Chemistry of Diazaphosphole−Phosphines. 3. Complexation Reactions of Substituted (Fluoro, Dimethylamino, or Trifluoroethoxy)diazaphosphinephospholes with Ru(II), Rh(I), and Rh(III) Precursors: The Crystal and Molecular Structures of Cyclopentadienylbis(κP-4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole Rhodium(I) and *trans*-Chlorocarbonylbis(κP-4-(dimethylaminophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole Rhodium(I)

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Metal complexes of a series of diphosphorus ligands, 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**), 4-(bis(dimethylaminophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**), and 4-bis(1,1,1-trifluoroethoxyphosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**3**), were prepared. Ligand **1** reacted with $CpRu(PPh_3)_2Cl$ to give the diastereotopic complex $CpRu(PPh_3)$(**1**)Cl (**4**). With $CpRh(CO)_2$ this same ligand gave $CpRh(\mathbf{1})_2$ (**5**), which was structurally characterized. The Cp−rhodium center carries two difluorophosphinodiazaphole ligands. The P−N bond distances, (1.670(4) and 1.672(3) Å), suggest partial multiple-bond character. $[Cp^*Rh(Cl)_2]$ with (**1**) gave $Cp^*Rh(Cl)_2$(**1**). Ligand **2** with $[Rh(CO)_2Cl]_2$ gave *trans*-Rh(CO)Cl(**2**)$_2$ (**7**), which was structurally characterized. The structure reveals two square-planar isomers in 75:25 ratio differing only in the interchange of Cl and CO. The two diazaphosphole ligands lie trans to each other and the planar diazaphosphole rings are oriented perpendicular to the square plane, stacked so that a mirror plane exists through the Cl−Rh−CO plane. The phosphorus−rhodium distance is 2.33 Å. The average P−N bond distance of the exo-phosphorus center and the dimethylamino groups is 1.683 Å, shorter than the normally accepted single-bond length. The dimethylamino nitrogen atoms on the exo-phosphorus are planar. Similarly, ligand **3** with $[Rh(CO)_2Cl]_2$ gave *trans*-[Rh(CO)Cl(**3**)$_2$] (**8**). The ligand action ranges in reactivity from a similarity to phenylphosphines through to PF_3, reflecting the variation in basicity induced by substituent changes on the exo-phosphorus.

Introduction

The nature of the ligand has a profound effect on the chemistry of a metal complex, and so design and "tailoring" of ligand properties can lead to new metal chemistry. Of particular recent interest in the evolution of homogeneous catalyst precursor species is the development of chelate ligands with multifunctional character particularly because such ligands can open reaction sites of different character while simultaneously maintaining one stable link to the metal center. In this way, potentially facile reversibility can be generated. Chelated ligands with differential reactivity have been termed "hemilabile".[1−3] An enormous number of different combinations exist with all manner of attachment types, and a particular ligand (or metal−ligand combination) can provide vastly improved (and unexpected) levels of catalytic performance.

Simple phosphines are widely used in support of homogeneous catalytic processes,[4] but development of the extensive substitutional chemistry and structural environments demonstrated by phosphorus opens an enormous potential for the development of hemilabile ligand chemistry incorporating phosphorus.

We have previously described[5] a set of 4-phosphinodiazaphospholes as potential multifunctional ligands with three possible coordination sites (Scheme 1), either

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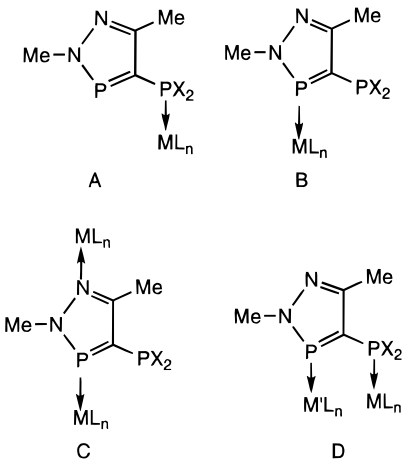
Scheme 1. Ligand System and Its Coordination Modes[a]



[a] In the present system X = F (**1**), X = NMe_2 (**2**), and X = OCH_2CF_3 (**3**).

of the two P(III) centers, the three-coordinate exocyclic phosphorus (A) or the two-coordinate ring phosphorus (B),[6,7] or the unsubstituted nitrogen (C) in the ring. Athough possible, this ligand is unlikely to act as a bis(phosphine) chelate, as is sometimes occasionally observed with bis(diphenylphosphino)methane(dppm), because the single backbone carbon connecting the two P(III) centers in the diazaphospholephosphine makes the bite angle too large to favor a single metal incorporated in a four-membered ring. More likely is the possibility that this ligand system would act as a bridge in a way similar to dppm (e.g., Scheme 1, D). Both of the modes (A[5,8,9] and B[6,7]) have been observed. The limited previous studies of the coordination chemistry of this bifunctional phosphinephosphole have not yet revealed situations in which both phosphorus centers are simultaneously involved in coordinate interactions.

In this report we describe the application of three selected diazaphospholephosphine ligands with Rh and Ru sources. Both of these elements have extensive phosphine coordination chemistry because of their widespread use in homogeneous catalytic systems[10−12] and offer opportunitues for coordination of either P(III) center.

Experimental Section

All experimental manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercial reagents were used as received. Solvents were dried and freshly distilled prior to use: diethyl ether was distilled from sodium benzophenone, hexane from sodium, acetonitrile from P_2O_5 (and then stored over CaH_2). The deuterated solvents, $CDCl_3$ and CD_2Cl_2, were distilled over P_2O_5 and stored over molecular sieves under argon before use.

NMR spectra were recorded on Bruker WH-200 and WH-400 spectrometers using the deuterium signal of the solvent as both the reference and the signal lock. Respective operating frequencies were as follows: ^{1}H (200.133 and 400.135 MHz), ^{13}C (50.323 and 100.614 MHz), ^{31}P (81.015 and 161.977 MHz), ^{19}F (188.313 and 376.503 MHz). External standards for ^{13}C and ^{1}H were $SiMe_4$ and for ^{31}P, 85% H_3PO_4. $CFCl_3$ was used as solvent, internal reference, and internal lock for ^{19}F spectra. Positive shifts lie downfield in all cases. NMR spectra were simulated with PANIC[13] or gNMR.[14] Chemical ionization (CI) mass spectra were recorded using an AEI MS50 spectrometer exciting with ammonia at 16 eV. Low-resolution mass spectra (electron impact, EI) were recorded at 16 or 70 eV on an AEI MS50 spectrometer. Infrared spectra were recorded as CH_2Cl_2 casts on KBr cells using a Nicolet 7199 infrared spectrometer. Elemental analyses were performed by the Microanalytical Services Laboratory at the University of Alberta. Melting points were determined on samples in sealed melting point capillaries and are uncorrected.

The parent diazaphosphole precursor, 4-(dichlorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole, and the ligands, 4-(difluorophosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**1**), 4-(bis(dimethylamino)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**2**), and 4-(bis(2,2,2-trifluoroethoxy)phosphino)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole (**3**), were prepared as described elsewhere[5] Organometallic precursors TlCp,[15] $CpRu(PPh_3)_2Cl$,[16] $[Rh(CO)_2Cl]_2$,[17] and $[Cp^*RhCl_2]_2$[18] were prepared as described in the literature.

Preparations. $CpRu(PPh_3)(1)Cl$ (4). To a solution of $CpRu(PPh_3)_2Cl$ (0.523 g, 0.72 mmol) in 25 mL of benzene was added the phosphole, **1** (0.1 mL, 0.72 mmol), via syringe. The solution was heated to reflux for 24 h. The solution was cooled, and the solvent was removed in vacuo to leave an orange oily material. The oil was washed with hot hexanes. Recrystallization from diethyl ether/dichloromethane yielded orange crystals. The yield of **4** was 0.357 g (76.7%), mp 112 °C. Anal. Calcd for $C_{27}H_{26}ClF_2N_2P_3Ru$: C, 50.20; H, 4.06; Cl 5.46; N, 4.34. Found: C, 50.15; H, 4.02; Cl 5.60; N, 4.37. MS (FAB, *m*/*z*): 646 (M, 17.8), 611 (M − Cl, 31.5), 429 (M − C − **1**, 100). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F) 843 (s), 792 (s). NMR data ($CDCl_3$) $^{31}P\{^1H\}$: P(σ^2), δ 258.90 (ddd, $^2J_{PP}$ 116 Hz, $^3J_{PF}$ 19

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Hz, $^3J_{PF}$ 15 Hz); P(σ^3), δ 216.59 (dddd, $^2J_{PP}$ 116 Hz, $^1J_{PF}$ 1131 Hz, $^1J_{PF}$ 1057 Hz, $^2J_{PPh3}$ 74 Hz); PPh_3, δ 48.16 (dd, $^2J_{PPh3}$ 74 Hz, $^3J_{PF}$ 7 Hz); ^{1}H, C−CH_3 δ 2.52 (s), P(σ^2)−N−CH_3 δ 3.97 (d, $^3J_{\sigma^2PH}$ 8.0 Hz), Cp δ 4.70 (s), phenyl H δ 7.3−7.6 (m); ^{13}C{^{1}H}, C−*C*H_3 δ 15.49 (s), P(σ^2)−N-*C*H_3 δ 44.88 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−*C*−P δ 138.32 (d, $^1J_{\sigma^2PC}$ 345 Hz), N−*C*−CH_3 δ 154.36 (s); ^{19}F, F_1, δ −27.55 (ddd, $^2J_{FF}$ 30 Hz, $^1J_{\sigma^3PF}$ 1057 Hz, $^3J_{\sigma^2PF}$ 19 Hz); F_2, δ −42.92 (dddd, $^2J_{FF}$ 30 Hz, $^1J_{\sigma^3PF}$ 1131 Hz, $^3J_{\sigma^2PF}$ 15 Hz, $^3J_{FPPh_3}$ 7 Hz).

