4240 *Organometallics* **1996,** *15,* 4240−4246

XPS Investigations of (1,4,7-trimethyl-1,4,7-triazacyclononane)$RhMe_3$ and [1,1,1-tris((dimethylphosphino)methyl)ethane]$RhMe_3$ and Their Rh−C Cleavage Derivatives. Comparison of Hard- and Soft-Ligated Rhodium Organometallics

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Received February 14, 1996[⊗]

The new molecules $P_3RhMe_{3-n}(OTf)_n$ are reported ($n = 0-2$; $P_3 = MeC(CH_2PMe_2)_3$; OTf = $OS(O)_2CF_3$). The known *fac*-$(Me_3P)_3RhMe_3$ was converted to *mer*-$(Me_3P)_3RhMe_{3-n}Cl_n$ (n = 1, 2) by cleavage with HCl in ether. X-ray photoelectron spectra (XPS) of these were recorded, and all except the $P_3RhMe_{3-n}Cl_n$ series afforded clean spectra. XPS were also obtained for the known $CnRhMe_{3-n}X_n$ (n = 0−2; X = Cl, Br, OTf; Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane), $CnRhX_3$ (X = Cl, Br), CnRhMe(OH)(OTf), and $[CnRhMe_2(CO)]OTf$. An X-ray crystal structure of P_3RhMe_3 is reported, and the geometry at the metal is compared among P_3RhMe_3, $(Me_3P)_3RhMe_3$, and $CnRhMe_3$. Core binding energies (BEs) for the series $L_3RhMe_{3-n}X_n$ (L_3 = Cn, P_3) change linearly with n for a given L_3 and X. For $CnRhMe_{3-n}X_n$, replacement of methyl by chloride or bromide gives similar ΔBE values (~0.7 eV), while triflate-for-methyl substitution gives a much larger ΔBE (1.2 eV). Triflate-for-methyl substitution in $P_3RhMe_{3-n}(OTf)_n$, however, causes a ΔBE of only 0.8 eV. Thus, the Rh($3d_{5/2}$) core binding energies in these complexes change less in triflate-for-methyl substitutions when the P_3 ancillary ligand is present than in the presence of Cn; apparently P_3 compensates for changes in electron density at the rhodium center more effectively than does Cn, presumably as a result of the greater polarizability of phosphorus (softer) compared to nitrogen (harder). The XPS trends for these series effectively mean that P_3 makes Rh^{III} a softer metal and Cn makes Rh^{III} a harder metal.

Introduction

Several recent publications[3] have focused on aspects of organometallic chemistry in the coordination sphere of rhodium coordinated to 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn). In addition to exploratory motivations, a primary goal of this work has been to view the organometallic chemistry of rhodium in the context of hard−soft acid−base formalism (hereafter HSABF).[4] That is, we wish to learn how a predominantly "hard", non-π-interacting array of ancillary ligands might alter hydrocarbyl chemistry in the coordination sphere of the metal compared to the same metal coordinated to conventionally "soft" ligands (Cp, PR_3, CO, π-arene, etc.), where the hard- and soft-ligated molecules are otherwise as structurally analogous as possible. In this context it is of interest to compare the behavior of $CnRh^{III}$ with that of (π-arene)Rh^{III} or $(R_3P)_3Rh^{III}$. Comparisons with CpRh, Cp*Rh, and (tpb)Rh (tpb = tris(pyrazolyl)borato) would also be interesting but are complicated by the anionic nature of the six-electron-donor ligands.

Core electron X-ray photoelectron spectroscopy (XPS) has been found to be a useful tool in characterizing ligand effects in transition-metal complexes.[5,6] In a photoelectron experiment, high-energy photons ($h\nu$ commonly greater than 1 keV) are applied to eject electrons from atomic core levels. If we measure the kinetic energy of the ejected electron (KE), the binding energy (BE) can be obtained as BE = $h\nu$ − KE − φ (where φ is the spectrometer work function). In simple terms, relatively electron-donating ligands will lower the binding energies (BEs) of the core level electrons and relatively electron-withdrawing ligands will raise their BEs. Relevant to HSABF, the effect of a facial tridentate ligand, L_3, on the relative hardness of the metal should be reflected in the magnitude of the *changes* in

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

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(3) (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (d) Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491.

(4) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734 and references therein.

(5) (a) Ballard, R. E. *Photoelectron Spectroscopy and Molecular Orbital Theory*; Wiley: New York, 1978. (b) Barr, T. L. *Modern ESCA*; CRC Press: Boca Raton, FL, 1994. (c) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.

(6) (a) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 6942. (b) Gassman, P. G.; Winter, C. H. *Organometallics* **1991**, *10*, 1592. (c) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. (d) Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 2890 and references cited therein.

S0276-7333(96)00109-4 CCC: $12.00

Table 1. Rh($3d_{5/2}$) and Rh($3d_{3/2}$) Core Binding Energies of Rh(III) Complexes and Standard Deviations (3σ) of the Former

	binding energy[a]		
compd	Rh($3d_{5/2}$)	3σ[b]	Rh($3d_{3/2}$)
$\mathrm{P_3RhMe_3}$ (**5**)	307.5	0.26	312.0
$\mathrm{P_3RhMe_2OTf}$ (**6**)	308.3	0.11	313.0
$\mathrm{P_3RhMe(OTf)_2}$ (**7**)	309.2	0.1	313.9
mer-$\mathrm{(PMe_3)_3RhMeCl_2}$ (**4**)	308.4	0.42	313.0
$\mathrm{CnRhMe_3}$ (**2**)	306.9	0.20	311.7
$\mathrm{CnRhMe_2Cl}$ (**8**)	307.6	0.1	312.3
$\mathrm{CnRhMeCl_2}$ (**9**)	308.3	0.1	313.0
$\mathrm{CnRhCl_3}$ (**10**)	309.3	0.17	314.0
$\mathrm{CnRhMe_2Br}$ (**11**)	307.6	0.11	312.4
$\mathrm{CnRhMeBr_2}$ (**12**)	308.3	0.1	313.0
$\mathrm{CnRhBr_3}$ (**13**)	309.0	0.1	313.7
$\mathrm{CnRhMe_2OTf}$ (**14**)	308.2	0.1	313.0
$\mathrm{CnRhMe(OTf)_2}$ (**15**)	309.4	0.15	314.1
$\mathrm{CnRhMe(OH)(OTf)}$ (**16**)	308.6	0.1	313.3
$\mathrm{[CnRhMe_2(CO)]OTf}$ (**17**)	309.5	0.27	314.2

