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Iminoarylphosphites with ferrocenylidene and cymantrenylidene fragments: Coordination properties and use in palladium-catalysed asymmetric allylic substitution

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Abstract

Complexation of the chiral *P*,*N*-bidentate ferrocene- and cymantrene-based iminoarylphosphites with $[Rh(CO)_2Cl]_2$, $[Rh(COD)(THF)_2]BF_4$, $[Pd(allyl)Cl]_2$, $[Pt(allyl)Cl]_4$, $[Pd(COD)Cl_2]$ and $[Pt(COD)Cl_2]$ was found to give chelate complexes $[Rh(CO)(\eta^2\text{-P,N})Cl]$, $[Rh(COD)(\eta^2\text{-P,N})]BF_4$, $[M(allyl)(\eta^2\text{-P,N})]BF_4$ (M = Pd, Pt) and *cis*-$[M(\eta^2\text{-P,N})Cl_2]$ (M = Pd, Pt), correspondingly. With the new *P*,*N*-ligands, up to 97% ee was achieved in the asymmetric Pd-catalysed alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate. In the enantioselective amination of 1,3-diphenyl-2-propenyl acetate with sodium diformylamide, up to 96% enantioselectivity was achieved.

Keywords: Arylphosphites; Asymmetric allylic substituton; Chiral *P*,*N*-ligands; Palladium; Platinum; Rhodium

1. Introduction

Organic reactions catalysed by chiral transition metal complexes are the basis of modern asymmetric synthesis. This statement was substantiated by the fact that three leading researchers working in this field of chemistry were awarded the Nobel Prize in 2001. The key to obtaining high catalytic results is targeted synthesis of optically active ligands. Of prime importance are phosphorus-containing compounds, including *P*,*N*-bidentate ones. Among them, chiral *P*,*N*-bidentate phosphites are particularly interesting. The first synthesis of ligands belonging to this class and their complexation with rhodium(I) was reported in 1993. [1]. However, they have been efficiently used in asymmetric catalysis only during the last five years. These compounds with three P–O and (or) P–N bonds offer a number of considerable advantages. First, they are synthetically accessible, because most of them can be synthesised rather simply and in high yield from a variety of optically active precursors. This makes possible a direct one-step phosphorylation of chiral compounds, whereas the synthesis of corresponding phosphine derivatives requires preliminary modification. Second, these compounds exhibit higher oxidative stability because of the absence of P–C bonds. Third, these compounds possess a pronounced π-acceptor ability, which allows the coordinated phosphites to stabilise low oxidation states of metal atoms, thus enhancing their electrophilicity. In general, replacement of carbon atoms by heteroatoms (oxygen and (or) nitrogen) in the first coordination sphere of phosphorus atom appeared to be a more efficient tool for control of the chemical stability of ligands and their donor–acceptor properties and steric features compared to traditional introduction of various substituents into benzene rings of the PAr_2 fragment typical of most phosphine systems. That made it possible to achieve impressive results in catalytic enantioselective allylation, conjugate addition of organometallics to enones, hydrosilylation and hydrogenation reactions [2,3]. Interestingly, most of the mentioned ligands have a cyclic phosphocentre in their structure, which

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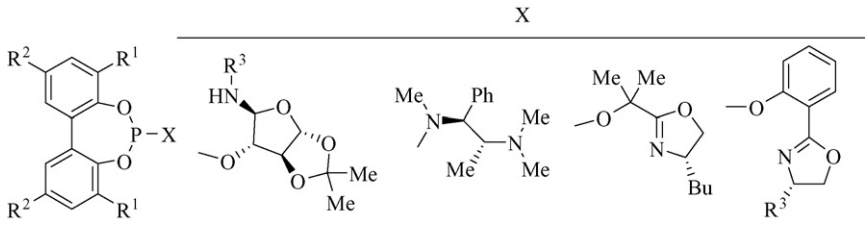


Fig. 1. *P*,*N*-phosphites with achiral cyclic phosphocentre.

is normally constructed on the base of effective chiral inductors, such as BINOL, TADDOL, dialkyltartrates and diamines [2–4]. *P*,*N*-phosphites possessing achiral cyclic phosphocentre are rare and derived exclusively from biphenyl-2,2′-diols [5–9] (Fig. 1).

Such aminophosphites and aminophosphoramidites were applied in asymmetric conjugate addition of Et_2Zn to cyclohexenone and addition of Me_3Al to vinyl epoxide [5,6], while phosphites containing an oxazoline fragment demonstrated high enantioselectivity in various Pd-catalysed allylation reactions [7–9]. At the same time, phosphocycle may significantly decrease a chelating ability of *P*,*N*-bidentate ligand, since the resulting metal chelate complex would represent a strained spiro structure with phosphorus as a spiro atom [10]. Besides, stereochemical characteristics of cyclic and acyclic phosphocentres are principally different. It is notable that most stereoselective and efficient phosphine ligands have achiral and acyclic PAr_2 fragments. Therefore, we started investigation of synthesis, complexation and catalytic application of optically active *P*,*N*-bidentate phosphite ligands also bearing achiral and acyclic phosphocentres [11–13]. Particular attention is paid to the ligands bearing a distant imino group. Like phosphitooxazolines, they contain a chiral block with an sp^2-nitrogen atom (Fig. 2), but can be prepared starting from imino alcohols, which are much more diverse and readily available synthons than hydroxyoxazolines. Thus, iminoarylphosphites afforded up to 82% ee in the Pd-catalysed alkylation of ethyl 3-penten-2-yl carbonate (so-called "unmanageable" substrate), ligand **3a** (X = ferrocenyl) being the best enantioselector [13].

In the present paper, we describe a detailed investigation of the coordination behaviour of these ligands and their application in another benchmark test, namely Pd-catalysed allylation of 1,3-diphenyl-2-propenyl acetate.

