Rhodium Complexes with Chiral Aminophosphinite Derivatives of Ephedrine

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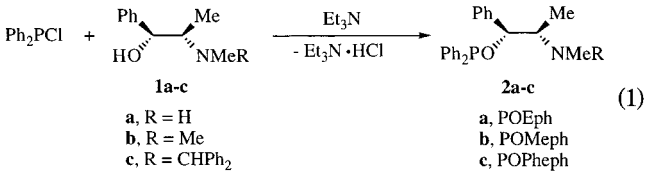
Aminophosphinites $Ph_2POCHPhCHMeNMeR$ (**2a**−**c**: **a**, R = H; **b**, R = Me; **c**, R = Ph_2-CH), prepared from the corresponding *N*-substituted (1*S*,2*R*)-ephedrines, cleanly react with $[Rh(CO)_2Cl]_2$ in benzene, affording complexes with P,N-chelating (**3a**, **4b)** or monodentate (**5b**,**c** and **7c**) ligands, depending on the steric bulk of the amino group and metal-to-ligand ratio. Treatment of the chloro-bridged dimer **7c** with $AgClO_4$ in methylene chloride gives the cationic complex **8c**, containing not only P,N-chelating aminophosphinite but also a Ph group of a *N*-diphenylmethyl fragment coordinated to Rh in an unusual η^2 fashion. Formation of the chiral center at nitrogen occurs stereoselectively, and complexes **3a** and **8c** exist as single diastereomers in the solid state and in solution. The structures of **3a** and **8c** were established by single-crystal X-ray diffraction.

Introduction

Metallocomplexes containing chiral P,N-chelating ligands have attracted considerable attention because they often display interesting structural, chemical, and catalytic properties.[1] The vast majority of these complexes, however, possess chirality associated with carbon and sometimes phosphorus atoms, while the nitrogen is sp^2-hybridized or bears identical substituents and therefore cannot be chiral. It is well-known that the N atom in an amino group undergoes very fast inversion of configuration; however, donation of the lone pair to a metal retards the inversion and the coordinated nitrogen becomes stereogenic. The formation of chiral N centers was proposed or implied in a number of publications;[2] however, structurally characterized complexes featuring stereogenic nitrogen are rare.[1a,3,4] Chiral amino alcohols such as ephedrine are very attractive for application in metalloorganic chemistry. They are inexpensive, are readily available in enantiomerically pure form, and can be easily transformed to the corresponding aminophosphinites.[5] The chemistry of an amino group is well-developed; thus, it is possible to introduce virtually any substituent at the nitrogen,[6,7] therefore allowing for fine-tuning of the coordination properties of these ligands. The affinity of "soft" transition metals toward N-donors is generally considered to be lower than that toward phosphorus; in contrast, the strength of the M−N bond is affected much more by steric effects than that of the corresponding M−P bond.[8] As a result, depending on the steric bulk of the N-substituents, aminophosphinites may act as chelating, monodentate, or bridging ligands. Here we wish to report the preparation and characterization of Rh complexes with aminophosphinite derivatives of ephedrine, emphasizing the factors which affect the structure of the complexes and the selectivity for the formation of chiral centers at nitrogen.

Results and Discussion

Preparation of Aminophosphinites 2a−c. The aminophosphinite ligands were prepared by treatment of *N*-substituted ephedrines with Ph_2PCl in the presence of Et_3N in benzene (eq 1) in a way similar to that described for prolinol based aminophosphinites.[5] The



1a-c
a, R = H
b, R = Me
c, R = $CHPh_2$

2a-c
a, POEph
b, POMeph
c, POPheph

(1)

compounds were isolated as colorless oils and characterized by ^{31}P, ^1H, and ^{13}C NMR. According to ^{31}P NMR spectra of the reaction mixture, the transformation of **1b** to **2b** was very clean and took less than 5 min at room temperature. Under the same conditions *N*-(diphenylmethyl)ephedrine (**1c**) reacted more slowly (ca. 6 h at

(1) See for example: (a) Gao, J.-X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087. (b) Yamada, T.; Ohkouchi, M.; Yamaguchi, M.; Yamagishi, T. *J. Chem. Soc., Perkin Trans.* **1997**, *1*, 1869. (c) Schnyder, A.; Togni, A.; Wiesli, U. *Organometallics* **1997**, *16*, 255. (d) Hampton, C. R. S. M.; Butler, I. R.; Cullen, W. R.; James, B. R.; Charland, J.-P.; Simpson, J. *Inorg. Chem.* **1992**, *31*, 5509 and references therein. (e) Payne, N. C.; Tobin, G. R. *Acta Crystallogr.* **1992**, *C48*, 45. (f) Yamamoto, K.; Tomita, A.; Tsui, J. *Chem Lett.* **1978**, 3.

(2) See for example: (a) Takehara, J.; Hashiguchi, S.; Fujii, A.; Shinichi, I.; Ikariya, T.; Noyori, R. *Chem. Commun.* **1996**, 233. (b) Brunner, H.; Weber, H. *Chem. Ber.* **1985**, *118*, 3380. (c) Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247. (d) Asami, M.; Inoe, S. *Chem. Lett.* **1991**, 685. (e) Yamada, S.; Mashiko, T.; Terashima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988.

