Wide-Bite-Angle Diphosphinines: Design, Synthesis, and Coordination Properties

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A wide-bite-angle diphosphinine ligand has been designed and synthesized, which exhibits structural features for a preferred formation of trans complexes. Due to the linear orientation of the lone-pair electrons of the phosphorus donors in combination with an appropriate P−P distance, trans coordination toward a Rh center was observed and the corresponding LRh(CO)I complex could be characterized crystallographically. Although typical reactivities usually observed for trans complexes were found, reaction of the diphosphinine with the cis-enforcing precursor $[Rh(nbd)_2]BF_4$ did result in the formation of several species at low temperature, to which cis-structures were attributed.

Introduction

The design and synthesis of diphosphine ligands which are exclusively trans-coordinating is a challenging research topic. Especially the evaluation of catalytic properties of such ligands deviating from the standard cis chelation has been an intriguing and rewarding research goal for many years.[1a] Only a limited number of P ligands are known that enforce trans coordination toward a transition-metal center.[1] Among these are the TRANSphos ligand introduced by Venanzi[2] and the TRAP ligand developed by Ito.[3] However, these ligands later appeared to be rather flexible and it was found that cis complexes are accessible as well.

Recently, we introduced a putative trans-coordinating ligand based on a spirobichroman backbone, the so-called SPANphos system.[4] True trans coordination was observed in several Pt, Pd, and Rh complexes and confirmed by ^{1}H and ^{31}P NMR spectroscopy as well as by X-ray diffraction. Lately, however, we observed that SPANphos also forms compounds of the type $[Rh(nbd)(SPANphos)]BF_4$, in which both norbornadiene and SPANphos act as cis chelating ligands.[5] DFT calculations indicated that the energies of cis and trans complexes of SPANphos might differ only by 4–10 kcal mol^{-1} and thus the cis-directing influence of norbornadiene suffices to form cis complexes.[5,6] Furthermore, it is worth mentioning that the orientation of the lone pair at the phosphorus atoms is as important as the P−P distance and this aspect of ligand design has so far mainly been neglected; if within a certain backbone conformation the orientation of the lone pairs does not comply with the trans configuration of the metal, a slight distortion leads just as easily to a cis complex.

During the course of investigations on functionalized phosphinines (phosphabenzenes, phosphorins)[7] we started to consider the possibility whether bidentate phosphinines might be more suitable candidates for the synthesis of exclusively trans-coordinating ligands toward a transition-metal center, compared to phosphines. In fact, these unique heterocycles exhibit remarkable structural (as well as electronic) features: the orientation of the phosphinine lone-pair electrons, responsible for σ-coordination, is significantly different from the situation in standard phosphines. While a pyramidal geometry is present in the latter species,[8] the formally sp^2-hybridized phosphorus atom in phosphinines shows an angle of approximately 120°

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(8) In (SPANphos)Rh(CO)Cl the corresponding angle is 108.65°.

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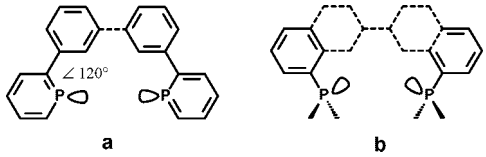


Figure 1. Large -bite-angle bidentate phosphorus based ligands: (**a**) trans-chelating bis-phosphinine ligands; (**b**) non-trans-chelating diphosphine ligand.

with the α-carbon atoms.[7b,9] This structural element of phosphinines in comparison to phosphines should in principle allow a simpler design of trans-chelating phosphorus ligands. As a matter of fact, analogues of bipyridine capable of coordinating in a trans fashion toward a metal center have been reported before, but their phosphorus homologues have remained unknown.[10] However, in combination with an appropriate aryl-based ligand backbone that locates the phosphorus atoms at the appropriate distance, the two lone pairs are expected to point in a linear way to one another (Figure 1, **a**), thus resulting in the ideal case in a true trans coordination with a P−M−P angle of 180° in which both P−P distance and lone-pair orientation contribute to this coordination mode. This ideal situation could in principle be achieved also with bidentate phosphine-based ligands, but due to the sp^3 hybridization of the phosphorus atoms, it would require a more elaborate backbone design or the orientation of the lone pairs would deviate from the ideal geometry (Figure 1, **b**).

