bonds, it seems possible on the basis of steric arguments that the long sought $I_3Cr(CO)_4^-$ may be a viable species and failures to prepare this material previously[13] could be for kinetic and not thermodynamic reasons.

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Registry No. 1, 67202-54-4; $[Et_4N]_2[(Ph_3Sn)_2Cr(CO)_4]$, 67202-48-6.

Supplementary Material Available: Tables of final thermal parameters and esds for non-hydrogen atoms of $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$ (1) (Table S-1), bond distances and angles with esds for $(C_2H_5)_4N^+$ in 1 (Table S-2), and final observed and calculated structure factors (Table S-3) (36 pages). Ordering information is given on any current masthead page.

Reactions of Alkylaluminum Reagents with Basic and Acidic Rhodium Compounds. X-ray Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)Rh(PMe_3)_2(Al_2Me_4Cl_2)$, a Rhodium–Lewis Acid Adduct[†]

James M. Mayer*[‡] and J. C. Calabrese

E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

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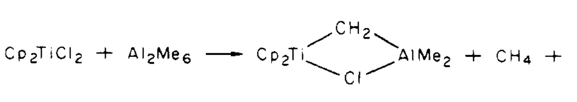
A series of alkylaluminum adducts of cyclopentadienylrhodium compounds have been prepared, including $CpRhL_2(AlMe_3)$ (L = PMe_3, PMe_2Ph, PEt_3), $CpRh(PMe_3)_2(AlEt_3)$, $CpRh(C_2H_4)(PMe_3)(AlMe_3)$, and $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$. The crystal and molecular structure at −100 °C of the last complex has been determined: space group $P2_1/n$, a = 15.696 (2) Å, b = 12.664 (2) Å, c = 12.544 (2) Å, β = 108.32 (1)°, V = 2367 (1) Å^3, Z = 4. The final conventional and weighted agreement indices on F_o for 4297 reflections with $F_o^2 > 2\sigma(F_o^2)$ are 0.025 and 0.029. The molecule has a normal "three-legged piano stool" geometry with a short, unbridged rhodium–aluminum bond (2.458 (1) Å). The structure of the $Al_2Me_4Cl_2$ ligand suggests that the complex can be described to some extent as a $Rh\text{–}AlMe_2$ cation with a weakly associated $AlMe_2Cl_2$ anion. NMR studies suggest that the trialkylaluminum adducts also have rhodium–aluminum bonds and that the aluminum ligand is extremely labile in solution. The kinetic parameters for dissociation of $AlMe_3$ from $CpRh(PMe_3)_2AlMe_3$ at 15 °C are k = 61 s^{-1}, $\Delta G^{\ddagger}$ = 14.4 (5) kcal/mol, $\Delta H^{\ddagger}$ = 18 (3) kcal/mol, and $\Delta S^{\ddagger}$ = 13 (10) eu. This $\Delta H^{\ddagger}$ corresponds roughly to the strength of the rhodium–aluminum dative bond. The acidic rhodium compounds $CpRhL(PMe_3)H^+$ react with trimethylaluminum not by deprotonation but by methyl for hydride exchange (making $CpRh(PMe_3)_2Me^+$ from $CpRh(PMe_3)_2H^+$) or methyl anion transfer ($CpRhMe(C_2H_5)PMe_3$ from $CpRh(C_2H_4)PMe_3(H)^+$).

The interactions of Lewis acidic reagents with metal carbonyl compounds have been extensively explored by Shriver and co-workers.[1] However, the chemistry of Lewis acids and metal complexes that do not contain an electronegative element like oxygen has received only sporadic attention.[2] Alkylaluminum reagents are extensively used in industrial processes like Ziegler–Natta polymerization.[3] Organoaluminum compounds have been used in transition-metal chemistry primarily as alkylating agents, although the Lewis acidity of aluminum also appears to be important,[4] as in the formation of "Tebbe's reagent" (eq 1, Cp = $\eta^5\text{-}C_5H_5$).[4a] We have investigated the reactions of alkylaluminum compounds with the very basic rhodium complexes prepared by Werner,[5] in order to study the Lewis acid chemistry of the aluminum reagents.



$$\mathrm{Cp_2TiCl_2 + Al_2Me_6 \longrightarrow Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2 + CH_4 + \tfrac{1}{2}Al_2Me_4Cl_2} \qquad (1)$$

Most of the examples of alkylaluminum–transition-metal complexes involve bridging carbonyls, alkyls, or hydrides;[6] there is only one firm example of an unbridged transition metal–aluminum bond: $[Cp(CO)_2Fe\text{–}AlPh_3]^-$.[7] The tungstenocene dihydride–trimethylaluminum adduct ($Cp_2WH_2\cdot AlMe_3$) was thought to contain a tungsten–aluminum bond,[8] but a recent crystal structure shows that

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[†] Contribution No. 3434.

