Study of the Bonding Properties of the New Ligands $C_5H_3N(2\text{-}R')(6\text{-}CH_2PPhR)$ toward Rhodium(I). Evidence for a Dynamic Competition for Bonding between O- and N-Donor Centers When R = *o*-Anisyl, R′ = Me

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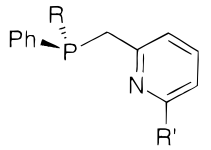
The bonding properties of the optically active chiral-at-P polydentate ligands $C_5H_3N(2\text{-}R')(6\text{-}CH_2PPhR)$ (R = Me, R′ = H, Me; R = *o*-anisyl, R′ = H, Me) and the achiral ligand $C_5H_3N(2\text{-}Me)(6\text{-}CH_2PPh_2)$ toward $(COD)Rh^+$ are reported. The results show that steric hindrance of the 2-position of the pyridyl ring induces a labile character of the Rh−N bond. Moreover, for R = *o*-anisyl and R′ = Me, a dynamic competition for bonding between the N- and O-donating centers is observed. Comparison of the solid state structures of complexes $[Rh(COD)(C_5H_4N(2\text{-}CH_2PPhMe)][BF_4]$ and $[Rh(COD)(C_5H_3N(2\text{-}Me)(6\text{-}CH_2PPh_2)][BF_4]$ shows a significant bond lengthening of the Rh−N bond in the latter complex, consistent with its fluxional behavior observed in solution.

Introduction

Optically active polydentate ligands combining phosphorus and nitrogen donor atoms are a class of ligands of increasing interest for application to enantioselective catalysis due to their efficiency in selected reactions, such as allylic substitution,[1,2] hydroboration of olefins,[3] hydrosilylation,[4,5] or transfer hydrogenation of ketones.[6−8] For these reasons, we are presently exploring new families of such ligands, the chirality center being either the phosphorus atom or a carbon in the hydrocarbon chain associating phosphorus to a pyridine ring.[9]

In this paper, we present the results concerning the study of the bonding properties of the new optically active chiral-at-P phosphines **4** and 2-methyl-6-((diphenylphosphino)methyl)pyridine **5**, shown in Chart 1, toward $[(COD)Rh]^+$. This study reveals the influence of the relative steric crowding around phosphorus and nitrogen on the coordination behavior of these ligands. In addition, a dynamic competition for bonding between two different N and O donor sites has been evidenced in solution for **4bb** associated to $[(COD)Rh]^+$. To the best of our knowledge, this constitutes the first observation of such a phenomenon in complexes containing hemilabile ligands.

Chart 1



R = Me, R' = H (**4aa**)
R = Me, R' = Me (**4ab**)
R = o-anisyl, R' =H (**4ba**)
R = o-anisyl, R' = Me (**4bb**)
R = Ph, R' = Me (**5**)

Results and Discussion

Synthesis of the Ligands. The optically active chiral-at-P phosphines $C_5H_3N(2\text{-}R')(6\text{-}CH_2PPhR)$ (**4aa** R = Me, R′ = H; **4ab** R = Me, R′ = Me; **4ba** R = *o*-anisyl, R′ = H; **4bb** R = *o*-anisyl, R′ = Me) have been synthesized following the quite general procedure developed by Jugé *et al.*[10] The principle of the synthesis is shown in Scheme 1. The starting material is the borane complex of (2*R*,4*S*,5*R*)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxaazaphospholidine, obtained by reaction of (bis(diethylamino)phenyl)phosphine with (−)-ephedrine followed by addition of a borane−dimethylsulfide complex.[10] Reaction with RLi gives the aminophosphine−boranes $H_3B{\cdot}P(Ph)(R)(N(Me)CH(Me)CH(Ph)OH)$ (**1a** R = Me; **1b** R = *o*-anisyl). Subsequent acidic methanolysis affords the alkyl- or arylphenylphosphinite−boranes $H_3B{\cdot}P(Ph)(R)(OMe)$ (**2a** R = Me; **2b** R = *o*-anisyl), and final reaction with $C_5H_3N(2\text{-}R')(6\text{-}CH_2Li)$ gives the phosphine−borane complexes $C_5H_3N(2\text{-}R')(6\text{-}CH_2P(BH_3)\text{-}PhR)$ (**3aa** R = Me, R′ = H; **3ab** R = Me, R′ = Me; **3ba** R = *o*-anisyl, R′ = H; **3bb** R = *o*-anisyl, R′ = Me). The corresponding phosphines **4** are then displaced by morpholine.

The phosphine $C_5H_3N(2\text{-}Me)(6\text{-}CH_2PPh_2)$ (**5**) has been synthesized in 63% yield by reaction of diphenylchlorophosphine with $C_5H_3N(2\text{-}Me)(6\text{-}CH_2Li)$ at low temperature (Scheme 2).

Reactivity of Ligands 4 and 5 toward $[Rh(COD)(THF)_2][BF_4]$. The ligands **4aa** (R = Me, R′ = H) and **4ba** (R = *o*-anisyl, R′ = H) react with $[Rh(COD)(THF)_2]$-

