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Rh(I) Coordination Chemistry of Chiral α-Aminophosphine(η^6-arene)chromium Tricarbonyl Ligands

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The diastereoselective addition of Ph_2PH to the chiral ortho-substituted η^6-benzaldimine complexes (η^6-*o*-X—C_6H_4-CH═NAr)$Cr(CO)_3$ (**1**, X = MeO, Ar = *p*-C_6H_4OMe; **2**, X = Cl, Ar = Ph) leads to the formation of the corresponding chiral aminophosphines (α-P,N) Ph_2P–$CH(Ar^1)$–$NHAr^2$ (**3**, Ar^1 = *o*-$C_6H_4(OCH_3)[Cr(CO)_3]$, Ar^2 = *p*-$C_6H_4OCH_3$; **4**, Ar^1 = *o*-$C_6H_4Cl[Cr(CO)_3]$, Ar^2 = Ph) in equilibrium with the starting materials. The uncomplexed benzaldimine (*o*-ClC_6H_4CH═NPh), **2′**, analogously produces an equilibrium amount of the corresponding aminophosphine Ph_2P–$CH(Ar^1)$–$NHAr^2$ (**4′**, Ar^1 = *o*-C_6H_4Cl, Ar^2 = Ph). Depending on the equilibrium constant, the subsequent addition of $^1/_2$ equiv of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) leads to either Ph_2PH oxidative addition in the case of **3** or to the corresponding [RhCl(COD)(α-P,N)] complexes [RhCl(COD)(Ph_2P–CH{*o*-$C_6H_4Cl[Cr(CO)_3]$}–NHPh)] (**5**) and [RhCl(COD)(Ph_2P–CH(*o*-C_6H_4Cl)–NHPh)] (**5′**) in the cases of the aminophosphines **4** and **4′**. The addition of the latter ligands, as racemic mixtures, to $^1/_4$ equiv of $[Rh(CO)_2Cl]_2$ leads to the [RhCl(CO)(α-P,N)$_2$] complexes [RhCO(Ph_2P–CH{*o*-$C_6H_4Cl[Cr(CO)_3]$}–NHPh)$_2$Cl] (**7**) or [RhCO(Ph_2P–CH(*o*-C_6H_4Cl)–NHPh)$_2$Cl] (**7′**) as mixtures of (R_C,S_C)/(S_C,R_C) and (R_C,R_C)/(S_C,S_C) diastereomers. The rhodium complexes **5** and **7′** have been fully characterized by IR and ^{31}P NMR spectroscopies and X-ray crystallography. These compounds exhibit intramolecular Rh–Cl··· H–N interactions in the solid state and in solution. The stability of the new rhodium complexes has been studied under different CO pressures. Under 1 atm of CO, **5** is converted to an unstable complex [$RhCl(CO)_2$(α-P,N)], **6**, which undergoes ligand redistribution leading to **7** plus an unidentified complex. This reaction is inhibited under higher CO or syngas pressure, as confirmed by the observation of the same catalytic activity in hydroformylation when styrene was added to a catalytic mixture that was either freshly prepared or left standing for 20 h under high CO pressure.

Introduction

Since the discovery that bidentate bifunctional P,N ligands increase considerably the activity and selectivity of Pd, Ni, Ru, and Ir catalysts relative to PR_3, their preparation has been the subject of extensive investigations.[1−7] It has been proposed that the nitrogen function increases the electron density on the metal and subsequently promotes the oxidative addition reactions.[8] When both heteroatom donors are separated by only one carbon atom (hereafter termed α-P,N ligand), the nitrogen function has been shown to coordinate to a second metal center[9,10] or to remain uncoordinated in a

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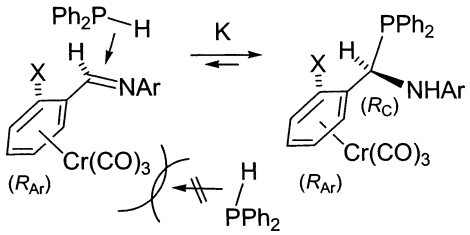
Scheme 1



X	Ar	imine	α-P,N	K
MeO	*p*-C_6H_4OMe	**1**	**3**	17
Cl	Ph	**2**	**4**	>1000
Cl[a]	Ph	**2′**	**4′**	330

[a] Without $Cr(CO)_3$.

mononuclear complex.[11] In the latter case, monodentate α-P,N ligands display a free amine group which may assist the proton-transfer steps in catalytic cycles, as was shown in Ni and Pd catalysis.[1,2]

We have recently described a synthesis of α-P,N ligands, where the N donor is a secondary amine function, which is based on the reversible addition reaction of Ph_2PH to a wide range of benzaldimines. The newly formed P−C bond was found to be stabilized by electron-withdrawing substituents on the N or C atom or by P coordination.[11] Moreover, the use of chiral (η^6-benzaldimine)tricarbonyl chromium complexes has allowed access to chiral versions of this ligand architecture via a diastereoselective reaction;[12] see Scheme 1.

By analogy with our reported stabilization of $Ph_2PCH(Ph)NHPh$ by coordination to Cu(I),[11] we explored whether the stabilizing coordination effect could be generalized to a metal center such as Rh(I) for potential applications to homogeneous catalysis work. We report in this paper the preparation of rhodium complexes, including some unusual features of the solid-state and solution properties and an initial testing of their catalytic behavior in styrene hydroformylation.