CpRh(1)$_2$ (5). To a solution of $[Rh(CO)_2Cl]_2$ (0.11 g, 0.29 mmol) in 10 mL of hexanes was added TlCp (0.19 g, 0.73 mmol). The solution was heated to reflux overnight and then filtered through Celite. The Celite was washed with 2.5 mL of hexanes to give a solution of $CpRh(CO)_2$. Phosphole **1** (0.1 mL, 0.72 mmol) was added to this solution by syringe, and the mixture was stirred at room temperature (22 °C) for 4 h. The solution was then reduced to half its volume and stored at −40 °C for 24 h, yielding X-ray quality orange crystals. A second crop was obtained by reducing the volume of hexanes and storing the concentrated solution at −40 °C. Total yield of **5** was 0.262 g (68.3%, mp 93−94 °C). Anal. Calcd for $C_{13}H_{17}F_4N_4P_4Rh$: C, 29.34; H, 3.22; N, 10.53. Found: C, 29.36; H, 2.86; N, 10.13. MS (FAB, *m*/*z*): 532 (M, 100), 350 (M − **2**, 85), 168 (CpRh, 66). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F), 835 (s), 786 (s). NMR data ($CDCl_3$): ^{31}P{^{1}H} (second order), P(σ^2), δ 259.9 (d(broad), $^2J_{PP}$ ∼175 Hz); P(σ^3), δ 188.5 (second order, $^2J_{\sigma^2P\sigma^3P}$ ∼175 Hz, $^2J_{\sigma^3P\sigma^3P}$ 102 Hz, $^1J_{PF}$ 1114 Hz, $^1J_{PRh}$ 306 Hz); ^{1}H, C−CH_3 δ 2.48 (s), P(σ^2)−N−CH_3 δ 3.97 (d, $^3J_{\sigma^2PH}$ 8 Hz), Cp δ 5.32 (s); ^{13}C{^{1}H}, C−*C*H_3 δ 15.49 (s), P(σ^2)−N−*C*H_3 δ 44.88 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−*C*−P δ 138.35 (d, $^1J_{\sigma^2PC}$ 35 Hz), N−*C*−CH_3 δ 154.48 (s); ^{19}F (second order), δ -36.13 ($^2J_{FRh}$ 19 Hz, $^3J_{\sigma^2PF}$ 18 Hz, $^1J_{\sigma^3PF}$ 1114 Hz); ^{103}Rh, δ −1278 ppm.

Attempt to Prepare [Rh(1)$_2$Cl]$_2$ from [Rh(CO)$_2$Cl]$_2$ or [Rh(cod)Cl]$_2$. A solution of phosphole **1** (0.1 mL, 0.72 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $[Rh(CO)_2Cl]_2$ (0.140 g, 0.36 mmol) (or of $[Rh(cod)Cl]_2$ (0.178 g, 0.36 mmol)) in 15 mL of dichloromethane and stirred for 4 h, during which time a red precipitate formed. In neither case did the ^{31}P{^{1}H} NMR spectrum indicate that the desired product had formed, so the reactions were not pursued further.

Cp*RhCl$_2$(1) (6). A solution of phosphole **1** (0.1 mL, 0.72 mmol) in 10 mL of dichloromethane was added dropwise at room temperature to a solution of $[Cp^*RhCl_2]_2$ (0.167 g, 0.36 mmol) in 15 mL of dichloromethane and stirred for 4 h The solution was reduced to ∼3 mL, 10 mL of hexanes was added, and the solution was stored overnight at room temperature (22 °C). During this time reddish-orange crystals of **6** (0.277 g, 78.3%, mp 135−140 °C (dec)) formed. Anal. Calcd for $C_{14}H_{21}Cl_2F_2N_2P_2Rh$: C, 34.24; H, 4.31; Cl, 14.44, N, 5.70. Found: C, 33.99; H, 4.20; Cl, 15.20, N, 5.82. MS (FAB, *m*/*z*): 491 (M + 1, 5). IR data (CH_2Cl_2 cast, cm^{-1}): ν(P−F), 756 (s), 786 (s). NMR data ($CDCl_3$): ^{31}P{^{1}H}, P(σ^2), δ 269.23 (d, $^2J_{PP}$ 103 Hz); P(σ^3), δ 188.78 (ddt, $^2J_{PP}$ 103 Hz, $^1J_{\sigma^3PF}$ 1171 Hz, $^1J_{\sigma^3PRh}$ 217 Hz); ^{1}H, C−CH_3 δ 2.48 (s), P(σ^2)−N−CH_3 δ 3.97 (d, $^3J_{\sigma^2PH}$ 8 Hz), C_5−(CH_3)$_5$ δ 1.95 (s); ^{13}C{^{1}H}, C−*C*H_3 δ 15.49 (s), P(σ^2)−N−*C*H_3 δ 44.88 (d, $^2J_{\sigma^2PC}$ 17 Hz), P−*C*−P δ 148.35 (d, $^1J_{\sigma^2PC}$ 35 Hz), N−*C*−CH_3 δ 156.70 (s), *C*$_5$−(CH_3)$_5$ δ 102.42 (d, $^1J_{CRh}$ 4 Hz) C_5−(*C*H_3)$_5$ δ 9.72 (s); ^{19}F, δ −62.18 ($^2J_{FRh}$ 12 Hz, $^3J_{\sigma^2PF}$ 13 Hz, $^1J_{\sigma^3PF}$ 1173 Hz).

***trans*-Rh(CO)Cl(2)$_2$ (7).** A solution of phosphole **2** (0.25 mL, 1.2 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $[Rh(CO)_2Cl]_2$ (0.117 g, 0.30 mmol) in 15 mL of dichloromethane and stirred for 4 h. The solution was concentrated to ∼5 mL, and hexane was added until the solution became slightly turbid. The solution was stored at −40 °C overnight to yield pale red crystals of **7** (0.149 g, 78.7%, mp 178 °C (dec)). Anal. Calcd for $C_{17}H_{36}ClN_8OP_4Rh$: C, 29.95; H, 5.65; Cl 11.05; N, 17.46. Found: C, 30.40; H, 5.89; Cl 11.35; N, 17.72. MS (FAB, *m*/*z*): 631 (M + 1, 5), 602 (M − CO, 22). IR data (CH_2Cl_2 solution, cm^{-1}): ν(CO), 1978 (s). NMR data ($CDCl_3$): ^{31}P{^{1}H}, P(σ^2), δ 246.92 (second order, "t", $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 51 Hz); P(σ^3), δ 103.34 ("dt", $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 51 Hz, $^1J_{\sigma^3PRh}$ 143 Hz); ^{1}H, C−CH_3 δ 2.43 (dd, $^4J_{PH}$ 0.9 Hz), P(σ^2)−N−CH_3 δ 4.03 (d, $^3J_{\sigma^2PH}$ 12.2 Hz), P(σ^3)−N−CH_3 δ 2.72 (d, $^3J_{\sigma^3PH}$ 7.6 Hz); ^{13}C-{^{1}H}, C−*C*H_3 δ 14.37 (s), P(σ^2)−N−*C*H_3 δ 41.88 (d, $^2J_{\sigma^2PC}$ 18 Hz), P−*C*−P δ 143.45 (dd, $^2J_{\sigma^2PC}$ 145 Hz, $^2J_{\sigma^3PC}$ 45 Hz), N−*C*−CH_3 δ 156.72 (dd, $^2J_{\sigma^2PC}$ 5 Hz, $^2J_{\sigma^3PC}$ 18 Hz).