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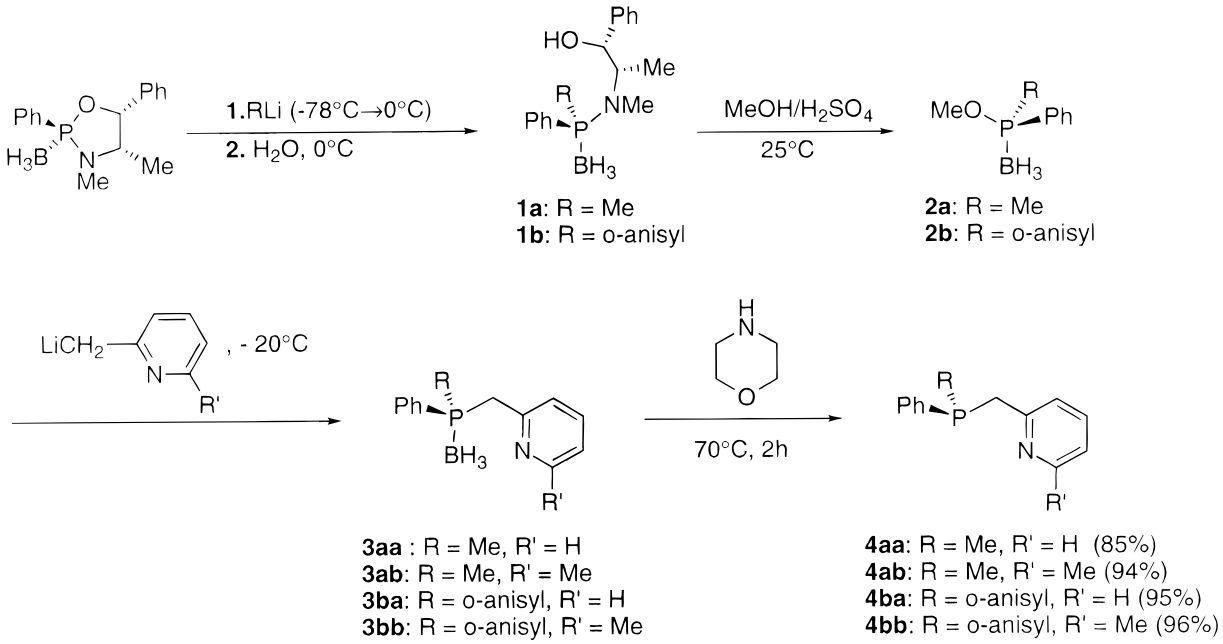
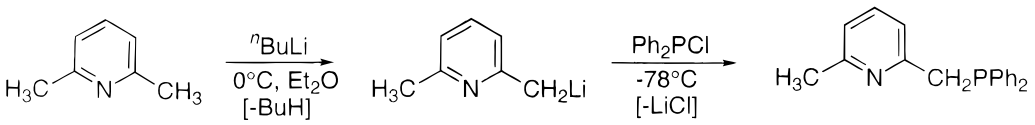
Scheme 1



Scheme 2



[BF_4] to give the complexes [Rh(COD)(**4aa**)][BF_4] (**6aa**) and [Rh(COD)(**4ba**)][BF_4] (**6ba**) in good yields. The complexes **6aa** and **6ba** are characterized by $^{31}P\{^1H\}$ NMR spectroscopy, with a doublet at 29.7 and 39.1 ppm, respectively, and J_{RhP} coupling constants of 152 Hz, typical for $[Rh(COD)(PR_3)_2]^+$ or $[Rh(COD)(P\text{-}N)]^+$-compounds.[11,12] In the ^1H NMR spectra, the olefinic protons in the *trans* position to phosphorus are observed at 5.43 (2H) ppm for both complexes,[13] while those in the *trans* position relative to nitrogen appear at much higher field, at 4.15 (1H) and 3.96 (1H) ppm for **6aa** and 3.83 (2H) ppm for **6ba**. The splitting of the latter type of olefinic protons observable in the case of **6aa** is a consequence of the asymmetry of the phosphorus environment.

The solid state structure of **6aa** has been confirmed by X-ray diffraction. The CAMERON drawing of the structure is shown in Figure 1. Table 1 contains a selection of bond distances and angles of interest. This structure determination has allowed us to establish the S_P configuration for the free ligand **4aa**, as expected from the synthetic method used.[10] The Rh−P and Rh−N bond lengths are in the range usually found in this family of complexes.[14,15] The Rh−C bonds *trans* to phosphorus (average value 2.237 Å) are longer than the Rh−C bonds *trans* to nitrogen (average value 2.128 Å). This phenomenon, attributed to a trans effect of the ligands, has previously been reported for similar complexes.[14,15]

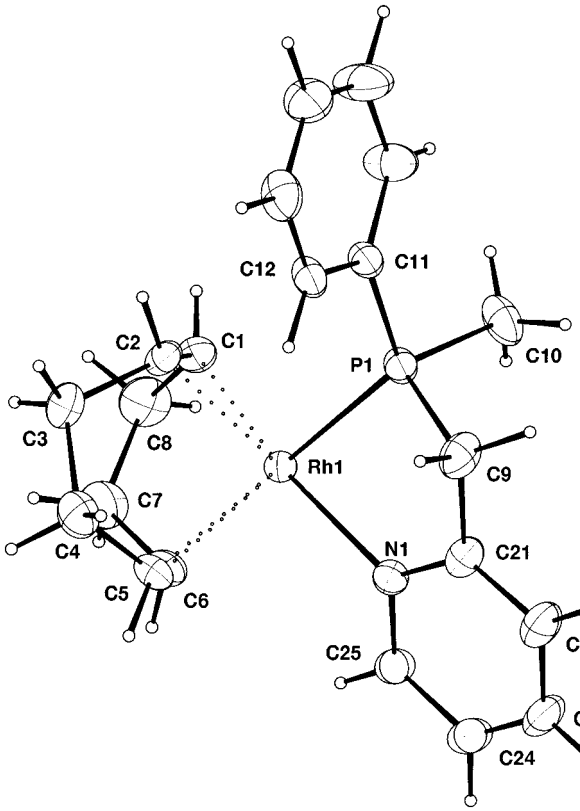


Figure 1. Perspective view of the cationic part of [Rh(COD)(**4aa**)][BF_4] (**6aa**). Ellipsoids are shown at the 50% probability level.

