Mendeleev Commun., 2001, 11(1), 33–35

Iminophosphites as new chiral P,N-bidentate ligands

Konstantin N. Gavrilov,*[a] Alexei I. Polosukhin,[b] Oleg G. Bondarev,[b] Andrei V. Korostylev,[b] Sergey E. Lyubimov,[a] Alexei A. Shiryaev,[a] Zoya A. Starikova[b] and Vadim A. Davankov[b]

[a] *Department of Chemistry, S. A. Esenin Ryazan State Pedagogical University, 390000 Ryazan, Russian Federation.*
Fax: +7 095 135 6471; e-mail: chem@ttc.ryazan.ru

[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation*

10.1070/MC2001v011n01ABEH001356

The coordination of new chiral P,N-hybrid ligands possessing a phosphite-type phosphorus donor centre and azomethine nitrogen to $[Rh(CO)_2Cl]_2$ and $PdCl_2(cod)$ was examined.

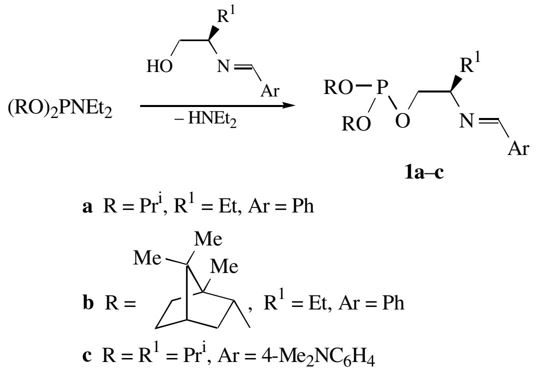
In the mid-1980's, H. Brunner introduced chiral phosphorus-containing ligands bearing a distant imino group — iminophosphines.[1] In the last years, such P,N-bidentate compounds were widely used in asymmetric metal complex catalysis and coordination chemistry.[2–5] Although they vary in molecular structure, all iminophosphines possess identical diphenylphosphine phosphorus centres. On the other hand, increasing the P-centre π-acidity of the P,N-bidentate ligand is well known to favour high chemical and optical yields in a number of catalytic reactions. The most effective way to increase the π-acidity and catalytic efficiency is to replace carbon atoms in the first coordination sphere of phosphorus by oxygen and/or nitrogen atoms. Some impressive results have been already achieved this way.[6–9] Hence, the inclusion of a distant imino group into a phosphorous acid ester molecule results in P,N-bidentate ligands of a new type, iminophosphites, which are promising for enantioselective catalysis.

In this study, we prepared the first optically active compounds of this class based on our previous experience in developing chiral aminophosphites.[9]

New chiral iminophosphites **1a–c** bearing a distant azomethine group have been obtained by one-step phosphorylation[†] of corresponding iminoalcohols[‡] (Scheme 1).

Compounds **1a–c**[§] are readily soluble in organic solvents and stable on keeping dry for several months. Their complexation[¶] leads to metal chelates with *cis*-oriented phosphorus and nitrogen atoms (Scheme 2).

In the case of **2a–c**, it is proved by ν(CO), ν(Rh–Cl) and ^1J(P,Rh) values (Table 1), which are characteristic of chlorocarbonyl Rh^I complexes with chelate-forming nitrogen-containing phosphites.[14] It should be added that ^1J(C,Rh) values are in the range 68–75 Hz typical of *cis*-[Rh(CO)Cl(PN)] chelates.[14] The presence of a Pd–P bond in the complexes **3a**,**b** is proved by δ_P and $\Delta\delta_P$ values (Table 2) typical of six-membered palladium chelates with acyclic nitrogen-containing phosphites.[15] Two equally intense ν(Pd–Cl) bands in the far IR region of **3a**,**b** result from the *cis*-configuration of chlorine ligands and different *trans*-influences of phosphorus and nitrogen centres (Table 2).



Scheme 1

Table 1 Selected spectroscopic data for compounds **2a–c** and **5**.