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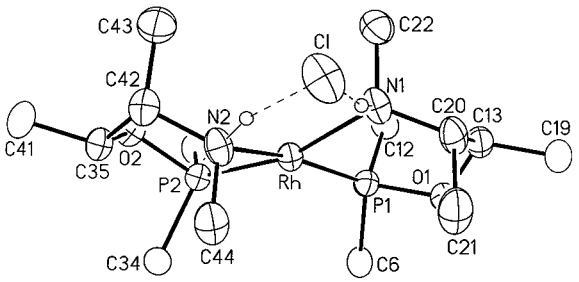


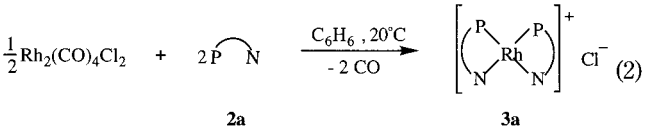
Figure 1. Perspective diagram of **3a** with 30% probability ellipsoids. The hydrogen atoms (except for *N*-H) and phenyl carbon atoms (except for *ipso*) are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3a

Rh−N(1)	2.182(3)	Rh−P(2)	2.1887(8)
Rh−N(2)	2.201(3)	O(1)−P(1)	1.633(3)
Rh−P(1)	2.1855(9)		
N(1)−Rh−P(1)	89.34(8)	C(22)−N(1)−Rh	106.7(2)
N(1)−Rh−N(2)	85.77(10)	C(22)−N(1)−C(20)	111.1(3)
N(2)−Rh−P(2)	88.98(7)	C(20)−N(1)−Rh	123.3(3)
P(1)−Rh−P(2)	98.74(3)		

room temperature). No intermediates were observed during this time. The ^{31}P NMR spectra showed only the signals of **2c** and unreacted Ph_2PCl (δ 113 and 82.5, respectively). Similar reaction of **1a** and Ph_2PCl at 20 °C led predominantly to the formation of *N*-(diphenylphosphino)ephedrine (identified by a signal at δ 60.5 in ^{31}P NMR);[5,9] however, heating the reaction mixture to reflux for ca. 30 min led to complete rearrangement to the desired **2a**. The reaction was accompanied by formation of unidentified side products (ca. 20%), and therefore column chromatography was employed in order to purify **2a**.

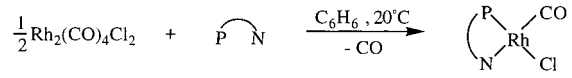
Reaction of POEph with $Rh_2(CO)_4Cl_2$. X-ray Structure of $[Rh(POEph)_2]^+Cl^-$ (3a). Treatment of a benzene solution of $Rh_2(CO)_4Cl_2$ with 2 equiv of **2a** led to the evolution of CO and clean formation of complex **3a** according to eq 2. According to the^{31}P NMR



spectra, complex **3a** was the only metalloorganic product even when less than 2 equiv of the aminophosphinite was used. The signal of unreacted **2a** appeared in the spectrum only when more than 2 equiv of the ligand was added. The complex was isolated in high yield as air-stable yellow crystals soluble in benzene, CH_2Cl_2, and methanol but insoluble in Et_2O and saturated hydrocarbons. The structure of **3a** was established by single-crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 1; selected bond distances and angles are presented in Table 1.

The coordination environment of the Rh is noticeably distorted from a square-planar geometry (the *trans*-P−Rh−N angles are 164.9 and 166.4°), with the distortion presumably due to steric repulsion between the *cis*-PPh_2 fragments. The observed arrangement with two phosphorus atoms *cis* to each other seems to be quite common for bis-P,N-chelated metallocomplexes and was reported for closely related $[Rh(PN)_2]PF_6$ (PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane)[10] and some Ru complexes.[11] The six-membered chelate rings of the complex adopt the thermodynamically more stable chair conformation with the bulky Ph groups at C(13) and C(35) in equatorial positions, while the sterically less demanding Me substituents at C(20) and C(42) occupy axial sites (chirality of the ligands dictates a *cis* orientation of the neighboring Ph and Me groups). Both nitrogen atoms possess the *R* configuration with the attached Me substituents in axial positions. It should be noted that the chiral centers at the N atoms in **3a** arise only upon coordination to the metal; therefore, another diastereomer with a sterically more favorable equatorial orientation of the *N*-Me groups could be formed. Since this does not happen, it seems reasonable to assume that the selective formation of the *R* diastereomer, which occurs despite unfavorable 1,3-diaxial interaction of the *N*-Me and *P*-Ph groups, is explained by the strong hydrogen bonding between the Cl anion and the two equatorial protons attached to the nitrogens. The *N*(H)···Cl interatomic separations (3.158(5) and 3.176(5) Å) in **3a** are consistent with strong Cl−H hydrogen bonds, while the hypothetical *S* diastereomer would possess two *trans*-*N*-H substituents in axial positions, a situation unsuitable for simultaneous formation of two hydrogen bonds with the Cl anion. The ^{1}H NMR spectrum of **3a** displays a broad resonance at 8.3 ppm which is typical for hydrogen-bonded *N*-H protons. It should be noted that formation of the chiral centers occurs stereoselectively and **3a** exists as a single diastereomer, not only in the solid state but also in solution, as can be seen from the ^{31}P{^{1}H} NMR of the reaction mixture (sharp doublet at 141 ppm) and ^{31}P-{^{1}H}, ^{13}C{^{1}H}, and ^{1}H NMR spectra of the isolated complex.[12]

Reaction of POMeph with $Rh_2(CO)_4Cl_2$. Characterization of Rh(POMeph)(CO)Cl (4b) and Rh-(POMeph)$_2$(CO)Cl (5b). In a comparison with **2a**, aminophosphinite **2b** gives two different products depending on the metal-to-ligand ratio employed. The reactions are very clean and occur easily at room temperature according to eqs 3 and 4. The complexes



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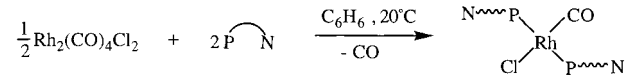

(4)

4b and **5b** were isolated in high yield and characterized by elemental analysis and IR and NMR spectra. The carbonyl group of the complex **4b** appears as a doublet

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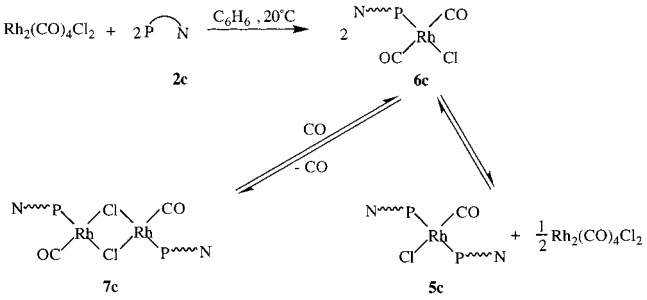
(12) The spectra recorded in CD_2Cl_2 at 173−313 K show the presence of a single diastereomer.

