Chiral α-P,N Ligands From a Diastereoselective Ph_2PH Addition to (η^6-Benzaldimine)tricarbonylchromium Complexes

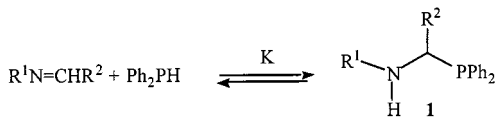
Jacques Andrieu,*[a] Clara Baldoli,[b] Stefano Maiorana,[b] Rinaldo Poli,*[a] and Philippe Richard[a]

Keywords: Aminophosphane / Chirality / Chromium complexes/ Diastereoselective reactions / P ligands

Chiral α-aminophosphane (α-P–C–N) ligands have been prepared by reversible addition of Ph_2PH to tricarbonylchromium benzaldimine complexes $(CO)_3Cr[\eta^6$-*o*-$C_6H_4(Y)(CH{=}NR)]$ (with Y, R = CH_3, CH_3 or CH_2COOCH_3; CH_3O, CH_3 or *p*-$CH_3OC_6H_4$; Cl, C_6H_5), with complete diastereoselectivity. These complexes are stabilized in solution by electron-withdrawing group(s) on the imine.

Introduction

Since the discovery that bifunctional P,N ligands increase considerably the activity and/or the selectivity of palladium, ruthenium, or rhodium catalysts,[1−4] the preparation of this type of ligand has been the subject of extensive investigations. As an example, pyridyl diphenylphosphane (2-$PyPPh_2$) crucially controls the activity and selectivity of alkyne methoxycarbonylation catalysts.[1] Other α-aminophosphane ligands are rare: compound $Ph_2PCH_2N(CH_3)_2$, having a tertiary amine function, is stable in the solid state and in solution,[5] while Et_2PCH_2NHtBu and $Ph_2PCH(Ph)NHPh$ have only been described in the solid state.[5,6] Recent studies by some of us have demonstrated *in solution* a reversible P−C bond cleavage of α-aminophosphane ligands with a secondary amine function (Scheme 1).[7] It was found, for instance, a $K = 50$ for $R^1 = R^2 =$ Ph and that electron-withdrawing substituents R^1 and R^2 or phosphorus coordination to Cu^I favor the formation of the P−C bond. This behavior rationalises previously reported unexpected P−C bond cleavage reactions.[6,8,9] We now report a stereoselective extension of this synthetic method leading to the preparation of chiral α-P,N ligands.

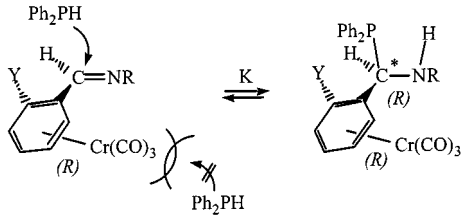


Scheme 1

[a] Laboratoire de Synthèse et d′Electrosynthèse Organométalliques, Faculté des Sciences "Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, F-21000 Dijon, France
Fax: (internat.) + 33-3/8039-6098
E-mail: andrieu@u-bourgogne.fr, poli@u-bourgogne.fr
[b] Dipartimento di Chimica Organica e Industriale e CNR Centro Studio Sintesi Stereochimica Speciali Sistemi Organici, Università di Milano,
Via C. Golgi 19, I-20133 Milano, Italy

Results and Discussion

The synthetic strategy consists in using chiral *ortho*-substituted benzaldimine $Cr(CO)_3$ complexes (Scheme 2). As it is well-known, in these complexes the coordination of the aromatic ring to the bulky $Cr(CO)_3$ fragment makes one imine diastereoface inaccessible to the phosphane attack. In addition the presence of the *ortho* substituent favours the conformation in which the *ortho* group is *anti* with respect to the imino moiety. These stereochemical features of planar-chiral chromium tricarbonyl complexes[10,11] and of $Cr(CO)_3$ complexed imines[12−15] in particular, have been previously exploited in stereoselective synthesis.



