2496 *Organometallics* **1996,** *15,* 2496−2503

Interconversion between Zwitterionic and Cationic Rhodium(I) Complexes of Demonstrated Value as Catalysts in Hydroformylation, Silylformylation, and Hydrogenation Reactions. Dynamic $^{31}P\{^1H\}$ NMR Studies of $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ and $[Rh(DPPB)_2]^+BPh_4^-$ in Solution

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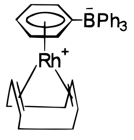
Received February 14, 1996[⊗]

Treatment of an orange solution of $[Rh(COD)(DPPB)]^+BF_4^-$ (**2**) in MeOH with 2 equiv of $NaBPh_4$ at room temperature (RT) afforded an orange precipitate, $[Rh(COD)(DPPB)]^+BPh_4^-$ (**3**), in 94% yield. Reaction of the cationic rhodium complex **3** with H_2 under ambient conditions in CH_2Cl_2 for 1 h gave the zwitterionic complex $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) in quantitative yield. Although **3** is stable in the solid state, it has the propensity in solution to convert to the zwitterionic complexes $(\eta^6\text{-}PhBPh_3)^-Rh^+(COD)$ (**1**) and $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) along with a small amount of $[Rh_x(DPPB)_{2x}]^{x+}[BPh_4^-]_x$. Addition of 1, 2, and 4 equiv of DPPB to the CD_2Cl_2 solution of $(\eta^6\text{-}PhBPh_3)^-Rh^+(NBD)$ (**6**) under N_2 resulted in the formation of $[Rh(NBD)(DPPB)]^+BPh_4^-$ (**7**) and $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) in ratios of 90/10, 57/43, and 0/100, respectively, while addition of 2 equiv of DPPB to the CD_2Cl_2 solution of **6**, under an atmosphere of H_2 at RT, gave **4** and **5** in an ratio of 35/65. "Slowed" η^6-$PhBPh_3^-$ rotation about the $(\eta^6\text{-}PhBPh_3)^-{-}Rh$ bond axis in $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) was established by a variable-temperature $^{31}P\{^1H\}$ NMR study. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) along with the low-temperature $^{31}P\{^1H\}$ COSY and EXSY NMR spectra demonstrated the presence of an equilibrium between $[Rh(DPPB)_2]^+$ (**5α**) and $[Rh(DPPB)(\mu\text{-}DPPB)]_2^{2+}$ (**5β**).

The zwitterionic rhodium complex **1**[1] is an effective and versatile catalyst for a variety of carbonylation reactions.[2−9] This complex, either by itself or in the presence of 1,4-bis(diphenylphosphino)butane (DPPB), can effect the highly regioselective hydroformylation of aryl and 1,1-disubstituted alkenes,[2,3] allyl acetates,[6] vinyl ethers,[2] vinylsilanes,[8] and vinyl sulfones and sulfoxides,[7] as well as α,β-unsaturated esters.[4,9] Complex **1** is also an excellent catalyst for the inter- and intramolecular silylformylation of alkynes.[10,11] Moderate yields of acids can be realized by the carbonylation of benzylic and allylic bromides with **1** under phase-transfer conditions.[12] Amines are isolated, usually in high yield, by the hydrogenation of imines catalyzed by **1** and DPPB.[13] Both cationic[6] and zwitterionic[12] intermediates have been proposed as key catalytic species in these reactions, and it was considered important to investigate the solution behavior of the zwitterionic $(\eta^6\text{-}PhBPh_3)^-Rh^+(diene)_n(DPPB)_{1-n}$ and the cationic $[Rh(diene)_n(DPPB)_{2-n}]^+BPh_4^-$ ($n = 0, 1$) complexes, in order to gain insight into the reactions catalyzed by **1** (with or without DPPB). Herein we report the preparation and demonstrate the facile interconversion of these rhodium complexes. The fluxionality of $(\eta^6\text{-}PhBPh_3)^-$-$Rh^+(DPPB)$ and $[Rh(DPPB)_2]^+BPh_4^-$ complexes is also demonstrated by variable-temperature $^{31}P\{^1H\}$ NMR spectra, which provide a detailed understanding of the solution behavior of these complexes.



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Results and Discussion

Preparation and Interconversion of η^6-$PhBPh_3$-Coordinated and Cationic Rhodium Complexes. Treatment of a clear orange solution of $[Rh(COD)(DPPB)]^+BF_4^-$ (**2**) with 2 equiv of $NaBPh_4$ in MeOH at room temperature (RT) afforded, in 94% yield, the orange complex $[Rh(COD)(DPPB)]^+BPh_4^-$ (**3**), which was characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. Its ^1H and $^{13}C\{^1H\}$ NMR spectra were essentially those of the cation

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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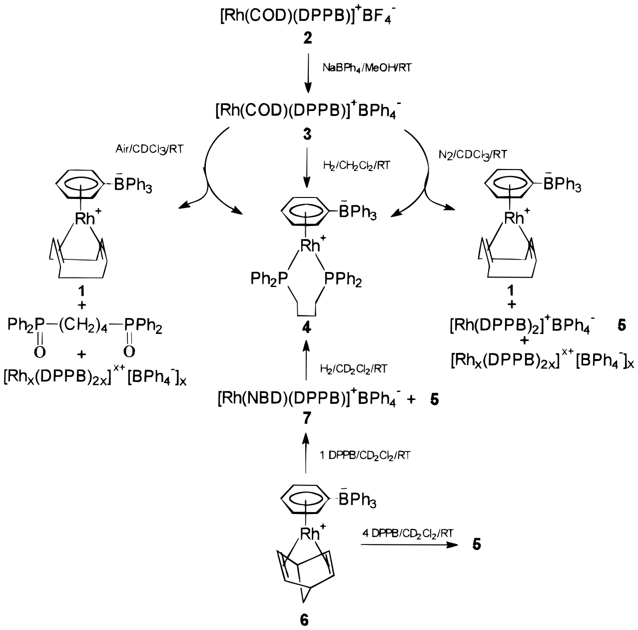
S0276-7333(96)00112-4 CCC: $12.00