Scheme 1



of doublets in the $^{13}C\{^1H\}$ NMR spectrum (J_{C-P} = 18 Hz; J_{C-Rh} = 71 Hz), indicating that there is only one phosphinite ligand in the molecule and that CO is *cis* to the phosphorus. The diastereotopic *N*-Me groups of the complex give two signals in the spectrum. Coordination of the nitrogen to the metal was unequivocally confirmed by the $^{15}N\{^1H\}$ NMR spectrum, which showed a doublet of doublets, due to coupling with Rh (J_{N-Rh} = 11.5 Hz) and phosphorus (J_{N-P} = 3.5 Hz). In contrast to the case for **4b,** complex **5b** shows a doublet of triplets in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum as a result of CO carbon coupling with Rh (J_{C-Rh} = 74.5 Hz) and with two P ligands (J_{C-P} = 17 Hz). The two phosphinites are equivalent (sharp doublet in $^{31}P\{^1H\}$ NMR) and hence are *trans* to each other. The *N*-Me groups of the complex appear as a single line in the $^{13}C\{^1H\}$ NMR spectrum, indicating that the two nitrogens of **5b** are equivalent and are not coordinated to the metal.

Reaction of POPheph with $Rh_2(CO)_4Cl_2$. Characterization of $Rh_2(POPheph)_2(CO)_2Cl_2$ (7c). X-ray Structure of $[Rh(POPheph)CO]^+ClO_4^-$ (8c). The reaction of $Rh_2(CO)_4Cl_2$ and 2 equiv of **2c** occurs according to eq 4 in the same way as described for **2b**. The resulting **5c** was isolated in high yield as an air-stable orange solid and characterized by elemental analysis and IR and NMR spectroscopy (see Experimental Section).

Treatment of $Rh_2(CO)_4Cl_2$ with 1 equiv of **2c** in benzene at room temperature leads to the appearance of two broad doublets at 125 (J_{P-Rh} = 192 Hz) and 110 ppm (J_{P-Rh} = 144 Hz) and a sharp doublet at 116 ppm (J_{P-Rh} = 136 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. The sharp doublet was identified as the signal of **5c** on the basis of its chemical shift and coupling constant. It seemed reasonable to assume that the reaction involves the set of equilibria shown in Scheme 1.

The removal of CO from the solution with a stream of inert gas resulted in the disappearance of the doublets of **5c** (116 ppm) and **6c** (110 ppm) from the NMR spectrum, while the doublet corresponding to **7c** became sharp. Bubbling CO through the solution restored the original equilibrium. Complex **7c** was isolated from the degassed reaction mixture in high yield and characterized by elemental analysis and IR and NMR spectra. The carbonyl groups of the complex appear as a doublet of doublets (δ 183.5, J_{C-P} = 19 Hz, J_{C-Rh} = 82 Hz) with the value of the C−P coupling constant indicative of a *cis* relationship between the CO and phosphorus. The amino groups of **7c** are equivalent and are not coordinated to rhodium, as indicated by a sharp singlet at

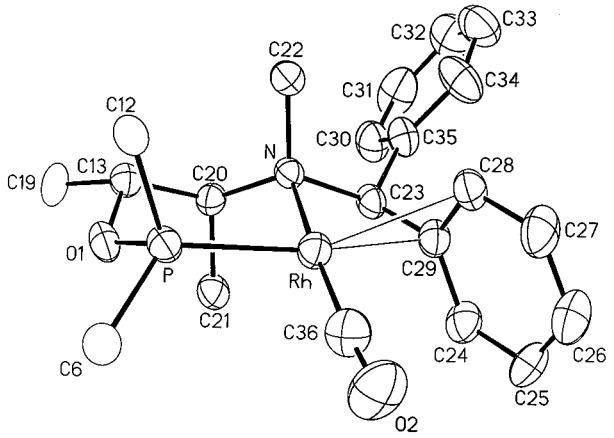


Figure 2. Perspective diagram of the cation of **8c** with 30% probability ellipsoids. All hydrogen atoms and non-*ipso*-phenyl carbon atoms on P and C(13) are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 8c

Rh−N	2.127(5)	C(28)−C(29)	1.434(11)
Rh−P	2.2015(16)	C(24)−C(29)	1.383(11)
Rh−C(36)	1.835(9)	C(24)−C(25)	1.370(12)
C(36)−O(2)	1.146(10)	C(25)−C(26)	1.404(13)
Rh−C(29)	2.334(6)	C(26)−C(27)	1.337(12)
Rh−C(28)	2.449(7)	C(27)−C(28)	1.405(12)
C(23)−C(35)	1.546(10)	P−O(1)	1.605(5)
C(23)−C(29)	1.514(10)		
N−Rh−P	92.34(13)	C(20)−N−Rh	114.9(4)
N−Rh−C(36)	174.4(3)	C(23)−N−Rh	95.2(3)
C(36)−Rh−P	92.4(3)	Rh−C(29)−C(28)	77.0(4)
C(20)−N−C(22)	109.9(5)	Rh−C(29)−C(24)	106.6(5)
C(22)−N−C(23)	111.9(5)	Rh−C(29)−C(23)	88.4(3)
C(22)−N−Rh	113.0(4)		