Scheme 2

The reaction between racemate complexes $(CO)_3Cr[\eta^6$-*o*-$C_6H_4(Y)(CH = NR)]$ (with Y, R = CH_3, CH_3 or CH_2COOCH_3; CH_3O, CH_3 or *p*-$CH_3OC_6H_4$; Cl, C_6H_5) and Ph_2PH in $CDCl_3$ leads to the formation of equilibrium quantities of the desired aminophosphane ligand (**2−6**) as a single diastereoisomer, within the detection limits of ^{31}P-NMR spectroscopy (Table 1). For the sake of semplicity, Scheme 2 shows this transformation for only one of the two enantiomers. The relative concentrations at equilibrium are determined by integration of the ^{1}H-NMR resonances of the imine and product methyne protons and/or the Ph_2PH and product ^{31}P-NMR resonances. With the exception of complex **6**, these constants are smaller relative to that previously reported for the formation of **1** ($R^1 = R^2 =$ Ph, Scheme 1).[7] Given the previously established electronic control on the equilibrium of Scheme 1, the presence of the

  1434−193X/99/1111−3095 $ 17.50+.50/0

$Cr(CO)_3$ moiety would be expected to enhance the formation of the P−C bond, while the presence of the Y substituent would provide an effect which depends on the relative σ and π donor/acceptor properties. It can therefore be concluded that, when R = Ph, the combination of the arene-coordinated $Cr(CO)_3$ group and the Cl substituent is sufficient for a quantitative P−C bond formation. For compound **5**, the electron-withdrawing effect of the $Cr(CO)_3$ moiety is not sufficient to compensate the overall donor properties of the two methoxy substituents. The individual effect of the $Cr(CO)_3$ moiety has been evaluated by comparing the formation of **6** with corresponding reaction of the $Cr(CO)_3$-free imine, forming product **7**. It can be observed that the constant *K* increases by at least a factor of 3 upon $Cr(CO)_3$ coordination.

Table 1. Results of the reaction between $(CO)_3Cr[\eta^6$-*o*-$C_6H_4(Y)(CH{=}NR)]$ and Ph_2PH[a]

	Y	R	d.e. (%)	% P−C[b]	*K*	δ_P (ppm)
2	CH_3	CH_3	> 98	44	3.1	10.4
3	CH_3O	CH_3	> 98	54	5.8	10.9
4	CH_3	CH_2COOCH_3	> 98	62	10.7	11.5
5	CH_3O	*p*-$CH_3OC_6H_4$	> 98	73	17	12.4
6	Cl	C_6H_5	> 98	> 99	> 1000	13.7
7	Cl	C_6H_5[c]	–	92	330	4.7

[a] Solvent = $CDCl_3$; $[imine]_0 = [Ph_2PH]_0 = 0.57$ M. – [b] Calculated by integration of the ^1H and ^{31}P resonances. – [c] Without the $Cr(CO)_3$ fragment.

The comparison between compounds **3** and **5** on one side and compounds **2** and **4** on the other side shows that *K* increases by changing R from CH_3 to *p*-$CH_3OC_6H_4$ and CH_2COOCH_3, respectively. These variations are consistent with the previously established electronic control on the stability of the P−C bond.[7] The comparison between compounds **2** and **3**, on the other hand, shows that *K* increases by changing Y from CH_3 to CH_3O, indicating that the methyl group is an even stronger donor than the methoxy group. While the nature of R and Y has an important effect on the equilibrium, the rate at which the equilibrium is achieved is not significantly changed (for instance, $t_{1/2}$ = 12 min for the formation of **6**, close to that observed for the formation of **1**).[7]

It is interesting to remark that the ^{31}P-NMR chemical shifts of the aminophosphane products **2**−**6** qualitatively correlate with their stability. The equilibrium constant increases as the ^{31}P-NMR resonance of the product shifts downfield. Both changes are related to the electronic properties of the substituents R and Y, while steric differences may be considered negligible. The strong variation of ^{31}P-NMR chemical shift between compounds **6** and **7**, on the other hand, may be attributed to the combination of a weak electronic effect (*K* changes only by a factor of ca. 3) and a larger steric effect.

The aminophosphane **6** was isolated by crystallization from $CHCl_3$ in 70% yield as yellow crystals and its absolute configuration has been confirmed by X-ray crystallography. The asymmetric unit contains both enantiomers and one $CHCl_3$ solvent molecule. It is interesting to note a dimeric structure (see Figure 1), the two monomer units being held together by two rare intermolecular P···H−N bridges. The P···N* and P*···N separations are 3.638 and 3.702 Å, respectively, which are similar to those found for compound $Ph_2P-C(S)-NHMe$ (3.607 Å).[16] It is to be noted that an (*R*) configuration for the (arene)tricarbonylchromium(0) unit induces an (*R*) configuration for the new stereocenter in the product (and vice versa), as predicted on the basis of the stereochemical considerations presented above.