***trans*-Rh(CO)Cl(3)$_2$ (8).** A solution of phosphole **3** (0.146 g, 0.42 mmol) in 10 mL of dichloromethane was added dropwise at room temperature (22 °C) to a solution of $[Rh(CO)_2Cl]_2$ (0.021 g, 0.053 mmol) in 15 mL of dichloromethane and stirred for 4 h. The solution was reduced to ∼3 mL, and 10 mL of hexanes was added. Storing the solution overnight at room temperature gave a light orange powder, **8** (0.068 g 75.3%, mp 189 °C (dec)). Anal. Calcd for $C_{17}H_{20}ClF_{12}N_4O_5P_4Rh$: C, 24.00; H, 2.37; Cl, 4.17, N, 6.59. Found: C, 24.06; H, 2.30; Cl, 4.28, N, 6.55. MS (FAB, *m*/*z*): 850 (M, 20). NMR data ($CDCl_3$): ^{31}P{^{1}H}, P(σ^2), δ 251.88 ("t", $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 52 Hz); P(σ^3), δ 159.78 (d"t", $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ 52 Hz, $^1J_{PRh}$ 187 Hz); ^{1}H, C−CH_3 δ 2.48 (s), P(σ^2)−N−CH_3 δ 3.97 (d, $^3J_{\sigma^2PH}$ 8.0 Hz), P(σ^3)−N−O−CH_2 δ 4.4−4.2 (m (broad)); ^{13}C{^{1}H}, C−*C*H_3 δ 15.49 (s), P(σ^2)−N−*C*H_3 δ 44.93 (d, $^2J_{\sigma2PC}$ 19 Hz), P−*C*−P δ 149.36 (d, $^1J_{\sigma^2PC}$ 30 Hz), N−*C*−CH_3 δ 155.03 (s); ^{19}F, δ −74.57 (s).

Results and Discussion

Reaction of (1) with CpRu(PPh$_3$)$_2$Cl; Formation of CpRu(PPh$_3$)(1)Cl (4). The reaction of **1** with $CpRu(PPh_3)_2Cl$ in refluxing benzene produced the monosubstituted diazaphospholephosphine complex $CpRu(PPh_3)$(**1**)Cl (**4**) in good yield. The ^{31}P{^{1}H} and the ^{19}F NMR spectra (Figure 1) confirmed the formulation, and in addition both the ^{31}P and ^{19}F NMR indicated that the fluorine atoms on the exo-phosphorus of the phosphinodiazaphosphole were diastereotopic due to the creation of a stereogenic ruthenium center through the substitution of one phosphine with the new ligand. A Newman projection of the complex is depicted in Figure 2. The ^{31}P{^{1}H} NMR spectrum showed a small downfield shift of 4 ppm (259.34 ppm) for the resonance of the σ^2P center, indicating that this center was not likely the donor site; however, the exo-phosphorus center also showed only a small downfield shift of 8 ppm to 200.04 ppm. The signal for the exo-phosphorus showed two different couplings to fluorine atoms as well as coupling to the phosphorus atom in the diazaphosphole ring. Coupling was also observed to the phosphorus of the triphenylphosphine coordinated to the ruthenium. The most dramatic spectral changes were found in the ^{19}F NMR spectrum because of the creation of the stereogenic center; one of the fluorine signals was shifted downfield (to −27.5 ppm, a shift of 59 ppm vs the free ligand) and showed coupling to both phosphorus centers of the diazaphosphole ring ($^1J_{PF}$ = 1057, $^3J_{PF}$ = 15 Hz) and to the other fluorine atom ($^2J_{FF}$ = 30 Hz). The other fluorine resonance was shifted downfield but by a lesser amount (to −41.0 ppm, a shift of 47 ppm vs the free ligand). This latter fluorine signal showed coupling to all three of the phosphorus atoms of **4** ($^1J_{PF}$ = 1131 Hz, $^3J_{PF}$ = 19 Hz, and $^3J_{(PPh3)F}$ = 7 Hz). Applying a Karplus-type relationship to this vicinal coupling suggests that the fluorine trans to the PPh_3 group should show a larger coupling to this phosphorus center than the fluorine gauche to the PPh_3, a coupling that should be very small. The ^{31}P{^{1}H} exo-phosphorus spectral region

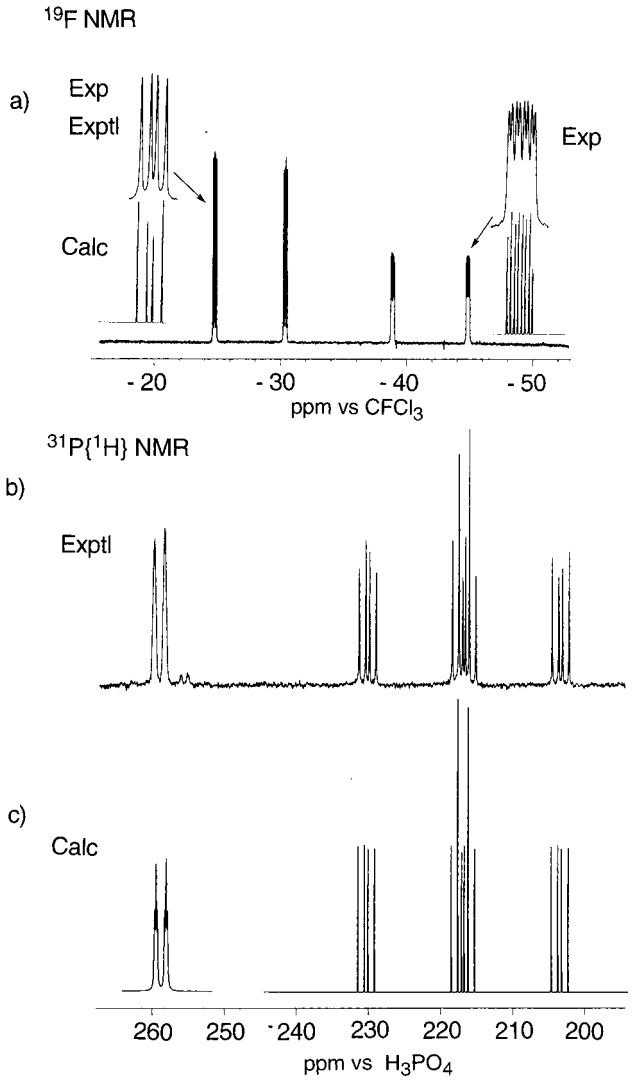

Figure 1. (a) Experimental ^{19}F NMR (188.313 MHz) spectrum of complex **4** in $CDCl_3$. The fine structure that appears in each of the two major doublets is illustrated in the expansions, and the simulated pattern for each of these multiplet units is illustrated below the expansion. (b) $^{31}P\{^1H\}$ NMR spectrum (81.015 MHz) of the diazaphosphole-phosphorus centers only for complex **4** (Ru) in $CDCl_3$. An additional signal due to PPh_3 (not illustrated) occurs at 48.16 ppm. (c) Simulated ^{31}P spectrum of **4**.

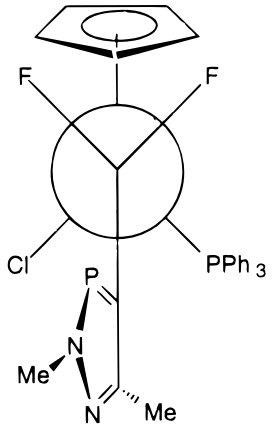

Figure 2. Newman projection of the structure of **4**.

and the ^{19}F NMR spectra were simulated, and their calculated spectra obtained with parameters given in Table 1 are also shown in Figure 1. It is interesting to note that with an excess of **1** only the monosubstituted product was obtained, in contrast to the behavior of Ph_2PH with the same Ru precursor, which gave both mono- and disubstituted phosphine products.[19] This might suggest that **1** possesses dominant bulky character, but as we show below and elsewhere,[5,9] multiple substitution with **1** is possible and the ligand packs nicely around the metal center. In this particular case, however, it is likely that the second replacement of **1** would introduce significant interference with the Cp ring, which inhibits further replacement by a second mole of **1**.