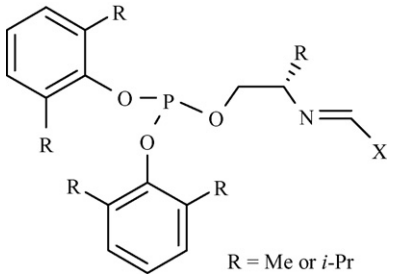


Fig. 2. Iminoarylphosphites with achiral acyclic phosphocentre.

2. Experimental

2.1. General comments

All reactions were performed under argon in dehydrated solvents. IR spectra were recorded on a Specord M80 or Nicolet 750 instrument. ^1H, ^{13}C, ^{19}F, ^{31}P, ^{195}Pt NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^1H, 100.6 MHz for ^{13}C, 376.31 MHz for ^{19}F, 162.0 MHz for ^{31}P; 86.48 MHz for ^{195}Pt). The complete assignment of all the resonances in ^{13}C NMR spectra was achieved using DEPT techniques. Chemical shifts (ppm) are given relative to Me_4Si (^1H and ^{13}C NMR), CF_3COOH (^{19}F NMR), 85% H_3PO_4 in D_2O (^{31}P NMR), 1 M H_2PtCl_6 in D_2O (^{195}Pt). Mass spectra were recorded with a Varian MAT 311 spectrometer (EI), a Finnigan LCQ Advantage spectrometer (electrospray ionization technique, ESI), an MSVKh TOF spectrometer with ionization by Cf-252 fission fragments (plasma desorption technique, PD). Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

Conversion of substrate **11** and optical purity of products **12** were determined using HPLC (Daicel Chiralcel OD-H column) as described previously [14]. Optical yields of product **13** were determined using HPLC ((*R*,*R*)-WHELK-01 column) according to the literature [15]. Optical yields of product **14** were determined using HPLC (Chiralcel OD column) according to the literature [16].

2,6-Dimethylphenol, 2,6-diisopropylphenol and PCl_3 were distilled immediately before use. Et_3N was twice distilled over KOH and then over a small amount of $LiAlH_4$ before use. (2*S*,3*S*)-2-Amino-3-methylpentan-1-ol (*L*-isoleucinol) and compounds **2a** and **3a** were prepared as published [17,13]. Starting substrate **11** and sodium diformylamide were synthesised as published [18,19]. 1-Methylpyrrolidin-2-one, dimethyl malonate, BSA (*N*,*O*-bis(trimethylsilyl) acetamide) and sodium *para*-toluene sulfinate were commercially available.

$[Rh(CO)_2Cl]_2$ [20], $[Rh(COD)Cl]_2$ [21], $[Rh(COD)(THF)_2]BF_4$ [22], $[Pd(allyl)Cl]_2$ [18], $[Pt(allyl)Cl]_4$ [23], $[Pd(COD)Cl_2]$ [24] and $[Pt(COD)Cl_2]$ [25] were synthesised using literature procedures. Rhodium(I) complexes **4a–c** were synthesised for the ^{31}P NMR and IR experiments in chloroform analogously to the known procedures [13,26]. The syntheses of palladium(II) complexes **7a–c** were performed by techniques similar to that reported [27].

Catalytic experiments: allylic alkylation of substrate **11** with dimethyl malonate, allylic sulfonylation with sodium *para*-toluene sulfinate and allylic amination with $NaN(CHO)_2$ were performed according to appropriate procedures [26,28].

*2.1.1. (2S,3S)-2-[(Cymantrenylidene)-amino]-3-methyl-pentan-1-ol (**2b**)*

(2*S*,3*S*)-2-Amino-3-methylpentan-1-ol (1.17 g, 10^{-2} mol) was dissolved in CH_2Cl_2 (30 mL). Formylcymantrene (2.32 g, 10^{-2} mol) and 2 g Na_2SO_4 were added to the above solution with stirring and the mixture refluxed for 3 h. After cooling to room temperature, the Na_2SO_4 was filtered off and washed with CH_2Cl_2 (10 mL). The CH_2Cl_2 was removed and the resulting residue was dried in vacuum (1 mmHg). Brown viscous oil, solidified on standing, 63% yield. ^{1}H NMR ($CDCl_3$), δ_H (*J*(H,H), Hz): 7.87 (s, 1H, CH=), 5.34 (m, 1H, H_{Cp}), 5.23 (m, 1H, H_{Cp}), 4.95 (m, 1H, H_{Cp}), 4.81 (m, 1H, H_{Cp}), 4.0 (br. s, 1H, OH), 3.73 (m, 2H, CH_2O), 2.93 (m, 1H, CHN), 1.66 (m, 1H, CH), 1.22 (m, 2H, CH_2), 0.91 (d, 3H, $^3J = 6.8$, CH_3), 0.85 (t, 3H, $^3J = 7.2$, CH_2CH_3). IR ($CHCl_3$), ν(CO), cm^{-1}: 2025, 1946. Anal. Calc. for $C_{15}H_{18}MnNO_4$: C, 54.39; H, 5.48; N, 4.23. Found: C, 54.58; H, 5.33; N, 4.02.

2.2. Preparation of bis-(aryl) chlorophosphites

2.2.1. General technique

1-Methylpyrrolidin-2-one (0.01 g, 0.1×10^{-3} mol) was added to a stirred mixture of appropriate 2,6-dialkylphenol (4×10^{-2} mol) and PCl_3 (1.76 mL, 2×10^{-2} mol). The mixture was refluxed for 30 min to become completely homogeneous. After cooling to room temperature, the reaction mixture was stirred for 20 min at 20 °C in vacuum (2 mmHg) to remove traces of HCl. The product was twice fractionally distilled in vacuum.

*2.2.2. Bis-(2,6-dimethylphenyl) chlorophosphite (**1a**)*

Colourless oil, 75% yield. bp 133–135 °C (1 mmHg). ^{31}P NMR ($CDCl_3$), δ_P: 174.3. The spectroscopic and physicochemical characteristics of this substance fully correspond to published data [11,12].