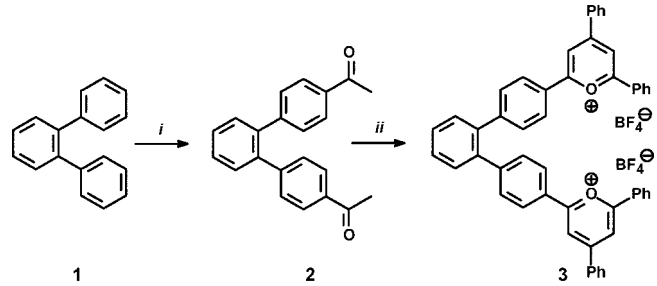
We report here on the design and preparation of a wide-bite-angle diphosphinine ligand containing an *o*-terphenyl backbone and its coordination properties toward Rh. This design exhibits special structural properties that are beneficial for the preferred formation of trans isomers: the right P−P distance as well as the most favorite orientation of the phosphorus lone pairs as a consequence of the sp^2 hybridization of all carbon and phosphorus atoms within the molecule.

Results and Discussion

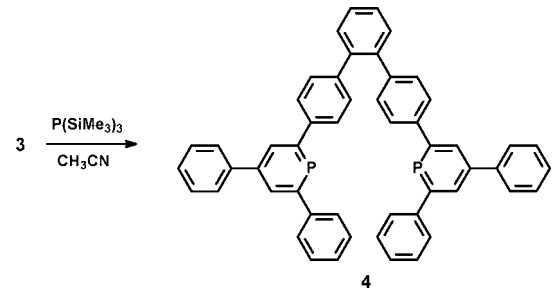
We chose the original and modular synthetic route toward phosphinines reported by Märkl et al. in the late 1960s[11] for the preparation of a bidentate diphosphinine, depicted in Figure 1. It should be mentioned here that a few bidentate diphosphinines have been reported in the literature before, but molecular modeling shows that these compounds are rather flexible and consequently not suitable for trans-only coordination.[12]

Selective double Friedel–Crafts acylation of *o*-terphenyl (**1**) with acetyl chloride in the presence of $AlCl_3$ afforded 4,4′-diacetyl-*o*-terphenyl (**2**) in high yields.[13] Subsequent reaction

Scheme 1. Synthesis of the Bis-Pyrylium Salt 3



Scheme 2. Synthesis of Bis-Phosphinine 4



of **2** with 4 equiv of the chalcone 1,3-diphenyl-2-propen-1-one and $HBF_4 \cdot Et_2O$ lead to the bis-pyrylium salt **3**, which was obtained as a red solid (Scheme 1).

The pyrylium salt **3** was further converted into the corresponding diphosphinine **4** by reaction with $P(SiMe_3)_3$[14] in acetonitrile (Scheme 2). Phosphinine **4** was obtained as a yellow solid and characterized by means of NMR spectroscopy and elemental analysis as well as mass spectrometry. It shows a single resonance at δ 184.3 ppm (C_6D_6) in the $^{31}P\{^1H\}$ spectrum, which is characteristic of an aromatic six-membered heterocycle.[11] In the ^1H NMR of **4** the pseudodoublet at δ 8.00 ppm with a coupling constant of $^3J_{H-P} = 4.4$ Hz is indicative of protons at the 3,5-positions of the phosphorus heterocycle, and these were identified with the help of ^1H-coupled ^{31}P NMR spectroscopy.

The calculated distance between the two phosphorus donors in **4** in its most stable conformation (4.64 Å, MM2) further suggests the preferred formation of trans complexes. Thus, upon reaction of 2 equiv of **4** with the rhodium(I) dimer $[Rh(CO)_2Cl]_2$, the formation of the single species (PP)Rh(CO)Cl was observed by NMR spectroscopy. This compound shows a doublet in the $^{31}P\{^1H\}$ spectrum at δ 164.2 ppm ($J_{P-Rh} = 173.0$ Hz, $CDCl_3$), which is indicative of the presence of the trans complex **5**(Figure 2).