Reactions with Rhodium Complexes. A convenient and standard route to a wide variety of mononuclear and binuclear Rh(I) complexes is the simple cleavage of the chloro-bridged dimeric complex $[Rh(cod)Cl]_2$ with the selected phosphine ligand. Stoichiometric reaction usually results in the formation of monomeric Rh(cod)(L)Cl complexes. With excess phosphine in noncoordinating solvents, such as pentane, displacement of the cyclooctadiene or related olefin ligands occurs in addition to cleavage of the dimer to yield $RhCl(phosphine)_3$ complexes.[10] This well-established chemistry along with our results[5,9] in other systems which indicates that **1** acts in a fashion similar to PF_3 offering a moderate σ donor capability coupled with good π acceptor properties[5,20,21] suggested that the difluorophosphinodiazaphosphole (**1**) would easily form complexes of the above types with a variety of rhodium(I) precursors. It was not obvious however whether the donor site would be the σ^2 ring phosphine or the exocyclic phosphine center, particularly in view of the fact that the basicity of the σ^3 center has been greatly reduced by fluorination. Also unclear was whether the bulk of the phosphole ring would influence the coordination abilities of the ligand. Rather surprisingly, then, we found that reaction of **1** with a variety of dimeric rhodium(I) precursors such as $[Rh(cod)Cl]_2$, $[Rh(coe)_2Cl]_2$, and $[Rh(CO)_2Cl]_2$ resulted only in the decomposition of both the starting phosphine **1** and the rhodium complexes and no identifiable complexes for reasons that are not clear. It is possible that **1** is such a poor σ donor that it cannot cleave the rhodium−chlorine bridge, but, even so, phosphorus trifluoride or dimethylaminodifluorophosphine reacts readily with a variety of rhodium(I) precursors with the replacement of either the π-alkene or carbon monoxide to give dimeric chloro-bridged complexes of the type $[RhCl(PR_3)_2]_2$.[11] It is therefore obvious that the chemistry of the difluorophosphinephosphole is different from these other fluorophosphines because we describe (below and elsewhere[5,9]) stable complexes of this ligand, which indicates that normal complexes are indeed accessible and that the difficulty encountered here in this particular Rh(I) system lies with a subtle interplay between this ligand and these particular precursors.

The Disubstituted Rh(I) Complex 5. Reaction of **1** with the monomeric rhodium(I) complex $CpRh(CO)_2$

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(20) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064−4065.
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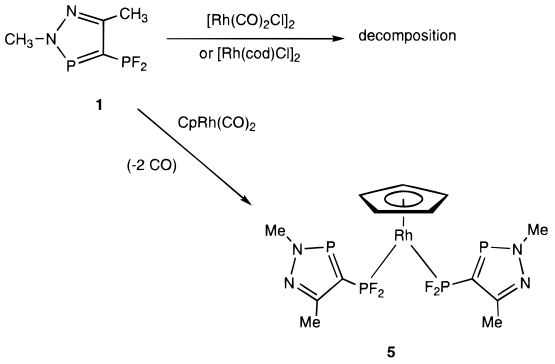
Table 1. $^{31}P\{^1H\}$ (and ^{19}F NMR) Data for Metal Complexes with 4-(Disubstituted)-2,5-dimethyl-2*H*-1,2,3σ^2-diazaphospholes[a,b]

complex	no.	$\delta\ \sigma^2$P (ppm)	$\delta\ \sigma^4$P (ppm)	$^2J_{PP}$ (Hz)	$^1J_{PRh}$ (Hz)	δ F (ppm)	$^1J_{\sigma^4PF}$ (Hz)	$^3J_{\sigma^2PF}$ (Hz)
CpRu(PPh_3)(**1**)Cl	**4**	258.90[c]	216.59[c]	116		−27.55[c]	1057	19
						−42.92[d]	1131	15
CpRh(**1**)$_2$	**5**	259.90[e]	188.52[e]	175[h]	306	−36.13[c]	1114	18
Cp*Rh(**1**)Cl_2	**6**	269.50[f]	188.23[e]	103	217	−62.32[g]	1171	13
trans-Rh(CO)(**2**)$_2$Cl	**7**	246.92[h]	103.34[h]	51[i]	143			
trans-Rh(CO)(**3**)$_2$Cl	**8**	251.88[h]	159.78[h]	52[i]	187			

[a] Chemical shifts δ in ppm in $CDCl_3$ with respect to 85% H_3PO_4 or $CFCl_3$ as appropriate. [b] In $CDCl_3$. [c] Doublet of doublet of doublets. [d] Doublet of doublet of doublet of doublets. [e] Doublet of triplets. [f] Doublet. [g] Doublet of doublet of triplets. [h] Second order. [i] $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$.

provided access to a difluorophosphinediazaphosphole−Rh(I) complex. Although in general phosphines replace only one CO in $CpRh(CO)_2$,[22] in this case **1** replaced both carbonyls to give **5** (eq 1), a reaction which is similar to the behavior of this Rh precursor with phosphites.[23] This parallel reinforces our impression that **1** behaves in ways similar to PF_3 and phosphites.[5,9]



(1)

The $^{31}P\{^1H\}$ and the ^{19}F NMR spectra for **5** (Figure 3) are both very complex by virtue of the number of spins involved and because the spectra are second order.[24] The $^{31}P\{^1H\}$ NMR spectrum for the resonance for the σ^4P center consisted of a 69-line pattern centred at 188.68 ppm, while the signal for the σ^2P center showed a broad doublet (259.81 ppm). The phosphorus spectrum reveals a specific large separation (306 Hz), which is the one-bond phosphorus−rhodium coupling constant (as verified by the inverse detection Rh NMR determination),[25] and the system is further complicated by the large triplet spacing due to $^1J_{PF}$. The complexity of the ^{31}P NMR spectrum precluded full simulation analysis, but (vide infra) insight was obtained from selective decoupling experiments combined with the analysis of the simplified spectra. The ^1H NMR spectrum reveals that the cyclopentadienyl protons are not coupled to the exo-phosphorus, in contrast to the behavior of the related rhodium complex Cp*Rh$(PF_3)_2$.[26,27] The fluorine signal was centered at −36.13 ppm and is dominated by the triplet created by $^1J_{PF}$ (which is approximately 1145 Hz). The ^{103}Rh chemical shift (−1280 ppm), measured by an inverse detection $^{31}P-^{103}Rh$ analysis,[25] lies in a range typical of many $CpRhL_2$ complexes.[28]

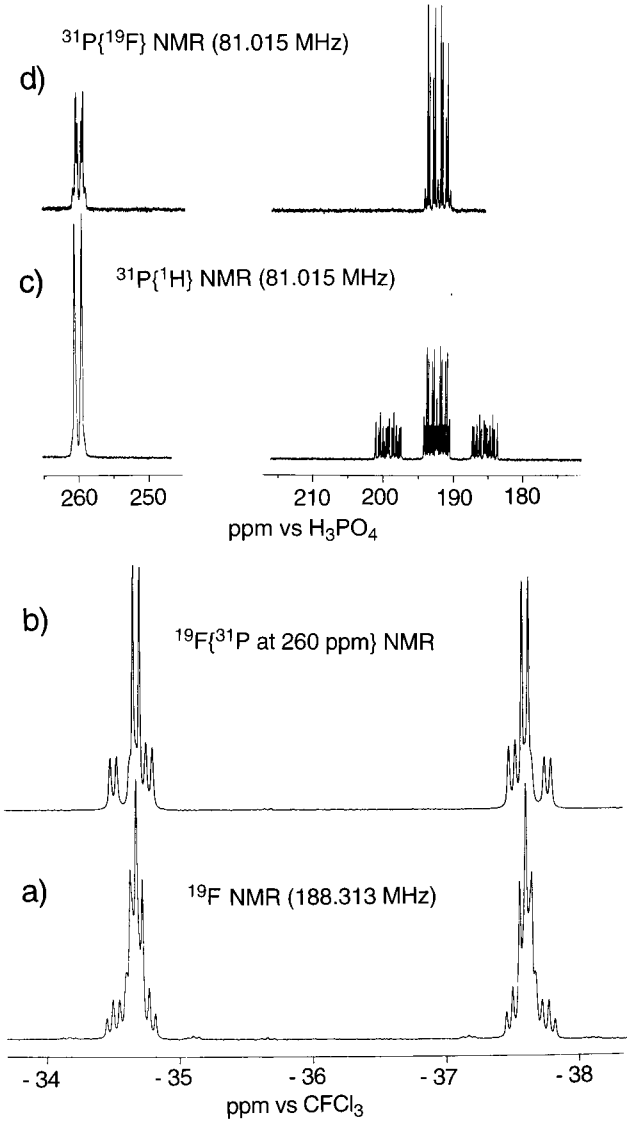


Figure 3. (a) ^{19}F NMR spectrum (188.015 MHz) of CpRh(**1**)$_2$ (**5**) in $CDCl_3$ and (b) the specifically σ^2 phosphorus-decoupled $^{19}F\{^{31}P$ at 260 ppm$\}$ NMR (188.313 MHz) spectrum of **5**. (c) $^{31}P\{^1H\}$ NMR spectrum (81.015 MHz) of CpRh(**1**)$_2$ (**5**) in $CDCl_3$ and (d) fluorine-decoupled $^{31}P\{^{19}F\}$ NMR spectrum of **5** in the same solvent.