*2.2.3. Bis-(2,6-diisopropylphenyl) chlorophosphite (**1b**)*

Colourless oil, 70% yield. bp 154–156 °C (1 mmHg). ^{31}P NMR ($CDCl_3$), δ_P: 173.3. MS (EI, 70 eV), *m*/*z* (I, %): 421 $[M]^+$ (28), 245 $[M - (2,6\text{-}Pr^i\text{-}PhO) + H]^+$ (100).

2.3. Preparation of ligands

2.3.1. General technique

A solution of appropriate chlorophosphite **1** (2.7×10^{-3} mol) in benzene (15 mL) was added dropwise to a stirred solution of a corresponding iminoalcohol **2** (2.7×10^{-3} mol) and Et_3N (0.4 mL, 2.7×10^{-3} mol) in the same solvent (15 mL) at 0 °C. Then the reaction mixture was heated up to boiling point, cooled down, stirred for 1 h at 50 °C, cooled down to room temperature and filtered. The solvent was removed in vacuum (40 mmHg) and the residue was dissolved in hexane (20 mL), filtered, evaporated and dried in vacuum (1 mmHg).

*2.3.2. (2S,3S)-Bis-(2,6-dimethyl-phenyl)-2-[(cymantrenylidene)-amino]-3-methyl-pentylphosphite (**3b**)*

Brown viscous oil, 63% yield. ^{31}P NMR ($CDCl_3$), δ_P: 136.2. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P), Hz): 223.8 (s, CO), 154.7 (s, CH=N), 148.9 (s, $C_{Ar}O$), 130.3 (d, $^3J = 2.4$, C_{Ar}), 130.1 (d, $^3J = 2.4$, C_{Ar}), 128.7 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 123.8 (s, $C_{Ar}H$), 95.2 (s, C_{Cp}(*ipso*)), 85.4, 83.7, 82.6, 81.8 (all s, C_{Cp}), 75.9 (d, $^3J = 3.6$, CHN), 63.6 (s, CH_2O), 36.7 (s, CH), 24.9 (s, CH_2), 17.6, 17.5, 17.4, 17.2 (all s, CH_3(Ar)), 15.6 (s, CH_3), 10.9 (s, CH_3). MS (EI, 70 eV), *m*/*z* (I, %): 604 $[M]^+$ (2), 484 $[M - (2,6\text{-Me-PhO}) + H]^+$ (100). Anal. Calc. for $C_{31}H_{35}MnNO_6P$: C, 61.69; H, 5.85; N, 2.32. Found: C, 61.80; H, 5.71; N, 2.13.

*2.3.3. (2S,3S)-Bis-(2,6-diisopropylphenyl)-2-[(ferrocenylidene)-amino]-3-methyl-pentylphosphite (**3c**)*

Red viscous oil, 86% yield. ^{31}P NMR ($CDCl_3$), δ_P: 137.2. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P), Hz): 161.1 (s, CH=N), 146.2 (s, $C_{Ar}O$), 146.0 (s, $C_{Ar}O$), 140.7 (d, $^3J = 2.0$, C_{Ar}), 140.5 (d, $^3J = 1.6$, C_{Ar}), 124.4 (s, $C_{Ar}H$), 124.2 (s, $C_{Ar}H$), 123.7 (s, $C_{Ar}H$), 80.6 (s, C_{Fc}(*ipso*)), 76.6 (s, CHN), 70.1, 70.0, 68.5, 68.3 (s, all C_{Fc}), 68.9 (s, C_{Cp}), 64.1 (s, CH_2O), 36.3 (s, CH), 27.1 (s, $CH(Pr^i)$), 26.9 (s, $CH(Pr^i)$), 25.3 (s, CH_2), 23.6, 23.5, 23.4, 23.3 (all s, $CH_3(Pr^i)$), 15.8 (s, CH_3), 10.9 (s, CH_3). MS (EI, 70 eV), *m*/*z* (I, %): 697 $[M]^+$ (3), 613 $[M - 2Pr^i + 2H]^+$ (37), 521 $[M - (2,6\text{-}Pr^i\text{-PhO}) + H]^+$ (100). Anal. Calc. for $C_{41}H_{56}FeNO_3P$: C, 70.58; H, 8.09; N, 2.01. Found: C, 70.84; H, 7.87; N, 1.91.

2.4. Preparation of rhodium complexes

*2.4.1. [Rh(COD)(η^1-**3a**)Cl](**5**)*

A solution of **3a** (0.249 g, 0.426×10^{-3} mol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of $[Rh(COD)Cl]_2$ (0.105g, 0.213×10^{-3} mol) in the same solvent (10 mL) at 20 °C. The reaction mixture was stirred for 1 h. The volume of solvent was reduced in vacuum (40 mmHg) to 1 mL, and then 10 mL of ether was added to induce the precipitation of the product. The precipitate obtained was separated by centrifugation, washed up with ether (10 mL) and dried in vacuum (1 mmHg). Red solid, 92% yield. ^{13}C NMR ($CDCl_3$), δ_C (*J*(C,P), Hz): 161.4 (s, CH=N), 149.6 (d, $^2J = 12.1$, $C_{Ar}O$), 149.3 (d, $^2J = 7.6$, $C_{Ar}O$), 130.1 (d, $^3J = 2.3$, C_{Ar}), 129.8 (d, $^3J = 2.3$, C_{Ar}), 128.5 (s, $C_{Ar}H$), 128.4 (s, $C_{Ar}H$), 124.2 (s, $C_{Ar}H$), 124.0 (s, $C_{Ar}H$), 111.3 (dd, ^1J(C,Rh) = 15.9, $^2J = 4.9$, COD, CH= *trans* P), 110.3 (dd, ^1J(C,Rh) = 17.4, $^2J = 4.9$, COD, CH= *trans* P), 80.3 (s, C_{Fc}(*ipso*)), 75.1 (d, ^1J(C,Rh) = 7.2, COD, CH= *trans* Cl), 73.0 (s, CHN), 71.3 (d, ^1J(C,Rh)= 12.5, COD, CH= *trans* Cl), 70.1, 70.0, 69.6, 69.3 (all s, C_{Fc}), 68.6 (s, C_{Cp}), 68.0 (s, CH_2O), 35.6 (s, CH); 32.9, 32.1, 28.1, 27.5 (all s, COD, CH_2), 24.9 (s, CH_2), 18.5, 18.4 (s, CH_3(Ar)), 15.5 (s, CH_3), 10.6 (s, CH_3). Anal. Calc. for $C_{41}H_{52}ClFeNO_3PRh$: C, 59.18; H, 6.30; N, 1.68. Found: C, 59.32; H, 6.46; N, 1.93.

