



HAL
open science

Chiral α -P,N Ligands From a Diastereoselective Ph₂PH Addition to (η^6 -Benzaldimine)tricarbonylchromium Complexes

Jacques Andrieu, Clara Baldoli, Stefano Maiorana, Rinaldo Poli, Philippe Richard

► **To cite this version:**

Jacques Andrieu, Clara Baldoli, Stefano Maiorana, Rinaldo Poli, Philippe Richard. Chiral α -P,N Ligands From a Diastereoselective Ph₂PH Addition to (η^6 -Benzaldimine)tricarbonylchromium Complexes. *European Journal of Organic Chemistry*, 1999, 1999 (11), pp.3095-3097. 10.1002/(SICI)1099-0690(199911)1999:113.0.CO;2-Q . hal-03299507

HAL Id: hal-03299507

<https://hal.science/hal-03299507>

Submitted on 28 Jul 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chiral α -P,N ligands from a diastereoselective Ph₂PH addition to (η^6 benzaldimine)tricarbonylchromium complexes

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

aminophosphine / chirality / chromium complexes/ diastereoselective reactions / P-ligands

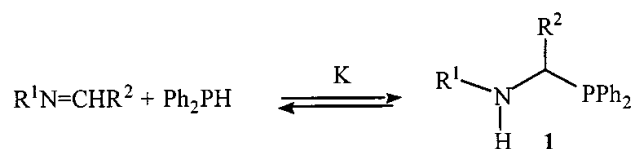
Chiral α -aminophosphine (α -P-C-N) ligands have been prepared by reversible addition of Ph₂PH to tricarbonylchromium benzaldimine complexes (CO)₃Cr[η^6 -*o*-C₆H₄(Y)(CH=NR)] (with Y, R = CH₃, CH₃ or CH₂COOCH₃; CH₃O, CH₃ or *p*-CH₃OC₆H₄; Cl, C₆H₅), with complete diastereoselectivity. These complexes are stabilized in solution by electron-withdrawing group(s) on the imine.

^[a] Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté des Sciences "Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, 21000 Dijon, France
Fax: +33-0380396098
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

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 diphenylphosphine (2-PyPPh₂) crucially controls the activity and selectivity of alkyne methoxycarbonylation catalysts.^[11] Other α -aminophosphine ligands are rare: compound Ph₂PCH₂N(CH₃)₂, having a tertiary amine function, is stable in the solid state and in solution,^[5] while Et₂PCH₂NH^tBu and Ph₂PCH(Ph)NHPPh 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 -aminophosphine ligands with a secondary amine function (Scheme 1).^[7] It was found, for instance, a $K = 50$ for R¹ = R² = Ph and that electron-withdrawing substituents R¹ and R² 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.

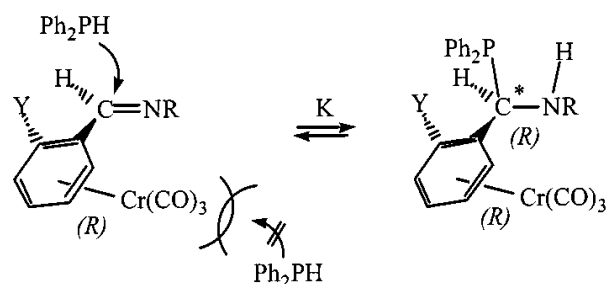


Scheme 1

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 $\text{Cr}(\text{CO})_3$ fragment makes one imine diastereoface inaccessible to the phosphine 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 $\text{Cr}(\text{CO})_3$ complexed imines^[12-15] in particular, have been previously exploited in stereoselective synthesis.