−342 ppm in the $^{15}N\{^1H\}$ NMR spectrum. The available spectral data do not contradict the proposed structure of **7c** as a dimer with two phosphinites coordinated in an *anti* fashion. We cannot exclude, however, that these ligands occupy *syn* positions in the dimer or that the complex exists as a mixture of both isomers. It seemed conceivable that substitution of the bridging chlorides with weakly coordinating anions such as perchlorate would destroy the dimeric structure of **7c**, bringing about coordination of the pendant amino group to the metal. Indeed, treatment of **7c** with $AgClO_4$ leads to precipitation of silver chloride and formation of the cationic complex **8c** containing P,N-chelating aminophosphinite and, surprisingly, a Ph group of the *N*-(diphenylmethyl) fragment coordinated to rhodium in an unusual η^2 fashion. The complex was isolated in high yield as yellow air-stable crystals soluble in CH_2Cl_2 and methanol and insoluble in THF and aromatic hydrocarbons. The structure of **8c** was established by single-crystal X-ray diffraction. An ORTEP plot and selected bond distances and angles of the complex cation are shown in Figure 2 and Table 2, respectively.

The coordination environment of the Rh is formed by a *cis* P,N-chelating aminophosphinite, a carbonyl group which is *trans* to the nitrogen, and a Ph group coordinated to the metal via the *ipso* and *ortho* carbons. The phenyl ring remains approximately planar (rms deviation 0.02 Å) and assumes a dihedral angle of 104° with the plane defined by the two coordinated carbons and the Rh atom. The Rh−*ipso*-C distance (2.334(6) Å) is very close to the average value for π-arene Rh complexes

(2.33(5) Å),[13] while the distance to the coordinated *ortho* carbon (2.449(7) Å) is substantially longer. A similar situation was reported for (η^3-$CH_2C_6Me_5$)Rh[$P(OPr^i)_3$]$_2$, which was described as the benzyl analogue of π-allyl Rh complexes.[14] The Rh−C(23) separation (2.746(7) Å) in **8c**, however, is too long for any bonding interaction, and **8c** thus represents a new example of still quite rare η^2-arene metallocomplexes.[15−17]

The six-membered P−N−Rh chelate is in a chair conformation. As anticipated, the bulky diphenylmethyl group at the nitrogen and Ph at C(13) occupy equatorial positions, rendering the sterically less demanding methyl substituents at C(20) and at the nitrogen in axial sites. The stereogenic N-center thus adopts the *S* absolute configuration. Coordination of Rh to one of the two Ph groups of the diphenylmethyl fragment brings about formation of a chiral center at C(23), with the absolute configuration depending on which phenyl is coordinated. The two possible diastereomers should differ from each other by the position of the uncoordinated Ph group relative to Me substituents at N and C(20). The observed structure of **8c** displays an *S* configuration at C(23) with the uncoordinated Ph group *cis* to the *N*-Me unit, while the hypothetical *R* diastereomer would possess the uncoordinated Ph *cis* to the Me group at C(20). The *cis* interaction in **8c** is relieved to some extent by pivoting of the diphenylmethyl group around the C(23)−N bond (the C(22)−N−C(23)−C(35) torsion angle is 31.8(5)°), while the *cis* interaction between the uncoordinated Ph and Me at C(20) is probably severe enough to prevent formation of the *R* diastereomer. The structure of **8c** thus incorporates six stereogenic centers. Two of them (C(13) and C(20)) were present in the ligand, while the others (C(23), C(28), C(29). and N) arise upon coordination of the η^2-Ph and amino groups to the metal. Formation of the new chiral centers occurs stereoselectively, and **8c** exists as a single diastereomer, not only in the solid state but also in solution ($^{31}P\{^1H\}$ NMR of the reaction mixture[18] and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra of the isolated complex).

Fluxional Behavior of 8c in Solution. The η^2-coordinated Ph group of **8c** gives six sharp resonances in the 125 MHz $^{13}C\{^1H\}$NMR spectra[19] recorded below 260 K (see Figure 3). At higher temperatures the signals of the *ortho* and *meta* carbons become broad and cannot be observed at 285 K. The *meta* carbons show a broad averaged resonance (δ 134.3) at 310 K, while the *ortho* carbons still cannot be seen in the spectrum. The signals of the *ipso* and *para* carbon atoms of the η^2-Ph group remain sharp in the temperature interval 210−310 K. Taken together, these data suggest that the observed fluxional behavior of **8c** is explained by restricted