The reaction of **4ab** (R = Me, R′ = Me) with [Rh(COD)$(THF)_2$][BF_4] in a 1:1 ratio is more complex, as the $^{31}P\{^1H\}$ NMR analysis shows the formation of three

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Rh(COD)(4aa)][BF_4] (6aa) and [Rh(COD)(3)][BF_4] (10), with Esd's in Parentheses

	6aa	10
Rh(1)−P(1)	2.255(1)	2.257(2)
Rh(1)−N(1)	2.116(3)	2.200(6)
Rh(1)−C(1)	2.131(4)	2.123(7)
Rh(1)−C(2)	2.138(4)	2,116(7)
Rh(1)−C(5)	2.217(4)	2.273(7)
Rh(1)−C(6)	2.275(4)	2.245(7)
P(1)−C(9)	1.817(4)	1.829(7)
C(9)−C(21)	1.512(6)	1.489(9)
N(1)−C(21)	1.348(5)	1.359(9)
N(1)−C(25)	1.341(5)	1.379(9)
C(1)−C(2)	1.375(7)	1.40(1)
C(1)−C(8)	1.501(7)	1.51(1)
C(2)−C(3)	1.520(6)	1.52(1)
C(3)−C(4)	1.508(6)	1.53(2)
C(4)−C(5)	1.497(7)	1.54(3)
C(5)−C(6)	1.369(7)	1.37(1)
C(6)−C(7)	1.516(7)	1.49(1)
C(7)−C(8)	1.497(7)	1.53(1)
P(1)−Rh(1)−N(1)	81.1(1)	77.5(1)
Rh(1)−P(1)−C(9)	98.9(1)	95.4(2)
Rh(1)−P(1)−C(11)	119.8(1)	118.7(2)
C(9)−P(1)−C(11)	105.8(2)	106.0(3)
Rh(1)−N(1)−C(21)	119.7(3)	113.8(4)
Rh(1)−N(1)−C(25)	123.1(3)	127.9(5)
C(21)−N(1)−C(25)	117.2(3)	118.2(6)

products. Two compounds in approximately the same proportion are observed at 62.5 (J_{RhP} = 170.8 Hz, **7ab**) and 43.3 ppm (J_{RhP} = 149.3 Hz, **8ab**), and a third in trace amount at 18.8 ppm (J_{RhP} = 149.4 Hz, **6ab**). Monitoring of the evolution of the mixture by $^{31}P\{^1H\}$ NMR spectrum shows the slow disappearance of **8ab** and the appearance of **7ab**. Concomitantly, the ^1H NMR spectrum shows the appearance of free 1,5-cyclooctadiene. Considering these observations, we propose the [Rh(**4ab**)$_2$][BF_4] formulation for **7ab**, which is consistent with the observed J_{RhP} value,[16,17] and the [Rh(COD)(**4ab**)$_2$][BF_4] formulation for **8ab**. The latter complex bears two ligands **4ab** η^1-bonded through the phosphorus atoms only. The third product **6ab** is the expected [Rh(COD)(**4ab**)][BF_4] complex, thus formed in very small amount only. Scheme 3 summarizes this analysis.

Comparison of the behavior of ligands **4aa**, **4ba**, and **4ab** shows that the introduction of the methyl group in the 2-position on the pyridyl ring prevents the easy complexation of this ring, favoring the initial coordination of two molecules of **4ab** in an η^1-mode of bonding through the less encumbered phosphorus site. This result prompted us to increase the steric bulk around phosphorus by replacing the methyl group by an aryl group, with the hope of restoring the expected η^2-mode of bonding. The first ligand we investigated is the achiral 2-methyl-6-((diphenylphosphino)methyl)pyridine (**5**).

$^{31}P\{^1H\}$ NMR analysis of the mixture resulting from the reaction of **5** with [Rh(COD)(THF)$_2$][BF_4] shows the formation of two products. The first complex observed in only trace amounts at 66.5 ppm has been formulated as [Rh(**5**)$_2$][BF_4] (**9**) on the basis on the J_{RhP} value of 173.2 Hz. The major complex appears at 49.8 ppm (J_{RhP} = 148.6 Hz). It has been isolated in a pure form and fully characterized as [Rh(COD)(**5**)][BF_4] (**10**). NMR data, however, suggests for the latter complex a nonrigidity phenomenon in solution. Indeed, its ^1H NMR spectrum recorded at room temperature does show the signals due to the complexed phosphine and to the methylenic protons of the 1,5-cyclooctadiene ligand, but the olefinic protons barely appear as a very broad signal approximately centered at 4.5 ppm. Only by lowering the temperature to 223 K could the two signals of the same intensity, characteristic of the olefinic protons in a *trans* position to the phosphorus atom and in a *trans* position to the nitrogen atom, be observed at 5.71 and 3.71 ppm, respectively. The coalescence temperature of these two resonances occurs at 303 K, which correspond to a $\Delta G^{\ddagger}$ value of 14 (± 1) kcal·mol^{-1}.[18] In the same temperature range, only a broadening of the doublet is observed in the $^{31}P\{^1H\}$ NMR spectra. These results are consistent with a reversible opening of the Rh−N bond, leading to an averaging of the olefinic proton environment, as shown in Scheme 4. A similar fluxional process has been invoked for the complex [(COD)Rh{(η^5-C_5H_4(2-C_5H_4N))Fe(η^5-$C_5H_4PPh_2$)}][PF_6] to explain some results of NMR spin-transfer experiments.[15]

An X-ray structure determination of **10** has been undertaken. A CAMERON perspective view of the complex is shown in Figure 2. Table 1 contains a selection of bond distances and angles of interest. Compared to **6aa**, the main structural difference concerns the Rh−N bond distances of 2.203(6) Å for **10** vs 2.116(3) Å for **6aa**. It is very likely that the observed lengthening of the Rh−N bond is due the steric crowding of the methyl group attached to the 2-position of the pyridine ring. It also has consequences on the geometry of the bonded ligands. Indeed, in **6aa**, the C(9) and C(21) atoms are, respectively, at 0.94 and 0.52 Å above the plane defined by Rh(1)−P(1)−N(1), while in **10**, the corresponding carbon atoms lie under the Rh(1)−P(1)−N(1) plane at −1.36 and −1.01 Å. These structural data corroborate our hypothesis of a facile opening of the Rh−N bond deduced from the NMR studies in solution.