*2.4.2. [Rh(COD)(η^2-**3a**)]BF_4 (**6**)*

2.4.2.1. Method A. A solution of **3a** (0.125 g, 0.213×10^{-3} mol) in THF (5 mL) was added dropwise to a stirred solu-

tion of $[Rh(COD)(THF)_2]BF_4$ (0.094g, 0.213×10^{-3} mol) in the same solvent (5 mL) at 20 °C. The reaction mixture was stirred for 1 h. The volume of solvent was reduced in vacuum (40 mmHg) to 1 mL, and then 10 mL of ether was added to induce the precipitation of the product. The precipitate obtained was separated by centrifugation, washed up with ether (10 mL) and dried in vacuum (1 mmHg). Orange solid, 94% yield.

2.4.2.2. Method B. To a stirred solution of **5** (0.177 g, 0.213×10^{-3} mol) in CH_2Cl_2 (5 mL) was added dropwise a solution of $AgBF_4$ (0.042 g, 0.217×10^{-3} mol) in THF (5 mL). The immediate formation of AgCl occurred as indicated by a white precipitate. The reaction mixture was stirred vigorously for 1 h. The cloudy reaction mixture was filtered through *Celite* to give an orange filtrate. The volume of filtrate was reduced in vacuum (40 mmHg) to 1 mL, and then 10 mL of ether was added to induce the precipitation of the product. The precipitate obtained was separated by centrifugation, washed up with ether (10 mL) and dried in vacuum (1 mmHg). Orange solid, 90 % yield. ^{13}C NMR ($CDCl_3$), δ_C (J(C,P), Hz): 175.2 (s, CH= N), 148.6 (d, $^2J = 16.3$, $C_{Ar}O$), 148.1 (d, $^2J = 14.8$, $C_{Ar}O$), 129.9 (d, $^3J = 11.0$, C_{Ar}), 129.5 (d, $^3J = 11.0$, C_{Ar}), 129.3 (s, $C_{Ar}H$), 129.1 (s, $C_{Ar}H$), 125.3 (s, $C_{Ar}H$), 125.2 (s, $C_{Ar}H$), 112.3 (d, ^1J(C,Rh) = 6.1, COD, CH= *trans* P), 109.2 (d, ^1J(C,Rh) = 14.8, COD, CH= *trans* P), 80.1 (s, C_{Fc}(*ipso*)), 80.0 (d, ^1J(C,Rh) = 6.8, COD, CH= *trans* N), 78.7 (d, ^1J(C,Rh) = 8.0, COD, CH= *trans* N), 74.0 (s, CHN); 72.7, 71.8, 71.5, 69.4 (all s, C_{Fc}), 70.0 (s, C_{Cp}), 67.3 (s, CH_2O), 38.0 (s, CH), 34.7, 31.2, 28.6, 25.3 (all s, COD, CH_2), 26.0 (s, CH_2), 17.9, 16.7 (s, CH_3(Ar)), 14.1 (s, CH_3), 10.9 (s, CH_3). ^{19}F NMR ($CDCl_3$), δ_F: −73.3. MS (PD), *m/z* (I, %): 796 $[M - BF_4^-]^+$ (100), 688 $[M - BF_4^- - COD]^+$ (90), 585 $[L]^+$ (24). Anal. Calc. for $C_{41}H_{52}BF_4FeNO_3PRh$: C, 55.74; H, 5.93; N, 1.59. Found: C, 55.88; H, 6.22; N, 1.39.

2.5. Palladium complexes

2.5.1. [Pd(allyl)(η²-3a)]BF₄ (7a)

Red solid, 94% yield. ^{13}C NMR (for major isomer) ($CDCl_3$), δ_C (J(C,P), Hz): 168.7 (s, CH=N), 149.2 (br. s, $C_{Ar}O$), 130.1 (br. s, C_{Ar}), 128.7 (br. s, $C_{Ar}H$), 125.6 (br. s, $C_{Ar}H$), 125.1 (d, $^2J = 7.9$, allyl, CH), 81.4 (d, $^2J = 42.8$, allyl, CH_2= *trans* P), 80.3 (s, C_{Fc}(*ipso*)), 73.2 (s, CHN), 71.8, 70.2, 69.5, 68.7 (all s, C_{Fc}), 69.3 (s, C_{Cp}), 67.4 (s, CH_2O), 55.3 (s, allyl, CH_2= *trans* N), 35.6 (s, CH), 24.8 (s, CH_2), 18.4, 18.2 (s, CH_3(Ar)), 15.4 (s, CH_3), 10.6 (s, CH_3). ^{19}F NMR ($CDCl_3$), δ_F: −74.0. MS (ESI), *m/z* (I, %): 732 $[M - BF_4^-]^+$ (100), 691 $[M - BF_4^- - allyl]^+$ (27), 585 $[L]^+$ (60). Anal. Calc. for $C_{36}H_{45}BF_4FeNO_3PPd$: C, 52.74; H, 5.53; N, 1.71. Found: C, 53.06; H, 5.90; N, 2.05.