[‡] Present Address: Department of Chemistry, University of Washington, Seattle, WA 98195.

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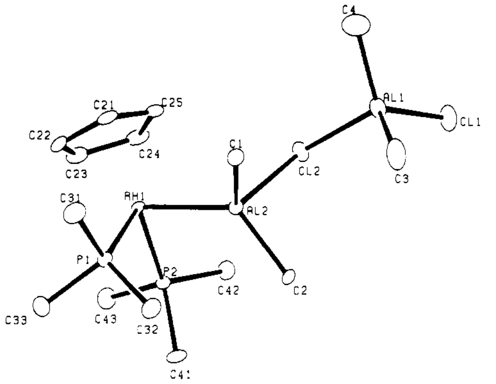

Figure 1. ORTEP drawing of $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$ (7). The hydrogen atoms are omitted for clarity.

the interaction is at least partially through bridging hydride ligands.[9] The deprotonation of $CpW(CO)_3H$ by trimethylaluminum was similarly thought to give a metal–metal bonded complex[10] (as trimethylgallium does[11]), but the aluminum fragment is actually bound to carbonyl oxygen atoms.[12] The site of basicity in a metal complex is often a function of the Lewis acid.[13]

Results

Addition of trialkylaluminum reagents to cold pentane solutions of cyclopentadienylrhodium bis(phosphine) complexes yield adducts (1–4, eq 2) as yellow precipitates.

$$CpRh(PR_3)_2 + {}^1/_2Al_2R'_6 \rightarrow CpRh(PR_3)_2(AlR'_3) \qquad (2)$$

$$\begin{aligned} &\mathbf{1},\ PR_3 = PMe_3,\ AlR'_3 = AlMe_3\\ &\mathbf{2},\ PR_3 = PMe_3,\ AlR'_3 = AlEt_3\\ &\mathbf{3},\ PR_3 = PMe_2Ph,\ AlR'_3 = AlMe_3\\ &\mathbf{4},\ PR_3 = PEt_3,\ AlR'_3 = AlMe_3 \end{aligned}$$

Reaction 2 is actually an equilibrium that lies far to the right except for **4** and the ethylene derivative **5** (eq 3)

$$CpRh(C_2H_4)PMe_3 + {}^1/_2Al_2Me_6 \rightleftharpoons \underset{\mathbf{5}}{CpRh(C_2H_4)(PMe_3)(AlMe_3)} \qquad (3)$$

where low temperature is necessary to favor the adducts. The dimethylphenylphosphine analogue of **5** has not been isolated because the equilibrium in this case is unfavorable. Trimethylaluminum does not appear to interact with $CpRh(PPh_3)_2$. $CpCo(PMe_3)_2$ binds trimethylaluminum strongly (eq 4), although solutions of **6** usually contain a small amount of $Me_3P{\cdot}AlMe_3$ (by ^{31}P NMR spectroscopy).

$$CpCo(PMe_3)_2 + {}^1/_2Al_2Me_6 \rightarrow \underset{\mathbf{6}}{CpCo(PMe_3)_2(AlMe_3)} \qquad (4)$$

Analogous adducts of alkylaluminum halides have not been isolated. However, addition of excess dimethylaluminum chloride to a solution of $CpRh(PMe_3)_2$ precipitates a yellow crystalline solid analyzing as a 2:1 aluminum–rhodium complex (**7**, eq 5). Compound **7** is insoluble in aromatic solvents and reactive toward polar solvents such as methylene chloride, THF, acetonitrile, and chlorobenzene; it has been characterized by an X-ray crystal structure, described below. A 1:1 iridium–aluminum adduct precipitates on mixing hexane solutions of diethylaluminum iodide and $CpIr(C_2H_4)_2$ (eq 6). This material is unstable in solution and has not been isolated in pure form.