[a] Polyethylene C(1s) BE assigned 284.6 eV. [b] For the $3d_{5/2}$ transitions. See the Experimental Section for a discussion of the estimation of 3σ.

the Rh($3d_{5/2}$) and Rh($3d_{3/2}$) BEs for $\mathrm{L_3RhXYZ}$ as ligands X, Y, and Z are varied systematically in the presence of a given $\mathrm{L_3}$. Such differences have been called "chemical shifts".[5]

The Cn-containing compounds that have been examined are $\mathrm{CnRhMe}_{3-n}\mathrm{X}_n$ ($n = 0-3$; X = Cl, Br, OTf, and some including OH or CO; listed in Table 1). The best soft analog of Cn might be 1,4,7-trimethyl-1,4,7-triphosphacyclononane, but that ligand appears to be synthetically inaccessible. On the other hand, the facially constrained 1,1,1-tris((dimethylphosphino)methyl)ethane, $\mathrm{MeC[CH_2(PMe_2)]_3}$ (abbreviated as $\mathrm{P_3}$) is available[7] and so has been used in the synthesis of analogs to the CnRh series. Although triphos ($\mathrm{MeC[CH_2(PPh_2)]_3}$) satisfies the facial coordination criterion and its rhodium chemistry is well-known,[8] it was decided that $\mathrm{P_3Rh}$ was likely to afford better comparisons with CnRh. Comparisons were also sought with *fac*-$\mathrm{(Me_3P)_3RhMe_3}$ (**1**)[9] and its derivatives, but these complexes did not yield reproducible XPS spectra.

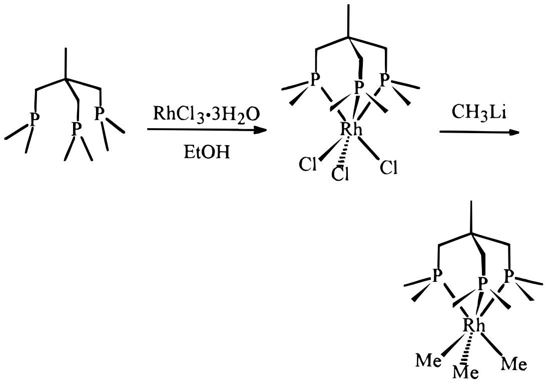
Results

Synthesis. XPS were measured on the numbered compounds in Table 1. Syntheses of the CnRh complexes **2** and **8**−**17** have been reported elsewhere.[3d] The synthesis of the facially coordinated complex $\mathrm{(Me_3P)_3RhMe_3}$ (**1**) was reported by Wilkinson and co-workers, and their procedure works very well without modification (eq 1).[9a] An alternate path to prepare **1** is to displace the Cn ligand of $\mathrm{CnRhMe_3}$ (**2**) with excess $\mathrm{PMe_3}$ at 108 °C (eq 2). It was originally anticipated that **1** should comprise a representative example of a soft-ligated analog of **2**, but **1** proved to be unstable to the conditions of XPS measurement. In addition, the published[9b] X-ray crystal structure of **1** does reveal substantial structural differences between it and **2** (see below). Stoichiometric treatment of **1** with 1 or 2 equiv of HCl (in $\mathrm{Et_2O/CH_2Cl_2}$) generates *mer*-$\mathrm{(Me_3P)_3RhMe_2Cl}$ (**3**) and *mer*-$\mathrm{(Me_3P)_3RhMeCl_2}$ (**4**), respectively. The structures of **3** and **4** were assigned from their ^{1}H and ^{31}P spectra.

$$\mathrm{Rh_2(OAc)_4} \xrightarrow[\mathrm{Et_2O}]{\text{excess PMe}_3} \xrightarrow{\mathrm{MgMe_2}} \underset{\mathbf{1}}{fac\text{-}\mathrm{(Me_3P)_3RhMe_3}} \qquad (1)$$

$$\underset{\mathbf{2}}{\mathrm{CnRhMe_3}} + \text{excess } \mathrm{PMe_3} \xrightarrow{108\ ^\circ\mathrm{C},\ \mathrm{C_6H_6}} \mathbf{1} + \mathrm{Cn} \qquad (2)$$

Because of the decomposition of **1** under conditions of XPS measurement, it was decided to use the known[7] chelate $\mathrm{MeC(CH_2PMe_2)_3}$ ($\mathrm{P_3}$), in place of the three $\mathrm{PMe_3}$ ligands, to prepare $\mathrm{P_3RhMe_3}$ (**5**). Addition of an ethanol solution of $\mathrm{P_3}$ to an ethanol solution of $\mathrm{RhCl_3{\cdot}3H_2O}$ resulted in the immediate precipitation of a yellow solid (presumably $\mathrm{P_3RhCl_3}$), which was not characterized but was treated directly with methyllithium in THF (eq 3).



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(3)

From this, $\mathrm{P_3RhMe_3}$ (**5**) was isolated as a snow-white solid in 24% yield. The solubility of $\mathrm{P_3RhMe_3}$ in relatively nonpolar organic solvents is similar to that of $\mathrm{CnRhMe_3}$; both dissolve in benzene but not in hexane. In contrast, *fac*-$\mathrm{(Me_3P)_3RhMe_3}$ (**1**) is very soluble in hexane. Stoichiometric treatment of **5** with 1 or 2 equiv of triflic acid in $\mathrm{Et_2O/CH_2Cl_2}$ generated $\mathrm{P_3RhMe_2(OTf)}$ (**6**) and $\mathrm{P_3RhMe(OTf)_2}$ (**7**), respectively. Complexes **5**−**7** have been fully characterized.

The closest triamine-coordinated structural analog of $\mathrm{P_3RhMe_3}$ would be $\mathrm{N_3RhMe_3}$, bearing the known[11] ligand $\mathrm{N_3}$ = 1,1,1-tris((dimethylamino)methyl)ethane. However, reaction between $\mathrm{N_3}$ and $\mathrm{RhCl_3{\cdot}3H_2O}$ in ethanol failed to give $\mathrm{N_3RhCl_3}$. CPK models suggest that $\mathrm{N_3}$ would be much more crowded than Cn in the coordination sphere of $\mathrm{RhCl_3}$.

Molecular Structure of $\mathrm{P_3RhMe_3}$ (5). Solution of the X-ray diffraction data of **5** shows the expected facial $\mathrm{P_3}$ coordination with average Rh−P and Rh−C bond lengths of 2.29 and 2.17 Å, respectively (Figure 1, Table 2). The average P−Rh−P angle in **5** is 89°, much closer

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(7) (a) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379. (b) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.

(8) (a) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vacca, A. *Organometallics* **1991**, *10*, 636 and references therein. (b) Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, *10*, 2209.