	IR/cm^{-1}		^{31}P NMR		^{13}C (CO) NMR		
	ν(CO), $CHCl_3$ (KBr)	ν(Rh–Cl) $CHCl_3$ (Nujol)	δ_P/ppm	^1J(P,Rh)/ Hz	δ_C(CO)/ ppm	^1J(C,Rh)/ Hz	^2J(C,P)/ Hz
2a	2019 (1999)	289 (285)	128.20	250.9	188.42	73.76	18.16
2b	2016 (2012)	290 (294)	130.22	254.3	187.46	72.95	18.77
2c	2014 (1996)	291 (288)	129.65	255.4	187.61	72.13	18.61
5	2022 (2011)	296 (296)	128.00	264.8	185.34	71.53	20.85

Table 2 Selected spectroscopic data for compounds **3a**,**b**.

	IR, ν(Pd–Cl)/cm^{-1}, $CHCl_3$ (Nujol)	^{31}P NMR ($CDCl_3$)	
		δ_P/ppm	$\Delta\delta_P^a$/ppm
3a	339, 328, 298 (335, 326, 295)	76.10	–63.1
3b	344, 294 (342, 284)	76.62	–64.2

[a] $\Delta\delta_P = \delta_P(\text{complex}) - \delta_P(\text{ligand})$.

A comparison between the spectral data for free and coordinated iminophosphites demonstrates significant downfield coordination shifts of the resonances of carbon atoms adjacent to phosphorus ($\Delta\delta_C$ 2–8 ppm) and nitrogen atoms. The azomethine carbon exhibits a large value of $\Delta\delta_C$ (9–11 ppm), which is indicative of binding an imine nitrogen atom to a metal atom.

Compounds **2a** and **2b** were isolated as single crystals and their structures were determined by X-ray diffraction studies.[††] The angular distortions of the Rh coordination geometries in both **2a** and **2b** molecules are almost equal, a Rh atom is situated at 0.073(2) Å (**2a**) and 0.101(2) Å (**2b**) from the P(1)Cl(1)N(1)C(1) basal plane. The chelate metal rings exhibit asymmetrically distorted Rh(1),C(3)-boat and N(1),O(2)-boat conformations in **2a** and **2b**, respectively.

[†] *General procedure.* An equimolar mixture of $(RO)_2PNEt_2$ [R = (1*S*)-endo-(–)-bornyl,[10] Pr^i [11]] (0.01 mol) and a corresponding iminoalcohol in toluene (20 ml) was stirred under reflux for 4 h. Then, the solvent was evaporated and the residue was distilled at 0.8 mmHg (65–80% yield). $[\alpha]_D^{20}$ = –4.63 (*c* 2.42, $CHCl_3$, **1a**), $[\alpha]_D^{15}$ = +17.35 (*c* 1, $CHCl_3$, **1b**), $[\alpha]_D^{20}$ = –7.71 (*c* 1.2, $CHCl_3$, **1c**).

[‡] Syntheses of the iminoalcohols {(2*R*)-2-[*N*-(benzylideneamino)]-3-methylpropan-1-ol[12] and (2*R*)-2-[*N*-(*p*-dimethylaminobenzylideneamino)]-3-methylbutan-1-ol, $[\alpha]_D^{19}$ = +9.82 (*c* 10, CH_2Cl_2)} are analogous to the described procedures.[13]

[§] All compounds gave spectroscopic and analytical data consistent with the proposed structure.

[¶] *General procedure.* A solution of **1a–c**, **4** (3.6×10^{-4} mol) in CH_2Cl_2 (5 ml) was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (1.8×10^{-4} mol) or $PdCl_2(cod)$ (3.6×10^{-4} mol) in the same solvent (15 ml) at 20 °C with stirring. The reaction mixture was stirred at 20 °C for 0.5 h. The excess of the solvent was then removed in a vacuum (40 mmHg), and 10 ml of hexane (in the case of **2a–c**, **5**) or diethyl ether (in the case of **3b**,**c**) was added to the residue. The precipitate obtained was separated by centrifugation, washed with hexane (10 ml) or diethyl ether and dried in a vacuum (1.5 mmHg) to give a product in 80–95% yield.