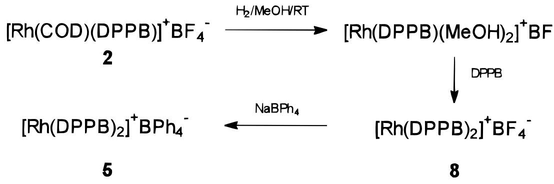
Scheme 1



of complex **2** and the BPh_4^- anion. The $^{31}P\{^1H\}$ spectrum showed a doublet at $\delta = 24.6$ ppm with $^1J_{Rh-P} = 143$ Hz. Complex **3**, soluble in $CHCl_3$, CH_2Cl_2, acetone, and THF but insoluble in MeOH and in hexane, is stable in the solid state. In solution, however, **3** has the propensity to convert to the zwitterionic complexes $(\eta^6\text{-}PhBPh_3)^-Rh^+(COD)$ (**1**) and $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**). When **3** was dissolved in $CDCl_3$ and allowed to stand in air for 7 days, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the solution indicated complete conversion of **3** to **1, 4**, and 1,4-bis(diphenylphosphino)butane dioxide ($\delta(^{31}P\{^1H\})$ 32.0 (s) ppm), along with some unidentified $[Rh_x(DPPB)_{2x}]^{x+}$ species (**4**/DPPB dioxide/$[Rh_x(DPPB)_{2x}]^{x+}$ = 32/42/26). Similar observations were made previously when an acetone solution of $[Rh(COD)(PPh_3)_2)]^+BPh_4^-$ [14] or $[Rh(P(OR)_3)_5]^+BPh_4^-$ [15] was exposed to air. When a $CDCl_3$ solution of **3** was kept under N_2 at room temperature for 6 days, **4** was also formed as the major product together with **1** and some phosphine-coordinated rhodium complexes (**4**/$[Rh_x(DPPB)_{2x}]^{x+}$ = 51/49), one of which was $[Rh(DPPB)_2]^+BPh_4^-$, (**5**; cf. Scheme 1 and discussion below). The complexity of ^1H NMR spectra of the solution in both the aerobic and anaerobic systems prevented us from determining the ratio of **1** and **4**. In both cases free 1,5-cyclooctadiene was detected by GC.

Reaction of complex **3** with H_2 at ambient pressure and temperature, in CH_2Cl_2 for 1 h, quantitatively afforded the zwitterionic complex $(\eta^6\text{-}PhBPh_3)^-Rh^+$(DPPB) (**4**) as deep red prismatic crystals and cyclooctane (cf. Scheme 1). This complex is soluble in CH_2Cl_2 and THF and partially soluble in $CHCl_3$. The η^6-$PhBPh_3$ coordination in **4** is clearly demonstrated by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. As observed in analogous complexes,[15-19] all protons and carbons on η^6-*Ph*BPh_3 show significantly high-field shifts compared to their noncoordinated analogs. The ^1H NMR *meta*, *ortho*, and *para* resonances of η^6-*Ph*BPh_3 appear well separated at δ 4.95, 5.63, and 6.81 ppm, respectively. The $^{13}C\{^1H\}$ spectrum of **4** possesses four signals at δ 98.01, 103.30, 106.41, and 153.50 (m) ppm, respectively, which are assigned to the coordinated η^6-*Ph*BPh_3. The $^{31}P\{^1H\}$ doublet of coordinated DPPB in **4** moves downfield to $\delta = 38.7$ ppm ($^1J_{Rh-P} = 200$ Hz), compared to that in the cationic complex **3** ($\delta = 24.6$ ppm, $^1J_{Rh-P} = 143$ Hz).

Scheme 2



The low solubility of $(\eta^6\text{-}PhBPh_3)^-Rh^+(COD)$ (**1**) in any solvent at RT prevented an NMR investigation of its reactivity. Thus, the closely related complex $(\eta^6\text{-}PhBPh_3)^-Rh^+(NBD)$ (**6**)[1] was prepared, followed by addition of 1 equiv of DPPB to a CD_2Cl_2 solution of **6** under N_2, affording $[Rh(NBD)(DPPB)]^+BPh_4^-$ (**7**). After the complete consumption of DPPB (in 60 min, as judged by ^1H and ^{31}P NMR), 90% of **6** was converted to **7** (δ-($^{31}P\{^1H\}$) 27.5 ppm, $^1J_{Rh-P} = 153$ Hz) and $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) (a broad band at $\delta(^{31}P\{^1H\})$ 21.3 ppm, **7**/**5** = 9/1). Bubbling H_2 through a CD_2Cl_2 solution of **7** for 1 h resulted in complete conversion to the zwitterionic complex $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) and norbornane. Reaction of 2 equiv of DPPB with **6** in CD_2Cl_2 at RT under N_2, for 150 min, resulted in the formation of **7** and **5** in the ratio of 57/43, while addition of 2 equiv of DPPB to the CD_2Cl_2 solution of **6** under 1 atm of H_2 at RT for 150 min gave **4** and **5** in the ratio of 35/65. Addition of 4 equiv of DPPB to the CD_2Cl_2 solution of **6** under N_2 at RT afforded complex **5**, quantitatively, in 60 min (cf. Scheme 1). The composition of $[Rh(DPPB)_2]^+BPh_4^-$, (**5**) was confirmed by the isolation of analytically pure compound via an independent route.

Hydrogenation of $[Rh(COD)(DPPB)]^+BF_4^-$ (**2**) in MeOH at RT (20 min) followed by the addition of 1 equiv of DPPB in CH_2Cl_2 afforded the known cationic complex $[Rh(DPPB)_2]^+BF_4^-$ (**8**)[20-23] as an orange-red solid, after removal of volatiles under vacuum. Addition of 4 equiv of $NaBPh_4$ (in MeOH) to the clear MeOH solution of **8** afforded the orange-red $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) in 99% yield (cf. Scheme 2). Interestingly, about 15% of **5** was converted to the zwitterionic $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) and DPPB, after a THF or CH_2Cl_2 solution of **5** was heated to 40 °C for 2 h.

Reaction of $(\eta^6\text{-}PhBPh_3)^-Rh^+(NBD)$ (**6**) with 200 psi/200 psi of H_2/CO at room temperature in CD_2Cl_2 or CH_2Cl_2 afforded a very air-sensitive red solution containing rhodium carbonyl complexes, $[Rh_x(CO)_y]^{z+}[BPh_4^-]_z$ (**9**), and aldehydes ($\delta(^1H)$ 10.01, 9.67, 9.64 ppm, $\delta(^{13}C\{^1H\})$ 202.7, 202.4, 192.7 ppm , $\nu(C{=}O) = 1717$ cm^{-1}). This solution possesses three strong infrared ν(CO) bands at

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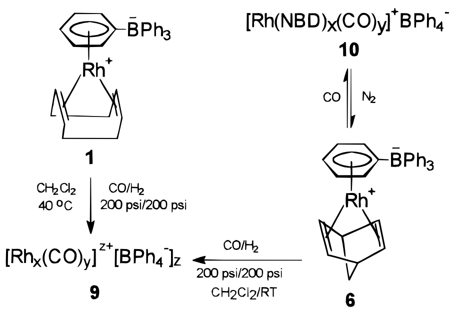
Scheme 3