(9) (a) Anderson, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446. (b) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *17*, 2071.

(10) (a) Feltham, R. D.; Brant, P. *J. Am. Chem. Soc.* **1982**, *104*, 641. (b) Andersson, S. L. T.; Watters, K. L.; Howe, R. F. *J. Catal.* **1981**, *69*, 212. (c) Nefedov, V. I.; Shubochkina, E. F.; Kolomnikov, I. S.; Baranovski, I. B.; Kukolev, V. P.; Golubnichaya, M. A.; Shubochkin, L. K.; Porai-Koshits, M. A.; Vol'pin, M. E. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1973**, *18*, 444. (d) Fisher, H. E.; Schwartz, J. *J. Am. Chem. Soc.* **1989**, *111* 7644.

(11) Kasowaki, W. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 3212.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of P_3RhMe_3 (5) Compared to Literature Values for $(Me_3P)_3RhMe_3$ (1)[a] and $CnRhMe_3$ (2)[b]

P_3RhMe_3 (**5**)		$(Me_3P)_3RhMe_3$ (**1**)		$CnRhMe_3$ (**2**)	
Ru−P2	2.282(2)				
Rh−P3	2.292(3)				
Rh−P4	2.285(3)				
av Rh−P	2.286(2)	av Rh−P	2.322 (3)	av Rh−N	2.222(6)
		Δ(Rh−P) **5** < **1**	0.036(5)	Δ(Rh−E) **5** > **2**	0.064(7)
Rh−C5	2.166(10)				
Rh−C6	2.175(11)				
Rh−C7	2.163(12)				
av Rh−C	2.168(7)	av Rh−C	2.148(8)	av Rh−C	2.057(10)
		Δ(Rh−C) **5** > **1**	0.020(15)	Δ(Rh−C) **5** > **2**	0.104(25)
C5−Rh−C6	85.5(4)				
C5−Rh−C7	85.6(5)				
C6−Rh−C7	85.9(4)				
av C−Rh−C	85.7(3)	av C−Rh−C	84.6(5)	av C−Rh−C	87.4(4)
		Δ(C−Rh−C) **5** > **1**	1.1(8)	Δ(C−Rh−C) **5** < **2**	1.7(7)
P2−Rh−P3	88.7(1)				
P2−Rh−P4	89.2(1)				
P3−Rh−P4	88.5(1)				
av P−Rh−P	88.8(1)	av P−Rh−P	97.2(2)	av N−Rh−N	80.1(2)
		Δ(P−Rh−P) **5** < **1**	8.4(3)	Δ(EhRh−E) **5** > **2**	8.7(3)

[a] Data for **1** from ref 9b. [b] Data for **2** from ref 3d.

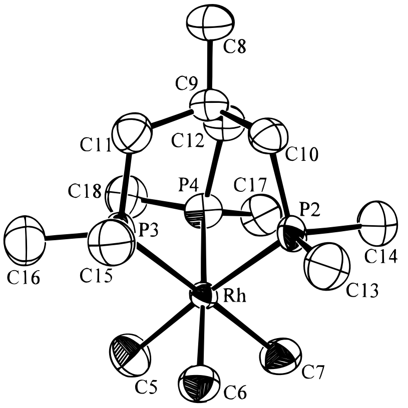

Figure 1. ORTEP view (50% probability) of P_3RhMe_3 (**5**) heavy atoms.

to the N−Rh−N angle of $CnRhMe_3$ (80°) than is the P−Rh−P angle of *fac*-$(Me_3P)_3RhMe_3$ (97°).[9b] Note that the Rh−P bonds of P_3RhMe_3 are 0.036 Å shorter on the average than those of *fac*-$(Me_3P)_3RhMe_3$, probably because of reduced steric crowding in **5** compared to **1**. On the other hand, this difference in Rh−P bonding has no discernible influence on the Rh−Me bonding, since the Rh−Me lengths and Me−Rh−Me angles are not statistically different in **1** and **5**. The size of the difference in trans influence of P and N on the Rh−C lengths, however, is substantial. A methyl group trans to the more strongly σ-bonding PR_3 in **5** exhibits an average Rh−C distance of 2.17 Å, while that trans to the more weakly σ-bonding NR_3 in **2** has an average Rh−C of 2.06 Å.

Since $CnRhMe_3$ and P_3RhMe_3 are relatively similar in structure, the comparison of their XPS data should be meaningful, particularly with regard to seeking reasons for reactivity differences between the Cn and phosphine-coordinated organorhodium complexes.

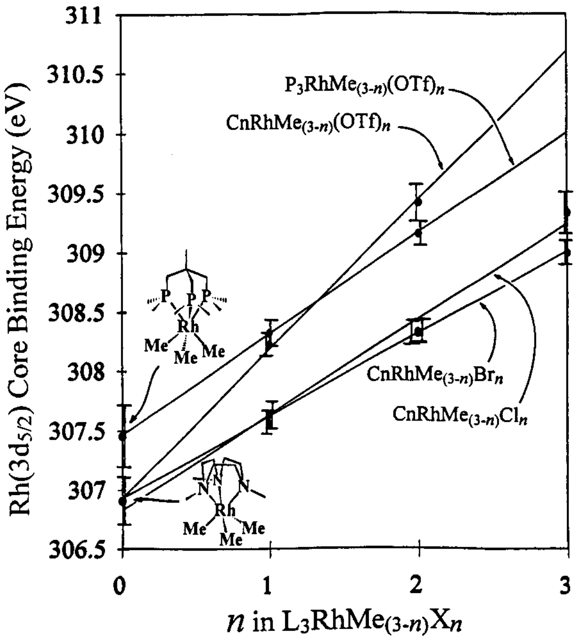

Figure 2. Plot of the Rh($3d_{5/2}$) core binding energies of many of the complexes listed in Table 1 versus "*n*", the number of unidentate non-methyl groups in $L_3RhMe_{3-n}X_n$ (L_3 = Cn, P_3). The least-squares lines for the four series are also plotted. The two least-squares lines for the $L_3RhMe_{3-n}X(OTf)_n$ series are extrapolated to n = 3, but the values for $L_3Rh(OTf)_3$ were not measured.