Scheme 2

The reaction between racemate complexes $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{Y})(\text{CH}=\text{NR})]$ (with Y, R = CH_3 , CH_3 or $\text{CH}_2\text{COOCH}_3$; CH_3O , CH_3 or $p\text{-CH}_3\text{OC}_6\text{H}_4$; Cl , C_6H_5) and Ph_2PH in CDCl_3 leads to the formation of equilibrium quantities of the desired aminophosphine ligand (**2-6**) as a single diastereoisomer, within the detection limits of ^{31}P NMR spectroscopy (Table 1). For the sake of simplicity, Scheme 2 shows this transformation for only one of the two enantiomers. The relative concentrations at equilibrium are determined by integration of the ^1H 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** ($\text{R}^1 = \text{R}^2 = \text{Ph}$, Scheme 1).^[7] Given the previously established electronic control

on the equilibrium of Scheme 1, the presence of the $\text{Cr}(\text{CO})_3$ 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 $\text{Cr}(\text{CO})_3$ group and the Cl substituent is sufficient for a quantitative P-C bond formation. For compound **5**, the electron withdrawing effect of the $\text{Cr}(\text{CO})_3$ moiety is not sufficient to compensate the overall donor properties of the two methoxy substituents. The individual effect of the $\text{Cr}(\text{CO})_3$ moiety has been evaluated by comparing the formation of **6** with corresponding reaction of the $\text{Cr}(\text{CO})_3$ -free imine, forming product **7**. It can be observed that the constant K increases by at least a factor of 3 upon $\text{Cr}(\text{CO})_3$ coordination.

Table 1. Results of the reaction between $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{Y})(\text{CH}=\text{NR})]$ 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 ₃ O	CH ₃	> 98	54	5.8	10.9
4	CH ₃	CH ₂ COOCH ₃	> 98	62	10.7	11.5
5	CH ₃ O	<i>p</i> -CH ₃ OC ₆ H ₄	> 98	73	17	12.4
6	Cl	C ₆ H ₅	> 98	>99	>1000	13.7
7	Cl	C ₆ H ₅ ^c	-	92	330	4.7

^aSolvent = CDCl₃; [imine]₀ = [Ph₂PH]₀ = 0.57 M. ^bCalculated by integration of the ¹H and ³¹P resonances. ^cWithout the $\text{Cr}(\text{CO})_3$ 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 CH₃ to *p*-CH₃OC₆H₄ and CH₂COOCH₃,

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 CH₃ to CH₃O, 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 ³¹P NMR chemical shifts of the aminophosphine products **2-6** qualitatively correlate with their stability. The equilibrium constant increase as the ³¹P 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 ³¹P 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 aminophosphine **6** was isolated by crystallization from CHCl₃ 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 CHCl₃ 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 Ph₂P-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.

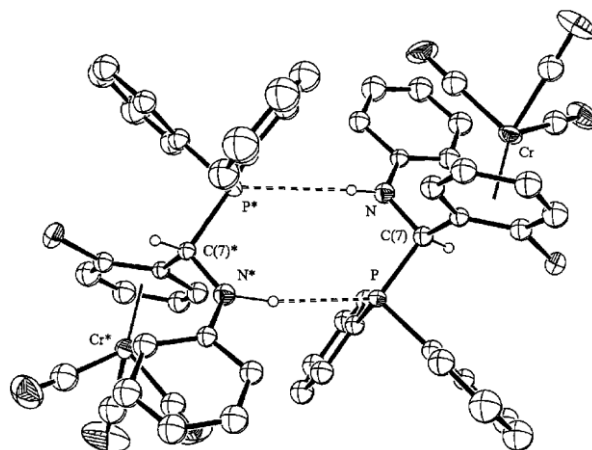


Figure 1. ORTEP view of compound **6** with ellipsoids shown at the 30% probability level. All hydrogen atoms are omitted for clarity, except those on the N, N*, C(7) and C(7)*, highlighting the hydrogen-bonding interactions and the absolute configuration at C(7) and C(7)*.