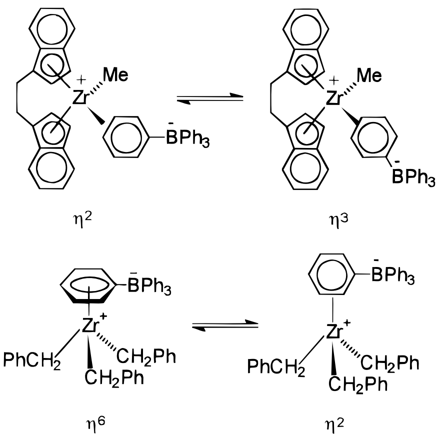


2072, 2042, and 1875 cm^{-1}, respectively, suggesting the existence of both terminal and bridging CO in the solution.[24] A similar solution resulted from the reaction of (η^6-PhBPh$_3$)$^-$Rh$^+$(COD) (**1**) with 200 psi/200 psi of H$_2$/CO at 40 °C for 24 h. Attempts to isolate these carbonyl complexes, however, failed. Bubbling CO through the solution of complex **6** for 2 h at RT resulted in the color changing from pale yellow to orange-red. An infrared spectrum of this solution showed three strong carbonyl stretching bands at 2076, 2051, and 1975 cm^{-1}, respectively, while the ^{1}H NMR spectrum indicated the presence of a large amount of **6**. Passing N$_2$ through the above solution at RT for 1 h resulted in bleaching of the above solution and the disapearance of ν(CO) bands from the IR spectrum, indicating the presence of a reversible process between complex **6** and [Rh(NBD)$_x$(CO)$_y$]$^+$BPh$_4^-$ (**10**; cf. Scheme 3). Similar observations were obtained after complex **6** was exposed to 200 psi of CO for 20 min and then to 1 atm of N$_2$. Treatment of (η^6-PhBPh$_3$)$^-$Rh$^+$(NBD) (**6**) with H$_2$ (no DPPB or CO) gave rhodium black.

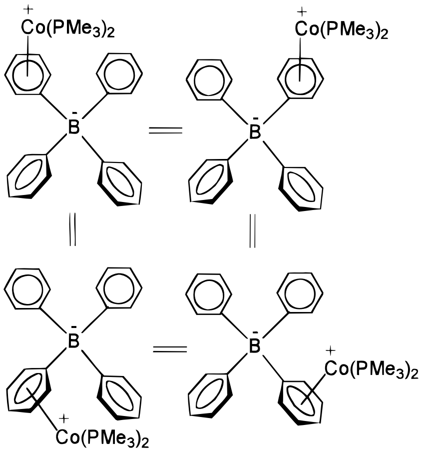
Fluxionality of (η^6-PhBPh$_3$)$^-$Rh$^+$(DPPB) (4). The conformational preferences and dynamic behavior of η^6-arene complexes have been subjects of longstanding interest to theoretical and experimental chemists.[25−31] The rotation of an ML$_n$ fragment around the η^6-arene−M bond axis is a well-known dynamic process and the rotational barrier is usually very low,[25,26,28,29] unless exceptional steric[32] and/or electronic[33] factors exist. In the latter case, this dynamic process has been unequivocally shown to be "slowed" on the NMR time scale at accessible temperatures.[31]

The fluxionality of η-tetraphenylborate−metal complexes has been previously demonstrated by NMR experiments.[19,34−37] These include the observations of hapticity exchange, with a phenyl ring of BPh$_4^-$ being coordinated to zirconium in an $\eta^2 \rightleftarrows \eta^3$ fashion in Cp′$_2$Zr$^+$Me(BPh$_4^-$) (Cp′$_2$ = 1,1′-(CH$_2$)$_2$(indenyl)$_2$)[35] or an $\eta^2 \rightleftarrows \eta^6$ fashion in (η-PhBPh$_3$)$^-$Zr$^+$(CH$_2$Ph)$_3$ (cf. Scheme 4),[36] and of the ethylene proton exchange in {[(C$_2$H$_4$)$_2$Rh(η^6-Ph)]$_2$BPh$_2$}$^+$[O$_3$SCF$_3$]$^-$.[19] Another interesting and unexplained "complicated exchange process"[37] is worth noting. The crystal structure of Co(PMe$_3$)$_2$BPh$_4$ clearly shows one phenyl ring η^6-coordinated to cobalt with a mirror plane bisecting the two PMe$_3$ ligands.[37] The fluxionality of this molecule, however, in CD$_2$Cl$_2$ resulted in the disappearance of the PMe$_3$ signal in the ^{31}P{^{1}H} spectrum and of all phenyl resonances in the ^{13}C{^{1}H} spectrum of (η^6-PhBPh$_3$)$^-$Co$^+$(PMe$_3$)$_2$, as well as an ill-resolved ^{1}H NMR spectrum at 295 K. At 183 K, a singlet appeared at 8.3 ppm in the ^{31}P{^{1}H} spectrum and a well-resolved ^{13}C{^{1}H} spectrum along with a partially resolved ^{1}H spectrum were observed.[37] These observations are in agreement with the Co(PMe$_3$)$_2$ moiety "creeping" among the four phenyl rings as shown in Scheme 5. So far, no "slowed" η^6-PhBPh$_3$ rotation about the η^6-PhBPh$_3$−ML$_n$ bond axis has been described in the literature, although many η^6-PhBPh$_3$−ML$_n$ complexes have been isolated and characterized by crystallographic and/or spectroscopic methods.[15−19,34,37−47]

Scheme 4



Scheme 5



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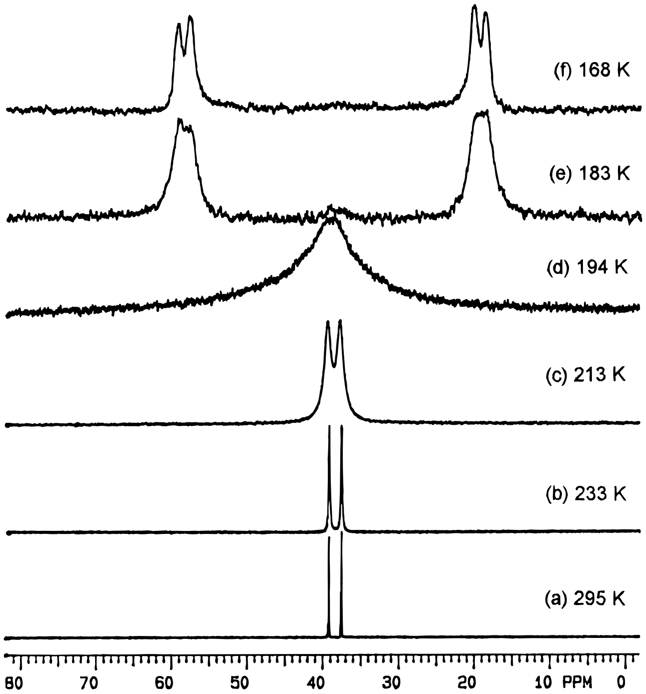
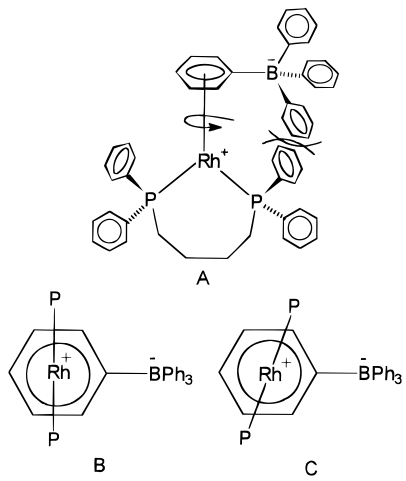


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) at 121.45 MHz in CD_2Cl_2/toluene-d_8 (2/1): (a) 295 K; (b) 233 K; (c) 213 K; (d) 194 K; (e) 183 K; (f) 168 K.