X-ray Photoelectron Spectra. The Rh($3d_{5/2}$) binding energies (BEs) of the organorhodium complexes are listed in Table 1, along with the estimated 3σ values for the $3d_{5/2}$ transitions (see the Experimental Section). The BEs are referenced to the C(1s) BE of polyethylene, assigned the value 284.60 eV. Since the Rh($3d_{5/2}$) band has a greater signal intensity than the Rh($3d_{3/2}$) band, its energy is regarded as more reliable. Much of our $3d_{5/2}$ data are also shown in graphic form in Figure 2, wherein the increasing BEs are plotted against "*n*", the number of non-methyl groups in $L_3RhMe_{3-n}X_n$ (L_3 = Cn, P_3). A significant amount of literature XPS data for rhodium compounds is available for comparison.[10]

It is interesting to note that $CnRhMe_3$ (**2**; Rh($3d_{5/2}$) = 306.9 eV) possesses the lowest BE among those reported here. This suggests that the Rh center in complex **2** is exceptionally electron rich. Replacement of methyl in **2** with chloride results in a 0.7 eV increase in BE for $CnRhMe_2Cl$ (**8**; 307.6 eV) and a further increase by 0.7 eV for $CnRhMeCl_2$ (**9**; 308.3 eV). These kinds of additive effects for such systematic changes are well established for organometallic complexes.[6] For example, replacement of methyl by chloride ligands was previously reported for a series of zirconocene derivatives where sequential replacement of methyl by chloride resulted in a 0.5 eV increase for each chloride[6e] (Cp_2ZrMe_2 [$Zr(3d_{5/2}) = 180.7$], $Cp_2ZrMeCl$ [181.2], and Cp_2ZrCl_2 [181.7 eV]). The BE values of the bromide-substituted species $CnRhMe_2Br$ (**11**; 307.6 eV) and $CnRhMeBr_2$ (**12**; 308.3 eV) are the same as those of the corresponding chlorides. In addition, $CnRhBr_3$ (**13**) exhibits a BE of 309.0 eV, so that each of the three Br-for-Me substitutions results in a ΔBE of 0.7 eV, resulting in a remarkably linear change in BE as a function of n, the number of Br-for-Me replacements. In contrast, replacement of the final methyl ligand in $CnRhMeCl_2$ (**9**) by chloride results in a 1.0 eV increase in BE for $CnRhCl_3$ (**10**; 309.3 eV). The reason for the apparently unique BE of **10** among these seven molecules is not certain. Both **10** and **13** ($CnRhBr_3$) are highly insoluble and are the only materials to be sampled as solid powders on the polyethylene rather than being deposited as methylene chloride solutions. It is possible that they actually have different structures. For example, **10** could be an ionic dimer such as $[CnRhCl(\mu\text{-}Cl)_2RhClCn]Cl_2$. However, we believe that the most probable explanation is that both series $CnRhMe_{3-n}X_n$ (X = Cl, Br) are essentially linear but with slightly different slopes, as represented in Figure 2. The uncertainties in the BEs certainly allow for this.

Overall, it appears that bromide and chloride ligands have very similar effects on the rhodium BEs in these CnRh molecules. The slightly greater electronegativity of Cl over Br (*ca.* 0.1−0.26, depending on the scale[12]) suggests the chloride complexes should have slightly higher BEs than the bromide analogues, consistent with the best-line interpretations of Figure 2. This was shown to be the case in a series of dihalotitanocene derivatives, where the chloride complexes were 0.1−0.3 eV higher in BE than the corresponding bromides.[6c,13] However, there are also a few reports where the trend goes in the other direction.[13,14] Clearly, σ-inductive effects and π-donor effects of the halide ligands, and the response of the ancillary ligands in the complex to the exchange of a halide for a methyl group, all combine in a way that is characteristic of a given system and is not identical for all metals. In addition, relaxation effects during photoionization may be different for different metal systems, so that the relative response of initial states and final states to ligand changes could also be different.

Replacement of a methyl ligand by triflate results in a 1.2−1.3 eV increase in the Rh binding energy, a much larger response than from Me-by-halide replacements. This greater response is attributed to the high electronegativity and weak coordination of the triflate ligand.[15] For $CnRhMe_2OTf$ (**14**) and $CnRhMe(OTf)_2$ (**15**), the ΔBE effect of replacement of methyl by triflate on the rhodium binding energy is additive. We were not able to prepare $CnRh(OTf)_3$ in pure form to extend the series, but extrapolation assuming continued linear behavior suggests a BE of *ca.* 310.7 eV (see Figure 2).

CnRhMe(OH)(OTf) (**16**; BE = 308.6 eV) is intermediate in electron richness between $CnRhMe_2OTf$ (**14**; 308.2 eV) and $CnRhMe(OTf)_2$ (**15**; 309.4 eV) so that a hydroxyl group is intermediate between methyl (ΔBE = 0.4 eV) and triflate (ΔBE = 0.8 eV) in electron withdrawal. If the effect on the rhodium BE upon replacement of methyl by hydroxyl is additive, then extrapolation predicts that the $Rh(3d_{5/2})$ BE of $CnRhMe(OH)_2$ would be 307.7 eV, which would mean that $CnRhMe(OH)_2$ would be more electron rich than $CnRhMe_2(OTf)$, CnRhMe(OH)(OTf), and $CnRhMe(OTf)_2$ by 0.5, 0.9, and 1.7 eV, respectively. Substitution of triflate by CO has a very large effect on binding energy, since $[CnRhMe_2(CO)]OTf$ has a higher BE than $CnRhMe_2(OTf)$ by 1.3 eV. This large change is attributable to the π-acidic character of CO and the overall cationic charge on the complex.

fac-$(Me_3P)_3RhMe_3$ (**1**) was not stable under XPS conditions; its binding energy determined at room temperature or at liquid-nitrogen temperature varied irreproducibly. A BE of 308.3 eV was obtained for *mer*-$(Me_3P)_3RhMe_2Cl$ (**3**), but this value is suspect since the sample was contaminated by a small amount of *mer*-$(Me_3P)_3RhMeCl_2$ (**4**), and the latter compound exhibited a BE of 308.4 eV. The chelated phosphine complex P_3RhMe_3 (**5**), on the other hand, provided good and reproducible spectra under XPS conditions. Its binding energy (307.5 eV) reveals that it is *less* electron rich than $CnRhMe_3$ (**2**; 306.9 eV). This result is supported by results of valence band ionization energies from UPS studies.[16] The ΔBE of 0.6 eV between **2** and **5** is consistent with the Cn ligand being more electron donating overall than the P_3 ligand in coordination with the $RhMe_3$ fragment. $P_3RhMe_2(OTf)$ (**6**; 308.3 eV), on the other hand, has the same BE as $CnRhMe_2(OTf)$ (**14**), and $P_3RhMe(OTf)_2$ (**7**; 309.2 eV) may be more electron rich than $CnRhMe(OTf)_2$ (**15**), but the ΔBE between them of 0.2 eV (6σ) is at the threshold of experimental significance. If the $P_3RhMe_{3-n}(OTf)_n$ series were to show the same essentially linear behavior as the halide series do, then extrapolation suggests that the BE of $P_3Rh(OTf)_3$ should be *ca.* 310.0 eV (see Figure 2).