Experimental Section

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 by standard methods. NMR measurements (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) were carried out with a Bruker AC200 spectrometer. $^1H-^1H$ and $^1H-^{13}C$ correlation spectra were recorded on a Bruker 500 DRX Advance instrument. The peak positions are reported with positive shifts in parts per million downfield of tetramethylsilane, as calculated from the residual solvent peaks (^1H and ^{13}C), or downfield of external 85% H_3PO_4 (^{31}P). The coordinated 1,5-cyclooctadiene (COD) C and H nuclei are labeled from 1 to 8, C_1 and C_2 being trans to P. IR spectra were recorded with a Bruker IFS 66V spectrophotometer using KBr optics. Elemental analyses were carried out by the analytical service of the LSEO with a Fisons Instruments EA1108 analyzer. The commercial compounds $[RhCl(COD)]_2$ and $[Rh(CO)_2Cl]_2$ (Strem) were used as received, and diphenylphosphine (Aldrich) was distilled prior to use. The α-aminophosphine ligands $Ph_2P-CH(Ar^1)-NHAr^2$ (**3**, $Ar^1 = o\text{-}C_6H_4(OCH_3)[Cr(CO)_3]$, $Ar^2 = p\text{-}C_6H_4OCH_3$; **4**, $Ar^1 = o\text{-}C_6H_4Cl[Cr(CO)_3]$, $Ar^2 = Ph$; **4′**, $Ar^1 = o\text{-}C_6H_4Cl$, $Ar^2 = Ph$) were isolated or generated as previously described.[12]

Synthesis of [RhCl(COD)($Ph_2P-CH\{o\text{-}C_6H_4Cl[Cr(CO)_3]\}-NHPh$)], 5. To a solution of **2** (57 mg, 0.162 mmol) in $CDCl_3$ (2 mL) was added Ph_2PH (30 μL, 0.162 mmol). After 3 h, the complete formation of the α-P,N ligand **4** was achieved. The solution was then transferred into $[RhCl(COD)]_2$ (40 mg, 0.081 mmol) and stirred for 3 h. The solvent was then removed, and the residue was dissolved in THF. The addition of pentane afforded the air-sensitive pale-yellow crystals **5**. Yield: 92 mg, 72%. ^1H NMR (C_6D_6): 8.00 (1H, s, br, NH), 7.94−6.86 (15H, m, aromatics), 7.28 (1H, d, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 6.00 (1H, dd, PCH, $^3J(H,H) = 10$ Hz, $^2J(P,H) = 13$ Hz), 5.96 (1H, s, br, H_1), 5.95 (1H, s, br, H_2), 4.57 (1H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 4.41 (1H, d, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 4.13 (1H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 3.08 (1H, s, br, H_5), 2.87 (1H, s, br, H_6), 2.22−1.45 (8 H, m, $H_{3,4,7,8}$). $^{13}C\{^1H\}$ NMR (C_6D_6): 231.6 (3C, s, $Cr(CO)_3$), 146.7−114.3 (m, C−aromatics), 116.9 (1C, s, C_6H_4Cl), 109.0 (1C, s, C_6H_4Cl), 106.5 (2C, m, C_1, C_2), 97.0 (1C, s, C_6H_4Cl), 94.1 (1C, s, C_6H_4Cl), 86.3 (1C, s, C_6H_4Cl), 85.3 (1C, s, C_6H_4Cl), 73.1 (1C, d, C_5, $^1J(Rh,C_{olefin}) = 12$ Hz), 71.9 (1C, d, C_6, $^1J(Rh,C_{olefin}) = 13$ Hz), 58.2 (1C, d, PCH, $^1J(P,C) = 20$ Hz), 33.1 (1C, s, C_3), 33.0 (1C, s, C_8), 29.4 (1C, s, C_4), 28.9 (1C, s, C_7). $^{31}P\{^1H\}$ NMR (C_6D_6): 44.1 (d, $^1J(Rh,P) = 155$ Hz). IR (CH_2Cl_2): 3285 (b, ν_{NH}), 1982 (vs, ν_{CO}), 1911 (vs, vb, ν_{CO}) cm^{-1}. IR (Nujol): 3288 (w, b, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{36}H_{33}Cl_2CrNO_3PRh$ (784.4): C, 55.12; H, 4.24; N, 1.70. Found: C, 55.15; H, 4.25; N, 1.70.

Synthesis of [RhCl(COD)($Ph_2P-CH(o\text{-}C_6H_4Cl)-NHPh$)], 5′. By using operating procedures identical with those described above for compound **5**, compound **2′** (35 mg, 0.162 mmol) and Ph_2PH (30 μL, 0.162 mmol) were initially mixed in $CDCl_3$. After 3 h, an equilibrium with the α-P,N ligand **4′** was achieved. The complex **5′** was obtained as single yellow crystals after addition to $[RhCl(COD)]_2$ (40 mg, 0.065 mmol) and workup as described in the previous section. Yield: 63 mg, 60%. ^1H NMR (C_6D_6): 9.26−6.50 (19H, aromatics + NH), 6.35 (1H, dd, PCH, $^2J(P,H) = 14.6$ Hz, $^3J(H,H) = 9$ Hz), 5.83 (2H, s, br, $H_1 + H_2$), 3.08 (1H, s, br, H_5), 2.90 (1H, s, br, H_6), 2.20−1.44 (8H, m, br, $H_{3,4,7,8}$). $^{13}C\{^1H\}$ NMR (C_6D_6): 147.4−113.4 (m, C−aromatics), 105.6 (s, br, $C_{1,2}$), 71.9 (d, 1C, C_5, $^1J(Rh,C_{olefin}) = 14$ Hz), 71.0 (d, 1C, C_6, $^1J(Rh,C_{olefin}) = 14$ Hz), 56.7 (d, 1C, PCH, $^1J(Rh,P) = 28$ Hz), 33.35 (s, 1C, C_3), 32.4 (s, 1C, C_8), 29.3 (s, 1C, C_4), 28.4 (s, 1C, C_7). $^{31}P\{^1H\}$ NMR (C_6D_6): 34.7 (d, $^1J(Rh,P) = 154$ Hz). Anal. Calcd for $C_{33}H_{33}Cl_2CrNPRh$ (648.4): C, 61.13; H, 5.13; N, 2.16. Found: C, 61.02; H, 5.18; N, 2.66.

