_2), 4.56 (t, 1H, $^3J_{H,H}=2.4$; CH_{Cp}), 4.90 (br s; CH_{Cp}), 5.06 (t, 1H, $^3J_{H,H}=1.2$; CH_{Cp}), 6.28 (br s, 1H; OH), 7.83 (s, 1H; CH=N). ^{13}C NMR ($CDCl_3$): δ 19.4 (s, CH*Me*), 23.3 (s, C*Me*), 27.6 (s, C*Me*), 33.9 (s, CH_2), 35.5 (s, CH_2), 38.4 (s, *C*Me_2), 41.1 (s, *CH*Me), 44.0 (s, CH), 47.0 (s, CH), 57.5 (s, OCH_2), 69.4 (s, NCH), 77.9, 86.2 and 86.9 (all s, CH_{Cp}), 94.2 (s, C_{Cp}), 104.9 (s, C_{Cp}), 153.5 (s, C=N), 223.5 (s, CO). MS (ESI), *m*/*z* (I, %): 398 (100) $[M+H]^+$, 380 (32) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 139 (20). Anal. Calcd for $C_{20}H_{24}MnNO_4$: C, 60.45; H, 6.09; N, 3.53. Found: C, 60.59; H, 5.96; N, 3.64.

4.4. Preparation of ligands

4.4.1. General technique. In 25 ml of benzene, appropriate phosphorylating reagent (1.5×10^{-3} mol) and Et_3N (0.21 ml, 1.5×10^{-3} mol) were dissolved. Then, with vigorous stirring and cooling to 0 °C, iminoalcohol **2** (0.46 g, 1.5×10^{-3} mol) for **4a** and **5a**, or iminoalcohol **3** (0.6 g, 1.5×10^{-3} mol) for **4b** and **5b** was added. The resulting mixture was stirred for 10 min at 0 °C, and then heated to reflux, allowed to cool to 20 °C, then $Et_3N\times HCl$ was filtered off. The solvent was removed in vacuum (40 Torr), and the residue was concentrated and dried in vacuum (1 Torr, 2 h).

4.4.2. (S_p)-2-((2-((*E*)-(Isopropylimino)methyl)cymantrenyl)methoxy)-1,3-diphenyl-1,3,2-diazaphospholidine 4a. Brown solid, 0.75 g, (91% yield). $[\alpha]_D^{25}=+17.6$ (*c* 0.5, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 23.9 and 23.8 (both s, Me (*i*-Pr)), 47.0 and 47.2 (both d, $^2J_{C,P}=4.4$ and 4.4; C^4 and C^5), 57.7 (s, $POCH_2$), 61.4 (s, NCH (*i*-Pr)), 80.8, 82.8 and 82.9 (all s, CH_{Cp}), 94.4 (s, C_{Cp}), 102.1 (d, $^2J_{C,P}=2.8$; C_{Cp}), 115.1–144.6 (C_{Ar}), 150.5 (s, C=N), 223.7 (c, CO). MS ESI, *m*/*z* (I, %): 544 (100) $[M+H]^+$, 286 (86) $[C_3H_7N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 241 (93) $[PhNCH_2CH_2N(Ph)P]^+$, 139 (51). Anal. Calcd for $C_{27}H_{27}MnN_3O_4P$: C, 59.67; H, 5.01; N, 7.73. Found: C, 59.81; H, 4.87; N, 7.61.

4.4.3. (S_p)-2-((2′-((*E*)-(1″*R*,2″*R*,3″*R*,5″*S*)-(2″,6″,6″-Trimethylbicyclo[3.1.1]heptan-3″-imino)methyl)cymantrenyl)-methoxy)-1,3-diphenyl-1,3,2-diazaphospholidine 4b. Light-brown solid, 0.9 g, (94% yield). $[\alpha]_D^{25}=-17.9$ (*c* 0.5, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 19.5 (s, CH*Me*), 23.3 (s, C*Me*), 27.7 (s, C*Me*), 33.6 (s, CH_2), 35.6 (s, CH_2), 38.5 (s, *C*Me_2), 41.4 (s, *CH*CH_3), 43.6 (s, CH), 47.1 (s, CH), 47.3 and 47.2 (both d, $^2J_{C,P}=9.6$ and 9.5; C^4 and C^5), 58.3 (s, OCH_2), 69.8 (s, NCH), 79.4, 83.4 and 84.0 (all s, CH_{Cp}), 93.9 (s, C_{Cp}), 102.4 (d, $^2J_{C,P}=2.8$; C_{Cp}), 115.1–144.7 (C_{Ar}), 150.5 (s, C=N), 223.8 (s, CO). MS (ESI), *m*/*z* (I, %): 638 (100) $[M]^+$, 380 (67) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 241 (39) $[PhNCH_2CH_2N(Ph)P]^+$, 139 (21). Anal. Calcd for $C_{34}H_{37}MnN_3O_4P$: C, 64.05; H, 5.85; N, 6.59. Found: C, 63.89; H, 5.97; N, 6.71.