It is worth of noting that a long Rh−N bond length of 2.26(3) Å has also been observed for the complex [Rh(NBD){(η^5-C_5H_3(1-CH_2NMe_2)(2-PPh_2))Fe(η^5-C_5H_5)}][PF_6],[14] a complex for which the olefinic protons of the norbornadiene ligand have been found to be equivalent in the room temperature ^1H NMR spectrum.

To summarize, the replacement of the methyl group of **4ab** by a phenyl group on phosphorus in **5** has restored the chelating behavior of this type of ligand. Nevertheless, the steric crowding around the nitrogen donor center likely induces the lability of the Rh−N bond.

Pursuing our investigations, we examined the behavior of 2-methyl-6-[(*S*)-((phenyl)(*o*-anisyl)phosphino)-methyl]pyridine (**4bb**), a ligand which possesses a similar steric crowding around phosphorus as **5** but has another potentially bonding site, the oxygen of the methoxy group. $^{31}P\{^1H\}$ NMR analysis of the reaction of **4bb** with [Rh(COD)(THF)$_2$][BF_4] shows the formation of [Rh(COD)(**4bb**)][BF_4] (**6bb**) only. Again, as for **10**, the ^1H NMR spectrum of **6bb** recorded at 293K (250

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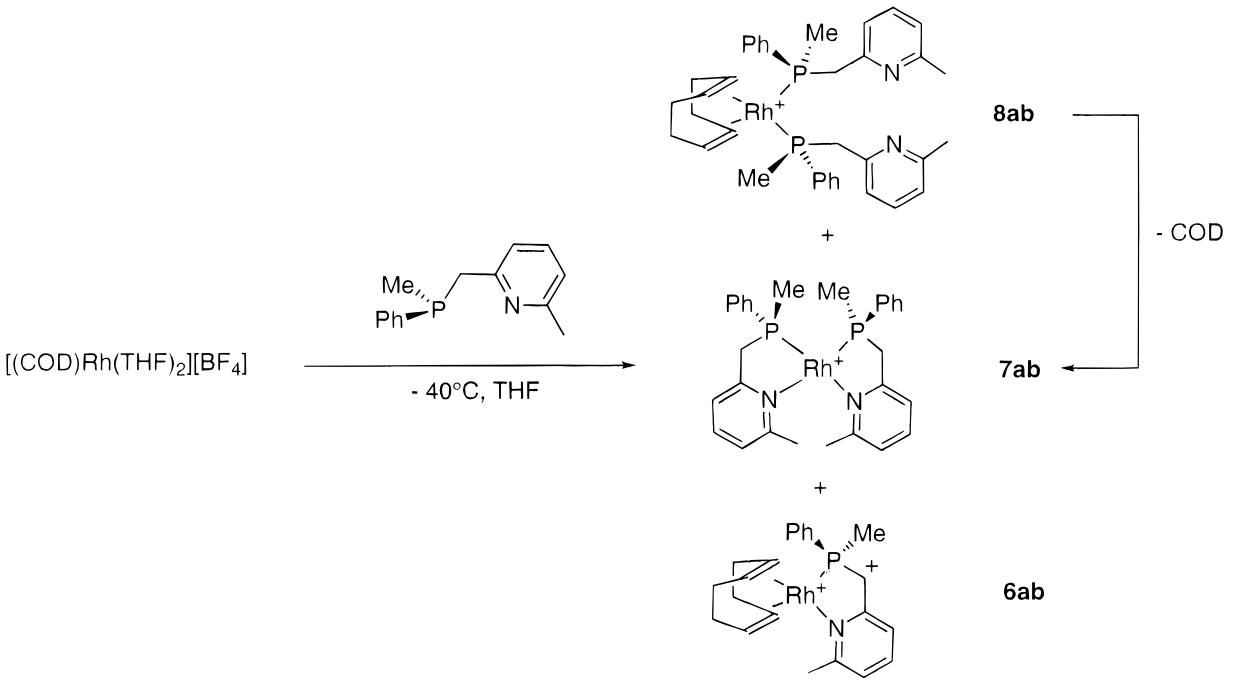
Scheme 3



Scheme 4

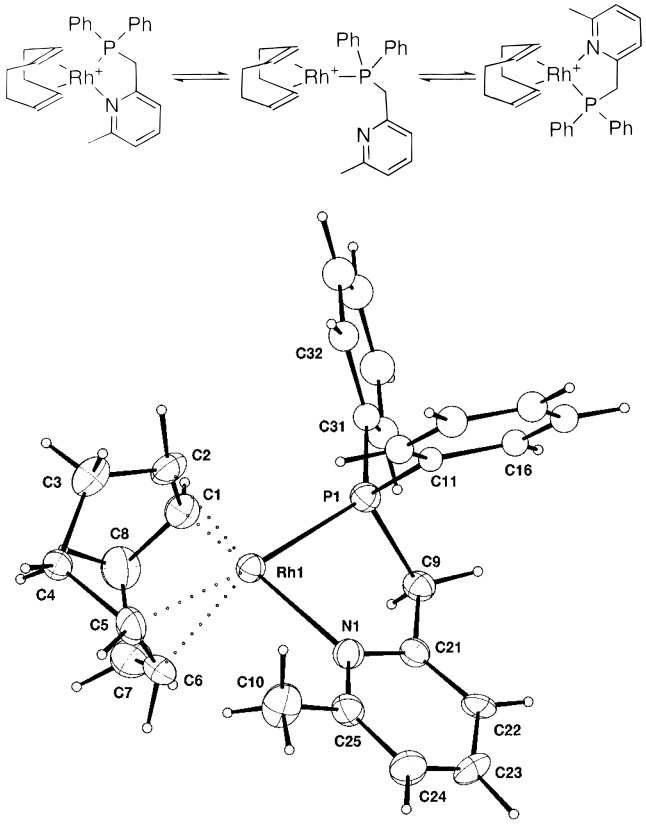


Figure 2. Perspective view of the cationic part of [Rh(COD)(**5**)][BF_4] (**10**). Ellipsoids are shown at the 50% probability level.