2.5.2. [Pd(allyl)(η²-3b)]BF₄ (7b)

Orange solid, 91% yield. ^{13}C NMR (for major isomer) ($CDCl_3$), δ_C (J(C,P), Hz): 222.3 (s, CO), 168.7 (s, CH=N), 148.4 (d, $^2J = 11.8$, $C_{Ar}O$), 147.6 (d, $^2J = 9.1$, $C_{Ar}O$), 129.9 (s, C_{Ar}), 129.7 (s, C_{Ar}), 129.5 (s, $C_{Ar}H$), 129.3 (s, $C_{Ar}H$), 125.8 (br. s, $C_{Ar}H$), 122.6 (d, $^2J = 10.4$, allyl, CH), 89.6 (s, C_{Cp}(*ipso*)), 86.7, 86.3, 85.4, 84.2 (all s, C_{Cp}), 81.8 (d, $^2J = 42.1$, allyl, CH_2= *trans* P), 75.5 (s, CHN), 69.9 (s, CH_2O), 54.7 (d, $^2J = 6.8$, allyl, CH_2= *trans* N), 37.8 (s, CH), 25.2 (s, CH_2), 17.9, 17.7, 17.5, 17.4 (all s, CH_3(Ar)), 13.9 (s, CH_3), 10.6 (s, CH_3). MS (ESI), *m/z* (I, %): 751 $[M - BF_4^-]^+$ (100), 710 $[M - BF_4^- - allyl]^+$ (58), 604 $[L]^+$ (15). Anal. Calc. for $C_{34}H_{40}BF_4MnNO_6PPd$: C, 48.74; H, 4.81; N, 1.67. Found: C, 49.07; H, 5.13; N, 1.84.

2.5.3. [Pd(allyl)(η²-3c)]BF₄ (7c)

Orange solid, 95% yield. ^{19}F NMR ($CDCl_3$), δ_F: −73.7. MS (ESI), *m/z* (I, %): 844 $[M - BF_4^-]^+$ (100), 697 $[L]^+$ (10). Anal. Calc. for $C_{44}H_{61}BF_4FeNO_3PPd$: C, 56.70; H, 6.60; N, 1.50. Found: C, 56.51; H, 6.42; N, 1.35.

2.6. Preparation of platinum complex [Pt(allyl)(η²-3a)]BF₄ (8)

Cationic platinum complex **8** was synthesised for the ^{31}P NMR and ESI-mass experiments as follows: a solution of **3a** (0.0234 g, 0.4×10^{-4} mol) in CH_2Cl_2 (0.5 mL) was added dropwise to a stirred solution of $[Pt(allyl)Cl]_4$ (0.011 g, 0.1×10^{-4} mol) in the same solvent (0.5 mL) at 20 °C. The reaction mixture was stirred for 1 h. Then, a solution of $AgBF_4$ (0.008 g, 0.4×10^{-4} mol) in THF (0.5 mL) was added dropwise. The cloudy reaction mixture was stirred vigorously for 1 h and the resulted solution was filtered through *Celite* to give an orange-yellow filtrate. Then, a 1 mL sample of the filtrate was transferred to a NMR tube or ESI-mass test tube and spectral experiments were carried out.

2.7. Preparation of palladium and platinum complexes cis-[M(L)Cl₂]

2.7.1. General technique

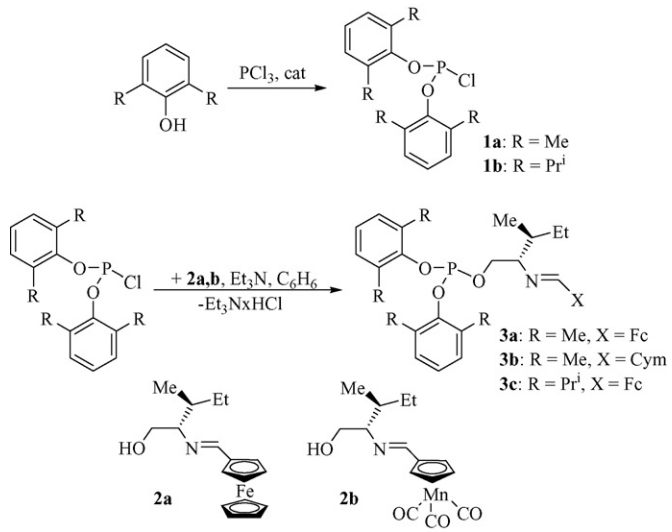
A solution of **3a** (0.125 g, 0.213×10^{-3} mol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of $[M(COD)Cl_2]$ (0.213×10^{-3} mol) in the same solvent (5 mL) at 20 °C. The reaction mixture was stirred for 1 h. The volume of solvent was reduced in vacuum (40 mmHg) to 1 mL, and then 10 mL of ether was added to induce the precipitation of the product. The precipitate obtained was separated by centrifugation, washed up with ether (2 × 10 mL) and dried in vacuum (1 mmHg).

2.7.2. cis-[Pd(3a)Cl₂] (9)

Red solid, 93% yield. ^{13}C NMR ($CDCl_3$), δ_C (J(C,P), Hz): 174.1 (s, CH=N), 148.5 (d, $^2J = 17.9$, $C_{Ar}O$), 146.5 (d, $^2J = 8.0$, $C_{Ar}O$), 129.9 (d, $^3J = 2.7$, C_{Ar}), 129.3 (d, $^3J = 2.7$, C_{Ar}), 129.1 (s, $C_{Ar}H$), 128.8 (s, $C_{Ar}H$), 125.4 (s, $C_{Ar}H$), 125.2 (s, $C_{Ar}H$), 80.5 (s, C_{Fc}(*ipso*)), 74.0 (s, CHN), 72.9, 71.2, 70.5, 69.8 (all s, C_{Fc}), 70.2 (s, C_{Cp}), 68.2 (d, $^2J = 2.7$, CH_2O), 36.4 (s, CH), 25.3 (s, CH_2), 18.2, 18.0 (s, CH_3(Ar)), 13.4 (s, CH_3), 10.4 (s, CH_3). Anal. Calc. for $C_{33}H_{40}Cl_2FeNO_3PPd$: C, 51.96; H, 5.29; N, 1.84. Found: C, 52.27; H, 5.02; N, 2.13.

