Novel Hemilabile (Phosphinoalkyl)arene Ligands: Mechanistic Investigation of an Unusual Intramolecular, Arene−Arene Exchange Reaction

Elizabeth T. Singewald, Xiaobo Shi, Chad A. Mirkin,* Susan J. Schofer, and Charlotte L. Stern

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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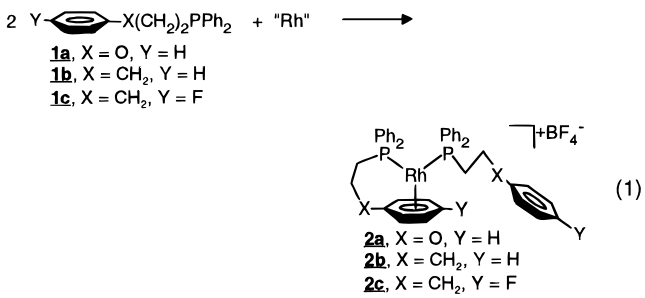
The novel, hemilabile (phosphinoalkyl)arene ligands $ArX(CH_2)_2PPh_2$ (**1a**, Ar = C_6H_5, X = O; **1b**, Ar = C_6H_5, X = CH_2; **1c**, Ar = FC_6H_4, X = CH_2) were synthesized and complexed to Rh(I) to form the bis(phosphine), η^6-arene piano stool complexes $[(\eta^6{:}\eta^1\text{-}ArX(CH_2)_2PPh_2)Rh(\eta^1\text{-}ArX(CH_2)_2PPh_2)]BF_4$ (**2a**−**c**). Complexes **2a**−**c** were fully characterized in solution, and complex **2a** was characterized by single-crystal X-ray diffraction methods. Two of these complexes, **2a**,**c**, undergo an unusual, degenerate η^6-arene, free arene exchange reaction which was studied by 2-D NMR EXSY experiments. A mechanism for the exchange reaction of **2a** which involves the formation of a square planar, *cis*-phosphine, *cis*-ether Rh(I) complex, $[Rh(\eta^2\text{-}PhO(CH_2)_2PPh_2)_2]BF_4$ (**13**), is proposed.

Introduction

Many variations of multidentate hybrid phosphine ligands have been studied and complexed to metal centers.[1] When complexed to transition metals, many of these ligands possess both substitutionally inert and labile groups and, therefore, are referred to as hemilabile ligands. Complexes formed from such ligands have found wide application in the area of homogeneous catalysis.[1a−c,e,i,m,r] The substitutionally labile groups in hemilabile ligands can be viewed as internal solvent molecules that stabilize a transition metal but in the presence of substrate can be easily displaced. The most widely studied hemilabile ligands have been phosphinoethers which can bind to metals in a bidentate, tridentate, or tetradentate fashion.[1a] In these examples, the ether is the substitutionally labile group and the phosphine is the substitutionally inert group. In addition to ether moieties,[1a,b] thioethers,[1d−i] alkenes,[1j−l] amines,[1m−s] and others have been used as labile functional groups in the design of hemilabile ligands.

On the basis of the ligand substitution chemistry of Rh^I(diphos)(η^6-arene) complexes,[2] we have designed a new type of hemilabile ligand that when complexed to Rh(I) employs a phosphine as a substitutionally inert group and an η^6-arene as the substitutionally labile moiety, compounds **2a**−**c**, eq 1. Significantly, the arene



(1)

ligand can temporarily occupy three coordination sites at the metal center and can be displaced in both reversible and irreversible reactions with more strongly ligating functional groups. The arene-based ligand substitution chemistry of compound **2a** is, in part, the subject of this paper. In addition, we report the discovery (previously communicated)[3] and a mechanistic study of a novel intramolecular exchange reaction between the η^6-arene and free arene moieties in compounds **2a**−**c**.

Although no examples of η^6-arene, free arene exchange reactions for (phosphinoalkyl)arene ligands have been reported previously, a variety of intramolecular and intermolecular arene−arene exchange reactions have been studied by others.[4,5] For example, several degenerate, intramolecular arene−arene exchange reactions which involve a haptotropic rearrangement of two

* Author to whom correspondence should be addressed. E-mail: camirkin@chem.nwu.edu.

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(1) (a) Allgeier, A. M.; Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Organometallics* **1994**, *13*, 2984. (b) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27. (c) Dilworth, J. R.; Miller, J. R.; Wheatley, N.; Baker, M. J.; Sunley, J. G. *J. Chem. Soc., Chem. Commun.* **1995**, 1579. (d) James, T. L.; Smith, D. M.; Holm, R. H. *Inorg. Chem.* **1994**, *33*, 4869. (e) Bressan, M.; Bonuzzi, C.; Morandini, F.; Morvillo, A. *Inorg. Chim. Acta* **1991**, *182*, 153. (f) Del Zotto, A.; Mezzetti, A.; Rigo, P.; Bressan, M.; Morandini, F.; Morvillo, A. *Inorg. Chim. Acta* **1989**, *158*, 151. (g) Del Zotto, A.; Mezzetti, A.; Dolcetti, G.; Rigo, P.; Pahor, N. B. *J. Chem. Soc., Dalton Trans.* **1989**, 607. (h) Del Zotto, A.; Rigo, P. *Inorg. Chim. Acta* **1988**, *147*, 55. (i) Bressan, M.; Morandini, F.; Morvillo, A.; Rigo, P. *J. Organomet. Chem.* **1985**, *280*, 1139. (j) Bennett, M. A.; Chiraratvatana, C.; Robertson, G. B.; Tooptakong, U. *Organometallics* **1988**, *7*, 1394. (k) Tau, W. D.; Meek, D. W.; Sorrell, T.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 3454. (l) Garrou, P. E.; Hartwell, G. E. *J. Organomet. Chem.* **1974**, *71*, 443. (m) Schumann, H. Hemlig, H.; Goren, N.; Blum, J. *J. Organomet. Chem.* **1995**, *485*, 209. (n) Del Zotto, A.; Mezzetti, A.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2257. (o) Hessler, A.; Fischer, J.; Kucken, S.; Stelzer, O. *Chem. Ber.* **1994**, *127*, 481. (p) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937. (q) Anderson, M. P.; Casalnuovo, A. L.; Johnson, B. J.; Mattson, B. M.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 1649. (r) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710. (s) Rauchfuss, T. B.; Clements, J. L.; Agnew, S. F.; Roundhill, D. M. *Inorg. Chem.* **1977**, *16*, 775.

(2) (a) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (b) Halpern, J.; Chan, A. S. C.; Riley, D. P.; Pluth, J. J. *Adv. Chem. Ser.* **1979**, *No. 173*, 16.

(3) Singewald, E. T.; Mirkin, C. A.; Levy, A. D.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2473. *Angew. Chem.* **1994**, *106*, 2524.

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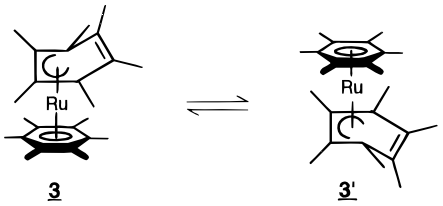
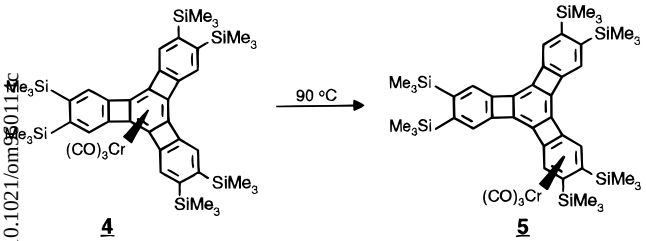
arene ligands have been reported. Finke *et al.* reported that a Ru complex undergoes a degenerate exchange process which involves a reversible η^6- to η^4-ring slippage reaction for the π-coordinated hexamethylbenzene ligands **3** and **3′** in eq 2.[4g] In another example of an



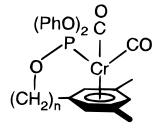
3 **3′** (2)

intramolecular arene−arene exchange reaction, a $Cr(CO)_3$ fragment undergoes a coordination shift from one arene to another in an aromatic polycyclic ligand, **4** to **5**, eq 3.[4a] However, this reaction is irreversible and nondegenerate since the starting and product complexes are chemically different.