4.4.4. (S_p,2*R*,5*S*)-2-((2′-((*E*)-(Isopropylimino)methyl)-cymantrenyl)methoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane 5a. Brown oil, 0.75 g, (98% yield). $[\alpha]_D^{25}=-95.1$ (*c* 0.5, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 23.8 and 23.9 (both s, Me (*i*-Pr)), 26.0 (d, $^2J_{C,P}=4.0$; C^7), 31.9 (s, C^6), 48.5 (d, $^2J_{C,P}=38.5$; C^8), 54.7 (d, $^2J_{C,P}=6.8$; C^4), 56.4 (d, $^2J_{C,P}=3.2$; $POCH_2$), 61.6 (s, NCH (*i*-Pr)), 63.1 (d, $^3J_{C,P}=8.4$; C^5), 81.1, 82.4 and 82.5 (all s, CH_{Cp}), 94.4 (s, C_{Cp}), 103.3 (d, $^2J_{C,P}=3.2$; C_{Cp}), 114.5–145.1 (C_{Ar}), 150.9 (s, C=N), 223.8 (s, CO). MS (ESI), *m*/*z* (I, %): 508 (72) $[M+H]^+$, 286 (88) $[C_3H_7N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 205 (100) $[C_{11}H_{14}N_2P]^+$, 139 (10). Anal. Calcd for $C_{24}H_{27}MnN_3O_4P$: C, 56.81; H, 5.36; N, 8.28. Found: C, 56.97; H, 5.51; N, 8.40.

4.4.5. (S_p,2*R*,5*S*)-2-((2′-((*E*)-(1″*R*,2″*R*,3″*R*,5″*S*)-(2″,6″,6″-Trimethylbicyclo[3.1.1]heptan-3″-imino)methyl)cymantrenyl)methoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo [3.3.0] octane 5b. Brown oil, 0.86 g, (95% yield). $[\alpha]_D^{25}=-91.4$ (*c* 0.5, C_6H_6). ^{13}C NMR ($CDCl_3$): δ 19.5 (s, CH*Me*), 23.3 (s, C*Me*), 26.0 (d, $^2J_{C,P}=3.6$; C^7), 27.7 (s, C*Me*), 31.9 (s, C^6), 33.5 (s, CH_2), 35.7 (s, CH_2), 38.5 (s, *C*Me), 41.4 (s, *CH*CH_3), 43.5 (s, CH), 47.3 (s, CH), 48.5 (d, $^2J_{C,P}=38.6$; C^8), 54.8 (d, $^2J_{C,P}=7.2$; C^4), 56.9 (d, $^2J_{C,P}=4.0$; $POCH_2$), 63.2 (d, $^3J_{C,P}=8.8$; C^5), 70.1 (s, NCH), 80.0, 83.3 and 83.5 (all s, CH_{Cp}), 94.1 (s, C_{Cp}), 103.4 (d, $^2J_{C,P}=3.2$; C_{Cp}), 114.6–145.1 (C_{Ar}), 150.6 (s, C=N), 223.9 (s, CO). MS (ESI), *m*/*z*

(I, %): 602 (100) $[M]^+$, 380 (85) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$, 205 (60) $[C_{11}H_{14}N_2P]^+$, 139 (7). Anal. Calcd for $C_{31}H_{37}MnN_3O_4P$: C, 61.89; H, 6.20; N, 6.99. Found: C, 61.76; H, 6.37; N, 7.12.

4.5. Palladium(II) complexes

4.5.1. [Pd(4a)(allyl)]$^+BF_4^-$ 8a. Yellow-brown powder, 0.29 g, (92% yield). Mp: 160–162 °C (dec.). ^{31}P ($CDCl_3$): δ_P 105.4 (br s) and 102.8 (br s). MS (ESI), *m*/*z* (I, %): 779 (12) $[M+H]^+$, 691 (100) $[M-BF_4]^+$, 650 (38) $[M-BF_4\text{-allyl}]^+$, 543 (36) $[L]^+$, 286 (39) $[C_3H_7N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$. Anal. Calcd for $C_{30}H_{32}BF_4MnN_3O_4PPd$: C, 46.33; H, 4.15; N, 5.40. Found: C, 46.19; H, 4.27; N, 5.29.