MHz) shows, for the 1,5-cyclooctadiene ligands, two complex signals at 2.49 and 2.19 ppm attributable to the methylenic groups and only one broad signal at 4.85 ppm for the ethylenic protons. Variable-temperature ^{1}H NMR experiments have been performed at 400 MHz in CD_2Cl_2 solutions. At 293 K, two broad resonances are observed at 5.45 and 3.97 ppm for the olefinic protons of the 1,5-cyclooctadiene ligand. At 253 K, the 5.45 ppm resonance splits into two signals of unequal intensity at 5.53 and 5.42 ppm. These signals move to 5.82 and 5.44 ppm when the temperature is lowered to 183 K. Changes in the 3.97 ppm region could not be analyzed due to the overlapping resonances of the methylenic group of the phosphine ligand. The most meaningful results concern the evolution of signals due to the methyl group in the 2-position on the pyridine ring and to the methoxy group. For the former, the sharp resonance observed at 2.77 ppm at 293 K broadens at 213 K, then splits into two resonances at 2.86 and 2.57 ppm at 183 K. Concomitantly, the sharp signal due to the methoxy group at 3.67 ppm at 293 K evolves into two broad resonances centered at 3.59 and 3.49 ppm at 183 K. In the same temperature range, the doublet observed at 46.8 ppm (J_{RhP} = 149 Hz) at 293 K in the $^{31}P\{^1H\}$ NMR spectrum splits into two doublets in a 3:2 intensity ratio at 183 K, one somewhat broad resonance at 52.4 ppm (J_{RhP} = 133 Hz) and the other at 42.7 ppm (J_{RhP} = 155 Hz). The coalescence temperature of these two resonances occurs at 243 K, which correspond to a $\Delta G^{\ddagger}$ value of 11 (± 1) kcal·mol^{-1}.[18]

Considering the behavior in solution of complex **10** and now taking into account the existence of an additional O donating site in the ligand **4bb**, a rational explanation of the behavior of the complex [Rh(COD)(**4bb**)][BF_4] (**6bb**) is the presence in solution of an equilibrium between two isomers in which the ligand is either η^2-P,O bound or η^2-P,N bound, as depicted in Scheme 5. Moreover, the results of the variable-temperature NMR studies suggest the former isomer is the major one, as at 183 K the corresponding methoxy and phosphorus resonances remain broad. This observation is not unforeseen as the Rh−O bond is expected to be more labile than the Rh−N one. To the best our knowledge this constitutes the first example of a dynamic competition between two different hemilabile[19] donating centers around the same metallic center.

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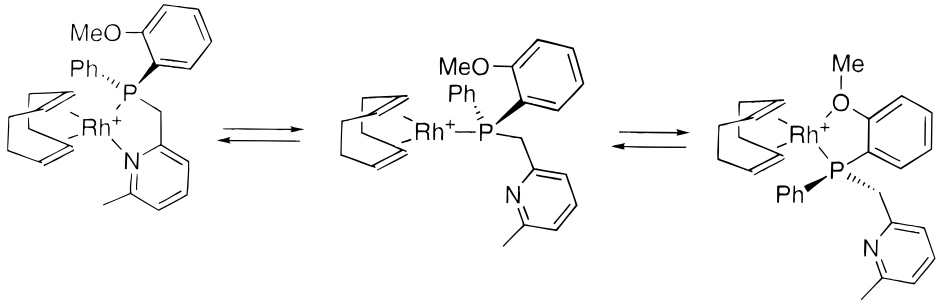
Scheme 5



In conclusion, this report on the bonding properties of the $C_5H_3N(2\text{-}R')(6\text{-}CH_2PPhR)$ ligands toward the $(COD)Rh^+$ entity stresses that an increase of the steric hindrance of the 2-position of the pyridyl ring (R′ = Me vs H) favors the labile character of the Rh−N bond. In that event, an additional potentially hemilabile center (R = *o*-anisyl) is likely to compete for bonding to Rh(I).

Experimental Section

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. The tetrahydrofuran and diethyl ether used for the syntheses were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following standard procedure and stored under nitrogen. NMR spectra were recorded on Bruker AC 200, WM 250, or AMX 400 instruments. Elemental analyses were performed in our laboratory on a Perkin-Elmer 2400 CHN analyzer. Optical rotations were measured with a Perkin Elmer 341 polarimeter using 10 cm cells. (2*R*,4*S*,5*R*)-3,4-Dimethyl-1,3,2-oxaaza-2-phospholidine−borane[10] has been prepared according to published procedures.

General Procedure for the Synthesis of the Aminophosphine−Boranes $H_3B{\cdot}P(Ph)(R)(N(Me)CH(Me)CH(Ph)OH)$ (1; 1a R = Me; 1b R = *o*-Anisyl). To a solution of 1.71 g (6 mmol) of (2*R*,4*S*,5*R*)-3,4-dimethyl-1,3,2-oxaaza-2-phospholidine−borane in 6 mL of THF cooled at −78 °C was slowly added 6.1 mmol of the appropriate RLi reagent (**1a** R = Me; **1b** R = *o*-anisyl). The solution was stirred at −40 °C for 1 h. Hydrolysis was done at 0 °C. After elimination of the solvents, the residue was dissolved in a minimum amount of dichloromethane and purified by chromatography on silica gel, using diethyl ether as eluant. The corresponding aminophosphine−borane **1** was obtained as a white solid after elimination of diethyl ether under vacuum.

1a (80% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.46−7.02 (m, 10H, C_6H_5), 4.65 (d, 1H, C*H*, J_{HH} = 6.9 Hz), 4.01 (m, 1H, C*H*), 2.41 (d, 3H, NCH_3, J_{HP} = 8.5 Hz), 2.10 (s, 1H, O*H*), 1.20 (d, 3H, CH_3, J_{HH} = 6.9 Hz), 1.8−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 66.1 (bm).