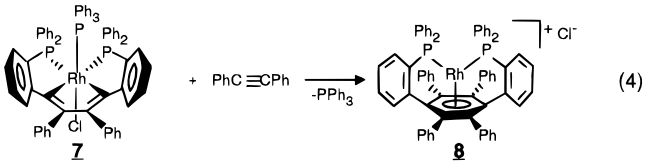
4 **5** (3)

A couple of ligand systems analogous to the one reported herein have been prepared by others. Rybinskaya *et al.* showed that arenes with pendant phosphite groups chelate to chromium and form the η^6-arene complexes **6a**−**c**.[6] Additionally, a bis(phosphine), η^6-

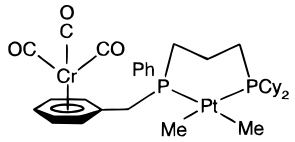


6a-c, n = 1-3

arene ligand can be generated on Rh(I) in a reaction involving alkyne insertion into a metallocyclopentadiene complex **7** to form complex **8**, eq 4.[7] However, no unusual arene ligand exchange processes were reported for **6**−**8**. Finally, Meek *et al.* prepared a novel (phosphinoalkyl)arene ligand which bridges two metal centers to form a heterobimetallic complex:[8]



7 **8** (4)



Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques or in an inert-atmosphere glovebox. Methylene chloride and pentane were dried over calcium hydride. THF and diethyl ether were dried over sodium/benzophenone. All solvents were distilled under nitrogen and degassed prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without purification. $RhCl_3 \cdot xH_2O$ was used on loan from Johnson-Matthey Chemical Co. A sample of $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_8H_{14})_2]_x$ was prepared according to literature methods.[9] β-Chlorophenetole was purchased from Pfaltz and Bauer Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. and used as received.

One dimensional ^1H NMR spectra were recorded either on a Varian Gemini 300 MHz, a Varian Unity 400 MHz, or a Bruker 600 MHz FT NMR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz FT NMR spectrometer at 121 MHz and referenced versus the external standard 85% H_3PO_4. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz FT NMR spectrometer at 75 MHz. One dimensional $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz FT NMR spectrometer at 282 MHz and referenced versus the external standard $CFCl_3$. ^1H and ^{19}F NMR exchange spectroscopy (EXSY) were performed on a Varian Unity 400 MHz FT NMR spectrometer at 400 and 376 MHz, respectively, using a standard NOESY pulse sequence with t_{mix} varying with temperature. All two dimensional NMR experiments were performed on a Varian Unity 400 MHz spectrometer. All coupling constants are reported as absolute values. Electrochemical measurements were carried out either on a PINE AFRDE4 or AFRDE5 bipotentiostat (cyclic voltammetry, CV) or a PAR 273A potentiostat/galvanostat (differential pulse voltammetry, DPV) using a Pt working electrode (0.02 cm^2), a Pt mesh counter electrode, and a Ag wire reference electrode. In all cases a n-Bu_4NPF_6 (0.1 M) solution in CH_2Cl_2 was used as the supporting electrolyte. All electrochemical data were referenced further versus the $FcH/[FcH]^+$ ($Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) redox couple. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a Fisions VG 70-250 SE mass spectrometer. FT-IR spectra were recorded on a Nicolet 520SX spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, NY.

Synthesis of $PhO(CH_2)_2PPh_2$ (1a). A THF solution of $KPPh_2$ (0.50 M, 0.020 mol) was added dropwise to a solution of $PhOCH_2CH_2Cl$ (3.13 g, 0.020 mol) in 200 mL of THF at 0 °C. The reaction was allowed to warm to room temperature over 12 h. The solution was filtered, 25 mL of silica gel was added, and the solvent was removed under vacuum. Chromatography of the crude reaction mixture on silica gel was performed in a glovebox under nitrogen. Two bands were eluted with 10% diethyl ether in pentane. The first band

(4) Intramolecular Exchange: (a) Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138. (b) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1992**, *11*, 3497. (c) Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084. (d) Nielson, R. M.; Weaver, M. J. *Organometallics* **1989**, *8*, 1636. (e) Traylor, T. G.; Goldberg, M. J. *Organometallics* **1987**, *6*, 2413. (f) Bandy, J. A.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2477. (g) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.

(5) Intermolecular exchange: (a) Decken, A.; Britten, J. F.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 7275. (b) Plitzko, K.-D.; Boekelheide, V. *Organometallics* **1988**, *7*, 1573. (c) Traylor, T. G.; Goldberg, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 3968. (d) Howell, J. A. S.; Dixon, D. T.; Kola, J. C.; Ashford, N. F. *J. Organomet. Chem.* **1985**, *294*, C1. (e) Traylor, T. G.; Stewart, K. J.; Goldberg, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 4445. (f) Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489. (g) Muetterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197.

(6) (a) Nesmeyanov, A. N.; Krivykh, V. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1979**, *164*, 159. (b) Vasyukova, N. I.; Nekrasov, Y. S.; Krivykh, V. V.; Rybinskaya, M. I. *J. Organomet. Chem.* **1980**, *201*, 283.

(7) Winter, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 241; *Angew. Chem.* **1976**, *88*, 260.

(8) McDougall, M. G.; Gallucci, J. C.; Meek, D. W. *Inorg. Chim. Acta* **1991**, *188*, 123.

(9) Porri, L.; Lionetti, A.; Allegra, G.; Immirizi, A. *Chem. Commun.* **1965**, 336.

contained $HPPh_2$ and was discarded. The second and major band contained **1a**. Vacuum evaporation of the solvent and recrystallization of the chromatographed product from ethanol afforded analytically pure **1a** (yield = 4.28 g, 0.014 mol, 70%). ^{1}H NMR (300 MHz, C_6D_6): δ 2.41 (t, J_{H-H} = 7.7 Hz, 2H, CH_2P), 3.92 (dt, $J_{H-H} = J_{P-H}$ = 7.7 Hz, 2H, CH_2O), 7.40−6.71 (m, 15H, Phs). $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6): δ −21.8 (s). EIMS: (70 eV, 190 °C) [M^+]: m/z 306. Anal. Calcd for $C_{20}H_{19}OP$: C, 78.42; H, 6.25. Found: C, 78.52; H, 6.44.

Synthesis of $Ph(CH_2)_3PPh_2$ (1b). Compound **1b** was synthesized in a route similar to **1a** and on a comparable scale. The reaction between $BrCH_2CH_2CH_2C_6H_5$ and $KPPh_2$ gave analytically pure **1b** (yield = 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79 (m, 2H, $CH_2CH_2CH_2$), 2.09 (dt, J_{H-H} = 7.3 Hz, J_{P-H} = 4.7 Hz, 2H, CH_2P), 2.76 (t, J_{H-H} = 7.3 Hz, 2H, CH_2-Ph), 7.43−7.15 (m, 15H, Phs). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −15.2 (s). EIMS: (70 eV, 190 °C) [M^+]: m/z 304. Anal. Calcd for $C_{21}H_{21}P$: C, 82.87; H, 6.95. Found: C, 82.62; H, 7.07.