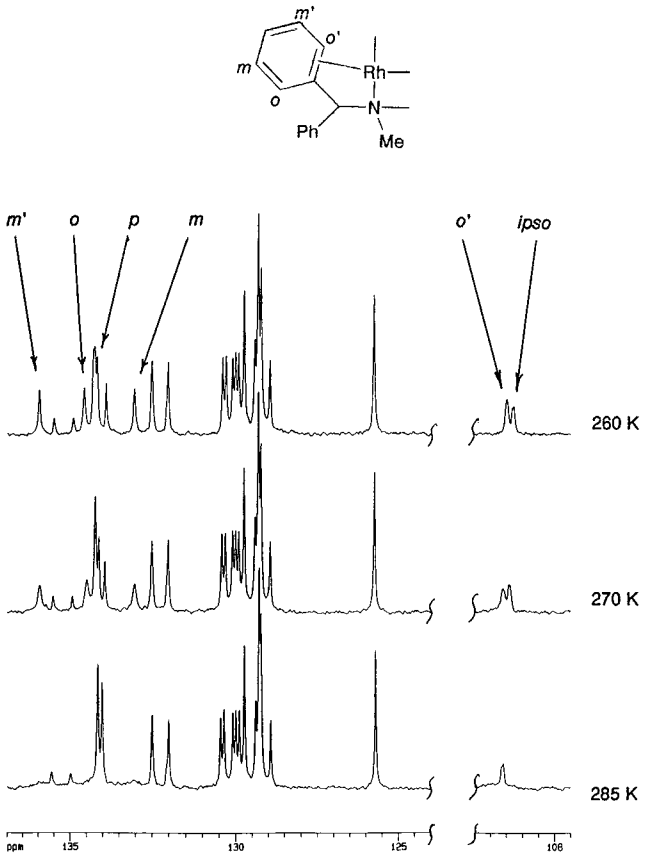


Figure 3. 125 MHz VT $^{13}C\{^1H\}$ NMR spectra (aromatic region) of **8c** in CD_2Cl_2.

rotation of the coordinated Ph group around the σ-bond (C(23)−C(29) on Figure 2). It should be noted that the other Ph groups of the complex have low rotational barriers, as indicated by the pairwise equivalence of the *ortho* and *meta* carbons in the VT $^{13}C\{^1H\}$ NMR spectra.

The *ortho* protons of the η^2-Ph group are nonequivalent and are well-separated from the other aromatic protons in the ^1H NMR spectra of the complex (see Figure 4). At 260 K they appear as sharp doublets centered at 8.6 and 7.9 ppm. Increasing the temperature leads to broadening and finally collapse of the signals at 305 ± 5 K. The value of the rotational barrier of the η^2-Ph group calculated for **8c** (13.7 ± 0.3 kcal/mol) compares well with the value obtained for "ring whizzing" in (η^2-arene)pentammineosmium(II) complexes (11.8−17.2 kcal/mol)[20] and is significantly higher than the corresponding value[14] for (η^3-$CH_2C_6Me_5$)Rh[$P(OPr^i)_3$]$_2$, where two sides of the benzyl ligand appear to be equivalent even at 193 K.

Conclusions

The present study demonstrates that coordination properties of aminophosphinites are very sensitive to the steric bulk of the amino group. Reaction of **2a** and $Rh_2(CO)_4Cl_2$ occurs with displacement of the Cl anion and all carbonyls from the coordination sphere of Rh(I). The two P,N-chelate cycles of the resulting complex **3a** remain intact in the presence of excess ligand, indicating high affinity of the NHMe fragment for the metal. The NMe_2 terminus of **1b** easily cleaves the Cl

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(17) Harman, W. D.; Gebhart, M.; Taube, H. *Inorg. Chem.* **1990**, *29*, 567.
(18) The spectrum shows a sharp doublet for **8c**, and other unidentified signals were of low intensity (ca. 5% altogether).
(19) The resonances were assigned using a combination of ^{13}C DEPT, COSY, TOCSY, NOESY, and HMQC techniques.
(20) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.

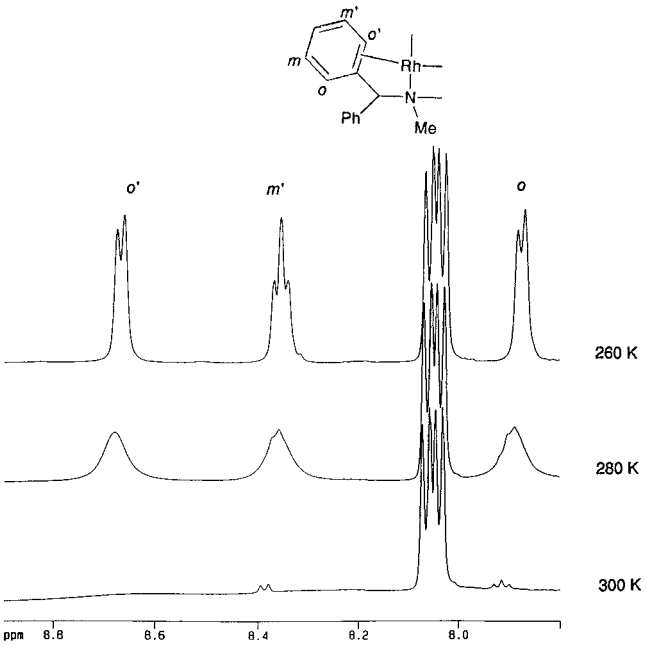

Figure 4. 500 MHz VT ^{1}H NMR spectra (fragment of aromatic region) of **8c** in CD_2Cl_2.

bridges but is not able to displace carbonyl, and the chelate ring in the formed **4b** can be opened by an excess of the ligand. The amino group of **2c**, which possesses a rather large *N*-(diphenylmethyl) substituent, is not able to cleave the relatively weak Cl bridges. The P,N-ligand in **7c** is connected to Rh only via phosphorus. It does not mean, however, that the $NMeCHPh_2$ fragment cannot be coordinated, and treatment of the complex with $AgClO_4$ leads to the formation of a chelate cycle. The affinity of the amino group of **2a**−**c** toward Rh(I) thus can be arranged in the following order: $-NHMe > CO > -OPPh_2 > -NMe_2 > \mu\text{-}Cl^- > -NMeCHPh_2 > ClO_4^-$.

The superior stability of the P,N-chelate in **3a** is probably explained by the formation of strong hydrogen bonds between the Cl anion and the two *N*-H protons. The hydrogen bonds render the *N*-H protons of the six-membered chelate rings in equatorial positions and thus define the configuration of the stereogenic nitrogen atoms in the complex. The selective formation of the chiral centers at the nitrogen in **8c** is governed by the well-known tendency of nonrigid six-membered rings to adopt a chair conformation with the sterically more demanding substituents in equatorial positions.