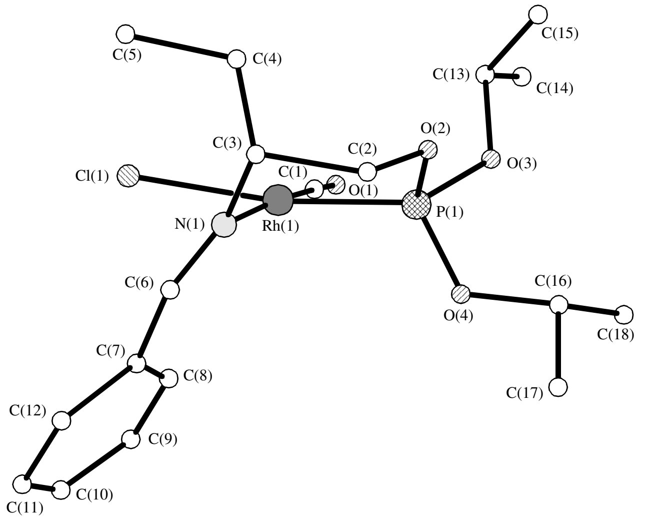
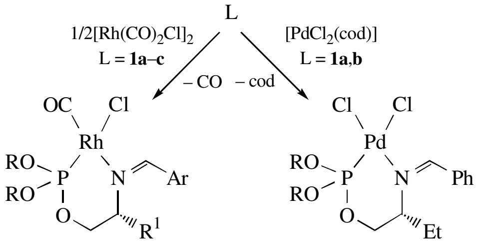


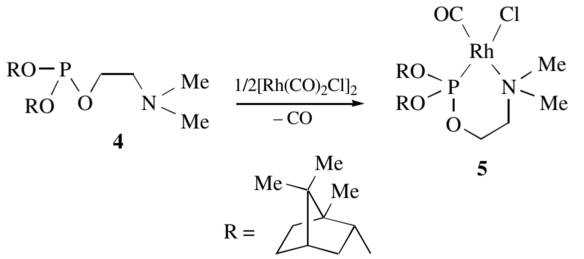
Figure 1 General view of a molecule of **2a**. Selected bond lengths (Å): Rh(1)–C(1) 1.813(6), Rh(1)–N(1) 2.123(4), Rh(1)–P(1) 2.186(2), Rh(1)–Cl(1) 2.400(2), O(2)–C(2) 1.436(7); principal bond angle (°): N(1)–Rh(1)–P(1) 88.02(13).

When designing chiral P,N-bidentate ligands, not only the π-acceptor ability of a phosphorus centre but also the δ-donor ability of nitrogen should be taken into account. Thus, in a series of ferrocene-based phosphinopyrazoles, optical yields in Rh-catalysed hydroboration–oxidation of alkenes[16,17] and in Pd-catalysed hydrosilylation–oxidation of alkenes[18] increased with the electron-donor ability of a pyrazole unit. In this connection, a concept of electronically non-symmetric ligands was suggested (the higher the π-acceptor ability of the P-centre and the δ-donor ability of the N-centre, the more electronically asymmetric the compound). This parameter can be estimated using the value of ν(CO) in the IR spectrum of the chlorocarbonyl complex [Rh(CO)Cl(PN)].[17] In particular, for structurally similar complexes with identical phosphorus centres and different nitrogen centres, a compound with a lower value of ν(CO) possesses a more active σ-donor nitrogen-containing centre and hence is more electronically asymmetric.[‡‡]



2a–c **3a,b**

Scheme 2



4 **5**

Scheme 3

On this basis, we synthesised a Rh(I) chlorocarbonyl complex with the same P-centre as in **2b** but bearing a tertiary amino group[§§] (Scheme 3).