Decoupling of the fluorine coupling interaction simplified the $^{31}P\{^1H\}$ NMR spectrum to an 11-line pattern. The signal for the σ^2P unit remained second order,

(22) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 243−247.
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(28) Goodfellow, R. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 521−561.

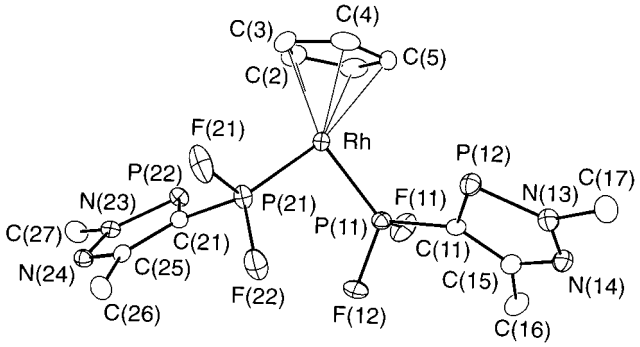


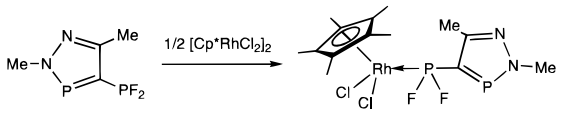
Figure 4. ORTEP[29] plot of the molecular structure of cyclopentadienylbis(κP-difluoro{2,5-dimethyl-1,2,3-diazaphosphol-4-yl}phosphine)rhodium(I), **5,** showing the atom-labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level, and all hydrogen atoms have been omitted for clarity.

which implies that both phosphorus centers in the diazaphosphole ring are magnetically inequivalent, and this complex should be considered as either an AA′DD′MM′M″M‴X or an AA′DD′M_2M′$_2$X type spin system.[24] Decoupling of the phosphorus signal at 260 ppm led to the simplification of the fluorine NMR spectrum to a 12-line pattern (Figure 3). From this spectrum, the fluorine−rhodium coupling was calculated to be 19 Hz, but the $^4J_{FF}$ value was not resolved. This spectrum also allows the calculation of the two-bond phosphorus−phosphorus coupling to the PF_2 moiety (102 Hz), which in turn yields a $^1J_{PF}$ value of 1114 Hz and a $^3J_{PF}$ coupling of 11 Hz. The analogous coupling constant values for the related Cp*Rh$(PF_3)_2$ complex[27] were $^2J_{PP}$ = 178 Hz, $^1J_{PF}$ = 1135 Hz, $^3J_{PF}$ = 6 Hz, and $^3J_{FRh}$ = 30 Hz. Unfortunately the ^{31}P data for this PF_3 complex were not reported,[27] as it would be of interest to ascertain if this complex also shows a larger than usual Rh−P coupling.

The infrared spectrum of **5** showed relatively broad P−F stretching frequencies compared to the sharp bands observed in the free ligand **1**. These peaks were shifted slightly to a higher frequency (835 and 786 cm^{-1}), relative to **1** (805 and 780 cm^{-1}), a shift that is expected since the σ* orbitals of the P−F are accepting electron density from the metal complex.

A solid-state structure determination of CpRh(**1**)$_2$ (**5**) showed a rhodium center subtended by a cyclopentadienyl ring and two difluorophosphinodiazaphole ligands as formulated (Figure 4).[29] The crystal structure details and metrical parameters are given in Tables 2−4. The structure is quite symmetric; excluding the Cp ring, the two phospholes are related by a C_2 axis through the Rh center. The angle between rhodium and the two exo-phosphorus centers, P(21)−Rh−P(11), is 94.56(5)°, smaller than that found for a similar (η^5-indenyl)-Rh$(PMe_3)_2$ complex (96.69°).[30] In **5** the phosphole rings are planar and the nitrogen at the 2-position in the ring is also planar, the sum of the angles about the nitrogen being 360°. The P(22)−N(23)−N(24) and the P(12)−N(13)−N(14) angles (117.3(3)° and 117.5(3)°, respectively) are wider than those observed for 2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphole itself (113.8°).[31] The carbon at the 4-position is also planar, with the P(21)−C(21)−P(22) angle being 121.6°, showing the sp^2 hybridization of the C(21). The angles about the two σ^{2}P centers, N(23)−P(22)−C(21) and N(13)−P(12)−C(11) are 88.6(2)° and 88.3(2)°, respectively. These angles are similar to that observed for the parent phosphole (88.2°).[31] Both the P(12)−N(13) and the P(21)−N(23) bond distances (1.670(4) and 1.672(3) Å) suggest some partial multiple-bond character when compared to the normally accepted P−N single (1.77 Å) and P=N double (1.57 Å) bond lengths.[32] Both two-coordinate phosphorus−carbon bond lengths show multiple bond character (P(12)−C(11) and P(22)−C(21) = 1.713 Å). A typical value for a P−C single bond is 1.84 Å, while that of a P−C double bond is 1.66 Å. The three-coordinate phosphorus−carbon bond lengths are shortened to 1.773 Å. The F(11)−P(11)−F(12) and F(21)−P(21)−F(22) bond angles are 95.3(2)° and 96.0(2)°, respectively, while the average P−F bond distance is 1.569 Å, which is longer than that previously observed[33] for the oxidized imino(difluoro)phosphinodiazaphosphole, where the P−F bond length was 1.537 Å. The difference in the P−F bond lengths of these two structures shows that the fluorines play a role in the bonding to the rhodium center by accepting electron density into the P−F antibonding σ* orbital formed from the phosphorus 3p orbital.

The Monosubstituted Rh(III) Complex, 6. Treating the rhodium(III) dimer, [Cp*RhCl_2]$_2$, with **1** readily gave the reddish-orange complex Cp*RhCl_2(**1**) (**6**) in high yield (eq 2). This precursor was used to explore both the possibility of forming a Rh(III) complex with this ligand and because the simplest possible reaction in this case is cleavage of the dimer, which was indeed observed. It is therefore a little surprising that simple dimer cleavage did not give the expected stable products in the case of the Rh(I) dimers used above.



1 6 (2)

The ^{31}P{^{1}H} NMR spectrum of **6** showed an $ADMX_2$ spin system[24] with an upfield shift for the exo-phosphorus center resonance (ca. 189 ppm) which is also coupled to the rhodium (216 Hz), to the σ^{2}P center (103 Hz), and to both fluorine atoms (1171 Hz). Although the magnitude of the rhodium−phosphorus coupling constant (216 Hz) in **6** was again larger than that normally observed for $^1J_{PRh}$, it is smaller than that observed in **5** (cf. 306 Hz). The relatively reduced $^1J_{PRh}$ value in this complex can be explained in terms of reduced π-bonding between the Rh(III) metal center and the phosphine as compared to that operative in the Rh(I) complexes.[34] The σ^{2}P center in **6** shifted slightly downfield (by 15 ppm to

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Table 2. Crystallographic Experimental Data for 5 and 7

	5	7
	A. Crystal Data	
empirical formula	$C_{13}H_{17}F_4N_4P_4Rh$	$C_{17}H_{36}ClN_8OP_4Rh$
fw (g/mol)	532.10	630.78
cryst dimens (mm)	0.37 × 0.22 × 0.08	0.35 × 0.18 × 0.07
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell params	*a*	*b*
a (Å)	14.653(2)	9.4866(9)
b (Å)	7.9711(8)	11.7338(13)
c (Å)	18.010(2)	14.9972(15)
α (deg)		68.686(8)
β (deg)	105.417(10)	73.004(8)
γ (deg)		66.764(7)
V (Å^3)	2027.9(4)	1407.2(2)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.743	1.489
μ (mm^{-1})	1.198	0.954
	B. Data Collection and Refinement Conditions:	
diffractometer	Enraf-Nonius CAD4[c]	Siemens P4/RA[d]
radiation (*λ*[Å])	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	incident beam (graphite crystal)	incident beam (graphite crystal)
temp (°C)	−50	−60
scan type	*θ*−2*θ*	*θ*−2*θ*
data collection 2*θ* limit (deg)	50.0	50.0
total data collected	3687 (−17 ≤ *h* ≤ 16, 0 ≤ *k* ≤ 9, 0 ≤ *l* ≤ 21)	5245 (0 ≤ *h* ≤ 11, −12 ≤ *k* ≤ 13, −17 ≤ *l* ≤ 17)
no. of ind reflns	3559	4916
no. of observations (*NO*)	2579 ($F_o^2 \geq 2\sigma(F_o^2)$)	2918 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXSI*-86[e])	direct methods (*SHELXSI*-86[e])
refinement method	full-matrix least-squares on F^2 (*SHELXSI*-93[f])	full-matrix least-squares on F^2 (*SHELXSI*-93[f])
absn corr method	DIFABS[g]	semiempirical (*ψ* scans)
range of absn corr factors	1.126−0.800	0.9965−0.8630
no. of data/restraints/params	3558 [$F_o^2 \geq -3\sigma(F_o^2)$]/0/239	4916 [$F_o^2 \geq -3\sigma(F_o^2)$]/2[e]/305
goodness-of-fit (*S*)[h]	1.002 [$F_o^2 \geq -3\sigma(F_o^2)$]	1.037 [$F_o^2 \geq -3\sigma(F_o^2)$][i]
final *R* indices,[i] $F_o^2 > 2\sigma(F_o^2)$	$R_1 = 0.0313$, $wR_2 = 0.0649$	$R_1 = 0.0623$, $wR_2 = 0.0776$
all data	$R_1 = 0.0688$, $wR_2 = 0.0747$	$R_1 = 0.1345$, $wR_2 = 0.0964$
largest diff peak and hole (e Å^{-3})	0.363 and −0.464	0.521 and −0.521