Synthesis of $4\text{-}FC_6H_4(CH_2)_3Cl$.[10] A slurry of $AlCl_3$ (2.05 g, 0.153 mol) in 50 mL of methylene chloride was treated with *tert*-$BuNH_2{\cdot}BH_3$ (2.67 g, 0.032 mol) and stirred for 5 min at 0 °C. The $AlCl_3$ dissolved giving a translucent gray solution. To this, a solution of $4\text{-}FC_6H_4C(O)CH_2CH_2Cl$ (0.954 g, 5.1 mmol) in 5 mL of methylene chloride was added via cannula. This reaction was stirred at room temperature and was monitored by thin-layer chromatography on silica gel plates using 10% methylene chloride in pentane. After 20 h, the translucent gray reaction solution was treated dropwise with HCl (25 mL, 0.1 M) during which the solution bubbled vigorously and became opaque. After all HCl was added, the reaction was stirred for an additional 15 min and then extracted with ethyl acetate. The combined organic layers were washed with HCl (40 mL, 0.1 M) and NaCl (saturated). After filtering of the organic layer through $MgSO_4$, the solvent was removed via rotary evaporation. The crude product was purified via column chromatography on silica gel. One band was collected with an eluent of 10% methylene chloride in pentane. The product was used without further purification (yield = 0.673 g, 3.9 mmol, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (m, 2H, $CH_2CH_2CH_2Cl$), 2.74 (t, 2H, J_{H-H} = 7.2 Hz, CH_2Ar), 3.50 (m, 2H, CH_2Cl), 6.98 (m, 2H, Phs), 7.14 (m, 2H, Phs). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): −117.9 (s).

Synthesis of $4\text{-}FC_6H_4(CH_2)_3PPh_2$ (1c). Compound **1c** was synthesized by reacting $4\text{-}FC_6H_4(CH_2)_3Cl$ with $KPPh_2$ in an manner analogous to the synthesis of **1a** (yield = 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78 (m, 2H, $CH_2CH_2CH_2P$), 2.08 (m, 2H, CH_2P), 2.73 (m, 2H, CH_2Ar), 6.99 (m, 2H, Phs), 7.10 (m, 12H, Phs). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): −118.2 (s). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −16.2 (s). HRFABMS [M^+]: Calcd, m/z 322.1287; found, m/z 322.1281.

Synthesis of $[(\eta^6\text{:}\eta^1\text{-}C_6H_5O(CH_2)_2PPh_2)Rh(\eta^1\text{-}PhO(CH_2)_2PPh_2)]BF_4$ (2a). $AgBF_4$ (0.27 g, 1.4 mmol) and $[Rh(\mu\text{-Cl})(\eta^2\text{-}C_8H_{14})_2]_x$ (0.50 g, 1.4 mmol) were reacted in 3 mL of THF for 45 min. The reaction was filtered to remove a dark gray precipitate and diluted to 75 mL with THF. Ligand **1a** (0.86 g, 2.8 mmol) in 75 mL of THF was added dropwise to the THF solution of $[(\eta^2\text{-}C_8H_{14})_2Rh(THF)_2]BF_4$[11] at −78 °C. After 2 h, the solvent was removed under vacuum. The crude product was recrystallized from a 1:10 mixture of methylene chloride and diethyl ether to afford analytically pure **2a** (yield = 0.89 g, 1.1 mmol, 80%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 1.76 (dt, J_{H-H} = 6.6 Hz, J_{P-H} = 9.6 Hz, 2H, CH_2P), 2.07 (m, 2H, CH_2P), 4.00 (m, 2H, CH_2O), 4.05 (m, 2H, CH_2O), 4.63 (t, J_{H-H} = 6.1 Hz, 1H, η^6-*p*-C_6H_5), 6.75 (d, J_{H-H} = 6.2 Hz, 2H, η^6-*o*-C_6H_5), 6.80 (d, J_{H-H} = 7.8 Hz, 2H, *o*-C_6H_5), 6.88 (m, 2H, η^6-*m*-C_6H_5), 7.00 (t, J_{H-H} = 7.4 Hz, 1H, *p*-C_6H_5), 7.28−7.47 (m, 22 H, Phs). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 32.6 (dd, J_{Rh-P} = 198.7 Hz, J_{P-P} = 38.6 Hz), 34.9 (dd, J_{Rh-P} = 210.4 Hz, J_{P-P} = 38.6 Hz). FABMS [M^+]: m/z 715. Anal. Calcd for $C_{40}H_{38}O_2P_2RhBF_4$: C, 59.88; H, 4.77. Found: C, 59.70; H, 4.91.

Synthesis of $[(\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3PPh_2)Rh(\eta^1\text{-}Ph(CH_2)_3PPh_2)]BF_4$ (2b). Compound **2b** is synthesized by an analogous route to **2a** but using ligand **1b** instead of **1a** (yield = 84%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.44 (m, 6H, CH_2P and 2 $CH_2CH_2CH_2$), 1.90 (dt, J_{H-H} = 4.8 Hz, J_{P-H} = 10.4 Hz, 2H, CH_2P), 2.37 (t, J_{H-H} = 7.2 Hz, 2H, $CH_2(\eta^6$-Ph)), 2.56 (t, J_{H-H} = 4.8 Hz, 2H, CH_2Ph), 4.68 (t, J_{H-H} = 6.0 Hz, 1H, η^6-*p*-C_6H_5), 6.78 (m, 2H, η^6-*m*-C_6H_5), 6.85 (d, J_{H-H} = 7.2 Hz, 4H, *o*-C_6H_5), 7.44−7.16 (m, 23H, Phs). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 34.6 (dd, J_{Rh-P} = 203.9 Hz, J_{P-P} = 40.6 Hz), 39.8 (dd, J_{Rh-P} = 198.8 Hz, J_{P-P} = 40.6 Hz). FABMS [M^+]: m/z 711. Anal. Calcd for $C_{42}H_{42}P_2RhBF_4$: C, 63.18; H, 5.31. Found: C, 62.63; H, 5.50.

Synthesis of $[(\eta^6\text{:}\eta^1\text{-}4\text{-}FC_6H_4(CH_2)_3PPh_2)Rh(\eta^1\text{-}4\text{-}FC_6H_4\text{-}(CH_2)_3PPh_2)]BF_4$ (2c). Compound **2c** is synthesized by an analogous route to **2a** but using ligand **1c** instead of **1a** (yield = 30%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.41 (m, 6H, CH_2P and 2 $CH_2CH_2CH_2$), 1.90 (m, 2H CH_2P), 2.29 (m, 2H, $CH_2(\eta^6$-Ar)), 2.56 (m, 2H, CH_2Ar), 6.75 (m, 4H, Phs), 6.90 (m, 4H, Phs), 7.13−7.48 (m, 20H, Phs). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2): −116.3 (s, F-C_6H_4), −125.5 (s, F-η^6-C_6H_4), −151.2 (s, BF_4). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 33.3 (dd, J_{Rh-P} = 200.3 Hz, J_{P-P} = 40.6 Hz), 40.6 (ddd, J_{Rh-P} = 204.4 Hz, J_{P-P} = 39.3 Hz, J_{P-F} = 5.2 Hz). HRFABMS [M^+]: Calcd m/z 747.1628; found, m/z 747.1657.

Synthesis of $[Rh(\eta^1\text{-}PhO(CH_2)_2PPh_2)_2(CO)_3]BF_4$ (9). Complex **2a** (0.010 g, 0.012 mmol) in CD_2Cl_2 (1 mL) was reacted with 1 atm of CO in an NMR tube for 15 min. The solution color changed from orange-red to bright yellow during the course of the reaction indicating the formation of **9**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.21 (m, 4H, CH_2P), 4.32 (m, 4H, CH_2O), 6.58 (d, J_{H-H} = 7.4 Hz, 4H, (*o*-C_6H_5)O), 6.96 (t, J_{H-H} = 7.4 Hz, 2H, (*p*-C_6H_5)O), 7.21 (m, 4H (*m*-C_6H_5)O), 7.64 - 7.51 (m, 20H, Ph_2P). $^{31}P\{^1H\}$ NMR (for ^{13}CO labeled **9**, 121 MHz, CD_2Cl_2, −77 °C): δ 31.5 (dq, J_{Rh-P} = 71.7 Hz, J_{P-C} = 14.1 Hz). $^{13}C\{^1H\}$ NMR (for ^{13}CO labeled **9**, 75 MHz, CD_2Cl_2, −77 °C): δ 185.2 (dt, J_{Rh-P} = 66.2 Hz, J_{P-C} = 14.4 Hz). FABMS [M^+ − 2CO]: m/z 743.