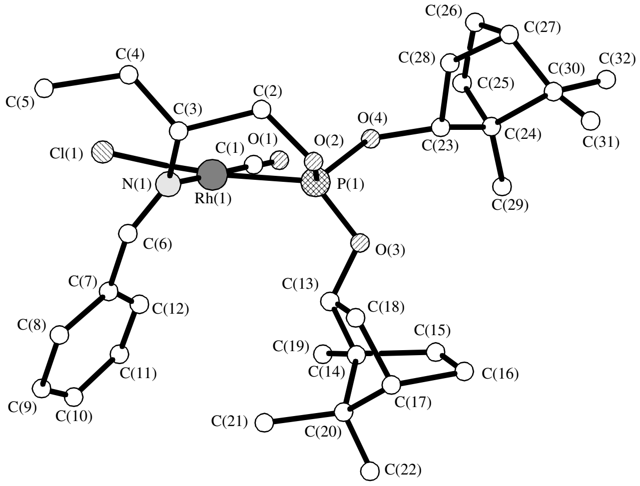


Figure 2 General view of a molecule of **2b**. Selected bond lengths (Å): Rh(1)–C(1) 1.833(7), Rh(1)–N(1) 2.114(5), Rh(1)–P(1) 2.164(2), Rh(1)–Cl(1) 2.405(2), O(2)–C(2) 1.441(7); principal bond angle (°): N(1)–Rh(1)–P(1) 86.1(2).

Selected spectral data for **5** are shown in Tables 1 and 2. Note that ν(CO) (in $CHCl_3$) for **2b** is 6 cm^{-1} lower than that for **5** (Table 1). It indicates a higher electron-donating ability of an imino group in comparison to an amino group and, therefore, a more pronounced electronic asymmetry of iminophosphite **1b**. An increase in the electron-donor ability of a nitrogen-containing unit causes a decrease of ^1J(P,Rh) (Table 1). A similar behaviour was observed when the spectral parameters of **2a** and its recently obtained[11] analogue **5** [R = Pr^i, ν(CO) 2022 cm^{-1} ($CHCl_3$), ^1J(P,Rh) 261.7 Hz ($CDCl_3$)] were compared.

[††] *Crystallographic data for* **2a**: at –80 °C crystals of $C_{18}H_{28}ClNO_4PRh$ are monoclinic, space group $P2_1$, $a = 9.042(4)$, $b = 8.727(4)$, $c = 13.904(7)$ Å, $\beta = 92.32(4)°$, $V = 1096.3(9)$ Å^3, $Z = 2$, $M = 491.74$, μ(MoKα) = 0.995 mm^{-1}, 2778 reflections were measured, 2567 ($R_{int} = 0.0443$) independent reflections were used in all calculations. The final $wR(F^2)$ was 0.0883 (all data), $R_1(F) = 0.0327$ [F, 2298 reflections with $I > 2\sigma(I)$]. All hydrogen atoms (except from six atoms) were located from the difference Fourier syntheses and refined in an isotropical approximation, the hydrogen atoms in two Me groups [$C(14)H_3$ and $C(15)H_3$] were placed in geometrically calculated positions and included in the refinement using the rigid model approximation with the temperature factors $U_{iso} = 1.5U_{eq}$(C), where U_{eq}(C) is the equivalent isotropical temperature factor for carbon atom bonding to the corresponding hydrogen atom.

Crystallographic data for **2b**·0.25CH_2Cl_2: at –163 °C crystals of $C_{32.25}H_{48}Cl_{1.50}NO_4PRh$ are tetragonal, space group $I4$, $a = 30.230(2)$, $b = 30.230(2)$, $c = 7.5935(5)$ Å, $V = 6939.5(7)$ Å^3, $M = 700.77$, $Z = 8$, μ(MoKα) = 0.688 mm^{-1}, 37077 reflections were measured, 9499 ($R_{int} = 0.0610$) independent reflections were used in all calculations. The final $wR(F^2)$ was 0.1431 (all data), $R_1(F) = 0.0606$ [F, 5092 reflections with $I > 2\sigma(I)$]. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement using the rigid model approximation with the temperature factors $U_{iso} = 1.2U_{eq}(C_i)$ or $1.5(C_{ii})$, where C_i and C_{ii} are sp^2- and sp^3-carbon atoms to which the corresponding hydrogen atom is attached. The solvate CH_2Cl_2 molecules are disordered over several positions in channels along a four-fold axis.