Synthesis of [RhCO($Ph_2P-CH\{o\text{-}C_6H_4Cl[Cr(CO)_3]\}-NHPh)_2Cl$], 7. A solution of **4** (87 mg, 0.16 mmol) in toluene (5 mL) was added to a solution of $[RhCl(COD)]_2$ (20 mg, 0.04 mmol) in toluene (5 mL). After stirring for 1 h, a CO stream was bubbled through the solution for 15 min, causing the formation of a yellow suspension. After stirring overnight, the mixture was concentrated to half its original volume and filtered. The yellow powder was washed two times with pentane (20 mL) and dried under vacuum. Yield: 80 mg, 80%. ^1H NMR ($CDCl_3$): 8.09−6.67 (30H, m, aromatics + 4H from C_6H_4Cl), 7.81 (2H, s, br, NH, exchange with D_2O), 5.82 (2H, m, PCH), 5.55 and 5.50 (2H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 5.00 and 4.95 (2H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz). ^1H NMR

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$[(CD_3)_2CO]$: 8.14−6.51 (32H, m, aromatics), 5.92 and 5.88 (2H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 5.80 and 5.77 (2H, t, PCH, $^3J(H,H) = {}^2J(P,H) = 5$ Hz), 5.35 and 5.31 (2H, t, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 5.28 and 5.22 (2H, d, C_6H_4Cl, $^3J(H,H) = 6$ Hz), 2.75 (2H, s, br, NH, exchange with D_2O). $^{13}C\{^1H\}$ NMR $[(CD_3)_2CO]$: 232.8 (s, $Cr(CO)_3$), 206.9 (Rh−CO, masked by acetone), 147.1−114.0 (m, C−aromatics), 108.1 and 108.0 (2C, s, C_6H_4Cl), 98.9 and 98.1 (2C, s, C_6H_4Cl), 89.3 and 89.1 (2C, s, C_6H_4Cl), 86.7 and 86.2 (2C, s, C_6H_4Cl), 57.8 (t, 2C, PCN, $^1J(P,C) = {}^2J(Rh,C) = 14$ Hz). $^{31}P\{^1H\}$ NMR $[(CD_3)_2CO]$: 36.98 and 34.54 (d, $^1J(Rh,P) = 129$ Hz) in 1:2 ratio. IR (THF): 3320 (br, ν_{NH}), 1994 (s, ν_{CO}, Rh−CO), 1980 (vs, ν_{CO}, $Cr(CO)_3$), 1914 (vs, br, ν_{CO}, $Cr(CO)_3$) cm^{-1}. Anal. Calcd for $C_{57}H_{42}Cl_3Cr_2N_2O_7P_2Rh$ (1242.2): C, 55.12; H, 3.41; N, 2.26. Found: C, 55.37; H, 3.48; N, 2.44.

Synthesis of [RhCO(Ph$_2$P−CH(*o*-C$_6$H$_4$Cl)−NHPh)$_2$Cl], 7′. To a solution of **2′** (59 mg, 0.27 mmol) in $CHCl_3$ (5 mL) was added Ph_2PH (49 μL, 0.27 mmol). After 3 h, an equilibrium with the α-P,N ligand **4′** was achieved. The solvent was removed and a solution of $[RhCl(COD)]_2$ (30 mg, 0.06 mmol) in THF (5 mL) was added. After stirring for $^1/_2$ h, CO was bubbled through the solution for 15 min. The resulting yellow solution was further stirred for 30 min and concentrated to 2 mL. The addition of pentane (10 mL) afforded the product as a yellow powder, which was isolated by filtration, washed with pentane (2 × 10 mL), and dried under vacuum (98 mg, 84%). A slow diffusion of pentane onto a THF solution of the product afforded suitable yellow crystals for the X-ray analysis. ^1H NMR (C_6D_6): 9.15−6.55 (38H, m, aromatics), 8.05 (2H, s, br, NH, exchange with D_2O), 6.48 (2H, m, PCH). ^1H NMR $[(CD_3)_2CO]$: 8.81−6.49 (38H, m, aromatics), 6.28 (2H, m, PCH), 2.88 (2H, s, br, NH, exchange with D_2O). $^{13}C\{^1H\}$ NMR (C_6D_6): 187.6 (2C, d, CO, $^1J(Rh,C) = 67$ Hz), 147.0−113.3 (m, C−aromatics), 57.0 and 56.7 (2C, d, PCH, $^1J(C,P) = 14$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): 31.68 and 29.87 (d, $^1J(Rh,P) = 128$ Hz). IR (THF): 3314 (w, b, ν_{NH}), 1990 (ws, ν_{CO}) cm^{-1}. IR (Nujol): 3296 (w, b, ν_{NH}) cm^{-1}. Anal. Calcd for $C_{51}H_{43}Cl_3N_2OP_2Rh$ (970.1): C, 63.14; H, 4.36; N, 2.89. Found: C, 62.99; H, 4.50; N, 3.40.