Synthesis of $[Rh(\eta^1\text{-}PhO(CH_2)_2PPh_2)_2(CO)_2]BF_4$ (10). Upon removal of the CO atmosphere and solvent from the NMR tube containing dissolved **9**, complex **10** is formed in quantitative yield as determined by NMR spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.20 (m, 4H, CH_2P), 4.33 (m, 4H, CH_2O), 6.67 (d, J_{H-H} = 8.0 Hz, 4H, (*o*-C_6H_5)O), 6.98 (t, J_{H-H} = 7.3 Hz, 2H, (*p*-C_6H_5)O), 7.23 (m, 4H, (*m*-C_6H_5)O), 7.67−7.48 (m, 20H, Ph_2P). $^{31}P\{^1H\}$ NMR (for ^{13}CO labeled **10**, 121 MHz, CD_2Cl_2, −71 °C): δ 18.9 (dt, J_{Rh-P} = 106.8 Hz, J_{P-C} = 15.5 Hz). $^{13}C\{^1H\}$ NMR (for ^{13}CO labeled **10**, 75 MHz, CD_2Cl_2, −71 °C): δ 185.7 (dt, J_{Rh-P} = 64.1 Hz, J_{P-C} = 16.0 Hz). FT-IR (CH_2Cl_2): ν_{CO} = 1997 (vs), 1932 (w) cm^{-1}. FABMS [M^+]: m/z 743 [M^+ − CO].

Reaction of 2a with Acetonitrile. In an NMR tube, complex **2a** was reacted with neat CD_3CN to form a mixture of *cis* and *trans* acetonitrile adducts in a 4:1 ratio, $[Rh(\eta^1\text{-}PhO(CH_2)_2PPh_2)_2(cis\text{-}CD_3CN)_2]BF_4$ (**11**) and $[Rh(\eta^1\text{-}PhO(CH_2)_2PPh_2)_2(trans\text{-}CD_3CN)_2]BF_4$ (**12**), respectively. In CD_2Cl_2 with 3 equiv of CD_3CN, a similar mixture of **11** and **12** is formed. If this reaction is performed at −78 °C, only the *cis* adduct **11** is formed. As the temperature is raised (up to 55 °C), *cis* adduct **11** slowly converts into the *trans* adduct **12**. Data for **11**: ^{1}H NMR (300 MHz, CD_2Cl_2, −45 °C) δ 1.62 (s, 6H, CH_3CN), 2.11 (m, 4H, CH_2P), 4.46 (m, 4H, CH_2O), 6.79 (d, J_{H-H} = 7.7 Hz, 4H, *o*-C_6H_5), 6.96 (t, J_{H-H} = 7.3 Hz, 2H, *p*-C_6H_5), 7.42−7.25 (m, 24H, Phs); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −45°C): δ 35.7 (d, J_{Rh-P} = 171.8 Hz). Data for **12**: ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C) δ 1.63 (s, 6H, CH_3CN), 2.94 (m, 4H, CH_2P), 4.56 (m, 4H, CH_2O), 6.78 (m, 4H, *o*-C_6H_5), 6.94 (m, 2H, *p*-C_6H_5),

(10) (a) The synthesis of this compound was previously reported in the literature; however, an improved synthesis and the spectroscopic characterization are reported herein: Olah, G. A.; Krishnamurty, V. V.; Singh, B. P.; Iyer, P. S. *J. Org. Chem.* **1983**, *48*, 955. (b) Procedure for reduction reaction was taken from: Lau, C. K.; Tardif, S.; Dufresne, C.; Scheigetz, J. *J. Org. Chem.* **1989**, *54*, 491.

(11) Postulated as the intermediate in the reaction of $[Rh(\eta^6\text{-}C_8H_{14})_2(\mu\text{-Cl})]_x$ with $AgBF_4$ in THF; for synthesis of $[Rh(\eta^6\text{-}C_8H_{14})_2(\mu\text{-Cl})]_x$ see ref 9.

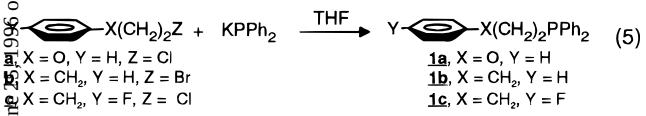
7.31−7.46, 7.68 (m, 24H, Phs); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, −45 °C) δ 22.8 (d, J_{Rh-P} = 130.1 Hz).

Crystal Structure of 2a. Single crystals of **2a** suitable for an X-ray diffraction study were grown by slow diffusion of a 1:10 mixture of methylene chloride and diethyl ether. The crystal was mounted on a glass fiber under degassed paratone-N oil. The data were collected at a temperature of −120 ± 1 °C using the ω-θ scan technique to a maximum 2θ value of 50.0°. In addition, the data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied with transmission factors of 0.80−0.86. Also, a correction for secondary extinction was applied (coefficient = 0.42235×10^{-7}). The structure was solved by Patterson methods with SHELXS-86. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were idealized.

NMR Kinetic Studies. Two dimensional exchange spectroscopy (EXSY) was used to determine the activation parameters for the arene−arene exchange reactions.[12] A standard NOESY pulse sequence ($\pi/2$, T_1, $\pi/2$, T_2, $\pi/2$) was used on a Varian 400 MHz FT NMR spectrometer. Mixing times ($T_2 = t_{mix}$) were varied with temperature. The rate of the exchange reaction (k) was determined by comparing the volumes of the cross peaks (V_{AB} and V_{BA}) and diagonal peaks (V_{AA} and V_{BB}) in the EXSY spectrum and evaluating with the mixing time in the equation $k = 1/t_{mix} \ln[(r+1)/(r-1)]$, where $r = (V_{AA} + V_{BB})/(V_{AB} + V_{BA})$.[12] From a plot of $\ln(k/T)$ versus $1/T$ modeled according to the Eyring equation, the $\Delta G^{\ddagger}_{298}$ values were calculated.[13]

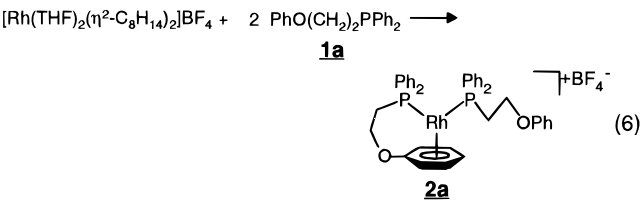
Results and Discussion

Synthesis and Characterization of Ligands 1a−c. The new hemilabile ligands **1a−c** were synthesized in high yield (70−83%) in the reaction between 1 equiv of $ArX(CH_2)_2Z$ with 1 equiv of $KPPh_2$, eq 5. They were isolated as white crystalline solids and fully characterized by ^1H NMR, ^{31}P NMR, and either high-resolution mass spectrometry or elemental analysis.