[a] Obtained from least-squares refinement of 37 reflections with 19.2° < 2*θ* < 27.7°. [b] Obtained from least-squares refinement of 32 reflections with 25.5° < 2*θ* < 28.0°. [c] Programs for diffractometer operation and data collection and reduction were those supplied by Enraf-Nonius. [d] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens. [e] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473. [f] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen: Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 < -3\sigma(F_o^2)$ except in the case of **5,** where one value having $F_o^2 < -3\sigma(F_o^2)$ was omitted). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger. [g] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. [h] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (*n* = number of data; *p* = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$). For **5** $a_0 = 0.0288$, $a_1 = 1.5071$, for **7** $a_0 = 0.0201$, $a_1 = 0$. [i] Distances involving the carbonyl group C(2)O(2) of the minor isomer were fixed as follows: *d*(Rh−C(2)) = 1.78(1) Å; *d*(C(2)−O(2)) = 1.12(1) Å. [j] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Table 3. Selected Interatomic Distances (Å) for Cyclopentadienylbis(κP-difluoro{2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphol-4-yl}phosphine)rhodium(I) (5)

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh	P(11)	2.1334(12)	P(21)	F(21)	1.576(3)
Rh	P(21)	2.1348(12)	P(21)	F(22)	1.563(3)
Rh	C(1)	2.257(5)	P(21)	C(21)	1.771(4)
Rh	C(2)	2.299(5)	P(22)	N(23)	1.672(3)
Rh	C(3)	2.231(5)	P(22)	C(21)	1.713(4)
Rh	C(4)	2.265(4)	N(13)	N(14)	1.355(5)
Rh	C(5)	2.237(4)	N(13)	C(17)	1.464(6)
P(11)	F(11)	1.574(3)	N(14)	C(15)	1.316(6)
P(11)	F(12)	1.562(3)	N(23)	N(24)	1.354(5)
P(11)	C(11)	1.774(4)	N(23)	C(27)	1.468(5)
P(12)	N(13)	1.670(4)	N(24)	C(25)	1.322(5)
P(12)	C(11)	1.713(4)			

269.23 ppm) and the two-bond phosphorus−phosphorus coupling ($^2J_{PP}$ = 103 Hz) showed a small decrease relative to uncoordinated **1**.

The ^{19}F NMR spectrum of **6** consisted of a resonance of an apparent doublet of triplets centered at −62.18 ppm with a one-bond phosphorus−fluorine coupling constant of 1171 Hz. Decoupling the phosphorus signal at 269 ppm collapsed the fluorine signal to a doublet of doublets. Values extracted from both spectra give values of 12 Hz for both $^3J_{\sigma^2PF}$ and $^2J_{FRh}$.

Reactions of 2 and 3 with Rhodium(I) Precursors. Formation of 7 and 8. In contrast to the treatment of **1** with $[Rh(CO)_2Cl]_2$, described above, which gave a product that could not be identified, **2** reacted smoothly with this precursor to yield exclusively the red, crystalline complex *trans*-Rh(CO)Cl(**2**)$_2$ (**7**), the expected product by analogy with analogous phosphine complexation reactions[35] We did not observe any condensed intermediates, but we did not conduct an extensive evaluation of the reaction pathway. We suggest that the steric bulk of **2** influences the reaction by directing it initially toward dimer cleavage (path B as described by Hughes)[35] as the first steps with intermediate formation of the monophosphine complex. The

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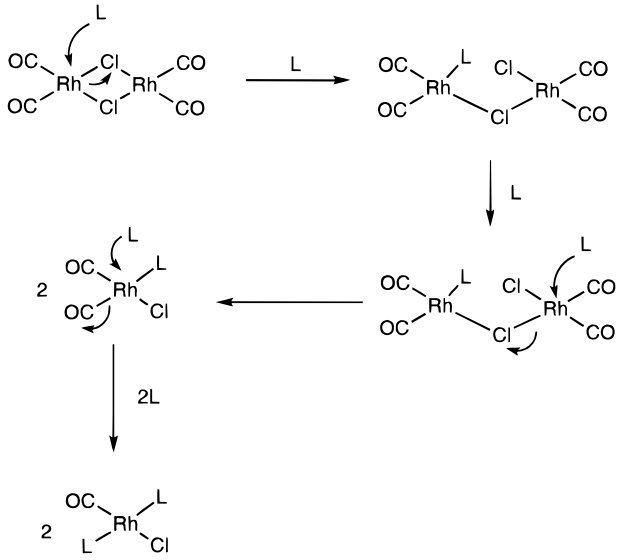
Table 4. Selected Interatomic Angles (deg) for Cyclopentadienylbis(κP-difluoro{2,5-dimethyl-2*H*-1,2,3σ²-diazaphosphol-4-yl}phosphine)rhodium(I) (5)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P(11)	Rh	P(21)	94.56(5)	N(13)	N(14)	C(15)	109.4(4)
Rh	P(11)	F(11)	115.95(13)	P(22)	N(23)	N(24)	117.3(3)
Rh	P(11)	F(12)	120.59(13)	P(22)	N(23)	C(27)	127.2(3)
Rh	P(11)	C(11)	119.02(14)	N(24)	N(23)	C(27)	115.5(3)
F(11)	P(11)	F(12)	95.3(2)	N(23)	N(24)	C(25)	108.8(3)
F(11)	P(11)	C(11)	100.7(2)	P(11)	C(11)	P(12)	119.4(2)
F(12)	P(11)	C(11)	101.0(2)	P(11)	C(11)	C(15)	130.4(3)
N(13)	P(12)	C(11)	88.3(2)	P(12)	C(11)	C(15)	110.2(3)
Rh	P(21)	F(21)	114.85(13)	N(14)	C(15)	C(11)	114.6(4)
Rh	P(21)	F(22)	119.87(12)	N(14)	C(15)	C(16)	118.4(4)
Rh	P(21)	C(21)	122.60(14)	C(11)	C(15)	C(16)	127.0(4)
F(21)	P(21)	F(22)	96.0(2)	P(21)	C(21)	P(22)	121.6(2)
F(21)	P(21)	C(21)	99.0(2)	P(21)	C(21)	C(25)	128.5(3)
F(22)	P(21)	C(21)	99.5(2)	P(22)	C(21)	C(25)	109.8(3)
N(23)	P(22)	C(21)	88.6(2)	N(24)	C(25)	C(21)	115.4(4)
P(12)	N(13)	N(14)	117.5(3)	N(24)	C(25)	C(26)	117.5(4)
P(12)	N(13)	C(17)	126.3(4)	C(21)	C(25)	C(26)	127.0(4)
N(14)	N(13)	C(17)	116.2(4)				

Scheme 2. Substitutional Process for the Formation of *trans*-[Rh(CO)Cl(2)$_2$]



process is outlined in Scheme 2. The first steps describe the cleavage of the dimer, and in the final stage, the second substitution, trans directed by **2** occurs. Ultimate formation of the trans product suggests that **2** is more trans directing than either Cl or CO in this final step. Further study of the substitutional process with these ligands would likely be rewarding.