Stability of Compound 6 under CO Pressure. A mixture of **4** (36 mg, 0.066 mmol) and $[RhCl(COD)]_2$ (16.5 mg, 0.033 mmol) was dissolved in 10 mL of $CHCl_3$, resulting in the formation of complex **5** as described above. The resulting yellow solution was introduced into the autoclave and pressurized with CO (300 psi) at 55 °C. After stirring for 12 h, the resulting red solution was analyzed by IR spectroscopy. IR ($CHCl_3$): 2097 and 2015 (s, ν_{CO}, Rh−CO), 1985 and 1916 (s, br, ν_{CO}, $Cr(CO)_3$) cm^{-1}. No stretching vibration corresponding to compound $Cr(CO)_6$ was observed.

Crystal Structure Analysis of Complexes 5 and 7′. Intensity data were collected on a Nonius Kappa charge-coupled device at 110 K for **5** and **7′**. The structure was solved by the heavy atom method and refined by full-matrix least-squares methods[13] with the aid of the WINGX program.[14] Non-hydrogen atoms were anisotropically refined. For **5**, the hydrogen atoms were located in the final difference Fourier maps and refined freely. For **7′**, with the exception of the NH hydrogen atom, which was located in the final difference Fourier maps and refined freely, all hydrogen atoms were included in a rigid model. Compound **7′** crystallizes with one pentane molecule, which is located on a fourfold inversion axis close to the inversion center (0, $^1/_4$, $^5/_8$), leading to disorder over two positions. However, the rather large values of the isotropic temperature factors may indicate a further disorder that was not resolved. Crystallographic data and selected bond lengths and angles for the compounds **5** and **7′** are reported respectively in Tables 1 and 2.

Table 1. Crystal Data and Structure Refinement for **5** and **7′**

	5	**7′**
chemical formula	$C_{36}H_{33}Cl_2NO_3PCrRh$	$C_{51}H_{42}N_2OP_2Cl_3Rh\cdot {}^1/_4C_5H_{12}$
fw	784.41	988.10
T, K	110(2)	110(2)
space group	$P\bar{1}$	$I4_1/a$
a, Å	11.9308(3)	42.6851(4)
b, Å	12.4015(3)	42.6851(4)
c, Å	12.5645(3)	10.2428(1)
α, deg	68.8459(15)	90
β, deg	89.439(2)	90
γ, deg	76.449(2)	90
V, Å^3	1679.76(7)	18 662.6(3)
Z	2	16
D_{calc}, g/cm^3	1.551	1.407
λ, Å	0.710 73	0.710 73
μ, mm^{-1}	1.058	0.647
$R(F_o)^a$ (all data)	0.047	0.076
$R_w(F_o^2)^b$ (all data)	0.080	0.090

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_c|$. ^{b} $R_w(F_o^2) = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2 + (0.038P)^2 + 1.37P]$ for **5** and $w = 1/[\sigma^2(F_o^2 + (0.033P)^2 + 27.39P]$ for **7′** and $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

Table 2. Selected Lengths (Å) and Angles (deg) for Compounds **5** and **7′**

5		**7′**	
Rh−Cl(2)	2.3978(6)	Rh−Cl(1)	2.3871(7)
Rh−P	2.3134(6)	Rh−P(1)	2.3358(7)
Rh−C(29)	2.230(3)	Rh−P(2)	2.3332(7)
Rh−C(30)	2.240(3)	Rh−C(1)	1.818(3)
Rh−C(33)	2.110(3)	C(1)−O	1.145(3)
Rh−C(34)	2.133(3)	N(1)−H	0.78(3)
Rh−Ct(1)^a	2.004(4)	N(1)−H···Cl(1)	2.40(3)
Rh−Ct(2)^a	2.128(3)	N(1)···Cl(1)	3.135(3)
P−C(10)	1.899(2)	N(2)−H	0.89(3)
C(10)−N	1.440(3)	N(2)−H···Cl(1)	2.24(4)
N−H	0.82(3)	N(2)···Cl(1)	3.116(3)
N−H···Cl(2)	2.42(3)		
N···Cl(2)	3.199(2)		
P−Rh−Cl(2)	93.32(2)	P(1)−Rh−Cl(1)	90.85(2)
Ct(1)−Rh−Ct(2)	86.2(2)	P(1)−Rh−C(1)	89.79(8)
Ct(2)−Rh−Cl(2)	87.3(1)	P(2)−Rh−Cl(1)	88.82(2)
Ct(1)−Rh−P	93.0(2)	P(2)−Rh−C(1)	90.48(8)
N−H···Cl(2)	158(3)	N(1)−H···Cl(1)	157(3)
		N(2)−H···Cl(1)	167(3)

^{a} Ct(1) is the centroid of C(29) and C(30), and Ct(2) is the centroid of C(33) and C(34).