Compound **5** was further characterized by means of IR spectroscopy, in order to compare the electronic properties of the phosphinine heterocycle with other phosphorus-containing ligands. The CO stretching frequency $\tilde{\nu}_{CO}$ in **5** was detected at

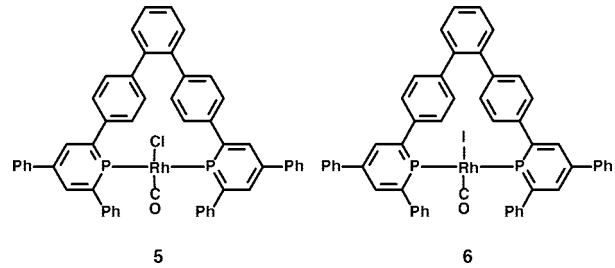


Figure 2. Rhodium complexes **5** and **6**.

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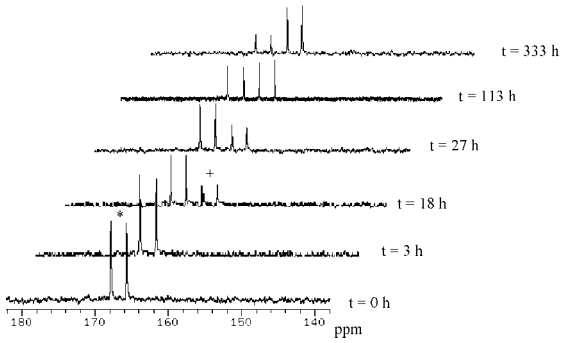


Figure 3. Reaction of **5** with MeI (8 equiv) in dichloromethane at room temperature, monitored by ^{31}P NMR spectroscopy: (*) Rh complex **5**; (+) Rh complex **6**.

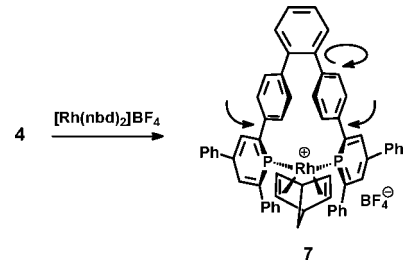
1992 cm^{-1}, suggesting that the electronic properties of **4** are in fact closer to those of phosphines than to those of phosphites (P[O(2-*t*-BuC$_6$H$_4$)]$_3$ $\tilde{\nu}_{CO}$ 2013 cm^{-1} and PPh$_3$ $\tilde{\nu}_{CO}$ 1978 cm^{-1} in L$_2$RhCl(CO) complexes[15]). In the ^{13}C NMR spectrum of **5** the corresponding signal of the CO ligand was observed as a multiplet at δ 183.5 ppm. Similar results have been reported by Breit et al. on monodentate triarylphosphinine/Rh(CO)Cl complexes.[16]

In order to obtain further information on the coordination preference of ligand **4**, the reactivity of **5** toward MeI was investigated. Treatment of **5** with MeI (8 equiv) did not result in any oxidative addition but only in slow halogen metathesis at room temperature. The corresponding (PP)Rh(CO)I complex **6** was observed by ^{31}P NMR spectroscopy as the only species formed (δ 162.0 ppm, J_{P-Rh} = 165.9 Hz; Figure 3). This conversion is completed within 18 h at T = 60 °C and excess MeI (140 equiv). Compound **6** was independently and quantitatively prepared by reaction of **4** with $^1/_2$ equiv of [Rh(CO)$_2$I]$_2$[17] in CH$_2$Cl$_2$. These results are in agreement with earlier observations that *trans*-[Rh(SPANphos)(CO)Cl] complexes do not undergo oxidative additions either[4b] and confirms that compound **5** is a monomeric Rh complex containing a trans-spanning ligand which does not isomerize to the cis form in solution (which would in fact lead to MeI oxidative addition).[18]

From the reaction of **5** with excess MeI, yellow crystals suitable for X-ray diffraction were obtained. Compound **6** crystallizes in the triclinic space group *P*1 (No. 1) with three independent molecules in the asymmetric unit. The molecular structure (see the Supporting Information) confirms halogen exchange and indeed the presence of the monomeric Rh complex **6**, containing the trans-spanning diphosphinine ligand **4**. Because the structure is pseudocentrosymmetric (Rh, P, and I atoms), strong restraints were introduced to obtain a stable refinement, with the consequence that bond lengths and angles can unfortunately not be discussed adequately here.