Experimental Section

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. (1*R*,2*S*)-*N*-(diphenylmethyl)ephedrine (**1c**) was prepared according to the published procedure.[7] Other chemicals were purchased from Aldrich and were used as received. The following instruments were used: Varian XL-300 and Bruker AMX 500 (NMR), Bomem MB-100 (FT-IR), and Perkin-Elmer 2400 Series II (combustion microanalysis). The natural-abundance $^{15}N\{^1H\}$ NMR spectra were acquired using 0.5−0.7 M solutions of the Rh complexes, a 10 mm probe, CH_3NO_2 as external standard, D1 = 12 s, and gated decoupling. Acceptable spectra were observed after 12−24 h.

Synthesis of Aminophosphinites (2a−c). A solution of Ph_2PCl (2.0 mL, 11.14 mmol) and Et_3N (4 mL) in 30 mL of benzene was added to a stirred solution of the corresponding ephedrine (11.16 mmol) in 30 mL of benzene. The resulting suspension was heated to reflux for 1 h, cooled, and filtered. The filtered white solid was washed with benzene (3 × 10 mL), and the combined filtrates were evaporated and dried under vacuum at 100 °C. The oily residue was stirred with heptane/Et_2O (4:1, 15 mL), the white precipitate which formed was filtered off, and the filtrate was passed through a short column with basic alumina (50 × 25 mm) and the column eluted with 30 mL of heptane/Et_2O (1:2 for **2a** or 2:1 for **2b**,**c**). Removal of the solvent in a vacuum afforded the corresponding **2a**−**c** as a colorless oil.

2a (POEph).[21] The compound was purified by column chromatography on basic alumina (250 × 25 mm, heptane−2:1 heptane/Et_2O). Yield: 63%. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 113.1. ^{1}H NMR ($CDCl_3$; δ): 1.1 (d, J = 6.4 Hz, 3H); 2.3 (s, 3H); 2.9 (m, 1H); 5.0 (dd, J_{H-H} = 4.6 Hz, J_{H-P} = 9.7 Hz, 1H); 7.2−7.7 (m, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 15.2 (s, Me); 33.8 (s, Me); 60.6 (d, J_{C-P} = 5.5 Hz, CH); 83.9 (d, J_{C-P} = 18.7 Hz, CH); 127.0−131.1 (12 lines, Ph); 140.1 (d, J_{C-P} = 2.5 Hz, Ph); 142.05 (d, J_{C-P} = 15.4 Hz, Ph); 142.15 (d, J_{C-P} = 20 Hz, Ph). $[\alpha]_D^{20}$ = −5.9° (c = 3.9, toluene).

2b (POMeph). Yield: 81%. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 112.8. ^{1}H NMR ($CDCl_3$; δ): 1.2 (d, J = 6.7 Hz, 3H); 2.3 (s, 6H); 3.0 (m, 1H); 5.1 (dd, J_{H-H} = 5.5 Hz, J_{H-P} = 8.9 Hz, 1H); 7.3−7.8 (m, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 9.6 (s, Me); 41.4 (s, Me); 65.1 (d, J_{C-P} = 6.2 Hz, CH); 83.4 (d, J_{C-P} = 18.6 Hz, CH); 127.0−131.2 (12 lines, Ph); 141.6 (d, J_{C-P} = 2 Hz, Ph); 142.1 (d, J_{C-P} = 17 Hz, Ph); 142.4 (d, J_{C-P} = 14 Hz, Ph). $[\alpha]_D^{20}$ = +21.4° (c = 22.5, benzene).

2c (POPheph).[21] Yield: 71%. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 112.2. ^{1}H NMR ($CDCl_3$; δ): 1.1 (d, J = 6.7 Hz, 3H); 2.1 (s, 3H); 3.2 (m, 1H); 4.4 (s, 1H); 4.8 (apparent t, $J_{H-H} \approx J_{H-P} \approx$ 8.5 Hz, 1H); 6.8−7.6 (m, 25H). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 9.5 (s, Me); 34.2 (s, Me); 59.3 (d, J_{C-P} = 7.4 Hz, CH); 74.1 (s, CH); 85.1 (d, J_{C-P} = 18.6 Hz, CH); 126.6−131.4 (18 lines, Ph); 141.8−142.1 (6 lines, Ph); 142.9 (s, Ph); 143.9 (s, Ph). $[\alpha]_D^{20}$ = +105° (c = 2.1, benzene).

Synthesis of ClRh(POEph)$_2$ (3a). POEph (1.8 mmol, 0.313 M in C_6H_6) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (170 mg, 0.437 mmol) in 6 mL of benzene. The resulting bright yellow solution was reduced in volume to ca. 5 mL under vacuum and diluted with 6 mL of heptane to form a voluminous yellow precipitate. Heating the reaction flask in boiling water led to transformation of the precipitate into a yellow oil which spontaneously crystallized. The flask was allowed to stay at room temperature for 1 h; the crystals were separated, washed with copious amounts of pentane, and dried under vacuum to give 670 mg (0.800 mmol, 91%) of analytically pure **3a** as a light yellow microcrystalline solid. Anal. Calcd for $C_{44}H_{48}ClN_2O_2P_2Rh$: C, 63.1; H, 5.8; N, 3.3. Found: C, 62.8; H, 5.6; N, 3.1. $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 141 (d, J_{P-Rh} = 189.5 Hz). ^{1}H NMR (C_6D_6; δ): 1.8 (d, J = 6.3 Hz, 3H); 2.8 (m, 4H); 4.7 (broad s, 1H); 6.7−7.8 (m, 15H); 8.3 (broad s, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6; δ): 14.8 (s, Me); 39.7 (s, Me); 61.2 (s, CH); 73.8 (s, CH); 126−141 (Ph). $^{15}N\{^1H\}$ NMR (1:10 C_6D_6/C_6H_6; δ): −364.3 (second-order m). $[\alpha]_D^{20}$ = +28° (c = 1.0, toluene).