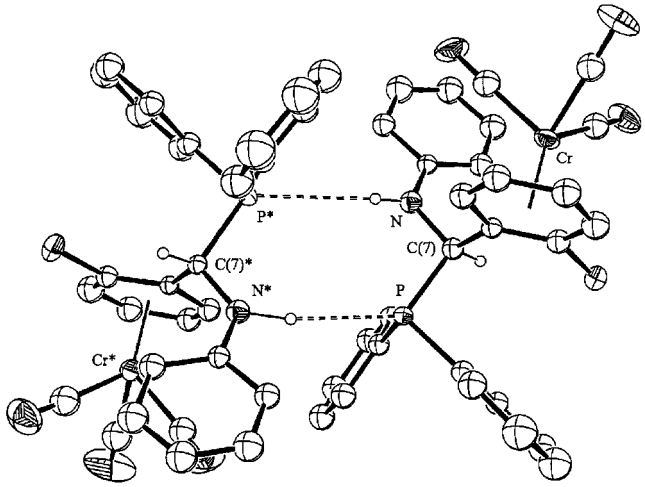


Figure 1. ORTEP view of compound **6** with ellipsoids shown at the 30% probability level; all hydrogen atoms are omitted for clarity, except those on the N, N*, C(7), and C(7)*, highlighting the hydrogen-bonding interactions and the absolute configuration at C(7) and C(7)*

In conclusion, we have described the use of an arene-coordinated tricarbonylchromium template for the diastereoselective addition of Ph_2PH to an imine, leading to chiral α-P−C−N ligands. Further information on the electronic control of the reversible P−C bond formation has been obtained by the use of various $Cr(CO)_3$ complexes' aromatic imine substrates. In addition to promoting the asymmetric induction, the $Cr(CO)_3$ moiety exerts an electronic contribution favouring the formation of the P−C bond. The coordination chemistry of the α-aminophosphane ligands obtained is currently under investigation in order to evaluate their potential in catalytic asymmetric reactions

Experimental Section

General Remarks: All manipulations were carried out under purified argon and in the dark using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. – ^1H- and $^{31}P\{^1H\}$-NMR measurements were carried out with a Bruker AC200 spectrometer. The peak positions are reported with positive shifts in ppm downfield of TMS as calculated from the residual solvent peaks (^1H) or downfield of external 85% H_3PO_4 (^{31}P). – IR spectra were recorded with a Bruker IFS 66V spectrophotometer with KBr optics. – Elemental analysis was carried out by the analytical service of the Laboratoire de Synthèse et d'Electrosynthèse Organométalliques with a Fisons Instruments EA1108 an-

alyzer. − The starting complexes $(CO)_3Cr[\eta^6$-o-$C_6H_4(Y)(CH=NR)]$ used in this study were obtained as previously described in the literature.[12−14,17]

Aminophosphanes 2−5: All experiments were conducted with identical operating procedures and concentrations. The equilibrium formation of product **5** is described in detail. Ph_2PH (50 μL, 0.287 mmol) was added to a solution of the benzaldiminetricarbonylchromium complex $(CO)_3Cr[\eta^6$-o-$C_6H_4(OCH_3)(CH=N$-p-$C_6H_4OCH_3)]$ (0.108 g, 0.287 mmol) in $CDCl_3$ (0.5 mL). The resulting solution was stirred at room temperature for 3 h. − ^{31}P NMR (81.03 MHz, $CDCl_3$): δ = 12.5 (s) and −36.6 (s), respectively, for **5** and the free Ph_2PH. − IR (ν_{CO}, $CHCl_3$): 1970 (b), 1904 (vb) cm^{-1}. − The equilibrium constant was determined by integration of the ^1H-NMR signals, whose intensity did not change over the subsequent 48 h.