Figure 1 illustrates the VT $^{31}P\{^1H\}$ NMR spectra of $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**) in CD_2Cl_2/toluene-d_8 at 121.45 MHz. At 295 K, **4** exhibits a sharp doublet at $\delta = 38.7$ ppm with $^1J_{Rh-P} = 200$ Hz. As the temperature decreases, the doublet gradually broadens and coalesces at 194 K. A further decrease of the temperature to 168 K results in the disappearance of the resonance at $\delta = 38.7$ ppm and the appearance of two sets of doublets at $\delta = 58.4$ and 19.2 ppm, respectively, with $^1J_{Rh-P} \approx 193$ Hz. The same spectra were obtained in neat CD_2Cl_2 at $T > 183$ K. This dynamic process was reversible as the solution was warmed. We were unable to lower the temperature further in order to resolve the two doublets to the expected two sets of doublets of doublets, due to the limitation of the NMR probe and the solvents used.

These observations may be attributed to the "slowed" rotation of the coordinated phenyl ring about the $(\eta^6\text{-}PhBPh_3)-Rh$ bond axis (cf. Chart 1A). Rapid rotation of η^6-$PhBPh_3$ about the $(\eta^6\text{-}PhBPh_3)-Rh$ bond axis at $T > 194$ K establishes the time-averaged symmetry plane (cf. Chart 1B) and gives a single phosphorus resonance (cf. Figure 1a−c). With $T < 194$ K, this rotation is slowed down and a conformation without the symmetry plane is adopted by complex **4** (cf. Chart 1C); and two sets of doublets are observed in the $^{31}P\{^1H\}$ spectrum (cf. Figure 1e,f). The anticipated P−P coupling is obscured due to the incomplete freezing of this rotation at the accessible temperature. Evidence for the dissymmetric conformer adopted by complex **4** at low temperature can be found from structural data for the analogous $(\eta^6\text{-}PhBPh_3)^-Rh^+L_2$ complexes (L = $P(OMe)_3$;[15,16] L_2 = 1,2-bis(diphenylphosphino)ethane (DPPE),[17] 1,1′-bis(diphenylphosphino)ferrocene (DPPF)[18]). The slowed η^6-phenyl ring rotation in **4**, in contrast to the reported analogs,[15−18] is presumably due to the size of the chelating ring, where the seven-membered chelate ring may force the phenyl groups on each phosphorus to be relatively closer to the phenyl groups of η^6-$PhBPh_3$ (cf. Chart 1A). This may impose a higher rotational barrier to η^6-$PhBPh_3$ about the $(\eta^6\text{-}PhBPh_3)-Rh$ bond axis.

Chart 1



Dynamic Behavior of $[Rh(DPPB)_2]^+BPh_4^-$ (5). It is well-known that the catalytic activity of the cationic $[Rh(PPh_2(CH_2)_nPPh_2)_2]^+$ (n = 1−6) complexes is dependent on the size of the chelating ring.[23,48−50] These complexes possess different solid-state structures,[21,22,51] solution behavior,[21,22,52] and chemical reactivity,[20,22,52−54] as n is varied from 1 to 6. The reaction of these complexes with CO and with H_2 illustrates major reactivity differences.[20,22,50,52−54] Reversible addition of H_2 gave *cis*-$[(H)_2Rh(PPh_2(CH_2)_nPPh_2)_2]^+$ with $n = 3$, while the $n = 1$ and 2 cationic rhodium precursors were unreactive toward H_2 and a mixture of hydrides was formed when $n = 4$.[53] The simple monocarbonyl adducts $[Rh(PPh_2(CH_2)_nPPh_2)_2CO]^+$ were isolated for $n = 1$ and 3[53−55] and no CO adduct was formed for $n = 2$, while a mixture containing some binuclear DPPB-bridged complex $[Rh_2(PPh_2(CH_2)_4PPh_2)_3(CO)_4]^+$ was obtained when $n = 4$.[20,53] In addition, variable-temperature ^{31}P NMR data indicated that the geometry of $[Rh(PPh_2(CH_2)_nPPh_2)_2]^+$ cations in solution varied from square planar ($n = 2$) to solvated trigonal bipyramidal with a solvent molecule occupying an equatorial position ($n = 3$) and to *unidentifiable, complicated species* ($n = 4$),[21] although

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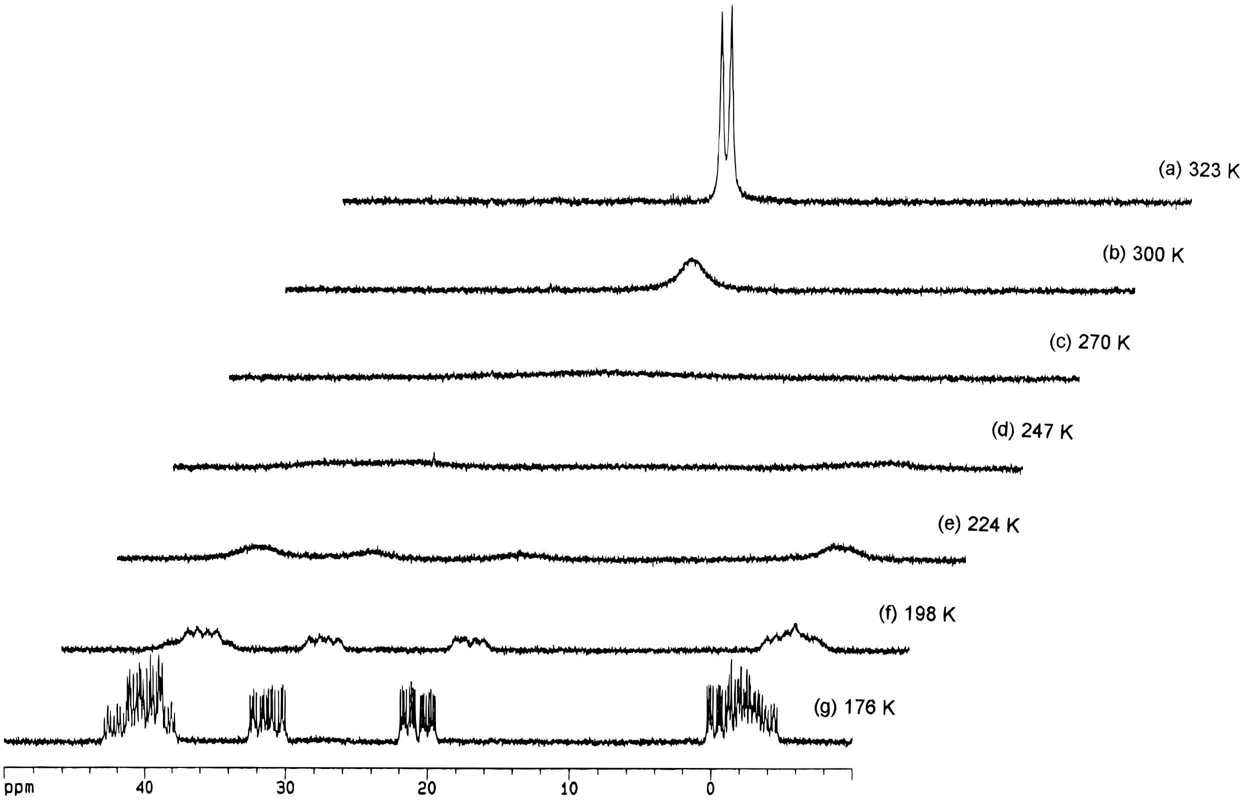
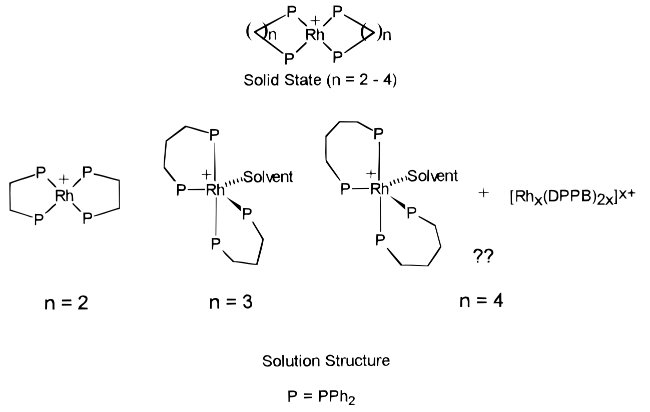