(5)

Synthesis and Characterization of Compounds 2a,b. Ligands **1a**,**b** react cleanly with Rh(I) precursors to form the new piano stool complexes **2a,b** with good yields (80−84%). For example, the bis(phosphine), η^6-arene piano stool complex **2a** was synthesized by the reaction of 2 equiv of ligand **1a** with 1 equiv of $[Rh(THF)_2(\eta^2\text{-}C_8H_{14})_2]BF_4$,[11] eq 6. Compound **2a** was isolated as an orange crystalline solid, and it has been characterized spectroscopically in solution and in the solid state by a single-crystal X-ray diffraction study. An ORTEP diagram of cation **2a** is shown in Figure 1, and crystallographic data are presented in Table 1. Selected bond distances and angles for **2a** are given in Table 2. The Rh−P and Rh−C bond distances are in the expected range for monomeric Rh compounds with bis(phosphine), η^6-arene piano stool geometry (Rh−P = 2.217−2.251 Å, Rh−C = 2.217−2.516 Å).[14] The Rh−P bond distance for the chelating phosphine ligand (2.228(1) Å) is shorter than the Rh−P bond distance for the monodentate phosphorus ligand (2.251(1) Å). The η^6-arene ring in complex **2a** is not planar but adopts a boat conformation with two short and four long Rh−C bond



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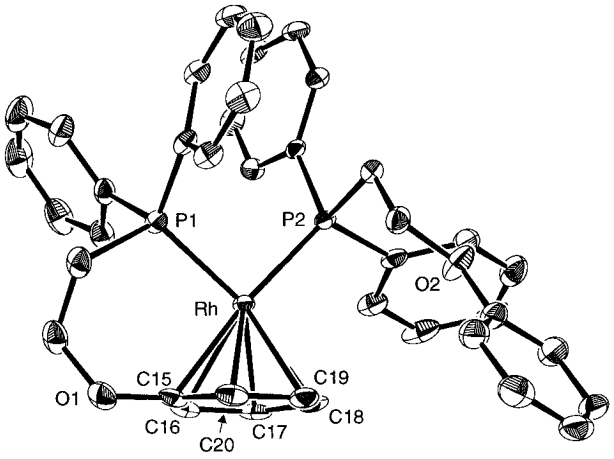


Figure 1. ORTEP diagram of **2a**. Thermal ellipsoids are given at 50% probability.

Table 1. Selected Crystal Data for 2a

formula	$C_{40}H_{38}BF_4O_2P_2Rh$
fw	802.4
cryst system	monoclinic
space group	$P2_1/c$
a, Å	10.595(3)
b, Å	17.116(5)
c, Å	19.564(5)
β, deg	92.16(2)
V, Å^3	3545(3)
Z	4
μ(Mo Kα), cm^{-1}	6.17
D_{calc}, g cm^{-1}	1.503
color	ruby red
size, mm	0.42 × 0.26 × 0.33
temp, K	153
diffractometer	Enraf-Nonius CAD-4
monochromator	graphite
scan method	$\omega-\theta$
radiation	Mo Kα (λ = 0.710 69 Å)
scan limit	$2 \le 2\theta \le 50.0$
reflcns collcd	6663
indepdt reflcns	6466
function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
obsd reflcts ($I > 3.00\sigma(I)$)	5133
variable paras	452
R(f), %	3.3
R(wf), %	4.3

Table 2. Selected Distances and Angles of 2a

Distances (Å)			
Rh−P1	2.228 (1)	Rh−C20	2.319 (3)
Rh−P2	2.251(1)	C15−C16	1.403(5)
Rh−C15	2.282(3)	C16−C17	1.400(5)
Rh−C16	2.350(3)	C17−C18	1.408(5)
Rh−C17	2.332(3)	C18−C19	1.407(5)
Rh−C18	2.270(3)	C19−C20	1.395(5)
Rh−C19	2.319(3)	C20−C15	1.424(5)
Rh-arene centroid	1.840(3)		

Angles (deg)			
C15−C16−C17	118.8(3)	C16−C17−C18	119.5(3)
C17−C18−C19	121.5(3)	C18−C19−C20	119.4(3)
C19−C20−C15	118.7(3)	C20−C15−C16	121.8(3)
P1−Rh−P2	93.28(9)		

(12) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.
(13) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: London, 1982.

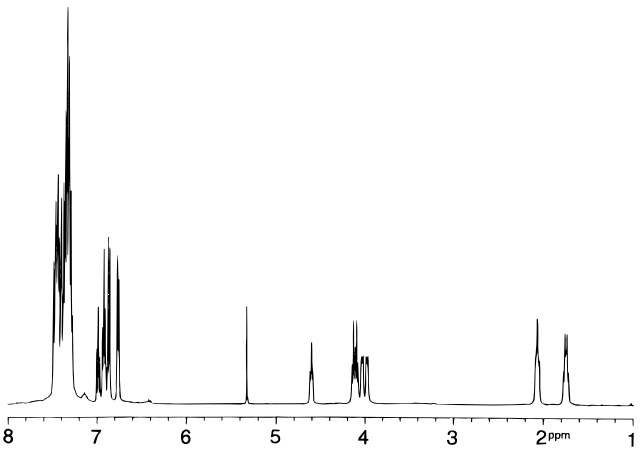


Figure 2. ^{1}H NMR spectrum of **2a** in CD_2Cl_2 at 20 °C.

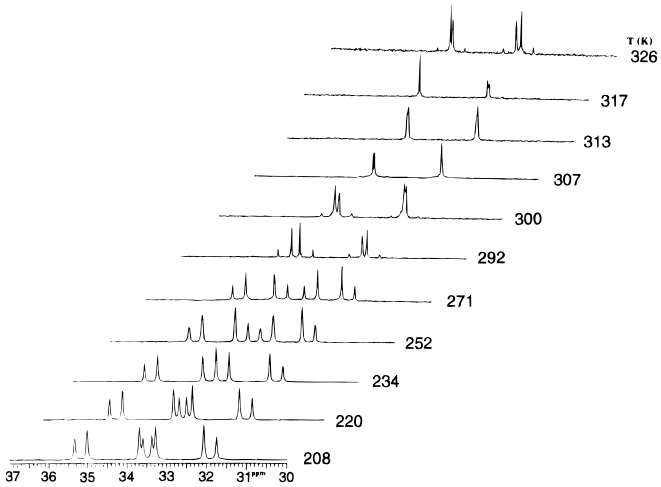


Figure 3. Variable-temperature ^{31}P NMR spectra of **2a** in THF-d_8 from 208 to 326 K.

distances. This deviation from planarity (0.020(3) Å) is a result of Rh d orbital and η^6-arene π-orbital overlap, which has been modeled extensively.[15] Several isoelectronic complexes with similarly distorted arenes have been reported in the literature.[14a,15]

Compound **2a** has been spectroscopically characterized, and all solution data are consistent with the solid-state structure. For example, the ^{31}P NMR spectrum of **2a** exhibits two resonances at δ 32.6 and 34.9 which are assigned to magnetically and chemically inequivalent P atoms due to coupling to each other and to the ^{103}Rh nucleus. Each resonance appears as a doublet of doublets (J_{Rh-P} = 210.4 and 198.7 Hz; J_{P-P} = 38.6 Hz), with coupling constants in the expected region for Rh complexes with this type of geometry (J_{Rh-P} = 190−209 Hz, J_{P-P} = 39−40 Hz).[14,16] Furthermore, in the ^{1}H NMR spectrum the two resonances at δ 2.07 and 1.76 can be assigned to the methylene protons α to the P atoms in the monodentate and chelated ligands, respectively, by comparision to the spectrum of the ligand. From the preceding assignments and a ^{31}P−^{1}H HETCOR NMR experiment of **2a**, the resonances at δ 32.6 and 34.9 have been assigned to the P atoms in the monodentate and chelated ligands, respectively.