Catalytic Runs. The hydroformylation reactions were carried out in a 300-mL stainless-steel Parr autoclave equipped with a magnetic drive, an internal glass vessel, and an immersion tube connected to a valve for solution withdrawals under pressure. The temperature was controlled by a rigid heating mantle and by a single-loop coil. The autoclave was purged three times under vacuum/argon before introducing the catalytic solution. The 1:1 CO/H_2 mixture was prepared by mixing the pure gases in a 500-mL stainless-steel cylinder before introduction into the autoclave at the desired pressure. Catalytic conditions were as follows: styrene/Rh = 1000, 12 mg of $[RhCl(COD)]_2$ in 35 mL of chloroform, *P*(syngas) = 600 psi, *T* = 55 °C. The zero time for the kinetic runs was considered to be the time at which the desired pressure was reached inside the autoclave. To maintain as constant as possible temperature and pressure conditions during each kinetic run, only a few milliliters of the catalytic solution mixture were

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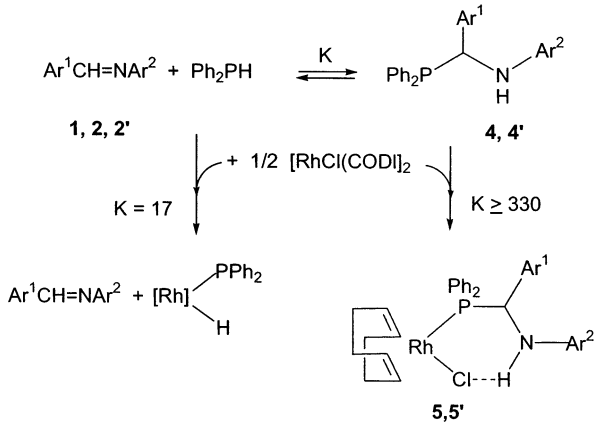
Scheme 2



carefully withdrawn each time from the autoclave. The $CHCl_3$ solvent was then rotary-evaporated at room temperature and the yellow-orange residue was analyzed by ^{1}H NMR spectroscopy to quantify the conversion by integration.

Results and Discussion

(a) Synthesis and Characterization. The same synthetic procedure previously used for the formation of Cu(I) complexes has now been applied to the formation of Rh(I) complexes. It consists of the addition of the stoichiometric amount of $[RhCl(COD)]_2$ to a mixture of Ph_2PH and the imines **1**, **2**, or **2′**, after it has reached thermodynamic equilibrium with the corresponding α-P,N product. When the $Cr(CO)_3$−benzaldimine **1** or **2** was used, this reaction led selectively to a single diastereomer as a racemic mixture. As shown in our previous study,[12] the resulting products **3** and **4** have the configuration $(R_{Ar},R_C)/(S_{Ar},S_C)$, where the first descriptor refers to the arene planar chirality and the second one refers to the chirality of the carbon center (see Scheme 1). The equilibrium constants shown in Scheme 1 had been determined during our previous study.[12] When the benzaldimine **1** was used, the ^{1}H NMR spectrum showed the presence of three different hydride complexes that are characterized by ^{1}H NMR resonances at −14.00 (hept), −17.20 (dt), and −18.70 (dt) ppm with coupling constants of 11.6, 35, and 26, and 11.6 and 24 Hz, respectively. However, the ^{31}P NMR spectrum exhibits only one broad signal at 9.0 ppm for all complexes. The mixture presumably results from Ph_2P−H oxidative addition to Rh(I), while the imine remained unreacted. These hydride products were not further characterized. Nevertheless, the phosphorus chemical shift excludes the formation of bridging phosphido moieties in dinuclear complexes. The use of **2** or **2′**, on the other hand, led to the desired mononuclear rhodium complexes **5** or **5′** without the observation of any product resulting from P−H oxidative addition (see Scheme 2).

This observation suggests that the outcome of the reaction is controlled by the relative concentration of free Ph_2PH and α-P,N in the reaction mixture. Because both reactions with the Rh(I) center are irreversible, the P−C bond-formation equilibrium is displaced completely either way, depending on which reactivity pathway prevails. Given the quantitative formation of **4**, the clean formation of **5** is not surprising. The quantitative formation of **5′**, however, shows that coordination to Rh(I) brings the same stabilizing effect previously demonstrated for Cu(I) toward the rupture of the ligand P−C bond. Hence, the presence of the $Cr(CO)_3$ fragment is not necessary to ensure the stability of the Rh(I) complex. However, its presence allows the introduction of chirality in complex **5**.

Both complexes **5** and **5′** are characterized by a doublet in the ^{31}P NMR spectra at 44.1 and 34.7 ppm, respectively, with a ^1J(Rh,P) coupling constant of 155 Hz in each case. An X-ray diffraction analysis of **5** (vide infra) confirms the monodentate (P) coordination of the ligand. Addition of 1 equiv (additional) of **4** or **4′** to **5** or **5′** does not induce displacement of the coordinated COD moiety (see Scheme 3, path a). However, when CO gas is introduced into this reaction mixture, the new complexes **7** or **7′** are formed (see Scheme 3, path b) via the formation of intermediates **6** or **6′** (see below for their identification). The same complexes can also be obtained directly by treatment of 4 equiv of the appropriate α-P,N ligand with $[Rh(CO)_2Cl]_2$ (path e).

