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Chiral α -P,N ligands from a diastereoselective Ph_2PH addition to $(\eta^6 \text{ benzaldimine})\text{tricarbonylchromium}$ complexes

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

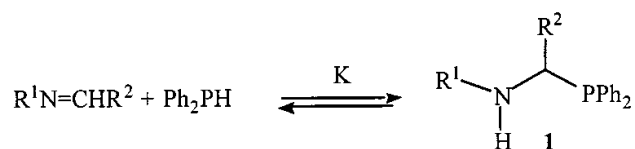
Chiral α -aminophosphine (α -P-C-N) ligands have been prepared by reversible addition of Ph_2PH to tricarbonylchromium benzaldimine complexes $(\text{CO})_3\text{Cr}[\eta^6\text{-}o\text{-C}_6\text{H}_4(\text{Y})(\text{CH}=\text{NR})]$ (with Y, R = CH_3 , CH_3 or $\text{CH}_2\text{COOCH}_3$; CH_3O , CH_3 or $p\text{-CH}_3\text{OC}_6\text{H}_4$; Cl, C_6H_5), with complete diastereoselectivity. These complexes are stabilized in solution by electron-withdrawing group(s) on the imine.

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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.^[1] 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)NPh 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 $R^1 = R^2 = \text{Ph}$ 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.

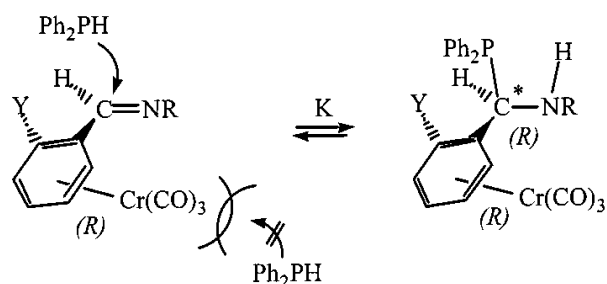


Scheme 1

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 $\text{R} = \text{Ph}$, 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.

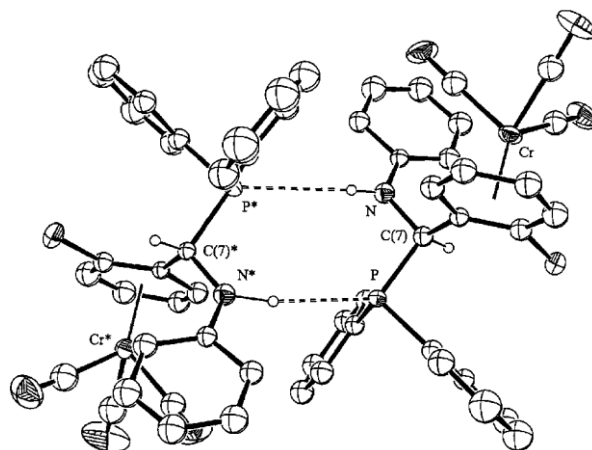


Figure 1. ORTEP view of compound **6** with ellipsoids shown at the 30% probability level. All hydrogen atoms are omitted for clarity, except those on the N, N*, C(7) and C(7)*, highlighting the hydrogen-bonding interactions and the absolute configuration at C(7) and C(7)*.

In conclusion, we have described the use of an arene-coordinated tricarbonylchromium template for the diastereoselective addition of Ph₂PH 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 -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): δ = 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, P2 $_1$ /c, $a = 11.267(2)$, $b = 28.202(4)$, $c = 18.014(3)$ Å, $\beta = 104.808(14)^\circ$, V = 5533.9(16) Å 3 , 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].

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