Synthesis of ClRh(CO)(POMeph) (4b). POMeph (2.6 mmol, 0.618 M in C_6H_6) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (505 mg, 1.3 mmol) in 12 mL of benzene. The resulting orange solution was evaporated, and the pale yellow mass was dissolved in 10 mL of hot MeOH and allowed to stay at room temperature for 1 h and then in a freezer (−17 °C) overnight. The precipitated yellow crystals were separated, rinsed with cold MeOH, and dried under vacuum to give analytically pure **4b** (1174 mg, 2.219 mmol, 85%). Anal. Calcd for $C_{24}H_{26}ClNO_2PRh$: C, 54.4; H, 5.0; N, 2.6. Found: C, 54.4; H, 5.0; N, 2.5. $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 134 (d, J_{P-Rh} = 184 Hz). ^{1}H NMR (C_6D_6; δ): 0.8 (d, J = 6.4 Hz, 3H); 1.75 (m, 1H);

(21) The compound was ≥95% pure according to ^{31}P NMR and contained up to 5% of heptane (^{1}H and ^{13}C NMR).

2.5 (s, 6H); 5.2 (d, J = 7.7 Hz, 1H); 6.8−7.9 (m, 15H). $^{13}C\{^1H\}$ NMR (C_6D_6; δ): 12.2 (s, Me); 47.7 (s, Me); 48.1 (s, Me); 70.8 (d, J_{C-P} = 3.8 Hz, CH); 77 (s, CH); 125.3−138.7 (Ph); 187.9 (dd, J_{C-Rh} = 71 Hz, J_{C-P} = 18 Hz, CO). $^{15}N\{^1H\}$ NMR (1:10 C_6D_6/C_6H_6; δ): −355.4 (dd, J_{N-Rh} = 11.5 Hz, J_{N-P} = 3.6 Hz). IR (KBr; ν_{CO}): 1985 cm^{-1}. $[\alpha]_D^{20}$ = +38.7° (c = 0.506, C_6H_6).

Synthesis of ClRh(CO)(POMeph)$_2$ (5b). POMeph (0.804 mmol, 0.618 M in C_6H_6) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (77 mg, 0.198 mmol) in 10 mL of benzene. The reaction mixture was evaporated under vacuum, and the resulting yellow oil was stirred with 10 mL of methanol to give a yellow precipitate that was separated, washed with MeOH (2 × 5 mL), and vacuum-dried to form 312 mg (0.349 mmol, 88%) of **5b** as a yellow microcrystalline solid. Anal. Calcd for $C_{47}H_{52}ClN_2O_3P_2Rh$: C, 63.2; H, 5.9; N, 3.1. Found: C, 63.5; H, 6.1; N, 3.0. $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 114 (d, J_{P-Rh} = 136.5 Hz). ^1H NMR (C_6D_6; δ): 1.3 (d, J = 6.6 Hz, 3H); 2.1 (s, 6H); 3.1 (quint, J = 6.9 Hz, 1H); 6.3 (m, 1H); 6.8−8.1 (m, 15H). $^{13}C\{^1H\}$ NMR (C_6D_6; δ): 10.6 (s, Me); 42.1 (s, Me); 65.3 (vt, J_{C-P} = 6.5 Hz, CH); 84.2 (s, CH); 127.8−141.8 (Ph); 186.8 (dt, J_{C-Rh} = 74.5 Hz, J_{C-P} = 17 Hz, CO). IR (KBr; ν_{CO}): 1992 cm^{-1}.

Synthesis of Rh$_2$(μ-Cl)$_2$(CO)$_2$(POPheph)$_2$ (7c). POPheph (1.028 mmol, 0.381 M in C_6H_6) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (200 mg, 0.514 mmol) in 15 mL of benzene, and nitrogen was passed through the homogeneous reaction mixture for 15 min. The resulting orange solution was diluted with 40 mL of heptane and reduced in volume to ca. 30 mL under vacuum to give a yellow precipitate and pale yellow solution. The precipitate was separated by decantation, washed with pentane (2 × 20 mL), and dried under vacuum to give 575 mg (0.421 mmol, 82%) of **7c** as a yellow microcrystalline solid. Anal. Calcd for $C_{72}H_{68}Cl_2N_2O_4P_2Rh_2$: C, 63.4; H, 5.0; N, 2.0. Found: C, 63.9; H, 5.2; N, 1.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 123 (d, J_{P-Rh} = 192 Hz). ^1H NMR ($CDCl_3$; δ): 1.5 (d, J = 6.5 Hz, 3H); 2.5 (s, 3H); 3.8 (m, 1H); 4.5 (s, 1H); 6.6 (dt, J_{H-H} = 9.5 Hz, J_{H-P} = 11.7 Hz, 1H); 6.8−8.0 (m, 25H). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 10.2 (s, Me); 34.2 (s, Me); 59.1 (d, J_{C-P} = 8 Hz, CH); 74.1 (s, CH); 85.9 (s, CH); 126.7−143.9 (Ph); 183.5 (dd, J_{C-Rh} = 82 Hz, J_{C-P} = 19 Hz, CO). $^{15}N\{^1H\}$ NMR (1:10 C_6D_6/C_6H_6; δ): −341.6 (s). IR (KBr; ν_{CO}): 1993 cm^{-1}.