The above results, although they clearly demonstrate the capability of ligand **4** to form preferentially trans complexes, do not disprove that **4** cannot form cis complexes under more cis-enforcing circumstances, as complexes of structure **5** or **6** would also form trans complexes with monodentate ligands.[19] As is the case with SPANphos, the metal fragment Rh(nbd)$^+$ provides a more stringent yardstick.[5] Thus, treatment of **4** with 1 equiv of [Rh(nbd)$_2$]BF$_4$ at room temperature did not result in the formation of any defined species according to ^{31}P NMR spectroscopy, while SPANphos did quantitatively give cis complexes under these reaction conditions (vide infra).

Scheme 3. Reaction of 4 with [Rh(nbd)$_2$]BF$_4$[a]



[a] Only a symmetric conformer is illustrated for clarity.

However, upon cooling the NMR tube to T = 240 K we did observe the presence of several Rh(**4**) species, such as compound **7** (Scheme 3). At least three different ABX patterns could be distinguished in the ^{31}P NMR spectrum, which were identified by means of NMR correlation experiments (see the Supporting Information). The low values of the corresponding P−P coupling constants of $^2J_{P-P'}$ = 53–61 Hz are in agreement with two different phosphorus atoms in relative cis positions (coupling constants of $^2J_{P-P}$ = 300–400 Hz are expected for two different phosphorus atoms in relative trans positions[4b]). The observed patterns reflect a reduced symmetry of the formed species in comparison to the trans complexes **5** and **6**, most likely due to a distorted ligand backbone in order to accommodate an "unnatural" cis coordination. Additional analysis of the mixture of compounds **7** by means of mass spectrometry further indicates the presence of monomeric Rh species of the type Rh(**4**)(nbd)$^+$ (*m*/*z* 917; [M − BF$_4$]$^+$). However, further investigations by means of (low-temperature) ^{31}P DOSY NMR spectroscopy, size-exclusion chromatography (GPC), vapor pressure osmometry (VPO), and differential scanning calorimetry (DSC) did not give any further insight into the nature of the observed Rh$^+$ species, although elemental analysis of the obtained orange powder is consistent with Rh complexes of the expected composition.[20] We attribute this unexpected coordination mode of ligand **4** to the flexibility of the *o*-terphenyl backbone. To confirm this, we performed an MM2 analysis[21] of the fragment Rh(**4**), and results are illustrated in Figure 4.

The MM2 analysis reveals that apart of the conformation leading to the trans complex, which represents the most stable one, other conformations are accessible without a significant increase of the total energy (3 kcal). Compressing of the ligand structure, along with rotation of the aryl moieties, can indeed

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(19) For a Rh(CO)Cl complex containing a trans-coordinating monodentate phosphinine, see ref 16.

(20) For compound **7** a composition was found which is consistent with the empirical formula C$_{59}$H$_{44}$BF$_4$P$_2$Rh·CH$_2$Cl$_2$·Et$_2$O. Substitution of the second norbornadiene ligand by an additional bidentate phosphinine to form a species of the composition Rh(**4**)$_2$BF$_4$ would lead to a much higher carbon content (76.8%). Furthermore, the presence of a potential bis-chelate to form Rh(**4**)$_2$BF$_4$ is rather unlikely, since free ligand is observed in the ^{31}P NMR spectrum upon reaction of Rh(nbd)$_2$BF$_4$ with excess bis-phosphinine **4**.

(21) Molecular mechanics calculations were performed using CAChe Worksystem Pro, version 6.1.1, from Fujitsu, using augmented MM2 force field parameters.

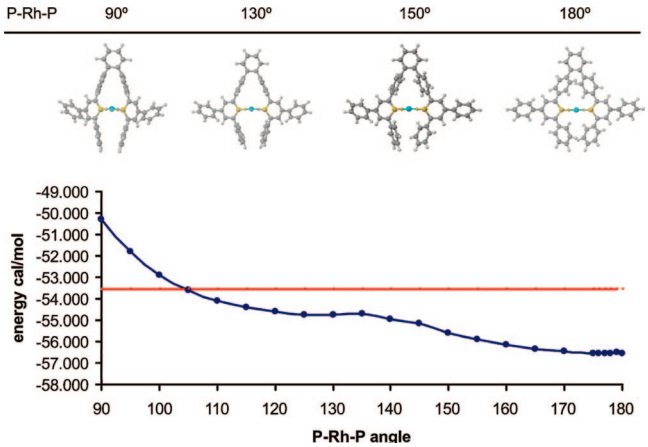

Figure 4. Potential energy diagram for the fragment Rh(**4**). The 3 kcal mol^{-1} over minimum energy threshold is marked as a straight line.

lead to a shorter P−P distance and formation of narrower bite angle species (Scheme 3).