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) at 202.46 MHz in CD_2Cl_2: (a) 323 K; (b) 300 K; (c) 270 K; (d) 247 K; (e) 224 K; (f) 198 K; (g) 176 K.

Chart 2



these complexes all possess the same general formula in the solid state (Chart 2).[21,23,51−55] "*A combination of solvated species and dimeric/polynuclear species*" was suggested by Anderson and Pignolet in the case of $n = 4$.[21]

In order to clarify the solution behavior of $[Rh(DPPB)_2]^+X^-$ ($X^- = BF_4^-$ and BPh_4^-), VT $^{31}P\{^1H\}$ NMR experiments, along with low-temperature $^{31}P\{^1H\}$ COSY and EXSY experiments, were performed. The VT $^{31}P\{^1H\}$ NMR spectra of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) in CD_2Cl_2 are shown in Figure 2. The $^{31}P\{^1H\}$ resonance of $[Rh(DPPB)_2]^+X^-$ ($X^- = BF_4^-$ and BPh_4^-) at 300 K appeared as a broad band (202.46 MHz, Figure 2b) or a broadened doublet (121.45 MHz) at about 21.5 ppm. This resonance, however, was resolved to a doublet at 202.46 MHz at 323 K (Figure 2a), while the broadened doublet at 121.45 MHz became a sharp doublet ($^1J_{RhP} = 136$ Hz) at 313 K. As the temperature decreases, the single ^{31}P resonance disappeared at 270 K (Figure 2c), and then gradually well-separated resonances appeared in the chemical shift range of −5 to +45 ppm (Figure 2d−f). These resonances eventually became well-resolved multiplets centered at 40.4, 31.3, 20.7, and −2.2 ppm, with an integration ratio of 2.5/1/1/2.5, respectively, at 176 K (Figure 2g). This process was also reversible with increasing solution temperature.

The analysis of the spectrum recorded at 176 K (Figure 2g) was at first complicated by the overlap of the resonances centered at 40.4 and −2.2 ppm. Attempts to assign this spectrum using any *single* species with a general formula of $[Rh_x(DPPB)_y]^{x+}$ failed. Therefore, exchange(s) between different Rh−DPPB complexes is (are) almost certainly occurring in this solution.

The $^{31}P\{^1H\}$ COSY data (Figure 3) clearly show the coupling connectivities between the individual ^{31}P resonances in the same species. On this basis there appears to be two species present. The $^{31}P\{^1H\}$ EXSY data (Figure 4) show that the two species are in slow exchange with each other. Although the assignment is not completely unambiguous due to some resonance overlap, the cross-peaks in the COSY and EXSY data are mutually exclusive. As shown in Figure 3, resonance D, centered at 31.3 ppm, is coupled with resonances M (strong), G (moderate), and A (weak), respectively. Resonance G centered at 20.7 ppm is coupled with A (strong), D (moderate), and M (weak), respectively, clearly demonstrating that resonances A, D, G, and M belong to the phosphines from the same species. This is confirmed by the $^{31}P\{^1H\}$ EXSY data, which do not show any exchange between sites D and G (Figure 4). Therefore, the other resonances (a, d, g, m) are assigned to another species. Computer simulation of the ADGMX and the adgmx multiplets gives the parameters reported in Scheme 6, which are consistent with the presence of a distorted-square-planar monomeric rhodium complex (**5α**) and a dimeric rhodium