2.7.3. cis-[Pt(3a)Cl₂] (10)

Red solid, 90% yield. ^{13}C NMR ($CDCl_3$), δ_C (J(C,P), Hz): 173.6 (s, CH=N), 148.0 (d, $^2J = 16.8$, $C_{Ar}O$), 146.1 (d, $^2J = 6.9$,



Scheme 1.

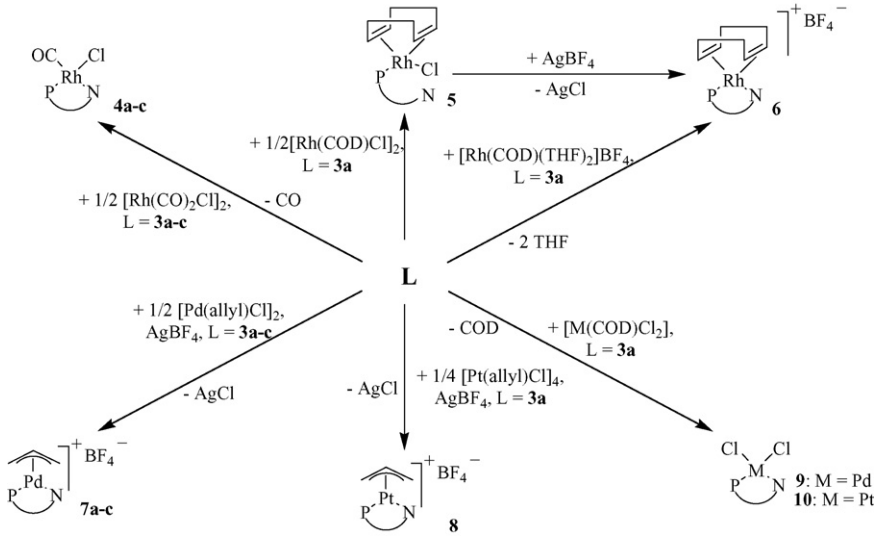
$C_{Ar}O$), 129.7 (s, C_{Ar}), 129.1 (s, C_{Ar}), 128.9 (s, $C_{Ar}H$), 128.5 (s, $C_{Ar}H$), 125.0 (s, $C_{Ar}H$), 124.8 (s, $C_{Ar}H$), 79.9 (s, C_{Fc}(*ipso*)), 74.8 (s, CHN), 73.8, 72.7, 71.6, 69.1 (all s, C_{Fc}), 70.1 (s, C_{Cp}), 68.4 (s, CH_2O), 36.2 (s, CH), 25.2 (s, CH_2), 17.9, 17.6 (s, CH_3(Ar)), 13.5 (s, CH_3), 10.1 (s, CH_3). MS (ESI), *m/z* (I, %): 851 $[M]^+$ (12), 816 $[M-Cl]^+$ (32), 780 $[M-2Cl]^+$ (100). Anal. Calc. for $C_{33}H_{40}Cl_2FeNO_3PPt$: C, 46.55; H, 4.74; N, 1.64. Found: C, 46.22; H, 4.47; N, 1.92.

3. Results and discussion

According to the previously described by us technique [13], ligand **3a** was prepared by direct phosphorylation of the imino alcohol **2a** with reagent **1a** (Scheme 1). For the catalytic study (vide infra), the related iminoarylphosphites **3b**,**c** were also prepared. They were obtained in a similar fashion using the same precursors, but from cymantrene based imino alcohol **2b** in the case of **3b** and with the bulky phosphorochloridite **1b** as phosphorylating reagent for the synthesis of **3c**. Phosphorochloridite **1a** can be easily prepared from 2,6-dimethylphenol and PCl_3 in the presence of Et_3N [11,12]. We also developed a simple solvent-free method for the synthesis of **1a**,**b** by using a catalytic amount of 1-methylpyrrolidin-2-one (see Section 2). This simple and time-saving procedure represents a handy method for the synthesis of convenient and cheap phosphorylating agents **1a**,**b**.

The compounds **3a–c** are red or brown viscous oils, which can be handled safely on air. All three ligands are well soluble in common organic solvents. Typically for iminoarylphosphites, their ^{31}P NMR spectra display a single peak near 136 ppm [13]. The structure of the new ligands **3b**,**c** was also unequivocally established by ^{13}C NMR, EI MS spectra and elemental analysis data. In the IR spectrum of **3b** (in $CHCl_3$), two strong bands attributable to the CO stretching frequencies are observed at 2026 and 1945 cm^{-1}.

Our earlier studies have shown that iminophosphites are suitable for chelation [11–13,27,28]. In the present study, the chelating ability of the **3a–c** was assessed by their reactions with square planar Rh^I and Pd^{II} precursors. Thus, reaction of **3a–c** with 0.5 equiv. $[Rh(CO)_2Cl]_2$ afforded complexes **4a–c** (Scheme 2). The ^{31}P NMR spectra of these complexes are characterised by doublets with ^1J(P,Rh) coupling constants in a narrow range of 275–279 Hz (Table 1). At the same time, the ν(CO) in the IR spectrum of chlorocarbonyl rhodium compounds [Rh(CO)(η^2-P,N)Cl] allows more sensitive estimation of the σ-donor/π-acceptor character of *P*,*N*-bidentate ligands and evaluation of the electron density at the metal [13,27,29]. Comparison of the CO stretching frequencies of **4a** and **4c** (Table 1) indicates lower π-acceptor ability of ligand **3c** due to +*I*-effect of the *iso*-propyl substituents in $P(OAr)_2$ fragment. On the other hand, the shift of 5 cm^{-1} to a higher frequency on going from **4a** to **4b** indicates that **3b** possesses a less active σ-donor nitrogen-containing centre because of the electron withdrawing $Mn(CO)_3$ group.