Synthesis of ClRh(CO)(POPheph)$_2$ (5c). Ph_2POPheph (0.721 mmol, 0.381 M in C_6H_6) was added to a solution of $Rh_2(CO)_4Cl_2$ (70 mg, 0.180 mmol) in 10 mL of benzene, and the reaction mixture was evaporated under vacuum. The obtained yellow mass was stirred with MeOH; a pale yellow solid was separated and vacuum-dried to give 387 mg (0.323 mmol, 90%) of **5c** as a light yellow powder. Anal. Calcd for $C_{71}H_{68}ClN_2O_3P_2Rh$: C, 71.2; H, 5.7; N, 2.3. Found: C, 71.1; H, 5.9; N, 2.3. $^{31}P\{^1H\}$ NMR (C_6D_6; δ): 115 (d, J_{P-Rh} = 136 Hz). ^1H NMR (C_6D_6; δ): 1.5 (d, J = 6.2 Hz, 3H); 2.4 (s, 3H); 3.7 (m, 1H); 4.5 (s, 1H); 6.6 (m, 1H); 6.8−8.1 (m, 25H). $^{13}C\{^1H\}$ NMR (C_6D_6; δ): 10.2 (s, Me); 34.6 (s, Me); 59.6 (vt, J_{C-P} = 8 Hz, CH); 74.4 (s, CH); 85.1 (s, CH); 126.8−144.4 (Ph); 186.8 (dt, J_{C-Rh} = 74.5 Hz, J_{C-P} = 17 Hz, CO). IR (KBr; ν_{CO}): 1986 cm^{-1}.

Synthesis of [Rh(CO)(POPheph)]ClO$_4$ (8c). $AgClO_4$ (0.733 mmol, 0.218 M in toluene) was added to a stirred solution of Rh$_2$(μ-Cl)$_2$(CO)$_2$(POPheph)$_2$ (500 mg, 0.366 mmol) in 10 mL of CH_2Cl_2. The bright yellow solution was filtered from precipitated AgCl diluted with 8 mL of benzene and reduced in volume to ca. 10 mL to give a brown oil and pale yellow solution. The oil crystallized upon standing overnight. The formed crystals were separated, washed with THF (3 × 10 mL), and dried under vacuum to give 526 mg of crude **8c**·C_6H_6 as green-yellow crystals. Recrystallization from CH_2Cl_2/C_6H_6 afforded analytically pure **8c**·C_6H_6 (482 mg, 0.584 mmol, 80%) as yellow crystals with a green tint. Anal. Calcd for $C_{42}H_{40}ClNO_6PRh$: C, 61.2; H, 4.9; N, 1.7. Found: C, 61.2; H, 4.7; N, 1.6. $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 128 (d, J_{P-Rh} = 209 Hz). ^1H NMR (CD_2Cl_2; δ): 2.1 (d, J = 6.3 Hz, 3H); 2.8 (s, 3H); 3.05 (m, 1H); 5.3 (m, 1H); 6.3 (s, 1H); 7.1−8.2 (m, 25H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ): 14.3 (s, Me); 46.2 (s, Me); 68.1 (d, J_{C-P} = 2.3 Hz, CH); 71.8 (s, CH); 77.1 (s, CH); 110.2 (d, J = 7.5 Hz, Ph); 126.1 (s, Ph); 129.2−138.1 (Ph); 187.1 (dd, J_{C-Rh} = 73 Hz, J_{C-P} = 21 Hz, CO). $^{15}N\{^1H\}$ NMR (1:10 CD_2Cl_2/CH_2Cl_2; δ): −356.7 (d, J_{N-Rh} = 10.5 Hz). IR (KBr; ν_{CO}): 2014 cm^{-1}. $[\alpha]_D^{20}$ = +45.1° (c = 1.35, CH_2Cl_2).

Table 3. Summary of Crystallographic Data for 3a and 8c

	3a	8c
formula	$C_{46}H_{48}ClN_2O_2P_2Rh$	$C_{36}H_{34}ClNO_6PRh$
fw	915.31	746.01
cryst dimens, mm	0.1 × 0.1 × 0.1	0.4 × 0.1 × 0.1
cryst syst	orthorhombic	tetragonal
lattice params		
a (Å)	10.9890(5)	10.6135(4)
b (Å)	19.4833(9)	10.6135(4)
c (Å)	20.1668(9)	34.797(2)
space group	$P2_12_12_1$	$P4_3$
Z	4	4
V, Å^3	4317.8(4)	3919.8(3)
d_{calcd}, g/cm^3	1.291	1.264
T, K	203(2)	204(2)
radiation (λ)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
abs coeff, mm^{-1}	0.568	0.585
transmissn (max/min)	0.801 520/0.609 815	0.928 077/0.778 905
$R(F)$,%[a]	4.07	3.96
$R_w(F^2)$,%[b]	9.55	10.75
GOF	1.058	1.015
Flack param	−0.03(3)	0.02(4)

[a] $R(F) = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $R_w(F^2) = \Sigma[(w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^{1/2}$;

Single-Crystal X-ray Diffraction Study of 3a and 8c. Crystal data and refinement parameters are summarized in Table 3. The crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into a benzene solution of **3a** or of THF into a solution of **8c** in CH_2Cl_2, respectively. The crystals were mounted on glass fibers with viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[22] Systematic absences in the diffraction data and unit cell parameters were consistent uniquely with the reported space group for **8c** and with $P4_1$, $P4_3$, $P4_122$, and $P4_322$ for **3a**. Only the solution in $P4_3$ yielded chemically reasonable and computationally stable results for the refinement of **3a**. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. Refinement of the Flack parameter yielded nil values, indicating that the true hands of the data sets were determined correctly. All non-hydrogen atoms were refined with anisotropic refinement parameters. All hydrogen atoms were treated as idealized contributions. All atomic scattering and anomalous dispersion factors are contained in the SHEXTL 5.1 program library.[23]

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Supporting Information Available: Listings of crystallographic details, atomic parameters, bond distances and angles, and isotropic and anisotropic thermal parameters and ORTEP drawings for **3a** and **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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