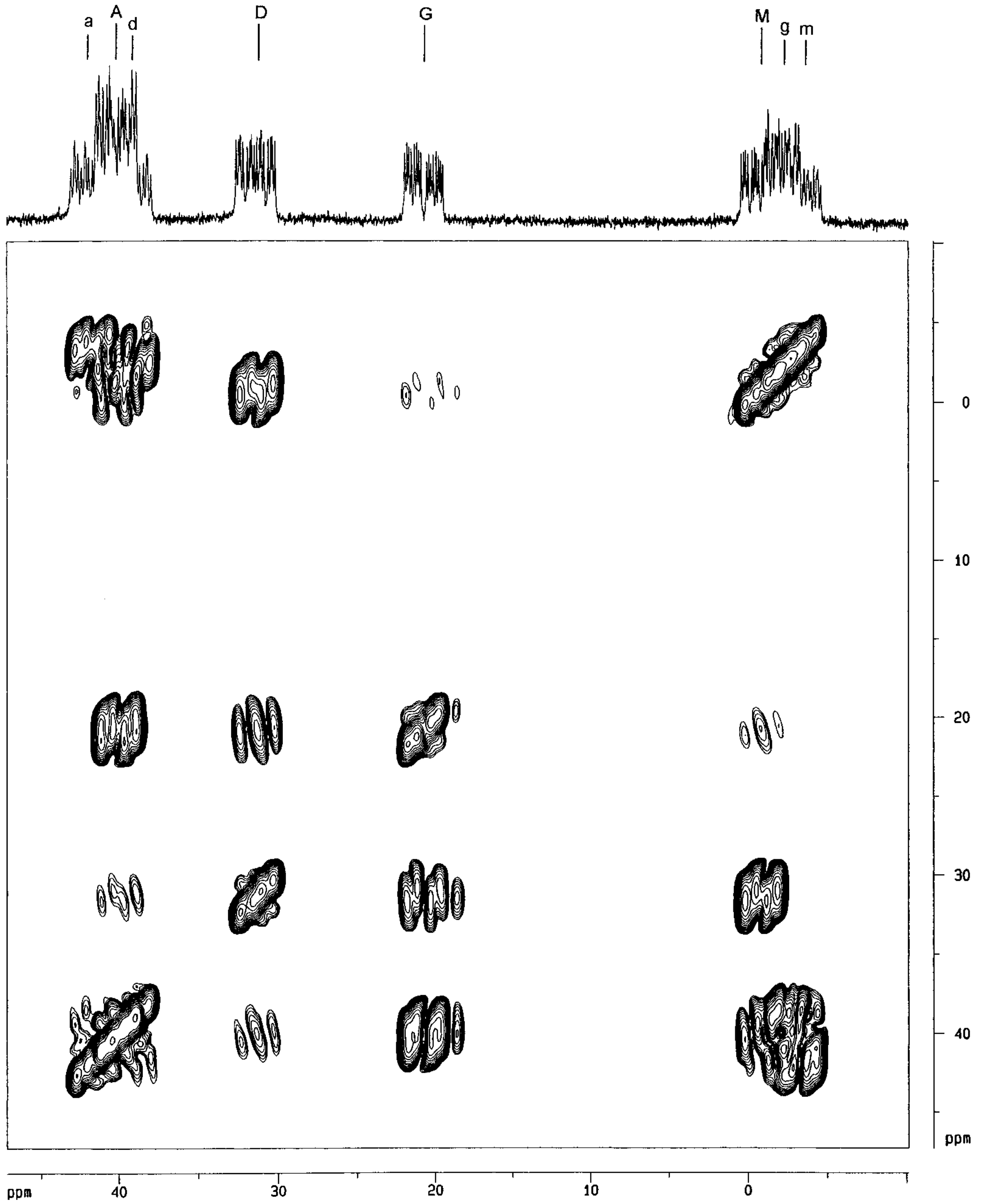


Figure 3. $^{31}P\{^1H\}$ COSY spectrum of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) at 202.46 MHz in CD_2Cl_2 at 176 K.

complex (**5**β) in a ratio of 100/75. The solvated trigonal-bipyramidal species as observed for a solution of $[Rh(PPh_2(CH_2)_3PPh_2)_2]^+$ and $[Rh(DPPF)_2]^+$ complexes (cf. Chart 2)[21,56] is ruled out, because a different coupling pattern would have resulted. The same spectra were obtained when the more strongly coordinating solvents THF-d_8 and acetone-d_6 were used, respectively, which confirms the above assumption. It is important to point out that no resonances for an uncoordinated phosphine ($\delta(^{31}P\{^1H\}$ -16 ppm)[23] are present in the VT ^{31}P NMR spectra. This rules out the presence of the monodentate-coordinated DPPB with one end dangling. The VT ^{31}P NMR spectra are independent of the anion (BF_4^- and BPh_4^-), which excludes possible exchange between coordinated phosphine and an η-$PhBPh_3^-$ coordinated species. This was further confirmed by the VT ^1H and $^{13}C\{^1H\}$ NMR spectra of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) in CD_2Cl_2, which demonstrated that the ^1H and $^{13}C\{^1H\}$ resonances of BPh_4^- always remained sharp in the temperature range of 176–300 K, as the ^1H and $^{13}C\{^1H\}$ resonance pattern of $[Rh(DPPB)_2]^+$ changed with a change in temperature.

In conclusion, this study has demonstrated that the zwitterionic $(\eta^6\text{-}PhBPh_3)^-Rh^+(diene)_n(DPPB)_{1-n}$ and the cationic $[Rh(diene)_n(DPPB)_{2-n}]^+BPh_4^-$ ($n = 0$, 1) complexes are interconvertible and coexist in solution. The size of the chelating ring probably rendered a "slowed" η^6-$PhBPh_3^-$ rotation about the $(\eta^6\text{-}PhBPh_3)^-$–Rh bond axis in $(\eta^6\text{-}PhBPh_3)^-Rh^+(DPPB)$ (**4**). This is the first example showing rotational fluxionality in η-tetraphenylborate-coordinated complexes. The VT $^{31}P\{^1H\}$ and low-temperature $^{31}P\{^1H\}$ COSY and EXSY NMR spectra of $[Rh(DPPB)_2]^+BPh_4^-$, (**5**) establish the coexistence of $[Rh(DPPB)_2]^+$ (**5**α) and $[Rh(DPPB)(\mu\text{-}DPPB)]_2^{2+}$ (**5**β) in solutions of complex **5**. It is clear that the solution geometries of $[Rh(PPh_2(CH_2)_nPPh_2)]^+$ are the "expected" square planar for $n = 2$, solvated trigonal bipyramidal for $n = 3$ (cf. Chart 2),[21] and a mixture of mono- and binuclear rhodium species for $n = 4$ (cf. Scheme 6).

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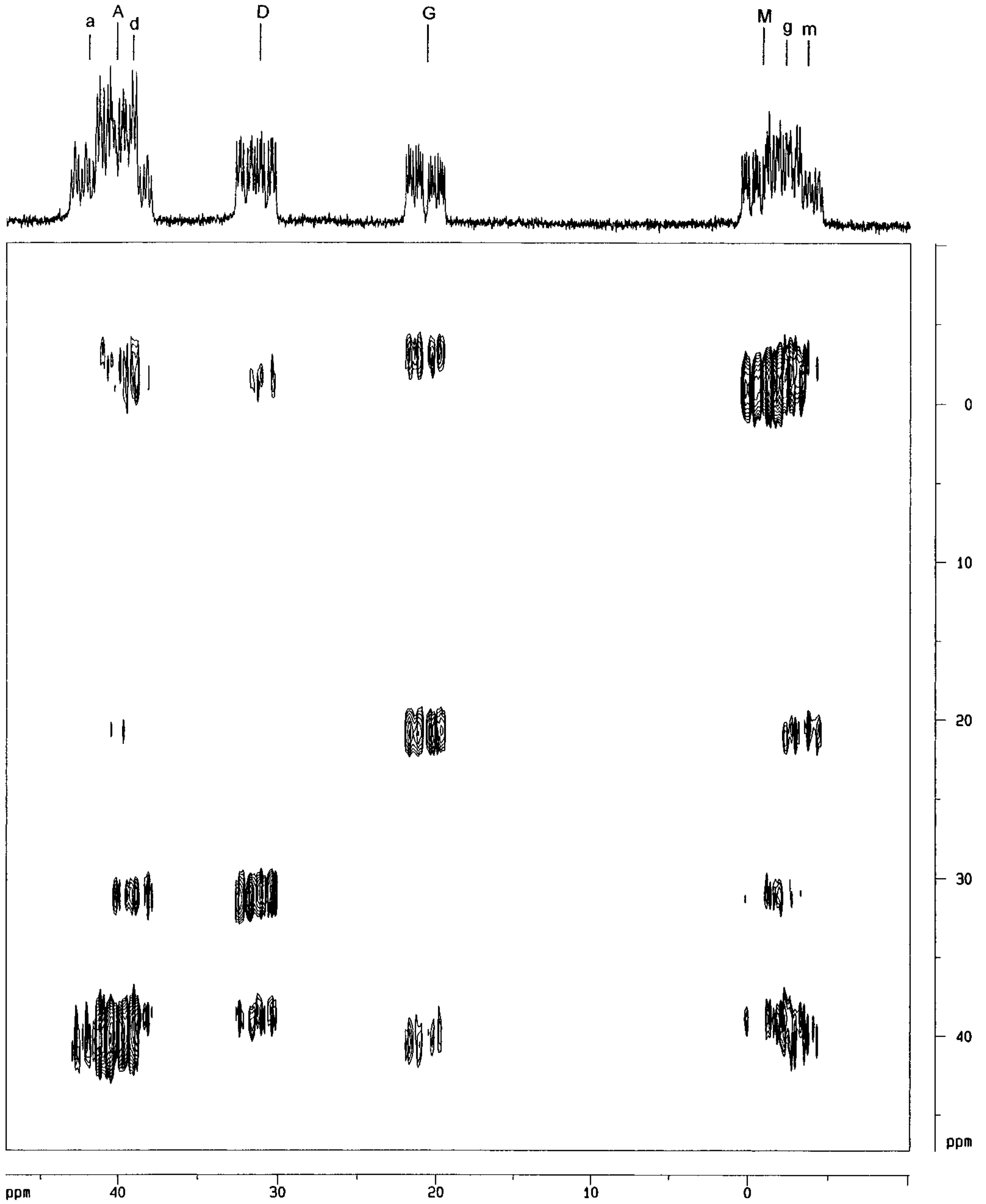