1b (93% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.60−6.86 (m, 14H, 2 × C_6H_5 and C_6H_4), 4.88 (d, 1H, C*H*, J_{HH} = 6.9 Hz), 4.32 (m, 1H, C*H*), 3.57 (s, 3H, OCH_3), 2.54 (d, 3H, NCH_3, J_{HP} = 8.1 Hz), 1.22 (d, 3H, CH_3, J_{HH} = 6.9 Hz), 0.3−2.0 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 69.1 (bm).

General Procedure for the Synthesis of Alkyl- and Arylphenylphosphinite−Boranes $H_3B{\cdot}P(Ph)(R)(OMe)$ (2; 2a R = Me, 2b R = *o*-anisyl). One molar equivalent of sulfuric acid was added to a 0.125 M solution of the appropriate aminophosphine−borane **1** in anhydrous methanol. The solution was stirred overnight, then filtered on a short column of silica gel to eliminate the acid in excess. The solvents were evaporated under vacuum, and the residue was extracted by dichloromethane and purified by chromatography. The corresponding alkyl- and arylphenylphosphinite−borane **2** was obtained as a colorless liquid after removal of the solvent under vacuum.

2a (80% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.81−7.44 (m, 5H, C_6H_5), 3.53 (d, 3H, OCH_3, J_{HP} = 12.1 Hz),1.68 (d, 3H, CH_3, J_{HP} = 9.2 Hz), 0.8 (dq, 3H, BH_3, J_{HP} = 14 Hz, J_{HB} = 97 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 113.3 (q, J_{PB} = 67 Hz). Anal. Calcd for $C_8H_{14}BO$: C, 57.2; H, 8.4. Found: C, 56.94; H, 8.28.

2b (80% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.84−6.84 (m, 9H, C_6H_5 and C_6H_4), 3.73 (d, 3H, OCH_3, J_{HP} = 12 Hz), 3.62 (s, 3H, CH_3), 1.8−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 106.2 (q, J_{PB} = 81 Hz). Anal. Calcd for $C_{14}H_{18}BO_2P$: C, 64.65; H, 6.98. Found: C, 64.94; H, 7.08.

General Procedure for the Synthesis of Phosphine−Borane $C_5H_3N(2\text{-}R')(6\text{-}CH_2P(BH_3)PhR)$ (3; 3aa R = Me, R′ = H; 3ab R = Me, R′ = Me; 3ba R = *o*-anisyl, R′ = H; 3bb R = *o*-anisyl, R′ = Me). To a solution of 5.94 mmol of 2-picoline (**3aa**, **3ba** R′ = H) or 2,6-lutidine (**4ab**, **4bb** R′ = Me) in 3 mL of diethyl ether was slowly added 1 molar equiv of ^{n}BuLi (3.7 mL of a 1.6 M hexane solution) at 0 °C, and the mixture was stirred for 1 h. The resulting solution was slowly added to a solution of 2.97 mmol of the appropriate alkyl- or arylphenylphosphinite−borane **2** dissolved in 3 mL of THF at −20 °C. The mixture was stirred at −20 °C for an additional 15 min, then at 0 °C for 1 h. Hydrolysis was done at room temperature by adding a minimum amount of water. After elimination of the solvents under vacuum, the residue was purified by chromatography on silica gel using a diethyl ether/hexanes mixture as eluent. The corresponding phosphine−borane complex **3** was obtained as an oil after elimination of the solvents.

3aa (77% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (m, 1H, C_5H_4N), 7.58−6.85 (m, 8H, C_6H_5 and C_5H_4N), 3.38 (d, 2H, PCH_2, J_{HP} = 11.1 Hz), 1.55 (d, 3H, PCH_3, J_{HP} = 10.1 Hz), 1.5−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 11.5 (q, J_{PB} = 52 Hz).

3ab (70% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.63−6.74 (m, 8H, C_6H_5 and C_5H_3N), 3.34 (d, 2H, PCH_2, J_{HP} = 10.9 Hz), 2.44 (s, 3H, CH_3), 1.58 (d, 3H, PCH_3, J_{HP} = 10.2 Hz), 1.7−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 18.0 (q, J_{PB} = 68 Hz).

3ba (70% yield): ^{1}H **NMR** ($CDCl_3$) δ 8.35 (m, 1H, C_5H_4N), 7.85−6.83 (m, 12H, C_6H_5, C_6H_4, and C_5H_4N), 4.01 (AB(X), 2H, PCH_2, $J_{H_aH_b}$ = 13.5 Hz, J_{H_aP} = 13.9 Hz, J_{H_bP} = 12.6 Hz), 3.70 (s, 3H, CH_3), 2.1−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 17.0 (q, J_{PB} = 52 Hz).

3bb (55% yield): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.79−6.84 (m, 12H, C_6H_5, C_6H_4 and C_5H_3N), 4.00 (AB(X), 2H, PCH_2, $J_{H_aH_b}$ = 13.2 Hz, J_{H_aP} = 15.7 Hz, J_{H_bP} = 13.5 Hz), 3.71 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3), 2.1−0.2 (m, 3H, BH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.01 MHz): δ 17.6 (m).

General Procedure for the Synthesis of the Phosphine $C_5H_3N(2\text{-}R')(6\text{-}CH_2$ P(Ph)(R)) (4; 4aa R = Me, R′ = H; 4ab R = Me, R′ = Me; 4ba R = *o*-Anisyl, R′ = H; 4bb R = *o*-Anisyl, R′ = Me). The appropriate phosphine−borane **3** (2−6 mmol scale) was dissolved in morpholine (10 mL) and heated under reflux for 2 h at 70 °C. After the reaction mixture was cooled, the excess morpholine was eliminated under vacuum and the residue was treated with a pentane/water mixture to eliminate most of the morpholine−borane