Note that in the ^{1}H NMR spectrum of **2a**, the resonances in the normal aromatic region (δ 6−9) integrate for 29 rather than the expected 30 protons (Figure 2).[17] From a COSY experiment, the resonance for the H atom *para* to the ether group on the η^6-coordinated arene ring is found at δ 4.6, which is *remarkably upfield* of the other aromatic resonances including the *para* H atom of the free arene ring (δ 7.0). It is well-known that arene resonances shift upfield upon coordination to a metal;[18] however, to the best of our knowledge this is the largest upfield shift for a proton on an arene complex of Rh yet reported. This significant upfield shift may result from an interaction of this proton with the ring current associated with the free arene ring. However, if this is the case, it is not evident in the solid state structure of **2a**, and it could not be detected in a ^{1}H NMR NOESY experiment of **2a** in CD_2Cl_2. The effects of aromatic ring current on nearby proton nuclei are well documented.[19] For example, in macrocyclic aromatic systems, the resonances for the internal hydrogens are shifted upfield well outside the range of resonances for normal aromatic hydrogens.[17,20]

The ^{31}P NMR spectrum of **2a** in THF-d_8 is temperature dependent, Figure 3. At 208 K, the spectrum appears as two doublets of doublets and looks much like the room-temperature spectrum of **2a** in CD_2Cl_2. As the temperature is raised, the two resonances move toward each other. At 313 K, they coincidentally have the same chemical shift and appear as a doublet (δ 33.2, J_{Rh-P} = 204.2 Hz) indicating that they are magnetically equivalent. Above 313 K, the two resonances cross over and the P−P coupling reappears. This effect could be misinterpreted as an indication of η^6-arene−free arene exchange at the Rh(I) center of **2a**, a process that if fast on the ^{31}P NMR time scale, would make the two P ligands magnetically equivalent. However, this is not what the spectrometer is detecting. Instead, what has been recorded is a temperature-dependent chemical shift phenomenon. Indeed, a plot of chemical shift as a function of inverse temperature shows a definite dependence for the two resonances, Figure 4. Note that one resonance exhibits a rough linear dependance while the other one is clearly nonlinear, probably due to the differences in solvent interactions between different parts of the molecule.[22a] This effect can be related to the temperature dependence of a shielding parameter in the equation which determines the chemical shift of ^{31}P nuclei.[21] Although not common, dramatic temperature-dependent chemical shifts have been observed in other organometallic systems.[22] Note that coalescence,

(14) (a) Singewald, E. T.; Mirkin, C. A.; Yap. G.; Liable-Sands, L. M.; Rheingold, A. L. unpublished results. (b) Alvarez, M.; Lugan, N.; Donnadieu, B.; Mathieu, R. *Organometallics* **1995**, *14*, 365. (c) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304. (d) Townsend, J. M.; Blount, J. F. *Inorg. Chem.* **1981**, *20*, 269. (e) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069.

(15) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(16) Sassano, C. A.; Mirkin, C. A. *J. Am. Chem Soc.* **1995**, *117*, 11379.

(17) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1991.

(18) (a) Price, J. T.; Sorensen, T. S. *Can. J. Chem.* **1968**, *46*, 515. (b) Mann, B. E. *Chem. Commun.* **1971**, 976. (c) Kohler, F. H. *Chem. Ber.* **1974**, *107*, 570.

(19) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*: VCH: New York, 1991.

(20) Sondheimer, F.; Calder, I. C.; Elix, J. A.; Gaoni, Y.; Garratt, P. J.; Grohmann, K.; Di Maio, G.; Mayer, J.; Sargent, M. V.; Wolovsky, R. *Aromaticity*; Spec. Publ. No. 21; Chemical Society: London, 1967; p 75.

(21) (a) Jameson, C. J.; De Dios, A. C.; Jameson, A. K. *J. Chem. Phys.* **1991**, *95*, 9042. (b) Jameson, C. J. *Bull. Magn. Reson.* **1980**, *3*, 3. (c) Jameson, C. J.; Rehder, D.; Hoch, M. *J. Am. Chem. Soc.* **1987**, *109*, 2589.

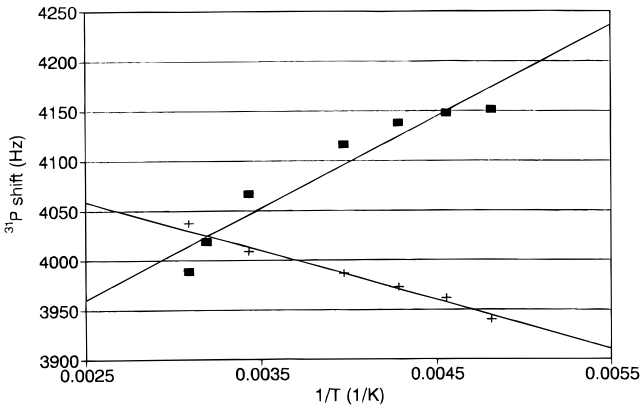
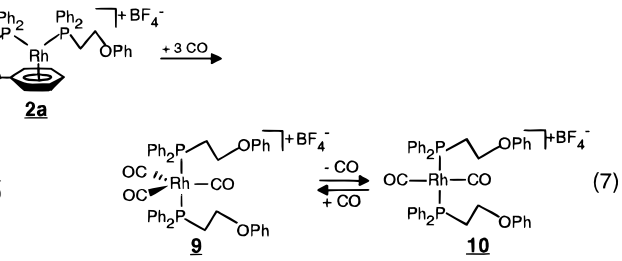


Figure 4. Plot of ^{31}P NMR chemical shifts of **2a** in THF-d_8 versus $1/T$. $1/T$ was arbitrarily chosen over T.

which would be an indication of an exchange process, is never observed in the variable-temperature NMR experiment, Figure 3.

Reactivity of 2a with Small Molecules. The (phosphinoalkyl)arene ligands in **2a** are extremely labile as evidenced by the reactivity of the complex with small molecules, such as CO, eq 7. When complex **2a** is



(7)

reacted with CO, the η^6-arene ligand is displaced and the tris(carbonyl) adduct, **9**, is formed, eq 7. Upon removal of the CO atmosphere and vacuum evaporation of the solvent, **9** loses a single carbonyl to form **10**. Using ^{13}CO, the products of these reactions were characterized by ^{31}P and ^{13}C NMR spectroscopy. The ^{31}P NMR spectrum of ^{13}CO-labeled **9** exhibits a single resonance for the magnetically and chemically equivalent phosphine ligands. This resonance appears at δ 31.5 as a doublet of quartets due to coupling of the ^{31}P nuclei with the ^{103}Rh nucleus (J_{Rh-P} = 71.7 Hz) and three ^{13}CO ligands (J_{P-C} = 14.1 Hz), Figure 5A. Removal of the ^{13}CO atmosphere results in the formation of **10** as evidenced by the new ^{31}P NMR resonance at δ 18.9, which appears as a doublet of triplets since the phosphines are now coupled to ^{103}Rh and only two ^{13}CO ligands rather than three, Figure 5B. The conversion of **9** to **10** by loss of one carbonyl is consistent with reactivity observed for one example of a related Rh phosphinoether complex, [Rh(η^2-CH$_3$O(CH$_2$)$_2$PCy$_2$)$_2$]-BPh$_4$.[23a] Other examples of similar Rh phosphinoether complexes are reported to lose two carbonyl ligands upon removal of the CO atmosphere.[23b–f]

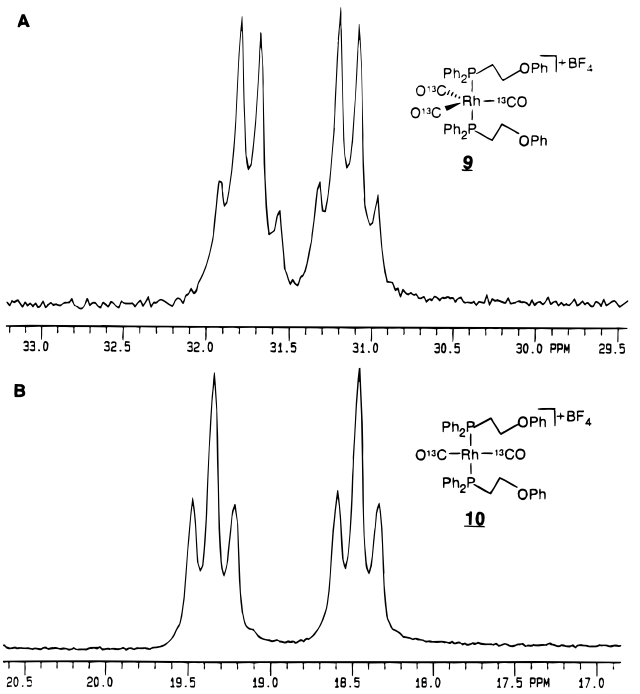
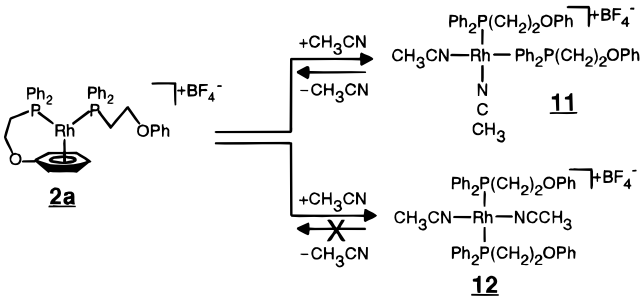


Figure 5. ^{31}P NMR spectra of **9** and **10** in CD_2Cl_2 at −77 and −71 °C, respectively.