Yellow crystals of **2a** and **2b**·CH_2Cl_2 were obtained from dichloromethane solutions by slow evaporation. A Bruker SMART (**2a**) or Syntex $P2_1$ diffractometer (**2b**·CH_2Cl_2) was used. The structures were solved using direct methods and refined by full-matrix least-squares on F^2. All calculations were performed using the SHELXTL PLUS 5.0 program. Atomic coordinates, bonds lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/75.

[‡‡] In the alkylation of dimethyl malonate with 1,3-diphenylprop-2-enyl acetate catalysed by $[Pd(All)Cl]_2$, ligands **1a** and **1c** gave *ee* 13 (*S*) and 57% (*S*), respectively (the chemical yield is quantitative). We are grateful to R. Hilgraf (University of Basel, Switzerland) for catalytic experiments.

[§§] Synthesis of ligand **4** was described previously.[10]

References

1 H. Brunnel and H. Weber, *Chem. Ber.*, 1985, **118**, 3380.

2 T. Hayashi, C. Hayashi and Y. Uozumi, *Tetrahedron: Asymmetry*, 1995, **6**, 2503.

3 H. Brunnel, I. Deml, W. Dirnberger, K.-P. Ittner, W. Reiβer and M. Zimmermann, *Eur. J. Inorg. Chem.*, 1991, 51.

4 A. Saitoh, K. Achiwa and T. Morimoto, *Synlett*, 1999, 483.

5 H. A. Ankersmit, B. H. Loken, H. Kooijman, A. L. Spek, K. Vrieze and G. van Koten, *Inorg. Chim. Acta*, 1996, **252**, 141.

6 J. M. Brunnel, T. Constantieux and G. Buono, *J. Org. Chem.*, 1999, **64**, 8940.

7 R. Hilgraf and A. Pfaltz, *Synlett*, 1999, 1814.

8 D. K. Heldmann and D. Seebach, *Helv. Chim. Acta*, 1999, **82**, 1096.

9 K. N. Gavrilov, A. V. Korostylev, O. G. Bondarev, A. I. Polosukhin and V. A. Davankov, *J. Organomet. Chem.*, 1999, **585**, 290.

10 K. N. Gavrilov, I. S. Mikhel, K. A. Lyssenko, M. Yu. Antipin, G. I. Timofeeva, A. I. Polosukhin and A. V. Korostylev, *Zh. Neorg. Khim.*, 1997, **42**, 593 (*Russ. J. Inorg. Chem.*, 1997, **42**, 520).

11 K. N. Gavrilov, A. V. Korostylev, O. G. Bondarev, A. V. Petrovskii, K. A. Lyssenko, A. I. Polosukhin and V. A. Davankov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 530 (*Russ. Chem. Bull.*, 2000, **49**, 533).

12 N. Heuser, M. Klein, J. Messinger, V. Buss, E. Raabe, C. Krueger, *J. Chem. Soc., Chem. Commun.*, 1987, 945.

13 H. Brunner, I. Deml, W. Dirnberger, B. Nuber and W. Reiber, *Eur. J. Inorg. Chem.*, 1998, 43.

14 K. N. Gavrilov, *Zh. Neorg. Khim.*, 1997, **42**, 433 (*Russ. J. Inorg. Chem.*, 1997, **42**, 368).

15 K. N. Gavrilov, A. V. Korostylev, G. I. Timofeeva, A. I. Polosukhin, O. G. Bondarev and P. V. Petrovskii, *Koord. Khim.*, 1998, **24**, 610 (*Russ. J. Coord. Chem.*, 1998, **24**, 570).

16 A. Snyder, L. Hintermann and A. Togni, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 931.

17 A. Schnyder, A. Togni and V. Weisli, *Organometallics*, 1997, **16**, 255.

18 A. Togni, R. Dorta, C. Köllner and G. Pioda, *Pure Appl. Chem.*, 1998, **70**, 1477.

Received: 6th July 2000; Com. 00/1682