The ^{31}P{^{1}H} NMR spectrum of **7** (Figure 5) shows the typical AA′XX′ pattern of a "deceptively simple triplet" for both phosphorus centers.[24] One of the P centers, the directly bound P(III) center, has superimposed on these "triplets" the large, essentially first-order, $^{1}J_{PRh}$ coupling, which, at 143 Hz, is larger than the outer line separation of the "triplet" (the value of which, 51 Hz, represents $|J_{AX} + J_{AX'}|$) and so gives a doublet of the "triplets". The other portion of the spectrum arising from the P(V) moiety gives only the "triplet" because $^{2}J_{PRh}$ is small. In the present case there is not a sufficient number of separated lines to allow a solution for the spectral parameters.[36] The exo-phosphorus center was shifted downfield relative to the free ligand (by 16 ppm to 103.34 ppm), while the chemical shift of the σ^2P

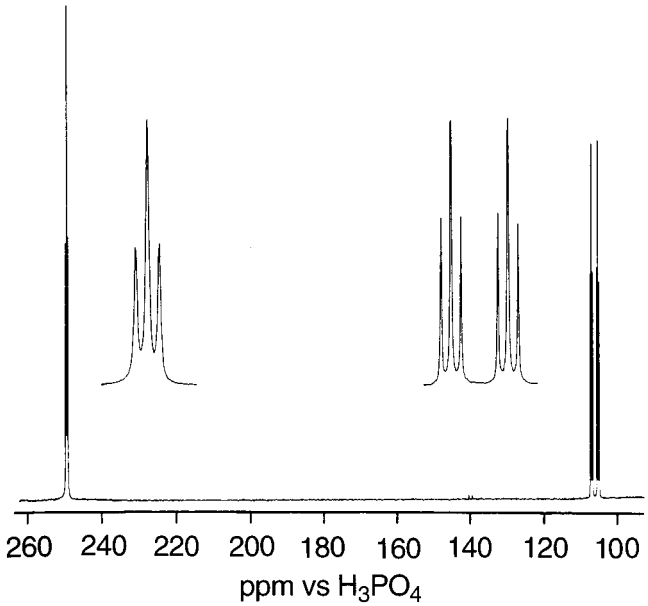


Figure 5. ^{31}P {^{1}H}NMR (161.977 MHz) spectrum of ((bis(bis{dimethylamino}{2,5-dimethyl-2*H*-1,2,3σ²-diazaphosphol-4-yl}phosphine)rhodium(I), **7**, in $CDCl_3$. The two regions shown in expansion are composed of deceptively simple "triplets" with the set at 160 ppm (due to the exocyclic phosphorus center) doubled by $^{1}J_{PRh} = 143$ Hz. The outer lines of each "triplet" unit are separated by $|^{2}J_{\sigma^2P\sigma^4P} + {}^{4}J_{\sigma^2P\sigma^4P'}| = 51$ Hz.

center was relatively unchanged. The value of $^{1}J_{PRh}$ is in keeping with typical Rh−P complexes, and the association of this coupling with the exocyclic phosphorus indicates the point of attachment.[37]

The solid-state structure of **7** (major isomer shown in Figure 6[29]) revealed the square-planar rhodium metal center wherein both diazaphosphole ligands lie trans to each other, as one would anticipate with a relatively bulky phosphine. Crystal parameters and metrical details are given in Tables 2, 5, and 6. One interesting feature of the structure is that the diazaphosphole rings are oriented perpendicular to the P(1)−Rh−CO−Cl−P(2) plane and stacked to create a mirror plane which contains the Cl−Rh−CO axis. The diazaphosphole rings

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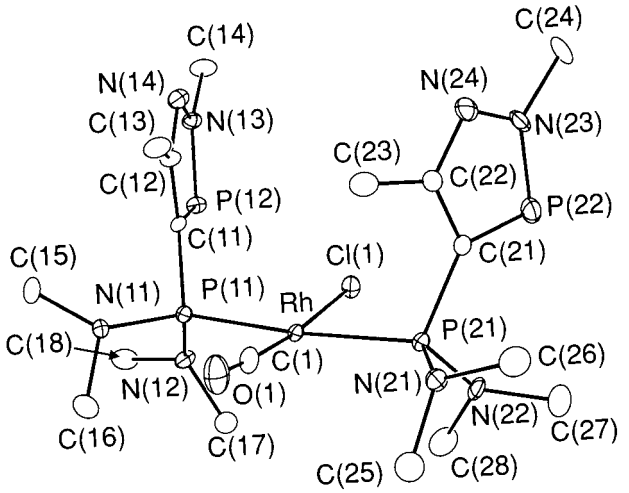

Figure 6. Perspective ORTEP[29] view of the major (75%) isomer of *trans*-chlorocarbonyl((bis(κP-bis{dimethylamino}-{2,5-dimethyl-1,2,3σ^2-diazaphosphol-4-yl}phosphine)-rhodium(I), **7**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The minor (25%) isomer of **7** differs only from that illustrated in that the Cl and CO positions relative to the "top" of the molecule are interchanged.

Table 5. Selected Interatomic Distances (Å) for *trans*-Chlorocarbonyl(bis(κP-bis{dimethylamino}-{2,5-dimethyl-2*H*-1,2,3σ^2-diazaphosphol-4-yl}-phosphine))rhodium(I) (7)

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh	Cl(1)	2.395(4)[a]	N(11)	C(15)	1.455(8)
Rh	Cl(2)	2.46(2)[b]	N(11)	C(16)	1.455(8)
Rh	P(11)	2.333(2)	N(12)	C(17)	1.462(8)
Rh	P(21)	2.326(2)	N(12)	C(18)	1.455(8)
Rh	C(1)	1.777(13)[a]	N(13)	N(14)	1.350(7)
Rh	C(2)	1.77(1)[b]	N(13)	C(14)	1.464(8)
P(11)	N(11)	1.695(5)	N(14)	C(12)	1.344(8)
P(11)	N(12)	1.683(6)	N(21)	C(25)	1.455(8)
P(11)	C(11)	1.784(7)	N(21)	C(26)	1.480(8)
P(12)	N(13)	1.678(6)	N(22)	C(27)	1.457(8)
P(12)	C(11)	1.704(7)	N(22)	C(28)	1.468(9)
P(21)	N(21)	1.686(6)	N(23)	N(24)	1.356(9)
P(21)	N(22)	1.668(6)	N(23)	C(24)	1.473(8)
P(21)	C(21)	1.795(7)	N(24)	C(22)	1.325(9)
P(22)	N(23)	1.679(7)	C(11)	C(12)	1.409(9)
P(22)	C(21)	1.712(7)	C(12)	C(13)	1.495(9)
O(1)	C(1)	1.13(2)[a]	C(21)	C(22)	1.413(10)
O(2)	C(2)	1.12(1)[b]	C(22)	C(23)	1.499(9)

[a] Major (75%) isomer. [b] Minor (25%) isomer.

of **7** are parallel to the CO−Rh−Cl axis and are parallel to each other. This symmetrical feature yields two isomers which differ in the relative positions of the chloride and the carbon monoxide ligands relative to the "top" of the molecule; these two substituents are readily interchanged to create two isomers. Both of the isomers were identified in the crystal, one of which is more predominant than the other (75:25). A similar result has been reported for the dimethylphenylphosphine analogue,[38] wherein the phenyl rings lie on the same side of the rhodium complex and are oriented toward the carbonyl group. In that case it was rationalized that the orientation of the phenyl rings arose from electronic interaction between the oriented phenyl rings and the carbonyl moiety, and a similar effect may be operational here. Once again, the phosphole rings are planar, and the angles about the σ^2P centers, C(11)−P(12)−N(13) and C(21)−P(22)−N(23), are 89.1(3)8° and 88.9(4)°, respectively. All characteristics of the phosphole rings are comparable to those shown by **5**. The phosphorus−rhodium distance is 2.33 Å, which is comparable to that of the Rh−P bond length (2.326 Å) in the $Rh(CO)_2Cl(PPh_3)$ complex.[39] The average P−N bond distance of the exo-phosphorus center and the dimethylamino groups is 1.683 Å, shorter than the normally accepted distance of 1.77 Å, again suggesting some multiple-bonding characteristics.[32] The dimethylamino nitrogen atoms are planar, with the sum of the angles about these nitrogen centers being 360°.

Replacing fluorine atoms on the exo-phosphorus center in **1** with alkoxy groups increases the basicity of the phosphine center, but the exocyclic phosphine center in this case is both less basic and less bulky in comparison with the amino derivative **2**. The reaction of **3** with $[Rh(CO)_2Cl]_2$ proceeded similarly to that demonstrated by **2** and resulted again in the formation of *trans*-[Rh(CO)Cl(**3**)$_2$] (**8**), which suggests that both **2** and **3** follow similar substitutional pathways. The $^{31}P\{^1H\}$ NMR spectrum of **8** was also second order, showing a spectrum consisting of two deceptively simple "triplets", similar to the patterns displayed by the complex formed by **2**. Surprisingly, the chemical shift of the exo-phosphorus signal in **8** was reduced only by 8 ppm (159.78 ppm) upon complexation, whereas the signal for the noncoordinated σ^2P center suffered a greater shift downfield of 14.5 ppm (251.88 ppm). The major spacing for $|^2J_{\sigma^2P\sigma^4P} + {}^4J_{\sigma^2P\sigma^4P'}|$ was 52 Hz. The $^1J_{PRh}$ coupling constant was 187 Hz and indicated that despite the smaller coordination shift, the exo-phosphorus was the coordination site.