Table 2. Crystal Data, Data Collection, and Refinement Parameters for Complexes 6aa and 10

	compound **6aa**	compound **10**
	Crystal Data	
chemical formula	$C_{21}H_{26}BF_4NPRh$	$C_{27}H_{30}BF_4NPRh$
molecular weight	512.37	589.22
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a (Å)	14.506(1)	10.780(1)
b (Å)	10.148(1)	14.603(2)
c (Å)	14.734(2)	16.959(3)
V (Å^3)	2169.0(5)	2590.5(8)
Z	4	4
ρ_{calcd} (g·cm^{-3})	1.57	1.51
no. of reflns for cell params	25	25
range for cell parameters (deg)	12−14	12−14
μ (mm^{-1})	8.86	7.52
F_{000}	1034.05	1195.52
	Data Collection	
data collection method	$\omega/2\theta$	$\omega/2\theta$
no. of indep reflns	6769	1905
no. of obsd reflns	5160	1729
obs criterion	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$
θ_{max} (deg)	23	23
range of hkl	0 g h g 20 −14 g k g 14 0 g l g 20	0 g h g11 0 g k g 16 −18 g l g 18
scan range θ (deg)	0.9 + 0.35 tan θ	0.8 + 0.35 tan θ
	Refinement	
R	0.0348	0.0406
R_w	0.0351	0.0398
abs corr	ψ-scans method	ψ-scans method
min/max corr	0.789−1.100	0.918−0.998
weighting scheme	Chebyshev	unit weights
coeff Ar	0.696, −0.624, 0.431 −0.302, 0.0377	
Flack's parameter	0.01(4)	
gof[a]	1.197	2.36
no. of reflns used	5160	1729
no. of params refined	299	256
residual electron density (e·Å^{-3})	−1.21 (min), 6.48 (max)	−1.76 (min), 0.82 (max)

[a] Goodness of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

complex formed. The phosphine, which stays in the pentane phase, was purified by chromatography on silica gel.

4aa (85% yield): $[\alpha]_D = -103°$ ($c = 2.48$, C_6H_6). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.47 (m, 1H, C_5H_4N), 6.91−7.54 (m, 8H, C_6H_5 and C_5H_4N), 3.20 (ABX, 2H, PCH_2, $J_{H_aH_b} = 13.0$ Hz, $J_{H_aP} = 2.2$ Hz, $J_{H_bP} = 0.0$ Hz), 1.26 (d, 3H, PCH_3, $J_{HP} = 5.1$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −29.4 (s). Anal. Calcd for $C_{13}H_{14}NP$: C, 72.53; H, 6.57; N, 6.50. Found: C, 72.62; H, 6.75; N, 6.41.

4ab (94% yield): $[\alpha]_D = -104°$ ($c = 1.65$, C_6H_6). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.65−7.49 (m, 8H, C_6H_5 and C_5H_3N), 3.23 (ABX, 2H, PCH_2, $J_{H_aH_b} = 12.9$ Hz, $J_{H_aP} = 1.7$ Hz, $J_{H_bP} = 0.0$ Hz), 2.49 (s, 3H, CH_3), 1.36 (d, 3H, PCH_3, $J_{HP} = 3.9$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −29.1 (s).Anal. Calcd for $C_{14}H_{16}NP$: C, 73.35; H, 7.23; N, 6.11. Found: C, 73.15; H, 7.35; N, 6.08.

4ba (95% yield): $[\alpha]_D = +61.4°$ ($c = 0.7$, C_6H_6). ^{1}H NMR ($CDCl_3$): δ 8.44 (m, 1H, C_5H_4N), 7.49−6.78 (m, 12H, C_6H_5, C_6H_4, and C_5H_4N), 3.60 (AB, 2H, PCH_2, $J_{H_aH_b} = 13.2$ Hz), 3.66 (s, OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.2 (s). Anal. Calcd for $C_{19}H_{18}NOP$: C, 74.24; H, 5.92; N, 4.56. Found: C, 74.01; H, 5.97; N, 4.51.

4bb (96% yield): $[\alpha]_D = +56°$ ($c = 0.57$, C_6H_6). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.49−6.77 (m, 12H, C_6H_5, C_6H_4, and C_5H_3N), 3.60 (AB, 2H, PCH_2, $J_{H_aH_b} = 13.4$ Hz), 3.65 (s, OCH_3), 2.46 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −20.0 (s). Anal. Calcd for $C_{20}H_{20}NOP$: C, 74.75; H, 6.29; N, 4.36. Found: C, 74.28; H, 6.50; N, 4.08.

Synthesis of 2-Methyl-6-((diphenylphosphino)methyl)-pyridine (5). To a solution of 5.2 mL (45 mmol) of 2,6-lutidine in 15 mL of diethyl ether at 0 °C was added 30 mL of a 1.6 M solution of ^{n}BuLi in hexane (48 mmol). The solution was stirred for 1 h at 0 °C and then added at −78 °C to a solution of 8.1 mL (45 mmol) of PPh_2Cl in 130 mL of diethyl ether. The reaction mixture was stirred for 1 h at low temperature, then the cooling bath was removed to allow the reaction mixture to warm up slowly to room temperature. The solvents were eliminated under vacuum, and the residue was distilled under vacuum, giving **3** as a pale yellow liquid (bp 190−195 °C at 10^{-1} mmHg) in 63% yield.

3: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50−7.25 (m, 11H, C_6H_5 and C_5H_3N), 6.87 (d, 1H, $J_{HH} = 7.8$ Hz, C_5H_3N), 6.72 (d, 1H, $J_{HH} = 7.8$ Hz, C_5H_3N), 3.60 (s, 2H, PCH_2), 2.48 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ −10.6. Anal. Calcd for $C_{19}H_{18}NP$: C, 78.33; H, 6.23; N, 4.81. Found : C, 78.12; H, 6.03; N, 4.42.

Synthesis of Complexes [Rh(COD)(4)][BF$_4$] (6) and [Rh(COD)(5)][BF$_4$] (10). General Procedure. To a solution of 0.2 g of $[Rh(COD)Cl]_2$ (0.4 mmol) in 10 mL of THF was added at room temperature 0.16 g of $AgBF_4$ (0.8 mmol). The mixture was stirred for 30 min. The solution of $[Rh(COD)(THF)_2][BF_4]$ thus formed was filtered to eliminate AgCl and cooled to −40 °C. To this was slowly added a solution of the appropriate phosphine (0.8 mmol) in THF (5 mL). After the reaction mixture was stirred for 1 h, 50 mL of diethyl ether were added to precipitate the complexes. They were recrystallized from a dichloromethane/diethyl ether mixture.