The solutions of compounds **7** and **7′** are characterized by two doublets in the ^{31}P NMR spectra with ^1J(Rh,P) of 128 Hz and only one carbonyl vibration in the IR spectra around 1990 cm^{-1} in a THF solution. These spectroscopic data are consistent with a *trans*-$[RhCl(CO)L_2]$ square-planar geometry,[15−17] which is confirmed by an X-ray diffraction study for **7′** (see below). The two ^{31}P NMR resonances are attributed to the different pairs of diastereomers $(R_C,R_C)/(S_C,S_C)$ and $(R_C,S_C)/(S_C,R_C)$, whose formation is due to the use of the racemic ligand. The resonances are observed at 37.0 and 34.5 ppm (1:2 ratio) for **7** and 31.7 and 29.9 ppm (1:1 ratio) for **7′**. Several resonances in the ^{1}H NMR spectrum are also distinct for the two diastereomeric pairs, whereas others overlap (see the Experimental Section). The complete resonance assignment was made possible by the spectroscopic analysis of $(R_{Ar},R_C)/(R_{Ar},R_C)$-**7**, obtained from optically pure (R_{Ar},R_C)-**4**, showing that the higher field resonance for **7** (major product) is due to the $(R_{Ar},R_C)/(S_{Ar},S_C)$ diastereomer.

The ν_{CO} in the mononuclear complexes allows an estimation of the σ-donor/π-acceptor character of the phosphine ligands and an evaluation of the electron density at the metal.[18,19] The comparison of the CO stretching frequencies of compounds **7** (1994 cm^{-1}) and **7′** (1990 cm^{-1}) with those of different *trans*-$[RhCl(CO)L_2]$ complexes indicates that the σ-donor/π-acceptor properties of ligands **4** and **4′** are comparable to those of diphenylpyrrolylphosphine and P(*p*-$CF_3C_6H_4$).[20,21] The shift of only 4 cm^{-1} to a higher frequency

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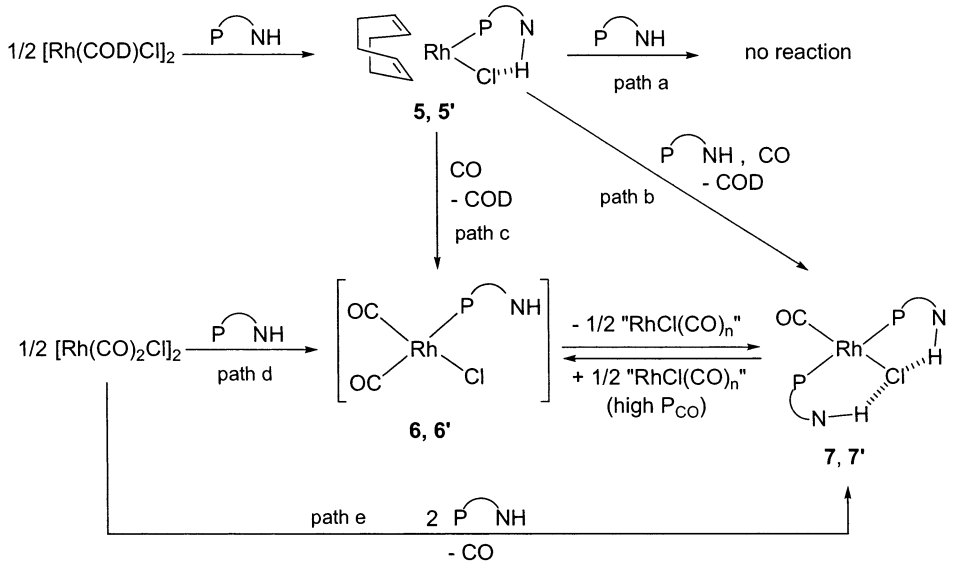
Scheme 3



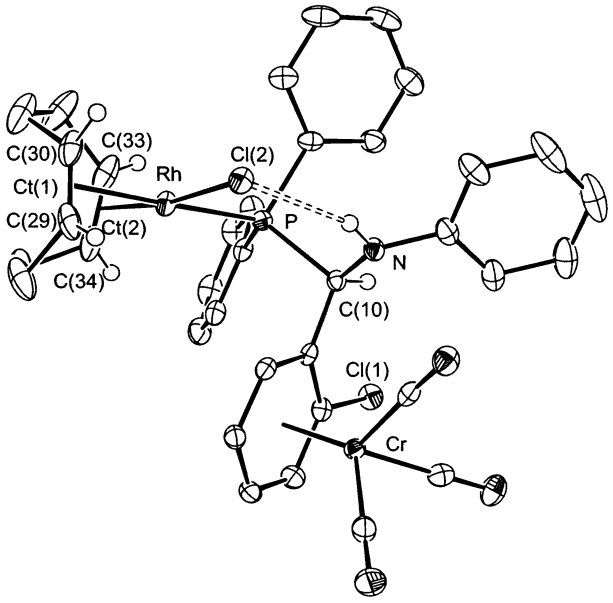


Figure 1. ORTEP view of complex **5**. Thermal ellipsoids are drawn at the 50% probability level. For clarity, only the relevant hydrogen atoms are shown.

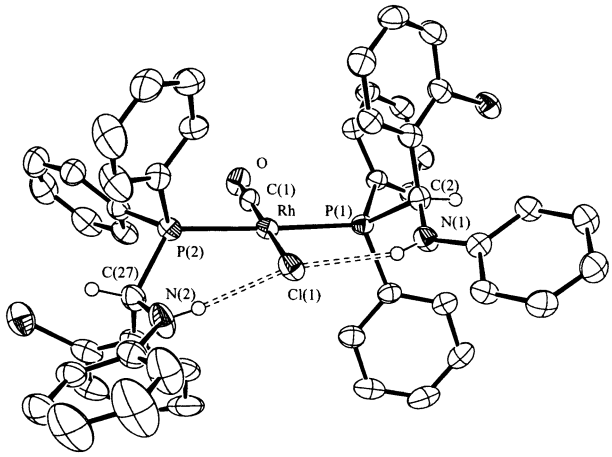


Figure 2. ORTEP view of complex **7′**. Thermal ellipsoids are drawn at the 50% probability level. For clarity, the pentane solvate molecule is omitted, and only the relevant hydrogen atoms are shown.

on going from **7′** to **7** indicates that ligand **4** is only slightly affected by the electron-withdrawing $Cr(CO)_3$ group.