Conclusions

In summary, we have designed and synthesized successfully a diphosphinine ligand that exhibits important structural features for the preferred formation of trans complexes. Due to the linear orientation of the lone-pair electrons of the phosphorus donors in combination with an appropriate P−P distance, trans coordination toward a Rh center and typical reactivities were observed. Yet, in this most favorable case up to now, the final test with the cis-enforcing precursor $[Rh(nbd)_2]BF_4$ did result in the formation of several species at low temperature to which unsymmetrical cis structures could be attributed. Consequently, embedding the two phosphinine units into a rigid aryl backbone should lead to an optimal structure and the development of truly trans-spanning diphosphinines. Current investigations carried out in our laboratories are thus focusing on bidentate diphosphinines with reduced flexibility of the backbone and their impact on homogeneous catalysis.[7,16,22]

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere, using modified Schlenk techniques, or in a Braun glovebox unless otherwise stated. All glassware was dried prior to use by heating under vacuum. All common solvents and chemicals were commercially available and were purchased from Aldrich Chemical Co. $P(SiMe_3)_3$,[14] 4,4′-diacetyl-*o*-terphenyl,[13] $[Rh(CO)_2I]_2$,[17] and 1,3-diphenyl-2-propen-1-one[23] were prepared according to the literature. The Rh precursors were obtained as a generous gift from Umicore AG & Co. Kg (Germany). MeI was degassed using the freeze–pump–thaw method. The solvents were taken from custom-made solvent purification columns filled with Al_2O_3. The elemental analyses were obtained from H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany, or were performed on a Perkin-Elmer 2400 Series II CHNSO analyzer at the Department of Chemical Engineering and Chemistry (TU/e). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian Mercury 200 and 400 and Bruker 500 spectrometers, and all chemical shifts are reported relative to the residual proton resonance in the deuterated solvents or referenced to an 85% aqueous solution of H_3PO_4. Mass spectra were either run by MALDI-TOF on a Bruker Autoflex spectrometer or by electrospray impact on a Waters LCT Premier spectrometer.

Bis-Pyrylium Salt 3. Tetrafluoroboric acid (52% ethereal solution, 8.04 g, 49 mmol) was added at 70 °C to a solution of 3.88 g (12.34 mmol) of 4,4′-diacetyl-*o*-terphenyl and 10.2 g (49 mmol) of 1,3-diphenyl-2-propen-1-one in 20 mL of 1,2-dichloroethane. The mixture was heated for 2 h and was subsequently cooled to room temperature. The red precipitate was filtered off, and the bis-pyrylium salt was obtained as a dark red solid after recrystallization from hot acetonitrile. Yield: 2.1 g (2.42 mmol), 20%. ^{1}H NMR (DMSO-d_6): δ (ppm) 7.67 (m, 8H), 7.73 (m, 8H), 7.82 (m, 4H), 8.54 (m, 12H, terphenyl H), 9.11 (s, 4H, heteroarom H). ^{13}C NMR (DMSO-d_6): δ (ppm) 115.5, 129.2, 129.5, 130.3, 130.4, 131.4, 131.6, 132.9, 135.5, 135.7, 139.0, 147.9, 165.3, 169.9, 170.4. ^{19}F NMR (DMSO-d_6): δ (ppm) −148.2, −148.3 (1:3). Anal. Calcd for $C_{52}H_{36}B_2F_8O_2$ (M_r = 866.46): C, 72.08; H, 4.19. Found: C, 72.45; H, 4.15.