[Rh(COD)(**4aa**)][BF_4] (**6aa**) (yellow solid, 75% yield): ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 8.12−7.31 (m, 9H, C_6H_5 and C_5H_4N), 5.43 (m, 2H, COD), 4.15 (m, 1H, COD), 3.96 (m, 1H, COD), 3.94 (AB(X), 2H, PCH_2, $J_{H_aH_b} = 17.0$ Hz, $J_{H_aP} = 12.2$ Hz, $J_{H_bP} = 10.6$ Hz), 2.7−2.1 (m, 8H, COD), 1.77 (dd, 3H, CH_3, $J_{HRh} = 1.2$ Hz, $J_{HP} = 10.0$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 29.7 (d, $J_{PRh} = 150.7$ Hz). Anal. Calcd for $C_{21}H_{26}BF_4NPRh$: C, 49.16; H, 5.11; N, 2.73. Found: C, 48.82; H, 4.90; N, 2.43.

[Rh(COD)(**4ba**)][BF_4] (**6ba**) (yellow solid, 81% yield): ^{1}H NMR ($CDCl_3$) δ 8.08−6.92 (m, 13H, C_6H_5, C_6H_4, and C_5H_4N), 5.43 (s, 2H, COD), 4.32 (AB(X), 2H, PCH_2, $J_{H_aH_b} = 16.7$ Hz, $J_{H_aP} = 12.4$ Hz, $J_{H_bP} = 11.5$ Hz), 3.83 (s, 2H, COD), 3.75 (s, 3H, OCH_3), 2.58−2.21 (m, 8H, COD). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.1 (d, $J_{RhP} = 152.4$). Anal. Calcd for $C_{27}H_{30}BF_4NOPRh$: C, 53.57; H, 5.01; N, 2.31. Found: C, 53.64; H, 5.11; N, 2.40.

[Rh(COD)(**4ab**)][BF_4] (**6ab**) (orange solid, 80% yield): ^{1}H NMR (CD_2Cl_2, 250 MHz, 273 K) δ 7.69−6.88 (m, 13H, C_6H_5 and C_6H_3N), 5.31 (b, 4H, COD), 4.54 (AB(X), 2H, PCH_2, $J_{H_aH_b} = 16.1$ Hz, $J_{H_aP} = 10.82$ Hz, $J_{H_bP} = 9.3$ Hz), 3.63 (s, 3H, OCH_3), 2.71 (s, 3H, CH_3), 2.57, 2.12 (m, 8H, COD). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.250 MHz, 273 K): δ 45.7 (d, $J_{PRh} = 149.6$ Hz). Anal. Calcd for $C_{28}H_{32}BF_4NOPRh$: C, 54.31; H, 5.21; N, 2.26. Found: C, 54.24; H, 5.10; N, 2.32.

[Rh(COD)(**5**)][BF_4] (**10**) (orange solid, 85% yield): ^{1}H NMR ($CDCl_3$, 200 MHz, 263 K) δ 8.58−8.04 (m, 13H, C_6H_5 and C_6H_3N), 6.55 (s, 2H, COD), 5.45 (d, 2H, CH_2, $J_{HP} = 9.8$ Hz), 4.56 (s, 2H, COD), 3.58 (s, 3H, CH_3), 3.36−2.90 (m, 8H, COD). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.01 MHz): δ 49.9 (d, $J_{PRh} = 148.4$ Hz). Anal. Calcd for $C_{27}H_{30}BF_4NPRh$: C, 55.04; H, 5.13; N, 2.38. Found: C, 54.94; H, 5.12; N, 2.27.

X-ray Crystallographic Analysis of 6aa and 10. Crystals of **6aa** and **10** suitable for X-ray diffraction were obtained through recrystallization from diethyl ether/methanol in the cold. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C. Cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° < 2θ(Mo Kα_1) < 28°. The space group was determined by careful examination of systematic extinctions in the listing of the measured reflections.

All calculations were performed on a PC-compatible computer. Data reductions were carried out using the RC93

program.[20] Full crystallographic data are given in Table 2. The structures were solved by using the SIR92 program,[21] which revealed the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses by using the CRYSTALS program.[22,23] The BF_4 counteranion in the structure of **6aa** has been found to be disordered. The best fit has been obtained considering two possible orientations of the anion around the boron atom. Each position has been refined with a structure occupancy factor of 0.66 and 0.33, respectively. However, a relatively large residual electron density remains in the vicinity of the BF_4 anion ($x = -0.1845$, $y = 0.4941$, $z = -0.0617$), which lead to the anormal value of the maximun of the residual electron density shown in Table 2 (6.48 e·Å^{-3}). The least-square refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and the calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - (\Delta F/6\sigma(F_o)^2]^2$, where $w' = 1/\sum_1^n A_r T_r(x)$ with a variable number of coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$, where x was $F_c/F_c(\max)$.[24] Models reached convergence with $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$ having the values given in Table 2. Atomic scattering factors were taken from the usual tabulations.[25] Anomalous dispersion terms for Rh, Cl, and P atoms were included in F_c.[26] All non-hydrogen atoms were allowed to vibrate anisotropically except the carbon atoms of the phenyl rings in the structure of **10**, which have been refined with isotropic temperature factors. For both structures, all of the hydrogen atoms were set in idealized positions (C−H = 0.99 Å). The absolute configuration of **6aa** was determined by refining the Flack's enantiopole parameter,[27] which is defined as $F_o^2 = (1 - x)F(h)^2 + xF(-h)^2$. The x value given in Table 2 agrees with the absolute configuration expected from the synthetic route.

Supporting Information Available: Tables of final values of all refined atomic coordinates, calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **6aa** and **10** (9 pages). Ordering information is given on any current masthead page.

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