Figure 4. $^{31}P\{^1H\}$ EXSY spectrum of $[Rh(DPPB)_2]^+BPh_4^-$ (**5**) at 202.46 MHz in CD_2Cl_2 at 176 K.

These findings are likely of significance in homogeneous catalysis involving zwitterionic and/or cationic rhodium complexes.

Experimental Section

General Considerations. The syntheses and manipulations of solutions were performed under a nitrogen or carbon monoxide atmosphere with standard Schlenk-line techinques. Solvents were dried and purified by standard methods. Infrared spectra were run on a Bomem MB-100 FT-IR spectrometer. All ^1H $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX-500, Varian XL-300, or Gemini 200 MHz spectrometer using $CDCl_3$ or CD_2Cl_2 as the solvent. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (reported with respect to 85% aqueous H_3PO_4, downfield shifts being positive) were acquired on the Bruker operating at 202.46 MHz using the decoupling coil of an inverse detection probe or on the Varian spectrometer operating at 121.45 MHz using a standard broad-band probe. The temperature was regulated within ±0.5 °C. The $^{31}P\{^1H\}$ COSY NMR data were collected (Bruker AMX-500) using a standard magnitude COSY-45 pulse sequence modified to incorporate continuous ^1H decoupling. The data consist of 64 slices, each with an acquisition time of 0.011 s using a spectral width of 11.6 kHz. Each slice was collected using 128 transients with a 0.5 s relaxation delay. The data were zero-filled to 512 points in each domain and Fourier-transformed using sine bell weighting. The EXSY spectrum was recorded using a standard phase-sensitive (TPPI) NOESY pulse program modified to incorporate continuous ^1H decoupling. The data consist of 200 slices, each with an acquisition time of 0.044 s using a spectral width of 11.6 kHz. Each of the slices was collected using 16 transients with a 0.5 s relaxation delay. The data were zero-filled to 512 points in each domain and Fourier-transformed using sine squared weighting. $RhCl_3{\cdot}3H_2O$, $[Rh(COD)(DPPB)]^+BF_4^-$ (**2**), and other chemicals were purchased from Aldrich and were used as received. $[Rh(COD)Cl]_2$,[57] $(\eta^6\text{-}PhBPh_3)^-Rh^+(COD)$ (**1**),[1] and $(\eta^6\text{-}PhBPh_3)Rh(NBD)$ (**6**)[1] were prepared by following literature procedures.

General Procedure for the Reaction of $(\eta^6$-PhBPh$_3)^-$Rh$^+$(NBD) (6) with CO or H_2/CO under High Pressure. In a 45-mL Parr autoclave fitted with a glass liner and

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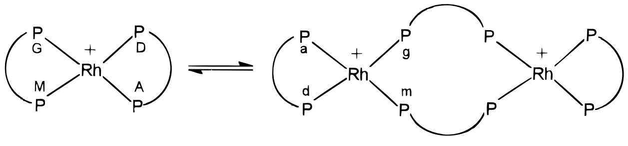
[57] Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

Scheme 6. $^{31}P\{^1H\}$ NMR Data for 5α and 5*β* at 176 K



5α **5β**

δ, ppm		J, Hz	
P_A = 40.0	P_a = 41.6	A,G = 283	a,m = 281
P_D = 31.3	P_d = 39.1	A,D = 34	a,d = 41
P_G = 20.7	P_g = -2.0	A,M = 54	a,g = 52
P_M = -0.9	P_m = -3.4	D,G = 54	d,g = 265
		D,M = 263	d,m = 48
		G,M = 30	g,m = 36
		Rh,A = 140	Rh,a = 139
		Rh,D = 142	Rh,d = 132
		Rh,G = 125	Rh,g =116
		Rh,M = 139	Rh,m = 121

P⌒P = $PPh_2(CH_2)_4PPh_2$

5α/**5β** = 100/75 (mol/mol)

stirring bar was added (η^6-$PhBPh_3$)$^-$Rh$^+$(NBD) (**6**; 50 mg) and CH_2Cl_2 (5 mL) or CD_2Cl_2 (1 mL). The CO line was flushed three times with CO, and the autoclave was fill-vented three times with CO to displace the air; subsequently, the pressure was increased to 200 psi with CO. When H_2 was required, the pressure was increased to 400 psi by filling with H_2, after the H_2 line was flushed three times. The solution was stirred in the autoclave at RT for the desired period of time. The excess CO (or H_2/CO) was released and the system disassembled, and the reaction solution was transferred to a Schlenk tube or an NMR tube under an atmosphere of N_2 or CO and subjected to IR and NMR tests.

General Procedure for the Reaction of (η^6-Ph-BPh$_3$)$^-$Rh$^+$(NBD) (6) with CO, H_2, or H_2/CO under Ambient Pressure. In a 25-mL Schlenk tube with a stirring bar, or an NMR tube, was added (η^6-$PhBPh_3$)$^-$Rh$^+$(NBD) (**6**; 50 mg) and CH_2Cl_2 (5 mL) or CD_2Cl_2 (1 mL). The system was frozen and thawed three times under N_2 first and then CO, H_2, or H_2/CO was slowly bubbled through for the desired period of time. The reaction solution was analyzed by IR and NMR.