(b) Unusual Features of 5 and 7′ Complexes in the Solid State and in Solution. The X-ray diffraction analyses of **5** and **7′** (see Figures 1 and 2) show that the aminophosphine ligands are only P-coordinated in the square-planar rhodium complexes. For complex **7′**, only one racemic diastereomer (R_C,R_C)/(S_C,S_C) is observed in the unit cell, whereas both diastereomers were present in the solution before crystallization. The essential geometrical features and metric parameters are quite typical for the $RhCl(CO)_2L$ and RhCl(COD)L structures.[22−24] The more interesting structural features in the complexes is(are) the intramolecular Rh−Cl···H−N interaction(s) between the NH amine function(s) and the Rh−Cl moiety. The N···Cl distances in the 3.12−3.20-Å range for **5** and **7′** (see Table 2) are significantly smaller than the sum of the N−H bond length and the van der Waals radii of H and Cl atoms[25] and even smaller than an analogous interaction (3.33 Å) recently reported for a palladium allyl complex.[26] Other reported intramolecular M−Cl···H−N interactions for neutral aminophosphine complexes involve four- or seven-membered rings,[27−29] but no previous example is available for six-membered rings.

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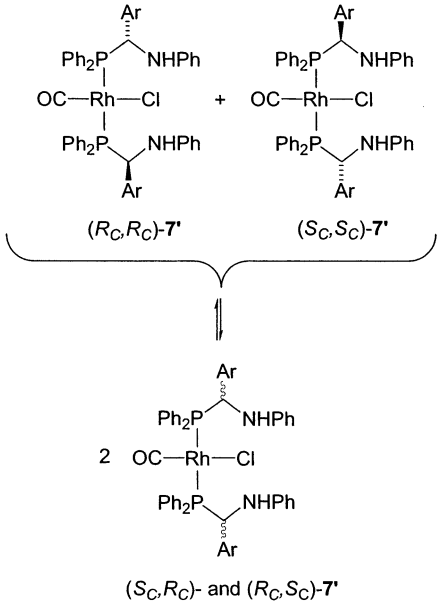
Scheme 4



The H-bonding interactions observed for **5** and **7′** in the solid state are maintained in CH_2Cl_2 and even in THF. This is demonstrated by the following IR spectroscopic results. The NH absorption band in the free ligand **4** is found at 3327 cm^{-1} in the solid state and 3409 cm^{-1} in a THF solution. This is due to the dimeric structure of **4** exhibiting P···H−N interactions.[12] Therefore, the solution band can be attributed to the stretching vibration of the free N−H moiety. Compound **5**, on the other hand, exhibits the N−H stretching vibration at 3283 cm^{-1} in THF and 3285 cm^{-1} in CH_2Cl_2 (these are close to the value of 3288 cm^{-1} observed for the solid dispersed in Nujol). Furthermore, a 10-fold dilution of the solution does not alter the form of the spectrum; notably, no absorption is visible in the free N−H region. The large red shift of about 125 cm^{-1} relative to the free N−H group indicates a rather strong H-bonding interaction. For compound **7′**, the N−H vibration is observed at 3312 cm^{-1} in a THF solution (a red shift of 97 cm^{-1} relative to free N−H) and 3296 cm^{-1} for the solid dispersed in Nujol. The lower shift for **7′** relative to **5** indicates a weaker H-bonding interaction, which can be rationalized on the basis of the higher NH/Cl ratio. It is important to remark that this H-bonding interaction does not engage the nitrogen lone pair. Consequently, the inversion at nitrogen should remain free, and no new chiral center is generated.

When crystals of the pure diastereomer (R_C,R_C)/(S_C,S_C)-**7′** are dissolved in C_6D_6, the compound immediately establishes an equilibrium with the (S_C,R_C)/(R_C,S_C) diastereoisomer (1:1 ratio; see Scheme 4). This is proven by the immediate recording of ^{31}P and ^1H NMR spectra. Therefore, a rapid intermolecular ligand-exchange process must occur. A similar phosphine-scrambling process has been previously reported for compounds RhCl(CO)(L)(L′), with L, L′ = triphenylphosphine, tricyclohexylphosphine, or dimethylphenylphosphine, and has been rationalized in terms of either the formation of dinuclear rhodium complexes[30] or through a dissociation−recoordination process.[31]

(c) Identification of the Dicarbonyl Complex *cis*-Rh(CO)$_2$Cl(L). When two equivalents of ligand **4** or **4′** (in equilibrium with **2′** and Ph_2PH) are added at room temperature to a THF solution of $[Rh(CO)_2Cl]_2$, an unstable mononuclear dicarbonyl derivative *cis*-Rh(CO)$_2$Cl(L) (**6** or **6′**) is formed (see Scheme 3, path d). The proposed geometry is demonstrated by the characteristic IR and ^{31}P NMR data.[32−37] The presence of only one doublet with ^1J(Rh,P) = 132 Hz (32.7 ppm for **6**, 28.1 ppm for **6′**) in the ^{31}P NMR spectrum and two carbonyl bands (at 2017 and 2095 cm^{-1} for **6** and 2015 and 2094 cm^{-1} for **6′**) in the IR spectrum unambiguously excludes the formation of a binuclear intermediate, which could result from the potential assembling character of the α-P,N ligands.[9,38,39]