Complex **2a** also reacts with excess acetonitrile to form a mixture of *cis*- and *trans*-bis(acetonitrile) adducts, **11** and **12**, eq 8. If **2a** is reacted with acetonitrile



(8)

at low temperature, only the *cis* adduct **11** forms; however, upon warming of the sample to room temperature, a fraction of **11** slowly converts to **12** until a mixture forms (4:1 *cis*:*trans*). Upon removal of the acetonitrile, the *cis* adduct **11** converts back to the starting material; however, the *trans* adduct, **12**, does not. At 55 °C in neat acetonitrile, a 1:2 ratio of **12** to **11** was formed. Acetonitrile adducts **11** and **12** are apparently the kinetic and thermodynamic products, respectively, in the reaction.

NMR Kinetic Studies. Although not detectible in the variable temperature one dimensional ^{1}H and ^{31}P NMR experiments, compound **2a** *does undergo* a facile, degenerate exchange reaction involving the η^6-arene and free arene rings in CD_2Cl_2 and THF-d_8, Scheme 1. The ether groups in compound **2a** are proposed to catalyze the exchange process possibly through the formation of the symmetrical *cis*-alkyldiphenylphosphine, *cis*-ether complex **13**, Scheme 1. This reaction was detected by a variable-temperature ^{1}H NMR EXSY experiment,[12] and the activation parameters for the exchange reaction were calculated from the Eyring equation.[13] EXSY is a useful technique for detecting exchange reactions with rates of 10^2–10^{-2} s^{-1}. This is in contrast to other one

(22) Examples of temperature-dependent chemical shifts: (a) Lindner, E.; Geprägs, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106. (b) Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1995**, *14*, 933. (c) Bianchini, C.; Farnetti, E.; Graziani, M.; Nardin, G.; Vacca, A.; Zanobini, F. *J. Am. Chem. Soc.* **1990**, *112*, 9190.

(23) (a) Lindner, E.; Wang, Q.; Mayer, H. A.; Fawzi, R.; Steimann, M. *Organometallics* **1993**, *12*, 1865. (b) Lindner, E.; Norz, H. *Chem. Ber.* **1989**, *123*, 459. (c) Lindner, E.; Norz, H. *Z. Naturforsch* **1989**, *44b*, 1493. (d) Lindner, E.; Andres, B. *Z. Naturforsch.* **1988**, *43b*, 369. (e) Lindner, E.; Andres, B. *Chem. Ber.* **1987**, *121*, 829. (f) Lindner, E.; Andres, B. *Chem. Ber.* **1986**, *120*, 761.

Table 3. Free Energy of Activation and $E_{1/2}$'s for 2a-c

	compd					
	2a	**2a**	**2b**	**2b**	**2c**	**2c**
$\Delta G^{\ddagger}_{298}$, kcal/mol (solvent)	17.7 (CD_2Cl_2)	14.1 (THF-d_8)	ND (THF-d_8)[a]	ND (CD_2ClCD_2Cl)[a]	23.2 (CD_2ClCD_2Cl)	20.2 (THF-d_8)
$E_{1/2}$ (mV)	573 (CH_2Cl_2)		515 (CH_2Cl_2)		605 (CH_2Cl_2)	

[a] ND = no detectible reaction; $E_{1/2}$ referenced versus FcH/FcH^+.

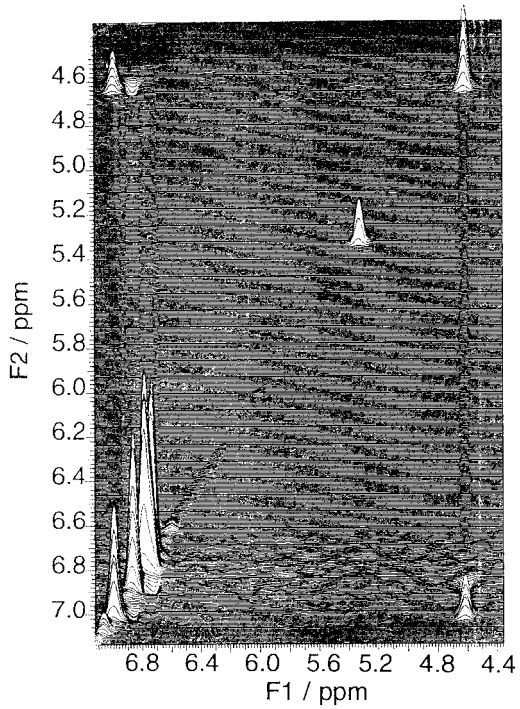
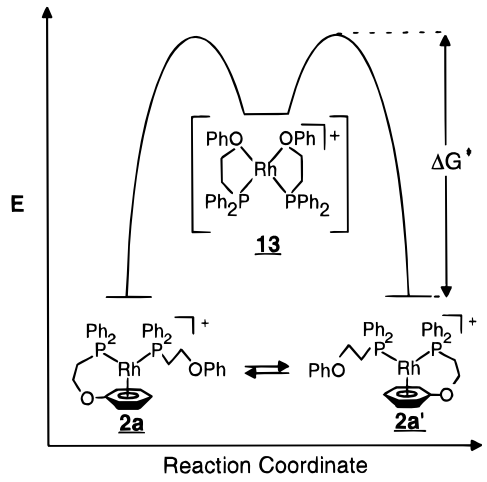


Figure 6. Aromatic region of the ^1H NMR EXSY spectrum of **2a** in CD_2Cl_2 at 30 °C.

Scheme 1



dimensional techniques, such as line shape analysis and spin saturation techniques, which measure rates of reactions above $10^{-1}-10^{4}$.[12] In a ^1H NMR EXSY spectrum, the one dimensional NMR spectrum is plotted along the diagonal, and the cross peaks are indicative of protons that undergo a chemical exchange reaction. The aromatic region of the ^1H NMR EXSY spectrum of **2a** is shown in Figure 6. A cross peak is observed which correlates the resonances at δ 4.6 and 7.0. These resonances are assigned to the H atoms which are *para* to the ether group on the η^6-arene and the free arene, respectively. The rate of the exchange reaction can be determined by integrating the area under the diagonal and cross peaks and relating these values to the mixing time (see Experimental Section). By performance of a variable-temperature EXSY experiment and determination of the rates of exchange over a range of temperatures, the activation parameters for the reaction can be calculated with the Eyring equation, Table 3.[13]

There are several notable features about the exchange reaction. First, the $\Delta G^{\ddagger}_{298}$ for **2a** in THF-d_8 is 3.6 kcal smaller than in CD_2Cl_2. Second, a symmetrical intermediate or a pair of intermediates that are mirror images of each other are necessary for this process since the overall reaction is degenerate. Because of the ability for Rh(I) to form stable square planar complexes, a reasonable intermediate in the exchange reaction between **2a** and **2a′** is the symmetrical, *cis*-diphenylphosphine, *cis*-ether Rh(I) complex **13**, Scheme 1. In the proposed intermediate the ether groups serve as internal solvent molecules, which occupy two coordination sites on the Rh(I) center during the exchange reaction.