Terphenyl Bis-Phosphinine 4. A 2.6 g (10.4 mmol) amount of $P(SiMe_3)_3$ was added dropwise at room temperature to a stirred solution of 2.2 g (2.54 mmol) of **3**, dissolved in 25 mL of acetonitrile. The resulting black reaction mixture was heated to T = 85 °C and refluxed for 8 h. Stirring was continued for 12 h at room temperature, and subsequently all volatiles were removed under vacuum. The resulting brown solid was chromatographed with petroleum ether/ethyl acetate (4:1), affording **4** as a yellow solid. Yield: 400 mg (0.55 mmol, 22%). ^{1}H NMR (C_6D_6): δ (ppm) 7.11–7.42 (m, 24H), 7.58 (m, 8H, terphenyl H), 8.00 (d, $^3J_{H-P}$ = 4.4 Hz, 4H, heteroarom H). ^{13}C NMR ($CDCl_3$): δ (ppm) 124.2, 124.6, 127.1, 127.4, 127.6, 127.8, 127.9, 128.3, 128.7, 128.9, 129.0, 129.9, 130.5, 130.8 (m), 131.7 (m), 140.0, 141.5, 141.9 (2 × d, J_{C-P} = 21.9, 23.0 Hz), 143.4, 144.1 (2 × d, J_{C-P} = 24.1, 13.8 Hz), 171.1, 171.6 (2 × d, J_{C-P} = 51.4, 51.8 Hz, C4). ^{31}P NMR (C_6D_6): δ (ppm) 184.2. Anal. Calcd for $C_{52}H_{36}P_2$ (M_r = 722.81): C, 86.41; H, 5.02. Found: C, 86.21; H, 5.12. Single mass analysis for $C_{52}H_{36}P_2$: m/z 761.1945 (M + K).

(PP)Rh(CO)Cl (5). A mixture of **4** (100.0 mg, 0.14 mmol) and $[Rh(CO)_2Cl]_2$ (27.0 mg, 0.07 mmol) was cooled to T = −40 °C, and CH_2Cl_2 (2.5 mL) was slowly added. The dark orange solution was slowly warmed to room temperature and subsequently filtered over Al_2O_3 (neutral)/Celite. Compound **5** was obtained as an orange solid after evaporating the solvent. Yield: 88.0 mg (1.0 mmol, 71%). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.16 (d, J_{H-H} = 9.3 Hz, 4H), 7.31 (d, J_{H-H} = 9.7 Hz, 2H), 7.33 (d, J_{H-H} = 9.7 Hz, 2H), 7.48–7.51 (m, 6H), 7.55–7.59 (m, 6H), 7.70 (m, 2H), 7.76 (d, J_{H-H} = 7.4 Hz, 6H), 7.85 (d, J_{H-H} = 7.7 Hz, 4H), 8.31 (pseudo-t, J_{H-H}, J_{P-H} = 10.8 Hz, 2H, heteroarom H), 8.36 (pseudo-t, J_{H-H}, J_{P-H} = 10.9 Hz, 2H, heteroarom H). ^{13}C NMR (CD_2Cl_2): δ (ppm) 127.7 (CH), 127.9 (CH), 128.0, 128.1, 128.3 (CH), 128.4 (CH), 128.7, 128.8 (CH), 128.9, 129.0, 129.1 (CH), 129.3, 130.5 (d, J_{CP} = 47.7 Hz, CH), 135.8 (heteroarom CH), 136.4 (heteroarom CH), 139.1, 139.2, 140.5, 140.6, 141.1, 141.3, 141.8, 142.2, 163.1, 183.5 (m, CO). ^{31}P NMR (CD_2Cl_2): δ (ppm) 166.6 (d, J_{P-Rh} = 173.1 Hz). Yellow-orange crystals of **5** are obtained by slow crystallization from CH_2Cl_2 at low temperature. Anal. Calcd for $C_{53}H_{36}ClOP_2Rh$ (M_r = 889.17): C, 71.59; H, 4.08. Found: C, 71.71; H, 4.38.

Reaction of 5 with MeI. To a solution of **5**, prepared from **4** (30 mg, 0.042 mmol) and $[Rh(CO)_2Cl]_2$ (8.0 mg, 0.021 mmol), in CH_2Cl_2 (0.8 mL) was added MeI (48 mg, 0.34 mmol, 8 equiv) at room temperature. The halogen metathesis under formation of **6** was recorded by means of ^{31}P NMR spectroscopy over a period of