Discussion

In interpretations of XPS data of a related series of compounds, the discussion usually begins with the mention of Koopmans' theorem.[5] In effect, this approximation assumes that electronic relaxation does not occur during an ionization event. Then it is generally noted that while Koopmans' theorem is a bad approximation, to the extent that there is electronic relaxation during electron ejection, it is probably reasonably similar for all of the molecules in a set of structurally related molecules and so can be ignored. Thus, *changes* in binding energy across a series of compounds with only minor structural variations should largely reflect *differences* in electron density in the

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[12] Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993; pp 182−199.

[13] (a) Nefedov, V. I.; Shubochkina, E. F.; Kolomnikov, I. S.; Baranovskii, I. B.; Kukolev, V. B.; Golubnichaya, M. A. *Zh. Neorg. Khim.* **1973**, *18*, 845. (b) *PHI Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin-Elmer, Physical Electronics Division: Eden Prairie, MN, 1979.

[14] Petrov, G. B.; Markovich, L. M.; Ryabtsev, A. V.; Belov, A. P. *J. Struct. Chem.* (*Engl. Transl.*) **1983**, *24*, 915.

[15] (a) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (c) Beck, W. *Inorg. Synth.* **1990**, *28*, 1.

[16] (a) Lichtenberger, D. L.; Subramanian, L.; Wang, L.; Flood, T. C. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA, March 1994; American Chemical Society: Washington, DC, 1994; INOR530. (b) Lichtenberger, D. L.; Subramanian, L.; Wang, L.; Wang, C.; Flood, T. C. Unpublished results.

ground state of the molecules (initial state) with only small contributions to *differences* in BE coming from the cations formed ("final" state).[5] In these kinds of studies, one cannot sort out the extent to which final state effects might contribute to or even dominate differences in ionization potentials. While this is an interesting question, it is not particularly important in the present context, since *changes* in the ionization potentials of a series of related compounds, whether they are dominated by initial-state or final-state effects, will parallel changes in many important chemical phenomena in which we are interested, such as heterolytic ligand dissociations and oxidations of all kinds including electrochemical and electron transfer oxidations and oxidative additions. Nevertheless, in the present study all of the CnRh and P_3Rh complexes under consideration (except $[CnRhMe_2(CO)]OTf$, **17**) are neutral, and they differ only in the extent of electron density at rhodium as a function of the cumulative electronegativity of the three unidentate ligands and/or, as suggested below, the polarizability of Cn vs P_3. The directions of the BE trends reported here follow a reasonable order for initial state effects with the expected ordering of Me < Br, Cl < OTf for reduction of electron density at rhodium.

Perhaps the most instructive insight into the relative electronic properties of the ligands shown here is the graphic illustration that the P_3 ligand affects the electron density of rhodium differently compared to the Cn ligand. The diagram of the XPS data of CnRh and P_3Rh complexes in Figure 2 illustrates that the binding energies of the $(L_3)RhMe_{3-n}(OTf)_n$ series (L_3 = Cn, P_3) give approximately linear (but three-point) plots with different slopes. $CnRhMe_3$ is *more* electron rich than P_3RhMe_3 ($\Delta BE = 0.6$ eV), but as methyl groups are replaced first by one and then two triflate groups, the incremental ΔBE is 1.2−1.3 eV in the CnRh series but ΔBE is only 0.8−0.9 eV in the P_3Rh complexes. If one assumes that the apparent linearity continues to $n = 3$ (as it does for $CnRhMe_{3-n}X_n$; X = Cl, Br), then $CnRh(OTf)_3$ would be *less* electron rich than $P_3Rh(OTf)_3$ ($\Delta BE \approx 0.7$ eV) (Figure 2). Clearly, P_3 compensates for electronic demands placed on the metal by its other ligands, either to donate or receive electron density, better than Cn does. One can couch the discussion in terms of nitrogen being a π-nonbonding, σ-donor ligand, while phosphorus is a σ-donor and a π-acid. The issue of whether phosphines, particularly trialkylphosphines, are π-acids has been debated over the years, with different types of data suggesting different answers.[17] The *simplest* rationalization for the BE trends of CnRh and P_3Rh is the difference in polarizability between nitrogen and phosphorus; i.e., nitrogen is "harder" and phosphorus is "softer". The XPS trends for these series effectively mean that P_3 makes Rh^{III} a softer metal and Cn makes Rh^{III} a harder metal.

Parenthetically, the observation that single triflate-for-methyl substitutions give significantly larger ΔBEs in the CnRh series than in the P_3Rh series may suggest that single-valued "ligand group shifts"[10a] that have been derived from XPS data on a large variety of complexes should be used with some caution. The electronic effect of a single ligand on a given metal center will be different as a function of the other ligands that are present, and the difference can be large.

In an attempt to put HSAB formalism on a quantitative footing, the "absolute hardness" of a chemical species has been defined[4] as $\eta = (I - A)/2$, where I and A are its ionization potential and electron affinity, respectively. For example, some representative molecules and their hardness parameters, η, are as follows: MeF, 9.4; NH_3, 8.2; NMe_3, 6.3; PH_3, 6.0; PMe_3, 5.9; MeI, 4.7. This number is said to be directly related to the size of the HOMO−LUMO gap, which, in turn, is related to the polarizability of the species and to its ability to engage in π-symmetry bonding either as a donor or an acceptor. All of these properties are relevant to the qualitative classification of species as hard or soft.[4] The hardness numbers suggest that NH_3 is substantially harder than PH_3, but NH_3 seems to be more softened by addition of three methyl groups than does PH_3, so that NMe_3 is only slightly harder than PMe_3. Presumably, the availability of species such as $(L_3)RhMe_{3-n}(OTf)_n$, where $L_3Rh = (NH_3)_3Rh$ and $(PH_3)_3Rh$, and the measurement of their XPS in combination with the present data might provide a semiquantitative correlation with hardness numbers, but at present there is too little data for this.