Scheme 2.

Table 1
Selected spectroscopic data for compounds **4a–c**; **5**, **6**; **7a–c**; **8**, **9** and **10** (in $CHCl_3$)

Compound	^{31}P NMR		IR, ν(CO) (cm^{-1})
	δ_P	^1J(P,M) (Hz)	
4a[a]	121.9	279.4[b]	2025
4b	120.2	274.7[b]	2032, 2030[d], 1944
4c	124.3	277.2[b]	2016
5	110.9	260.0[b]	
6	101.8	263.2[b]	
7a	136.9 (31%), 134.8 (69%)		
7b	121.7 (60%), 121.1 (40%)		2025, 1943
7c	116.0 (53%), 111.5 (47%)		
8	102.4 (45%), 102.2 (55%)	7083[c], 6861[c]	
9	74.1		
10	47.0	6138.2[c]	

[a] According the literature [13].
[b] ^1J(P,Rh).
[c] ^1J(P,Pt).
[d] For Rh—CO fragment.

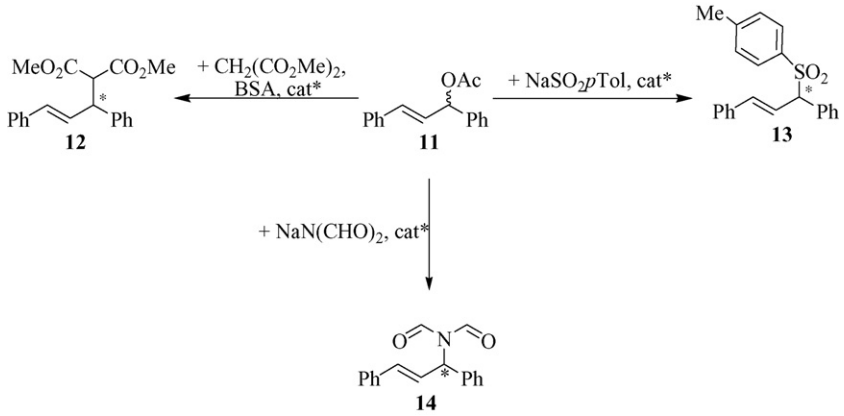
In complex **5**, iminoarylphosphite **3a** acts as a monodentate *P*-ligand (Scheme 2). Thus, the ^{31}P NMR spectrum of **5** (in $CDCl_3$) shows a doublet with ^1J(P,Rh) = 260.0 Hz (Table 1). As was shown by ^{13}C NMR spectroscopy (see Section 2), the 1,5-cyclooctadiene ligand is a part of complex **5**. Noteworthy is the asymmetric arrangement of this ligand, which is manifested in the fact that each carbon atom exhibits its own signal. This seems to be due to the influence of the bulky organophosphorus ligand, which causes a distortion of the geometry of the metal complex. The chemical shift of the CH=N carbon resonance does not show significant change upon coordination of the ligand (**3a**, δ_C 160.6 [13]; **5**, δ_C 161.4); this is consistent with the absence of interaction between the nitrogen and metal atoms. The IR spectrum of complex **5** in $CHCl_3$ exhibits only one ν(Rh—Cl) absorption band at 284 cm^{-1} in the far-IR region. Therefore, a chloride, a bidentate 1,5-cyclooctadiene ligand and a phosphorus atom complete the square planar geometry about the rhodium centre in **5**. The coordination of the nitrogen donor atom can be readily achieved by treatment of **5** in CH_2Cl_2 with a chloride scavenger such as $AgBF_4$ in THF. As a result, the complex **6** is quantitatively obtained (Scheme 2), in which the presence of a chelating *P*,*N*-ligand is proved by ^{31}P NMR (Table 1) and ^{13}C NMR (for example, δ_C 175.2 (s, CH=N), see Section 2) spectroscopy. Chelate formation was also inferred from the PD MS spectrum, which showed the expected $[M - BF_4^-]^+$ peak. Structure of complex **6** was also proved by its alternative synthesis from $[Rh(COD)(THF)_2]BF_4$ (Scheme 2).

The cationic palladium complexes **7a–c** were obtained with iminoarylphosphites **3a–c** and 0.5 equiv. $[Pd(allyl)Cl]_2$ in the presence of $AgBF_4$ (Scheme 2). The data of ^{13}C, ^{19}F, ^{31}P NMR, IR spectroscopy and ESI MS spectrometry (Table 1; Section 2) are in a good agreement with the suggested structures of the complexes. Duplication of peaks in the ^{31}P NMR spectra of compounds **7a–c** indicates the presence of their *exo*- and *endo*-isomers [13,27]. Stability of the obtained metal chelates **7a** and **7c** is indicated by the fact that addition of equimolar amount of corresponding ligands to their solutions in $CDCl_3$ did not cause any changes. Resulting ^{31}P NMR spectra contained exclusively signals of complexes **7a** and **7c** and free **3a** and **3c**.

Structure of the platinum complex **8**, which was prepared in situ, is analogous to **7a–c**. The ^{31}P NMR spectrum of **8** shows pseudotriplets δ_P 102.4, ^1J(P,Pt) = 7083.0 Hz (45%) and δ_P 102.2, ^1J(P,Pt) = 6861.5 Hz (55%). Its PD MS spectrum contains intense peaks at *m*/*z* 821(24%) and 780 (100%), corresponding to the $[M - BF_4^-]^+$ and $[M - BF_4^- - allyl]^+$ ions.