Aminophosphane 6: Ph_2PH (50 μL, 0.287 mmol) was added to a solution of the complex $(CO)_3Cr[\eta^6$-o-$C_6H_4(Cl)(CH=NPh)]$ (0.181 g, 0.474 mmol) in $CHCl_3$ (10 mL). The resulting solution was stirred at room temperature for 3 h, filtered, and concentrated to half volume. Addition of pentane afforded the complex **6** as yellow crystals (0.188 g, 70%). − ^1H NMR (200 MHz, $CDCl_3$): δ = 7.41−4.53 (m, 20 H, aromatics + NH), 4.12 (dd, 1 H, PCH, $^2J_{PH}$ = 3.4 Hz, $^3J_{HH}$ = 7.3 Hz). − ^{31}P NMR (81.03 MHz, $CDCl_3$): δ = 13.7 (s). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 231.61 (s, CO), 145.37−84.68 (m, aromatics), 51.39 (d, PCH, $^1J_{PC}$ = 18.5 Hz). − IR (ν_{CO}, $CHCl_3$): 1980 (b), 1917 (vb) cm^{-1}. − $C_{56}H_{42}Cl_2Cr_2N_2O_6P_2 \cdot 1/2\ CHCl_3$ (1135.5): calcd. C 59.75, H 3.75, N 2.48; found C 59.90, H 3.75, N 2.59.

Crystal Structure Analysis of 6: $(C_{28}H_{21}ClNPO_3Cr)_2 \cdot CHCl_3$, M = 1195.12. Enraf−Nonius CADA diffractometer, Mo-K_α radiation (λ = 0.71073 Å), T = 293 K; monoclinic, $P21/c$, a = 11.267(2), b = 28.202(4), c = 18.014 (3) Å, β = 104.808(14)°, V = 5533.9(16) $Å^3$, Z = 4, D_x = 1.434 g cm^{-3}, μ = 0.744 mm^{-1}. The structure was solved by Patterson methods and subsequent difference Fourier analysis.[18] Due to the weak diffracting power of the crystal, the refinement was performed on the 2338 observed reflections [$I > 2\sigma(I)$] among the 5365 unique reflections collected. The model was refined isotropically except for the Cr, Cl, and P atoms. Except one hydrogen atom bonded to a nitrogen atom located in the final fourier difference map, hydrogen atoms were included in their calculated positions and refined with a riding model. A final refinement on F^2 with 2338 intensities [$> 2\sigma(I)$] and 292 parameters converged at $wR(F^2)$ = 0.208 and $R(F)$ = 0.081. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-127927. 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.at.uk].

Acknowledgments

We acknowledge the Conseil Régional de Bourgogne, the MENRT, the CNRS and CNR for their financial support to this work.

[1] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247−253.
[2] H. Yang, M. Alvarez, N. Lugan, R. Mathieu, *J. Chem. Soc., Chem. Commun.* **1995**, 1721−1722.
[3] H. Brunner, A. F. M. Mokhlesur Rahman, *Chem. Ber.* **1984**, *117*, 710−724.
[4] G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067−2089.
[5] K. Isslieb, H. Oehme, D. Wienbeck, *J. Organomet. Chem.* **1974**, *76*, 345−348.
[6] A. N. Pudovik, G. V. Romanov, V. M. Pozhidaev, *Z. Obsch. Chim.* **1978**, *48*, 1008−1013; *Chem. Abstr.* **1978**, *89*, 109752k.
[7] J. Andrieu, J. Dietz, R. Poli, P. Richard, *New J. Chem.* **1999**, *23*, 581−583.
[8] K. Kellner, A. Tzschach, *Z. Chem.* **1984**, *24*, 365−375.
[9] P. H. M. Budzelaar, *J. Org. Chem.* **1998**, *63*, 1131−1137.
[10] A. Solladié-Cavallo, in: *Advances in Metal-Organic Chemistry*, vol. 1 (Ed.: L. S. Liebenskind), JAI Press, Greenwich, **1989**, p. 99.
[11] S. G. Davies, T. D. McCarthy, in *Comprehensive Organometallic Chemistry II*, vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, p. 1039.
[12] S. Maiorana, C. Baldoli, P. Del Buttero, M. Di Ciolo, A. Papagni, *Synlett* **1996**, 258.
[13] P. Kündig, L. H. Xu, P. Romanenes, G. Bernardinelli, *Synlett* **1996**, 270.
[14] C. Baldoli, P. Del Buttero, E. Licandro, A. Pagagni, *Tetrahedron* **1996**, *52*, 4849−4856.
[15] M. Uemura, N. Taniguchi, *Tetrahedron* **1998**, *54*, 12775−12788.
[16] V. W. Hiller, K. Wurst, U. Kunze, *Acta. Crystallogr.* **1987**, *C43*, 2235−2236.
[17] E. P. Kündig, B. Schnell, G. Bernardinelli, *Synlett* **1999**, 348−350.
[18] G. M. Sheldrick, University of Göttingen, Göttingen, Federal Republic of Germany, **1997**.

Received April 21, 1999
[O99229]