Overall, the XPS data provide a graphic qualitative illustration of the relatively hard properties of Cn and the relatively soft behavior of P_3 with Rh complexes and point to the possibility that different organometallic chemistry may be observed in the hard and soft systems. Only a few precedents for hard organorhodium species of the type (hydrocarbyl)Rh(*saturated* amine) are known. Very early examples are the series $[(NH_3)_5RhR]^{2+}$ (R = H, Et, Pr, Bu) and $[(NH_3)_4(H_2O)RhEt]^{2+}$ reported by Wilkinson *et al.* in the late 1960s.[18] Recently, the Wilkinson group has reported[9b] preparations of *fac*-(tmeda)(THT)$RhMe_3$ and *fac*-(tmeda)(CO)$RhMe_3$ (tmeda = $Me_2NCH_2CH_2NMe_2$, THT = *c*-SC_4H_8). No reactivity was reported for any of these compounds. Initial results of investigations of the organometallic reactivity of CnRh show that they do have some unusual properties. For example, $[CnRhMe(OH)(H_2O)]^+$ very slowly polymerizes ethylene *in water*,[3b] and $[CnRh(H)Me(PMe_3)]^+$ exhibits the highest thermal stability reported to date for a Rh(H)Me moiety.[3c] We have recently observed that $[(tacn)Rh(H)Et(PMe_3)]^+$ (tacn = 1,4,7-triazacyclononane) is even more stable than $[CnRh(H)Me(PMe_3)]^+$.[19]

Perhaps the most pronounced hard−soft reactivity comparison so far is the observed relative propagation vs transfer rate ratios in reactions of ethylene with $CnRhMe(OTf)_2$ (which gives polyethylene),[3a] $[Cp^*Rh(H)(CH_2{=}CH_2)P(OMe)_3]^+$ (which gives butenes),[20] and $[MeC(CH_2PPh_2)_3]RhMe_2(BF_4)$ (which shows only reductive elimination of ethane; no insertion).[8b] In general, very high propagation/transfer ratios are much more characteristic of early-transition-metal polymerization catalysts (hard, electrophilic metal cations), and usually the reverse is seen with late-transition-metal olefin alkylation catalysts. Even though XPS BEs indicate that

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[17] (a) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758 and references therein. (b) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064. (c) Wang, S. P.; Richmond, M. G.; Schwartz, M. *J. Am. Chem. Soc.* **1992**, *114*, 7595. (d) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492.

[18] Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1801.

[19] Zhou, R.; Flood, T. C. Submitted for publication.

[20] Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691 and references therein. In contrast, the cobalt analogue $[Cp^*Co(H)(CH_2{=}CH_2)P(OMe)_3]^+$ gives high-molecular-weight polyethylene: Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634 and references therein.

$CnRhMe_3$ is more electron rich than P_3RhMe_3, it also illustrates that cationic CnRh-containing species with highly electronegative groups are more electrophilic than complexes containing more polarizable L_3, such as $(R_3P)_3Rh$ and, one can interpolate, probably CpRh or Cp*Rh. Thus, one can infer that $[CnRhR(CH_2{=}CH_2)(OTf)]^+$ is likely to be a much harder and stronger electrophile than $\{[MeC(CH_2PPh_2)_3]RhR_2(CH_2{=}CH_2)\}^+$ and probably a stronger one that $[Cp^*RhR(CH_2{=}CH_2)P(OMe)_3]^+$. This difference may account for the "early-transition-metal-like" behavior of $CnRhMe(OTf)_2$ toward ethylene. Consistent with features of this rationale, cationic nickel and palladium alkyls in nitrogen-coordinated ligand environments have recently been reported to polymerize ethylene and α-olefins with very large propagation/transfer ratios and very high reactivity.[21]

Efforts to develop the organometallic chemistry of (saturated amine)$_n$Rh-based molecules continue, particularly with regard to contrasts with the reactivity of conventional soft analogues.

Experimental Section

General Considerations. All reactions involving organometallic compounds, unless otherwise mentioned, were carried out under an atmosphere of N_2 or Ar purified over reduced Cu catalyst (BASF R3-11) and Aquasorb. Flamed-out glassware and standard vacuum-line, Schlenk, and N_2-atmosphere box techniques were employed. Benzene, ether, hexanes, pentanes, and THF were distilled from purple solutions of sodium/benzophenone, and CH_2Cl_2 was distilled twice from CaH_2. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

XPS Experiments. Rh($3d_{5/2}$) and Rh($3d_{3/2}$) binding energies were measured on a PHI-548 X-ray photoelectron spectrometer using Mg Kα X-rays. A solution of *ca.* 0.5 mg of compound in *ca.* 1 mL of CH_2Cl_2 was prepared in a nitrogen-atmosphere glovebox. A few (3−4) small drops of the solution were evaporated onto a polyethylene-coated aluminum chip to form a thin layer of the metal complex on the polyethylene surface.[6d] $CnRhCl_3$ and $CnRhBr_3$, which are insoluble in CH_2Cl_2, were pressed onto a polyethylene chip as a powder. The C(1s) binding energy of polyethylene was assigned a value of 284.60 eV as an internal reference. All spectra were recorded at high resolution (pass energy 25 eV) at room temperature and a pressure of *ca.* 5×10^{-9} Torr. Three separate runs of each compound (four runs with $CnRhCl_3$, **10**) were performed on separately prepared samples, and at least one measurement was made on a different day than the other two as a check of the spectrometer reproducibility. Half-height widths of the $3d_{5/2}$ band were typically 1−2 eV, but the peaks were well-shaped and could be computer-fitted[6d] to Gaussian curves with good precision. Thus, the peak maxima were readily reproducible with well-behaved materials with the *range* of the three measurements on a given compound usually spanning a difference of less than 0.15 eV, and less than 0.10 eV with most compounds. As an indication of the dispersion of measurements, a standard σ was calculated for each compound where $\sigma = [\sum(BE_{av} - BE)^2/(n - 1)]^{1/2}$. Since three measurements do not constitute a statistical sample, a better overall indication of the precision of the method could be gained by calculating σ over all 40 individual measurements that we made in this study (excluding **17**, which is charged, and **4**, which gave particularly poor spectra). This more meaningful σ value was 0.035 eV, and so $3\sigma = 0.11$ eV. To use a general σ value is to ignore that some samples are not as well-behaved as others; therefore, the 3σ value calculated for each compound is recorded in Table 1. Where this value is less than 0.1 eV, a value of 0.1 is assigned in recognition of the fact that a set of three measurements is frequently accidentally more precise than is realistic.