4.5.2. [Pd(4b)(allyl)]$^+BF_4^-$ 8b. Light-brown powder, 0.31 g, (90% yield). Mp: 171–173 °C (dec.). ^{31}P ($CDCl_3$): δ_P 107.2 (br s). MS (ESI), *m*/*z* (I, %): 872 (6) $[M]^+$, 785 (100) $[M-BF_4]^+$, 380 (35) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$. Anal. Calcd for $C_{37}H_{42}BF_4MnN_3O_4PPd$: C, 50.97; H, 4.86; N, 4.82. Found: C, 51.11; H, 4.95; N, 4.69.

4.5.3. [Pd(5a)(allyl)]$^+BF_4^-$ 9a. Yellow-brown powder, 0.29 g, (91% yield). Mp: 182–184 °C (dec.). ^{31}P ($CDCl_3$): δ_P 119.4 (br s) and 117.9 (br s). MS (ESI), *m*/*z* (I, %): 743 (100) $[M+H]^+$, 655 (88) $[M-BF_4]^+$, 614 (24) $[M-BF_4\text{-allyl}]^+$. Anal. Calcd for $C_{27}H_{32}BF_4MnN_3O_4PPd$: C, 43.72; H, 4.35; N, 5.67. Found: C, 43.86; H, 4.51; N, 5.54.

4.5.4. [Pd(5b)(allyl)]$^+BF_4^-$ 9b. Light-brown powder, 0.32 g, (95% yield). Mp: 178–180 °C (dec.). ^{31}P ($CDCl_3$): δ_P 120.5 (br s). MS (ESI), *m*/*z* (I, %): 836 (4) $[M]^+$, 749 (100) $[M-BF_4]^+$, 675 (26), 380 (18) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$. Anal. Calcd for $C_{34}H_{42}BF_4MnN_3O_4PPd$: C, 48.86; H, 5.06; N, 5.03. Found: C, 48.68; H, 4.82; N, 5.19.

4.5.5. [Pd(5b)(allyl)]$^+SbF_6^-$ 10. Light-yellow powder, 0.37 g, (93% yield). Mp: 185–187 °C (dec.). ^{31}P ($CDCl_3$): δ_P 116.7 (br s). MS (ESI), *m*/*z* (I, %): 749 (100) $[M-SbF_6]^+$, 602 (18) $[L]^+$, 380 (54) $[C_{10}H_{17}N{=}CH(CH_2C_5H_3)Mn(CO)_3]^+$. Anal. Calcd for $C_{34}H_{42}F_6MnN_3O_4PPdSb$: C, 41.47; H, 4.30; N, 4.27. Found: C, 41.61; H, 4.41; N, 4.18.

4.6. Pd-catalyzed allylic amination of 1,3-diphenyl acetate with pyrrolidine

4.6.1. General procedure. A solution of $[Pd(allyl)Cl]_2$ (3.7×10^{-3} g, 1×10^{-5} mol) and appropriate ligand (2×10^{-5} mol–4×10^{-5} mol) in 5 ml of appropriate solvent was stirred for 40 min [alternatively, the presynthesized complex **9a** or **9b** (2×10^{-5} mol) was dissolved in appropriate solvent (5 ml)]. Then, 1,3-diphenylallyl acetate (0.1 ml, 5×10^{-4} mol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.12 ml, 1.5×10^{-3} mol) was added and the reaction mixture stirred for 48 h. After that, resulting solution was filtered through Celite. The solvent was removed in vacuum (40 Torr), and the residue dried in vacuum (10 Torr, 12 h) to obtain ((*E*)-1,3-diphenylallyl)pyrrolidine **14** as a cream crystalline solid. All spectroscopic data of compound **14** are in good agreement with published data.[27]

4.7. X-ray crystallographic study of iminoalcohol 3

X-ray structure of **3**. Crystal data: $C_{20}H_{24}MnNO_4$, MW = 397.35 g mol^{-1}, light-brown needles, monoclinic, space group $P2_1$, $Z=2$, $a=6.825(2)$, $b=19.095(6)$, $c=22.284(7)$ Å, $\beta=93.394(8)°$, $R_1=0.0749$.

All calculations were performed on an IBM PC/AT using the SHELXTL software (G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI 53719, USA). Crystallographic data for structure **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (reference no CCDC 279754). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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