The fluorine NMR spectrum of **8** showed a single resonance at −74.50 ppm for the fluorines of the trifluoroethoxy group, which were unchanged from those of uncomplexed **3**. Unlike the parent diazaphosphole spectrum however, coupling of ^{19}F to either the σ^2P center or the protons was not resolved. Consistently, the proton spectrum showed only two broadened resonances for the diastereotopic protons (4.353 and 4.585 ppm). Even at higher magnetic fields, the coupling to other nuclei remained unresolved.

The $^{31}C\{^1H\}$ NMR spectrum of **8** showed an upfield shift for the resonance for the carbon at the 4-position of the ring which was coupled to both phosphorus centers (135.26 ppm, $^1J_{\sigma^2PC}$ = 84 Hz, $^1J_{\sigma^3PC}$ = 42 Hz). The carbon at the 5-position of the ring showed only coupling to the exo-phosphorus center (155.57 ppm, $^2J_{\sigma^4PC}$ 10 Hz). The resonance for the trifluoromethyl carbon showed coupling to the exo-phosphorus (122.19 ppm, $^3J_{\sigma^4PC}$ = 9 Hz, $^1J_{CF}$ = 277 Hz). Coupling to only the fluorines was observed in the methylene carbon signals (64.83 ppm, $^2J_{CF}$ = 39 Hz), but the coupling to the phosphorus was unresolved.

No significant change in the P−O stretching frequency (1165 cm^{-1}) of **3** was observed on coordination.

Relative Ligand Character. The lack of systematic substitutional patterns of the phosphinediazaphosphole ligands investigated herein does not allow for a complete

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Table 6. Selected Interatomic Angles (deg) for *trans*-Chlorocarbonyl(bis(κP-bis{dimethylamino}-{2,5-dimethyl-2*H*-1,2,3σ²-diazaphosphol-4-yl}phosphine))rhodium(I) (7)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Rh	P(11)	86.71(10)[a]	N(22)	P(21)	C(21)	106.2(3)
Cl(1)	Rh	P(21)	87.18(10)[a]	N(23)	P(22)	C(21)	88.9(4)
Cl(1)	Rh	C(1)	173.6(4)[a]	P(11)	N(11)	C(15)	124.4(5)
Cl(2)	Rh	P(11)	92.9(7)[b]	P(11)	N(11)	C(16)	115.5(5)
Cl(2)	Rh	P(21)	92.7(7)[b]	C(15)	N(11)	C(16)	112.6(6)
Cl(2)	Rh	C(2)	172.4(14)[b]	P(11)	N(12)	C(17)	120.0(5)
P(11)	Rh	P(21)	173.33(8)	P(11)	N(12)	C(18)	120.1(5)
P(11)	Rh	C(1)	93.6(4)[a]	C(17)	N(12)	C(18)	112.5(6)
P(11)	Rh	C(2)	88.1(12)[b]	P(12)	N(13)	N(14)	117.3(5)
P(21)	Rh	C(1)	92.1(4)[a]	P(12)	N(13)	C(14)	125.8(5)
P(21)	Rh	C(2)	85.9(12)[b]	N(14)	N(13)	C(14)	116.9(6)
Rh	P(11)	N(11)	117.4(2)	N(13)	N(14)	C(12)	108.5(6)
Rh	P(11)	N(12)	111.7(2)	P(21)	N(21)	C(25)	114.8(5)
Rh	P(11)	C(11)	110.7(2)	P(21)	N(21)	C(26)	123.0(5)
N(11)	P(11)	N(12)	109.4(3)	C(25)	N(21)	C(26)	111.5(6)
N(11)	P(11)	C(11)	103.8(3)	P(21)	N(22)	C(27)	123.2(6)
N(12)	P(11)	C(11)	102.5(3)	P(21)	N(22)	C(28)	120.6(5)
N(13)	P(12)	C(11)	89.1(3)	C(27)	N(22)	C(28)	112.4(6)
Rh	P(21)	N(21)	117.5(2)	P(22)	N(23)	N(24)	117.8(5)
Rh	P(21)	N(22)	112.0(2)	P(22)	N(23)	C(24)	126.7(7)
Rh	P(21)	C(21)	109.7(2)	N(24)	N(23)	C(24)	115.5(7)
N(21)	P(21)	N(22)	108.9(3)	N(23)	N(24)	C(22)	107.5(7)
N(21)	P(21)	C(21)	101.5(3)	Rh	C(1)	O(1)	175.9(13)[a]
Rh	C(2)	O(2)	177.9(44)[b]	C(11)	C(12)	C(13)	127.5(7)
P(11)	C(11)	P(12)	122.9(4)	P(21)	C(21)	P(22)	126.0(4)
P(11)	C(11)	C(12)	126.4(5)	P(21)	C(21)	C(22)	124.5(6)
P(12)	C(11)	C(12)	109.9(5)	P(22)	C(21)	C(22)	108.9(5)
N(14)	C(12)	C(11)	115.2(7)	N(24)	C(22)	C(21)	116.9(7)
N(14)	C(12)	C(13)	117.1(6)	N(24)	C(22)	C(23)	116.7(7)
C(21)	C(22)	C(23)	126.4(7)				

[a] Major (75%) isomer. [b] Minor (25%) isomer.

classification of the ligand properties which devolve from the substitutions on the exocyclic phosphorus center, but some understanding can be gleaned from the IR spectra. The carbonyl infrared stretching frequency ν(CO) for **7** is 1978 cm^{-1}, which is comparable to values for *trans*-(phosphine)Rh(CO)Cl with the ligands PPh_3 (1980 cm^{-1})[40] and $(C_6F_5)_2PPh$ (1982 cm^{-1}),[41] thus suggesting that **2** behaves with a basicity and back-donation character similar to these aryl phosphines. The ν(CO) stretching frequency of **8** is 2010 cm^{-1}, which suggests that the ligating characteristics of **3** are more similar to those of the phosphites $P(OMe)_3$ (2014 cm^{-1})[42] and $P(OPh)_3$ (2018 cm^{-1}),[43] and this is reinforced by the fact that in substitution reactions with $CpRh(CO)_2$ both CO ligands are replaced, a reaction characteristic of phosphites but not phosphines. Here and elsewhere[5,9] we observe substitutional behavior and reactivity characteristics of the difluorophosphinediazaphosphole that are very similar to those of PF_3; unfortunately the appropriate Rh(I) complex of **1** was not obtained, and so the comparison within this series cannot be completed.

Summary

The diazaphoaphole phosphine set of ligands exhibits varied chemistry which illustrates the effect of the substituents on the exocyclic phosphine. The difluoride did not give carbonyl products with Rh(I), although it forms stable CpRu and CpRh complexes and a Cp*Rh complex. This ligand, **1,** readily substitutes both CO ligands in $CpRh(CO)_2$ to give $CpRh(\mathbf{1})_2$. Elsewhere[5,9] we have shown that the difluoride is a good coordinating and also reducing[9] ligand. The replacement of one of the PPh_3 groups in the complex $CpRu(PPh_3)_2Cl$ with the difluorophosphinophosphole ligand gave the asymmetric ruthenium complex $CpRu(PPh_3)(\mathbf{1})Cl$, wherein the fluorine atoms were diastereotopic. The $^{31}P\{^1H\}$ NMR spectrum of this complex gave a complex second-order splitting pattern for the exo-phosphorus centre. A very large one-bond phosphorus−rhodium coupling constant value of 306 Hz was observed. Reaction of **1** with the dimeric complex $[Cp^*RhCl_2]_2$ gave $Cp^*Rh(\mathbf{1})Cl_2$. In contrast to **1**, the related ligands **2** (the bis(dimethylamino)) and **3** (the bis trifluoroethoxy) analogues gave the expected *trans*-Rh(I) complexes, wherein the CO stretching frequencies reflect the basicity of the ligand, a measure that could not however be obtained for the difluoride ligand, **1**.

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Supporting Information Available: Full structure reports containing atomic coordinates, full tables of interatomic distances and angles, torsional angles, tables of equivalent isotropic displacement parameters, anisotropic displacement parameters, selected least-squares planes, and derived hydrogen atom positions for **5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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