Table 3. Crystallographic Data for P_3RhMe_3 (5)

empirical formula	$C_{14}H_{36}P_3Rh$
cryst size (mm)	$0.3 \times 0.2 \times 0.4$
cryst syst	orthorhombic
space group	$Pna2_1$ (No. 33)
a (Å)	14.454(1)
b (Å)	9.492(2)
c (Å)	14.258(1)
V (Å^3)	1956.4(4)
molecules per unit cell (Z)	4
fw	400.3
calcd density (g cm^{-3})	1.364
radiation	Mo Kα (0.710 69 Å)
2θ(max) (deg)	45
no. of rflns collected	1402
no. of rflns used ($I > 3\sigma(I)$)	1202
no. of params refined	163
final agreement factor	$R(F) = 0.0339$

One general concern in XPS measurements is sample charging, or the accumulation of positive change on the sample as electrons are continuously ejected. For nonconducting samples deposited on a conducting matrix, if the sample layer is very thin, the matrix effectively dissipates the charge. For thick samples or samples on a nonconducting matrix, such as polyethylene, charging can become a problem and is generally evidenced by a gradual shifting of the peak to higher BE, increasing broadening, and deterioration of the peak shape. Typically a flood gun (no pun intended) is used to correct for charging, but for our XPS measurements of organometallic species in general,[6] there was concern that electron bombardment might lead to reduction reactions with conversions to other species whose ionizations would then complicate the spectra. Since some charging is likely without the flood gun, the polyethylene surface was intentionally chosen as an internal standard because it was believed that it would charge at the same rate as the sample and thus give a consistent reference point. The large organic carbon content of the compounds in this series may contribute to their charging being similar to the polyethylene surface. A balance in sample loading must be struck: if loading is too heavy, often a broader carbon 1s signal is seen due to the different types of carbon ionizations from the organometallic complex (CO, Cp, aryl, etc.) underneath the polyethylene standard. If the sample loading is too light, the metal signal is too low. This sensitivity to surface loading indicates that photoelectrons coming off the surface are dominant in determining the overall signal. Since the sample is in intimate contact with the carbon surface, the charging effects are likely to be very similar for the sample and the surface of the standard. Additionally, care has been taken in all these investigations to use series of compounds which are as similar as possible, other than the variation in the groups to be tested. This maximizes the chances that charging effects from compound to compound will be very similar. Phenomenologically, shifting of the energy of the sample with respect to the standard over the time the spectrum is acquired is never seen, and while not all samples give ideal line shapes or signal to noise, the shapes of the peaks do not change with time either. These observations for XPS measurements over a large number of different organometallic series[6] give considerable confidence that the data are meaningful.

X-ray Crystallographic Structure Determination of P_3RhMe_3 (5). Slow evaporation in air of a methylene chloride−toluene solution of **5** resulted in formation of single crystals, the structure of which was found to be orthorhombic and of point group $Pna2_1$. Crystal and crystallographic parameters are given in Table 3. Data were collected at room temperature on a Siemens P2$_1$ diffractometer with Mo Kα radiation ($\lambda = 0.710\,69$ Å) up to a 2θ maximum of 50°. The x and y coordinates of the Rh atom were located from a Patterson

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[21] Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

map,[22] and the *z* value was fixed at the arbitrary value of $^1/_2$. The other non-hydrogen atoms were located from a series of difference Fourier maps, and the entire structure was refined[22] anisotropically to a final agreement factor of $R = 3.39\%$. No attempt was made to locate the H atoms. Final atomic coordinates are given in the Supporting Information.

Synthesis of $(Me_3P)_3Rh$ and P_3Rh Complexes. *fac*-$(Me_3P)_3RhMe_3$ (1). Method 1. The preparation of Wilkinson *et al.*[9a] was used. ^1H NMR (C_6D_6): δ 0.30 (m, RhCH_3), 0.93 (second-order d, J_{PH}(apparent) = 5.6 Hz, PCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 6.50 (dddd, $J_{RhC} = 22.8$, $J_{PC}(trans) = 113.6$, $J_{PC}(cis) = 13.6$, 8.7 Hz, RhCH_3), 17.86 (m, PCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −17.99 (d, $J_{RhP} = 83.0$ Hz).

Method 2. From CnRhMe$_3$. A solution of CnRhMe$_3$ and an excess of PMe$_3$ in C_6D_6 was sealed in an NMR tube and heated at 108 °C for 24 h. The proton spectrum showed only the presence of excess PMe$_3$, free Cn, and *fac*-$(Me_3P)_3RhMe_3$, the last two in a 1:1 molar ratio.

***mer*-$(Me_3P)_3RhMe_2Cl$ (3).** An ether solution of HCl (0.276 mL of 0.770 N solution, 0.213 mmol) was slowly added to a stirred solution of 80 mg (0.213 mmol) of $(Me_3P)_3RhMe_3$ in 8 mL of CH_2Cl_2 at −78 °C, under nitrogen. Ten minutes after completion of the addition, the solution was warmed slowly to 22 °C and stirring was continued for 30 min. Solvents were removed under vacuum, and the yellow solid was vacuum-dried for 3 h. The conversion was quantitative. ^1H NMR (C_6D_6): δ −0.14 (m, RhCH_3), 0.54 (m, RhCH_3), 1.00 (d, $J_{PH} = 6.4$ Hz, P(CH_3)$_3$), 1.15 (vt, $J_{PH} = 3.0$ Hz, 2P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −21.39 (dt, $J_{RhP} = 85.1$ Hz, $J_{PP} = 29.2$ Hz, *P*Me$_3$), −5.52 (dd, $J_{RhP} = 109.5$ Hz, $J_{PP} = 29.2$ Hz, 2*P*Me$_3$).

***mer*-$(Me_3P)_3RhMeCl_2$ (4).** The procedure was the same as the preceding, except that 2 equiv of HCl was used in this case. The transformation afforded yellow product quantitatively. ^1H NMR (C_6D_6): δ 0.61 (m, RhCH_3), 0.90 (d, $J_{PH} = 9.8$ Hz, P(CH_3)$_3$), 1.31 (vt, $J_{PH} = 3.5$ Hz, 2P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −8.26 (dd, $J_{RhP} = 96.7$ Hz, $J_{PP} = 32.4$ Hz, 2*P*Me$_3$), 8.01 (dt, $J_{RhP} = 135.7$ Hz, $J_{PP} = 32.4$ Hz, *P*Me$_3$).

1,1,1-Tris((dimethylphosphino)methyl)ethane (P$_3$). This ligand was prepared by the method of Whitesides *et al.*[7a] as modified by Bleeke *et al.*[7b] in 48% overall yield from P_2Me_4 as a yellow liquid collected at 74−77 °C/0.2 mm. ^1H NMR (C_6D_6): δ 0.91 (d, $J_{PH} = 2.9$ Hz, PCH_3), 1.15 (s, CH_3), 1.71 (d, $J_{PH} = 3.5$ Hz, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −61.54 (s).