Under a di-nitrogen purge, the unstable complexes **6** and **6′** rapidly undergo quantitative decarbonylation to afford complexes **7** and **7′**, respectively, as shown by the IR and ^{31}P NMR monitoring. The IR spectrum of the crude mixture also showed two weak carbonyl bands at 2070 and 2080 cm^{-1}, while no additional ^{31}P resonance is observed in the NMR spectrum. Therefore, the transformation of **6** to **7** must be accompanied by the formation of a second product that does not contain phosphine ligands. However, the IR data are not consistent with the formation of $[Rh(CO)_2Cl]_2$. This product is formulated as "RhCl(CO)$_n$" in Scheme 3. We have not made any further attempt to fully characterize this byproduct. A separate experiment shows that complexes **5** and **5′** transform into **6** and **6′** immediately when exposed to CO at atmospheric pressure (path c), but these are converted completely to the same final mixture within 30 min. On the other hand, the solutions obtained by decomposition of **6** (or **6′**) regenerate these precursors when pressurized under CO (see also the following catalytic studies). It is interesting to note that a similar behavior was observed by Alper et al. for the analogous complex RhCl(CO)$_2$(L-κ^1-P) (L = $Ph_2POCH(Ph)CH(Me)NHMe$),[17] whose transformation into $[RhCl(CO)L_2]$ and $[RhCl(CO)_2]_2$ was proposed on the basis of ^{31}P NMR spectra. In another study, the formation of a μ-CO species was found when using a pyridinylphosphine ligand.[38] Our IR investigation excludes the formation of such species, although it could play a role as an intermediate, as found for other ligand-redistribution processes.[30]

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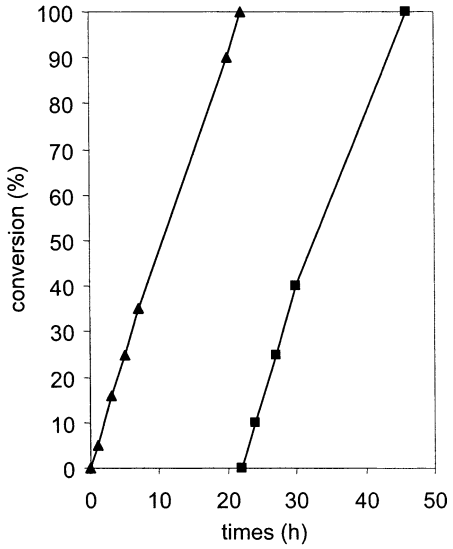

Figure 3. Rate conversion for the styrene hydroformylation with complex **5** (see the Experimental Section for the catalytic conditions). (▲) Styrene introduced at $t = 0$. (■) Styrene introduced after 20 h.

Independent of how complex **6** is generated, it remains the major species in solution, as shown by IR spectroscopy, when it is maintained overnight under a high CO pressure (20 atm). The subsequent release of the CO pressure induces the evolution of **6** to **7** as previously described. The stabilizing effect of the high CO pressure suggests that the initial step of the ligand-redistribution process in Scheme 3 is a CO dissociation. To establish the reversibility of this ligand-redistribution process, the decomposed mixture obtained as described above (containing no residual complex **6**) was pressurized with CO (20 atm) for several hours in an autoclave. Upon depressurization, an immediate IR analysis revealed the presence of compound **6** together with **7** and the subsequent quantitative transformation into **7**.

Further evidence that complex **6** is stable under a high CO pressure was obtained through hydroformylation catalysis studies. A first run was carried out by charging the autoclave with $[RhCl(COD)]_2$, ligand **4** (L/Rh = 1), styrene, the chloroform solvent, and syngas. A kinetic follow-up (triangles in Figure 3) shows a turnover frequency of 45 h^{-1}. It is interesting to note the absence of any induction period.

A second experiment was carried out under the same conditions. However, the precatalyst solution was initially equilibrated overnight under a CO pressure in the absence of styrene to ensure the quantitative formation of compound **6**. The autoclave was then depressurized, and the complete and slow transformation of **6** to **7** was verified by IR spectroscopy. At this point, styrene was introduced, and the subsequent catalytic run (squares in Figure 3) indicates the same turnover frequency as that for the previous experiment. These results suggest that the same catalytic species is present in both systems and confirm that the ligand-redistribution process can be reversed only under high CO pressure.

Conclusion

We have shown that chiral α-aminophosphine ligands form stable Rh(I) complexes, provided that the equilibrium constant of the ligand formation from the benzaldimine and diphenylphosphine is sufficiently high. Otherwise, the diphenylphosphine oxidative addition reaction prevails. The Rh(I) complexes containing one or two monodentate (P) α-P,N ligands display Rh−Cl···H−N interactions with the dangling secondary amine function in the solid state and in solution. The NMR and IR studies have highlighted ligand-redistribution processes in solution, some of which are dependent on the CO pressure. The stabilization of dicarbonyl rhodium compounds by high CO pressure allows the formation of a hydroformylation catalytic precursor. The influence of the P,N ligand on the hydroformylation catalytic activity will be the topic of a separate contribution.[40]

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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