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14 days. ^{31}P NMR (CH_2Cl_2) for **6**: δ (ppm) 162.0 ppm (d, J_{P-Rh} = 165.9 Hz). The transformation of **5** (40 mg, 0.045 mmol) is completed within 18 h at T = 60 °C with 140 equiv of MeI (0.4 mL, 0.9 g, 6.4 mmol). Yellow needles of **6** are formed by slow crystallization from CH_2Cl_2 at low temperature. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.05–7.15, 7.22–7.62, 7.65–7.80 (3 × m, 32H, arom H), 8.30 (q, 4H, J_{H-P} = 10.6 Hz, J_{H-Rh} = 20.3 Hz, heteroarom H). ^{13}C NMR ($CDCl_3$): δ (ppm) 126.4, 127.1, 127.8, 128.3, 128.8, 129.1, 130.2, 130.5, 135.8, 136.6, 139.1, 140.0, 140.6, 141.1, 141.4, 141.7, 142.0, 143.0, 161.7. ^{31}P NMR (CD_2Cl_2): δ (ppm) 159.2 (d, J_{P-Rh} = 165.9 Hz). Anal. Calcd for $C_{53}H_{36}IOP_2Rh$ (M_r = 980.63): C, 64.92; H, 3.69. Found: C, 65.25; H, 4.04. Compound **6** was independently characterized by ^{31}P NMR spectroscopy by reaction of $[Rh(CO)_2I]_2$ (8.0 mg, 0.014 mmol) with **4** (20.0 mg, 0.028 mmol) in CH_2Cl_2 (0.5 mL), leading quantitatively to the complex (**4**)Rh(CO)I.

Reaction of 3 with Rh(nbd)BF$_4$ (Compounds 7). $[Rh(nbd)_2]BF_4$ (20.0 mg, 0.053mmol) and **4** (38.7 mg 0.053 mmol) were dissolved in 10 mL of distilled CH_2Cl_2, and the solution was stirred for 1 h. Evaporation of the solvent rendered quantitatively the mixture of compounds **7** as an orange powder after washing with Et_2O. Attempts to obtain crystals from the resulting solutions were unsuccessful. Different techniques (see the Supporting Information) have been applied in an effort to elucidate the nuclearity of compounds **7**. ^{31}P NMR (202.46 MHz, CD_2Cl_2, 298 K): δ (ppm) 179 (br), 173–163 (br), 155 (br). ^{31}P NMR (202.46 MHz, CD_2Cl_2, 240 K): δ (ppm) 178.57 (dd, $^1J_{Rh-P_a}$ = 183.4 Hz, $^2J_{P_b}-P_a$ = 53.3 Hz, P_a), 171.71 ($^1J_{Rh-P_c}$ = 174.9 Hz, $^2J_{Pd-P_c}$ = 59.0 Hz, P_c), 170–164 (m), 164.02 ($^1J_{Rh-P_d}$ = 174.9 Hz, $^2J_{P_d}-P_c$ = 59.0 Hz, P_d), 155.65 (dd, $^1J_{Rh-P_b}$ = 172.4 Hz, $^2J_{P_a}-P_b$ = 53.3 Hz, P_b). Anal. Calcd for $C_{59}H_{44}BF_4P_2Rh$ (M_r = 1004.65): C, 70.54; H, 4.41. Found: C, 66.03; H, 5.31. This composition is consistent with the empirical formula $C_{59}H_{44}BF_4P_2Rh \cdot CH_2Cl_2 \cdot Et_2O$ (C, 66.06; H, 4.85). MS (MALDI+ve): m/z 917 $(M - BF_4)^+$.

Molecular Mechanics Calculations. Molecular mechanics calculations have been performed using augmented MM2 force field parameters, as implemented in CAChe v. 6.1.1 (for a detailed list of parameters used in the calculations see the Supporting Information). Minimum energy conformations have been located by using a block diagonal Newton–Raphson algorithm with a convergence criterion of 0.001 kcal mol^{-1}.

To find the minimum energy conformation of the ligand coordinated to a metal, only the fragment ligand−Rh has been evaluated. The hybridization of the metal center has been defined as "unconfigured" in order to avoid having the P−Rh−P bending contribute to the energy balance. A global minimum has been located at a bite angle of 179°.

The potential energy at different bite angles has been calculated to estimate the strain energy of the ligand on chelation at different bite angles.[24] The fragments ligand−Rh have been minimized containing locked P−Rh−P angles at different values (but still neglecting this bending contribution to the total energy; see the Supporting information).

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Supporting Information Available: Text, figures, and tables giving details of the single crystal X-ray diffraction study of compound **6**, attempts to characterize compounds **7**, and parameters used for the MM calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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