P_3RhMe_3 (5). First 20 mL of deoxygenated ethanol was used to dissolve 1.00 g (3.80 mmol) of $RhCl_3{\cdot}3H_2O$ in a 100 mL, two-necked, round-bottom flask which was equipped with a condenser. Under N_2, 15 mL of an ethanol solution of P$_3$ (1.13 mL of P$_3$ in 14 mL of ethanol) was slowly added to the dark red solution of RhCl$_3$ with stirring. This resulted in immediate precipitation of light yellow solids. Addition was finished in 10 min. The mixture was stirred at room temperature for 20 min and then was heated at reflux for 6 h. The room-temperature mixture was filtered in air. The yellow solid was washed with 3 × 8 mL of ethanol, then 3 × 8 mL of ether, and 3 × 8 mL of pentane and then vacuum-dried to yield 1.42 g of yellow solid. This solid (presumably P_3RhCl_3) was mixed with 0.507 g of CH$_3$Li (80% by weight); 35 mL of THF was added, and the mixture was stirred. Reaction was initiated in *ca.* 2 min, whereupon the color of the solution turned red-brown and the solution became homogeneous. This was stirred at room temperature for 1 day. Wet THF was slowly added to the reaction mixture with stirring until bubbling ceased. Solvent was evaporated. The residue was extracted with stirring by 70 mL of benzene under reflux for 40 min. The room-temperature solution was filtered, and the residue was washed with 3 × 5 mL of benzene. Evaporation of benzene gave 0.33 g of a light yellow mixture of 80% P_3RhMe_3 and 20% P_3RhMe_2Cl. This was further treated with 90 mg of CH$_3$Li (80% by weight) in 12 mL of THF with stirring for 1 day. Workup as just mentioned yielded 0.23 g (15%) of snow white product. The residue of the first benzene extraction was extracted with 75 mL of CH_2Cl_2 at room temperature for 1 h. The solution was filtered, the solvent was evaporated, and 0.35 g of yellow solid was obtained (partially P_3RhMe_2Cl). This was treated with 0.20 g of CH$_3$Li (80% by weight) in 12 mL of THF and stirred for 1 day. The workup procedure was as usual. From this 0.14 g (9%) of light yellow product was obtained (The color was due to contamination by a trace amount of P_3RhMe_2Cl, but the product was quite pure enough for most purposes.) Combined yield: 0.37 g (24% based on Rh). ^1H NMR (C_6D_6): δ 0.45 (m, RhCH_3), 0.59 (q, $J_{PH} = 2.5$ Hz, CH_3), 0.69 (vq, CH_2), 0.94 (vt, P(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.35 (m, RhCH_3), 15.73 (m, PCH_3), 38.09 (m, CC_4), 38.48, (q, $J_{PC} = 8.6$ Hz, CH_3), 39.16 (m, PCH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −11.93 (d, $J_{RhP} = 77.9$ Hz). Anal. Calcd for $C_{14}H_{36}P_3Rh$: C, 42.01; H, 9.07. Found: C, 42.34; H, 9.06.

P_3RhMe_2OTf (6). To a stirred solution of 0.100 g (0.250 mmol) of P_3RhMe_3 in 10 mL of CH_2Cl_2 at −78 °C was slowly added 0.337 mL of a 0.705 N (0.237 mmol) triflic acid ether solution under nitrogen. The solution turned milky white during the addition. Then 5 min after completion of the addition, the solution was slowly warmed to room temperature and was stirred at this temperature for 40 min. The solvent was then reduced to *ca.* 2 mL under reduced pressure, and 15 mL of pentane was added by syringe to induce precipitation of the product. The mother liquor was removed by cannula, and the solid was washed with pentane (2 × 15 mL). The solid was dried under vacuum for several hours; 0.116 g (91%) of milky white solid was obtained. ^1H NMR (CD_3SOCD_3): δ −0.06 (Rh(CH_3)$_2$), 1.12 (CCH_3), 1.36, 1.41, 1.52, 1.66 (CH_2, PCH_3). $^{31}P\{^1H\}$ NMR (CD_3SOCD_3): δ −18.27 (dd, $J_{RhP} = 74.5$ Hz, $J_{PP} = 35.4$ Hz, 2*P*Me$_2$), 14.56 (dt, $J_{RhP} = 113.8$ Hz, $J_{PP} = 35.4$ Hz, *P*Me$_2$). Anal. Calcd for $C_{14}H_{33}P_3F_3SO_3Rh$: C, 31.47; H, 6.23. Found: C, 31.21; H, 6.38.

$P_3RhMe(OTf)_2$ (7). A solution of triflic acid in ether (0.691 mL of a 0.705 N solution, 0.487 mmol) was slowly added to a stirred solution of 0.100 g (0.250 mmol) of P_3RhMe_3 in 10 mL of CH_2Cl_2 in a Schlenk flask under nitrogen at −78 °C. The solution became cloudy during the addition. Five minutes after the completion of the addition, the solution was slowly warmed to room temperature and the mixture was stirred at this temperature for 50 min. The white precipitates were allowed to settle, and the mixture was cooled to 0 °C. The supernatant was removed by cannula. The residue was warmed to room temperature, and 15 mL of benzene was added. The supernatant was again removed by cannula, and the solid was washed again with 15 mL of benzene. The resulting solid was dried under vacuum for several hours; 0.143 g (91%) of snow white solid was obtained. ^1H NMR (CD_3SOCD_3): δ 0.63 (RhCH_3), 1.18 (CCH_3), 1.39, 1.56, 1.76, 1.81 (CH_2, PCH_3). $^{31}P\{^1H\}$ NMR (CD_3SOCD_3): δ −13.33 (dt, $J_{RhP} = 71.2$ Hz, $J_{PP} = 28.7$ Hz, *P*Me$_2$), 33.55 (dd, $J_{RhP} = 122.6$, $J_{PP} = 28.6$ Hz, 2*P*Me$_2$). Anal. Calcd for $C_{14}H_{30}P_3F_6S_2O_6Rh$: C, 25.16; H, 4.52. Found: C, 25.62; H, 4.53.

Acknowledgment. The work at both the University of Southern California and the University of Minnesota was supported by the National Science Foundation (USC, Grant No. CHE-9317570; UM, Grant No. CHE-8921744-06). We thank Dr. Paul A. Deck and Prof. Robert Bau for helpful discussions and Hongshi Zhen for experimental assistance. We are grateful to Prof. John Evans and his group (UM) for the use of their XPS instrument and for helpful discussions.

Supporting Information Available: Tables giving complete crystallographic data for **5** (4 pages). Ordering information is given on any current masthead page.

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[22] Sheldrick, G. M. SHELX-76; Cambridge University, Cambridge, U.K., 1976.