Synthesis of [Rh(COD)(DPPB)]$^+$BPh$_4^-$ (3). An excess of $NaBPh_4$ (0.23 g, 0.66 mmol) in 5 mL of methanol was added, drop-by-drop, into a clear orange-yellow solution of [Rh(COD)(DPPB)]$^+$$BF_4^-$ (**2**; 0.21 g, 0.29 mmol) in 20 mL of MeOH. An orange-red precipitate soon formed, and after the solution was stirred for about 10 min, the precipitate was collected and washed three times with 20 mL of H_2O, followed by 20 mL of MeOH, and then air-dried (0.26 g, 94%): mp 167−168 °C dec; ^1H NMR ($CDCl_3$, 22 °C) δ 7.48, 7.40 (m, 28H, P−*Ph* and H_{ortho} of B−*Ph*), 6.98 (t, $J = 7.0$ Hz, 8H, H_{meta} of B−*Ph*), 6.83 (t, $J = 7.0$ Hz, 4H, H_{para} of B−*Ph*), 4.37 (s, broad, 4H, C*H*=C*H*), 2.30, 2.17, 1.50 (broad signals, 16H, −C*H*$_2$−); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22 °C) δ 164.10 (q, $J_{B-C} = 49.6$ Hz, C_{ipso} of B−*Ph*), 136.32, 133.05, 132.95, 132.84, 132.28 (m), 131.67, 129.49, 129.39, 129.29, 125.40, 125.35, 121.48 (phenyl carbons), 100.50 (m, *C*H=*C*H), 31.50 (m), 30.38, 24.67 (−*C*H$_2$−); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22 °C) δ 24.6 (d, $J_{RhP} = 143.1$ Hz). Anal. Calcd for $C_{60}H_{60}BP_2Rh$: C, 75.32; H, 6.32. Found: C, 75.13; H, 6.15.

Synthesis of (η^6-PhBPh$_3$)$^-$Rh$^+$(DPPB) (4). [Rh(COD)(DPPB)]$^+$$BPh_4^-$ (**3**; 0.15 g, 0.16 mmol) was dissolved in 10 mL of CH_2Cl_2 in a Schlenk tube. The system was first flushed with nitrogen and then with hydrogen. Continuous stirring of this solution for 60 min under H_2 at RT resulted in a color change from orange-red to deep red and the disappearance of COD, which was converted to cyclooctane (^1H NMR). Hexanes (1 mL) was then added slowly after the reaction solution was concentrated to about 3 mL. This solution was allowed to stand under N_2 at RT overnight. The resulting deep red prisms were filtered, washed with cold CH_2Cl_2 (2 × 3 mL), and air-dried (0.13 g, 99%): mp >202 °C dec; ^1H NMR (CD_2Cl_2, 22 °C) δ 7.34−6.98 (m, 35H, *Ph*), 6.81 (t, $J = 6.2$ Hz, 1H, H_{para} of η-*Ph*−B), 5.63 (d, $J = 6.2$ Hz, 2H, H_{ortho} of η-*Ph*−B), 4.95 (t, $J = 6.2$ Hz, 2H, H_{meta} of η-*Ph*−B), 2.17 (s, broad, 4H, −C*H*$_2$−), 1.72 (s, broad, 4H, −C*H*$_2$−); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ 161.57 (q, $J_{B-C} = 50.2$ Hz, C_{ipso} of B−*Ph*), 153.50 (m, C_{ipso} of η-Ph−B), 138.59 (m), 136.52, 132.87 (t, $J_{P-C} = 5.0$ Hz), 130.15, 128.55 (t, $J_{P-C} = 5.0$ Hz), 126.46, 123.20 (phenyl carbons), 106.41, 103.30, 98.01 (η-*Ph*−B carbons), 29.47 (t, $J_{P-C} = 16.2$ Hz, P−*C*H$_2$−), 24.39 (−*C*H$_2$−); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C) δ 38.7 (d, $J_{RhP} = 200.3$ Hz). Anal. Calcd for $C_{52}H_{48}BP_2Rh$: C, 73.60; H, 5.70. Found: C, 73.29; H, 5.47.

Synthesis of [Rh(DPPB)$_2$]$^+$BF$_4^-$ (8).[20−23] Because of the low solubility of $[Rh(COD)Cl]_2$ in acetone, alternative methods were used here to synthesize [Rh(DPPB)$_2$]$^+$$BF_4^-$.

Method A. To a solution of $[Rh(COD)Cl]_2$ (0.0826 g, 0.17 mmol) in 10 mL of CH_2Cl_2 and 2 mL of MeOH was added 0.0853 g (0.44 mmol) of $AgBF_4$ in 2 mL of acetone. The resulting precipitate was filtered, and DPPB (0.29 g, 0.68 mmol) was added to the filtrate. Hydrogenation of the reaction mixture under 200 psi of H_2 at RT afforded a deep red solution. Removal of volatiles under vacuum resulted in an orange-red solid, which was recrystallized from CH_2Cl_2/*n*-pentane (0.31 g, 91%).

Method B. [Rh(COD)(DPPB)]$^+$$BF_4^-$ (0.052 g, 0.072 mmol) was dissolved in 15 mL of MeOH in a Schlenk tube. The system was first flushed with nitrogen and then with hydrogen. Continuous stirring of this solution for 20 min under H_2 at RT, followed by the addition of 0.031 g (0.072 mmol) of DPPB in 10 mL of CH_2Cl_2, resulted in a solution color change from orange-red to deep red. This reaction mixture was stirred for another 2 h. Removal of volatiles afforded **8** (0.072 g, 96%).

Synthesis of [Rh(DPPB)$_2$]$^+$BPh$_4^-$ (5). Addition of excess $NaBPh_4$ (0.13 g, 0.38 mmol) in 5 mL of MeOH to a deep red solution of [Rh(DPPB)$_2$]$^+$$BF_4^-$, (**8**; 0.083 g, 0.079 mmol) in 15 mL of MeOH resulted in the formation of an orange-red precipitate. The precipitate was collected and washed three times with 10 mL of H_2O followed by 10 mL of MeOH and then air-dried (0.10 g, 99%): mp 234−236 °C dec; ^1H NMR (CD_2Cl_2, 27 °C) δ 7.40−7.10 (m, broad, P−*Ph*), 7.33 (m, H_{ortho} of B−*Ph*), 7.04 (t, $J = 7.0$ Hz, H_{meta} of B−*Ph*), 6.87 (t, $J = 7.0$ Hz, H_{para} of B−*Ph*) (total 60H), 2.13, 1.66 (broad signals, 16H, −C*H*$_2$−); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 27 °C) δ 164.70 (q, $J_{B-C} = 49.9$ Hz, C_{ipso} of B−*Ph*), 136.23, 134.9 (m), 133.19, 130.61, 128.68, 125.97, 125.91, 125.86, 122.03 (phenyl carbons), 31.16 (broad), 25.02 (−*C*H$_2$−); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 27 °C) δ 21.5 (s, broad, at 202.46 MHz), 21.5 (broadened doublet, at 121.45 MHz). Anal. Calcd for $C_{80}H_{76}BP_4Rh$: C, 75.36; H, 6.01. Found:, C, 75.04; H, 5.85.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for the award of a collaborative project grant in support of this research.

OM960112S