In an effort to test the viability of this mechanism, complex **2b** was synthesized, characterized, and studied by ^1H and ^{31}P NMR spectroscopy. With **2b**, there is no possibility for the formation of an intermediate such as **13** since the ether moieties have been replaced by methylene groups. The ^{31}P NMR spectrum of **2b** in CD_2Cl_2 consists of two resonances, one for each phosphine, with a coupling pattern similar to that observed in the ^{31}P NMR spectrum of **2a** in CD_2Cl_2. Like the ^1H NMR spectrum of **2a**, the ^1H NMR spectrum of **2b** in CD_2Cl_2 exhibits an upfield resonance for the *para*-H atom of the η^6-arene (δ 4.68). This large upfield shift associated with the *para*-H atom seems to be a general phenomenon for complexes of this type.

Significantly, by ^1H NMR EXSY an arene−arene exchange reaction *could not* be detected for complex **2b** in CD_2Cl_2 or in THF-d_8 at temperatures comparable to the EXSY studies of **2a**. Even in dioxane-d_8 at temperatures near 100 °C, no exchange reaction could be detected. The $\Delta G^{\ddagger}$ for arene−arene exchange in **2b**, which is much higher than for **2a**, is likely due to a combination of two factors: (1) **2b** does not have internal ethers which can facilitate the arene−arene exchange reaction through an intermediate comparable to **13**, and (2) the η^6-arene in **2b** is bound more strongly to the Rh(I) center than the η^6-arene in **2a**. Others have shown that as the electron-donating properties of arenes are increased, their binding affinities for Rh(I) also increase.[24] Indeed the arene in **2b** is more electron rich than the arene in **2a** as evidenced by electrochemistry for the two complexes, Table 3. The Rh(I)/Rh(II) redox couple can be used as a diagnostic tool to determine the relative electron-donating properties of the arenes, when coordinated to Rh(I), in these isostructural complexes.[25] Compound **2a** is 58 mV more difficult to oxidize than

(24) (a) Espinet, P.; Bailey, P. M.; Downey, R. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1048. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

(25) Reversible Rh(I)/Rh(II) couples are unusual for mononuclear organometallic compounds; however, this tends to be a property common to this class of compounds. A detailed study of this redox couple in a series of piano stool complexes has been undertaken, ref.[14a]

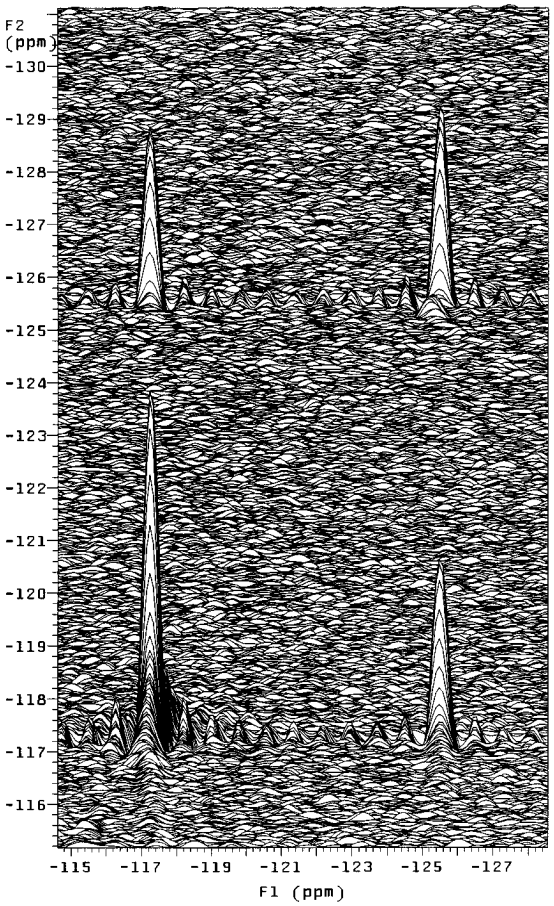
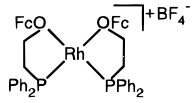


Figure 7. The ^{19}F NMR EXSY spectrum of **2c** in CD_2ClCD_2Cl at 60 °C.

2b, showing that the anisole-like ligand in **2a** (when coordinated to Rh(I)) is less electron donating than the tolyl-like ligand in **2b**. If the binding strength of the η^6-arene is the dominant factor controlling the activation barrier, then a Rh complex with an arene that is less electron rich than the arene ligands in **2a**,**b** is likely to have the lowest barrier to exchange.

To test this hypothesis, complex **2c**, which has a relatively electron-deficient η^6-arene ligand and does not possess ether groups, was synthesized and characterized. Note that the $E_{1/2}$ of complex **2c** is 32 mV more positive than the $E_{1/2}$ of **2a** indicating that the F atom significantly decreases the electron-donating properties of the arene for **2c**. Although an arene−arene exchange reaction for **2c** could not be detected by ^{19}F NMR EXSY in CD_2Cl_2, it was observed in CD_2ClCD_2Cl at elevated temperatures, Figure 7; CD_2ClCD_2Cl has a higher boiling point than CD_2Cl_2. In the EXSY experiment, a cross peak is observed, which correlates the resonances for the two F atoms on the exchanging arene rings. The $\Delta G^{\ddagger}_{298}$ determined from an Eyring plot of the EXSY data for **2c** in CD_2ClCD_2Cl is 5.5 kcal higher than the $\Delta G^{\ddagger}_{298}$ for **2a** in CD_2Cl_2, Table 3. Even though it has a more strongly binding arene than **2c**, compound **2a**'s barrier to exchange is lower than **2c**'s. Although $\Delta G^{\ddagger}_{298}$ is affected by solvent, the same trend that is observed in halogenated solvents is observed for **2a**,**c** in THF-d_8. The $\Delta G^{\ddagger}_{298}$ for **2c** in THF-d_8 is 6.1 kcal higher than the $\Delta G^{\ddagger}_{298}$ for **2a** in THF-d_8. This reinforces the importance of the proposed intermediate **13** in the **2a** to **2a′** arene exchange reaction even in a mildly coordinating solvent such as THF, Scheme 1. This is reasonable since we know from other studies that THF *does not* displace the ether groups in the isoelectronic model compound **14**.[26] Even though the η^6-arene in **2c** binds significantly



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less strongly than the η^6-arene in **2a**, the barrier to exchange for **2a** is lower than for **2c** in both a potentially coordinating solvent (THF-d_8) and a solvent which is less likely to coordinate (CD_2Cl_2 and CD_2ClCD_2Cl). Note that the solvent polarities for CD_2Cl_2 and CD_2ClCD_2Cl are comparable,[27] suggesting that the difference in the $\Delta G^{\ddagger}_{298}$ for the arene−arene exchange processes involving **2a**,**c** is dependent on the solvent polarity and not necessarily the coordinating properties of the solvent systems studied herein. This is in contrast to the intramolecular arene exchange reactions observed for (diarylalkane)tricarbonyl chromium complexes.[4e] Traylor and Goldberg determined that the rate of the arene−arene exchange reaction increased in the presence of coordinating solvents such as ketones and ether moieties and via a detailed kinetic investigation proposed an intermediate which is a solvent adduct. Unlike their systems, we propose that the arene−arene exchange between **2a** and **2a′** is not catalyzed by a coordinating solvent but by its internal ether groups.

Conclusions

In summary, we have reported the design, synthesis, and characterization of a new class of hemilabile ligand based on the strongly binding phosphine and weakly binding arene moieties. Rh(I) complexes formed from these ligands undergo novel η^6-arene, free arene exchange reactions with rates that are dependent on the electron richness of the arene, polarity of the solvent, and the presence of ether groups that can catalyze the reaction. We conclude that the internal ethers in these complexes facilitate the exchange reaction most likely through the formation of a square planar, *cis*-phosphine, *cis*-ether Rh(I) intermediate.

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Supporting Information Available: Listings of crystallographic data, including Cartesian coordinates, thermal parameters, and complete bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

OM960114C

(26) Singewald, E. T.; Mirkin, C. A.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1624; *Angew. Chem.* **1995**, *107*, 1725.

(27) Isaacs, N. S. *Physical Organic Chemistry*; Wiley and Sons: New York, 1987; p 180.