Neutral palladium and platinum complexes of **3a** could also be synthesised. Thus, reactions of **3a** with $[M(COD)Cl_2]$ (M = Pd, Pt) afforded compounds **9** and **10** (Scheme 2) in high yields. The structure of the products is supported by ^{31}P, ^{13}C NMR and IR spectral data. In particular, δ_P value for complex **9** (Table 1) is typical for six-membered palladacycles based on *P*,*N*-bidentate phosphites with acyclic phosphorus centres [10,13]. Besides ^{31}P NMR data (Table 1), coordination of the phosphorus atom to platinum in complex **10** was also confirmed by ^{195}Pt NMR spectroscopy (a doublet at δ_{Pt} −2610.0, ^1J(Pt,P) = 6143.6 Hz). Comparison of the ^{13}C NMR spectral parameters of the free and coordinated iminoarylphosphite **3a** revealed substantial downfield coordination shifts of the signals for the CH=N carbon atom ($\Delta\delta_C$ = 13.5 ppm for **9** and $\Delta\delta_C$ = 13 ppm for **10**). The *cis* orientation of chloride ligands was confirmed by observation of two ν(Pd—Cl) absorption bands at 337 and 292 cm^{-1} and two ν(Pt—Cl) absorption bands at 344 and 298 cm^{-1} in the far-IR spectral region of solid complexes **9** and **10**. High stability of the metal chelate based on **3a** is again notable, since ^{31}P NMR monitoring detected no reaction between complex **10** and free ligand **3a**, just as in the case of **7a** (vide supra).

Iminoarylphosphites **3a–c** and complexes **6**, **7a–c** and **9** were tested in asymmetric Pd-catalysed allyic substitution (Scheme 3). The results of allylic alkylation are summarised in Table 2. In general, catalytic systems with ligand **3a** demonstrated rather high enantioselectivity (Table 2, entries 1–5). Complex **7a** afforded excellent chemical (92%) and optical (97%) yields of product **12**. In contrast to π-allyl palladium pre-



Scheme 3.

Table 2
Enantioselective allylic alkylation of **11** with dimethyl malonate (BSA, NaOAc, 20 °C, 48 h)

Entry	Ligand	Catalyst	Solvent	Conversion of **11** (%)	ee (%)
1	**3a**	$[Pd(allyl)Cl]_2$/2L	THF	69	86 (*R*)
2	**3a**	**7a**	THF	70	93 (*R*)
3	***3a***	***7a***	CH_2Cl_2	*92*	*97* (*R*)
4	**3a**	**9**	THF	34	75 (*R*)
5	***3a***	***9***	CH_2Cl_2	*31*	*88* (*R*)
6	**3b**	$[Pd(allyl)Cl]_2$/2L	THF	34	38 (*R*)
7	**3b**	**7b**	THF	53	16 (*R*)
8	**3c**	$[Pd(allyl)Cl]_2$/2L	THF	46	56 (*R*)
9	**3c**	**7c**	THF	49	74 (*R*)
10	**3c**	**7c**	CH_2Cl_2	60	73 (*R*)

cursors, *cis*-dichloride complex **9** is sufficiently less active and slightly less enantioselective (Table 2, entries 4 and 5). More bulky homologue iminoarylphosphite **3c** provided some lower enantioselectivity (up to 74% ee), presumably due to steric overcrowding in a transition state [30]. Cymantrene-based ligand **3b** afforded not more than 38% ee (Table 2, entries 6 and 7), probably because $Mn(CO)_3$ is a more electron-withdrawing (vide supra) and a bulkier group [31] compared to the Cp ring in ferrocene.

It should be noted that steroselectivity of iminoarylphosphites **3a–c** in allylation of 1,3-diphenyl-2-propenyl acetate depends sufficiently on the nature of nucleophile. Thus, in allylic sulfonylation (Scheme 3) ligand **3a** demonstrated surprisingly low enantioselectivity, and highest optical yield of product **13** (36% ee) was achieved not with palladium complexes, but with rhodium complex **6** (Table 3, entries 1–3). At the same time, ligands **3c** and especially **3b** showed substantially better results—up to 50 and 67% ee, correspondingly. In the case of **3b**, strong correlation between enantioselectivity and the nature of anion in the applied palladium catalyst was observed (Table 3, entries 4 and 5).

Table 3
Enantioselective allylic sulfonylation of **11** with $NaSO_2pTol$ (THF, 20 °C, 48 h)

Entry	Ligand	Catalyst	Isolated yield (%)	ee (%)
1	**3a**	$[Pd(allyl)Cl]_2$/2L	33	5 (*R*)
2	**3a**	**7a**	55	20 (*R*)
3	***3a***	***6***	*50*	*36* (*S*)
4	**3b**	$[Pd(allyl)Cl]_2$/2L	34	2 (*R*)
5	***3b***	***7b***	*40*	*67* (*R*)
6	**3c**	**7c**	65	50 (*R*)

The $[Pd(allyl)Cl]_2$/2L (L = **3a**) catalytic system in the allylic amination of **11** with $NaN(CHO)_2$ in CH_3CN (standard reaction time 48 h, 20 °C) provided only 26% conversion of **11**, but excellent optical yield (96% (*S*)) of product **14**. In THF, conversion was 21% (58% ee (*S*)).

In conclusion, iminoarylphosphite **3a** was found to be a versatile chelating agent for a wide range of metal precursors ($[Rh(CO)_2Cl]_2$, $[Rh(COD)(THF)_2]BF_4$, $[Pd(allyl)Cl]_2$, $[Pt(allyl)Cl]_4$, $[Pd(COD)Cl_2]$, $[Pt(COD)Cl_2]$), and a representative stereoinductor for various Pd-catalysed allyic substitution processes.

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