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 $\alpha\text{-P-C-N}$ ligands. Further information on the electronic control of the reversible P-C bond formation has been obtained by the use of various $\text{Cr}(\text{CO})_3$ -complexes aromatic imine substrates. In addition to promoting the asymmetric induction, the $\text{Cr}(\text{CO})_3$ moiety exerts an electronic contribution favouring the formation of the P-C bond. The coordination chemistry of the α -aminophosphine 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 an atmosphere of purified argon and in the dark using standard Schlenk techniques. All solvents were dried and deoxygenated prior to use. ^1H and $^{31}\text{P}\{^1\text{H}\}$ -NMR measurements were carried out on 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). The IR spectra were recorded on a Bruker IFS 66V spectrophotometer with KBr optics. The elemental analysis was carried out by the analytical service of the Laboratoire de Synthèse et d'Electrosynthèse Organométalliques with a Fisons Instruments EA1108 analyzer. The starting complexes $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{Y})(\text{CH}=\text{NR})]$ used in this study were obtained as previously described in the literature.^[12-14,17]

Aminophosphines 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 benzaldimine chromium tricarbonyl complex $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{OCH}_3)(\text{CH}=\text{N-}p\text{-C}_6\text{H}_4\text{OCH}_3)]$ (0.108 g, 0.287 mmol) in CDCl_3 (0.5 ml). The resulting solution was stirred at room temperature for 3 hrs. ^{31}P NMR (81.03 MHz, CDCl_3): $\delta = 12.5$ (s) and -36.6 (s) ppm 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 H^1 NMR signals, whose intensity did not change over the subsequent 48 hours.

Aminophosphine 6: Ph_2PH (50 μl , 0.287 mmol) was added to a solution of the complex $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{Cl})(\text{CH}=\text{NPh})]$ (0.181 g, 0.474 mmol) in CHCl_3 (10 ml). The resulting solution was stirred at room temperature for 3 hrs, filtered and concentrated to half volume. Addition of pentane afforded the complex **6** as yellow crystals (0.188 g, 70%). ^1H NMR (δ , 200 MHz, CDCl_3): 7.41-4.53 (m, 20H, aromatics + NH), 4.12 (dd, 1H, PCH, $^2J_{\text{PH}} = 3.4$ Hz, $^3J_{\text{HH}} = 7.3$ Hz). ^{31}P NMR (δ , 81.03 MHz, CDCl_3): 13.7 ppm (s). ^{13}C NMR (δ , 50.32 MHz, CDCl_3): 231.61 (s, CO), 145.37-84.68 (m, aromatics), 51.39 (d, PCH, $^1J_{\text{PC}} = 18.5$ Hz). IR (ν_{CO} , CHCl_3): 1980 (b), 1917 (vb) cm^{-1} . Elemental analysis: Calcd for $\text{C}_{56}\text{H}_{42}\text{Cl}_2\text{Cr}_2\text{N}_2\text{O}_6\text{P}_2 \cdot 1/2\text{CHCl}_3$: C 59.75, H 3.75, N 2.48; Found: C 59.90, H 3.75, N 2.59.

Crystal Structure Analysis of 6: $(\text{C}_{28}\text{H}_{21}\text{ClNPO}_3\text{Cr})_2 \cdot \text{CHCl}_3$, Mw = 1195.12. Enraf-Nonius CADA diffractometer, Mo-K α radiation ($\lambda = 0.71073$ Å), T = 293 K; monoclinic, P21/c, $a = 11.267(2)$, $b = 28.202(4)$, $c = 18.014(3)$ Å, $\beta = 104.808(14)^\circ$, V = 5533.9(16) Å³, Z = 4, $D_x = 1.434$ g cm^{-3} , $\mu = 0.744$ 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 : int. code + 44(1223)336-033 ; E-mail : deposit@ccdc.cam.ac.uk].

Acknowledgments

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

References

- [1] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, 455, 247-253.
- [1] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, 455, 247-253.
- [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. Solladie´-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, 12775212788.
- [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