$$CpRh(PMe_3)_2 + Al_2Me_4Cl_2 \rightarrow \underset{\mathbf{7}}{CpRh(PMe_3)_2(Al_2Me_4Cl_2)} \qquad (5)$$

$$CpIr(C_2H_4)_2 + {}^1/_2Al_2Et_4I_2 \rightarrow \underset{\mathbf{8}}{CpIr(C_2H_4)_2(AlEt_2I)} \qquad (6)$$

Table I. Fractional Coordinates ($\times 10^4$) in the Structure of $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$ (7)[a]

atom	x	y	z
Rh(1)	149.3 (1)	2403.7 (1)	1921.6 (1)
Cl(1)	2669.0 (5)	404.3 (6)	−1753.6 (7)
Cl(1*)	1513.7 (11)	4030.0 (12)	573.4 (15)
Cl(2)	1386.2 (4)	1375.7 (5)	−172.2 (5)
P(1)	686.6 (4)	3701.0 (5)	3194.5 (5)
P(2)	753.7 (4)	1018.0 (5)	3017.6 (5)
Al(1)	2168.5 (6)	1917.7 (6)	−1369.4 (7)
Al(2)	1507.6 (5)	2587.6 (6)	1359.4 (6)
C(1)	1506 (4)	4036 (4)	569 (4)
C(2)	2736 (1)	2140 (2)	2265 (2)
C(3)	3182 (3)	2808 (3)	−553 (4)
C(4)	1259 (3)	2479 (3)	−2672 (3)
C(21)	−827 (2)	3323 (2)	555 (2)
C(22)	−1313 (2)	2997 (2)	1289 (2)
C(23)	−1341 (2)	1902 (2)	1280 (2)
C(24)	−862 (2)	1536 (2)	552 (2)
C(25)	−584 (2)	2414 (2)	71 (2)
C(31)	282 (2)	5003 (2)	2652 (3)
C(32)	1878 (2)	3963 (2)	3831 (2)
C(33)	292 (2)	3620 (2)	4406 (2)
C(41)	1710 (2)	1153 (2)	4279 (2)
C(42)	1075 (2)	−93 (2)	2310 (2)
C(43)	−57 (2)	385 (2)	3574 (3)

[a] C(1) and Cl(1*) are disordered in the crystal, with an occupancy of 0.67 C(1) and 0.33 Cl(1*).

X-ray Crystal Structure of $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$ (7). The crystal structure of **7** consists of discrete molecules, drawn in Figure 1 along with the atom numbering scheme. Fractional atomic coordinates are listed in Table I; relevant bond distances and angles are listed in Table II. The geometry about rhodium is well described as a "three-legged piano stool", as expected for $CpML_3$ complexes. The rhodium–phosphorus and rhodium–carbon bond lengths (average 2.254 (1) and 2.265 (7) Å) are within the range found for other Rh–PMe_3 and CpRh complexes.[14] Included in this comparison is the structure of $CpRh(C_2H_4)PMe_3$[15] which we have also solved.[16] The bond lengths (Å) in $CpRh(C_2H_4)PMe_3$—

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(16) $RhPC_{10}H_{18}$: M_w = 272.138; orthorhombic; space group $Pna2_1$; a = 10.686 (1), b = 8.779 (1), c = 12.123 (1) Å; temp = −100 °C; V = 1137.3 Å^3; D(calcd) = 1.589 g/cm^3 for Z = 4; trapezoidal block 0.30 × 0.29 × 0.34 mm; μ = 15.69 cm^{-1}; 1218 diffractometer reflections with $I > 2\sigma(I)$; final R = 0.021, R_w = 0.027 for 53 independent variables (Rh, P, C anisotropic). There is a pseudomirror plane in the structure that contains the Rh and P atoms and one methyl group (C11) and relates the two ethylene carbon atoms to two of the Cp ring atoms, causing strong correlations in the least squares.

Table II. Interatomic Distances (Å) and Angles (deg) in $CpRh(PMe_3)_2(Al_2Me_4Cl_2)$ (7)[a]

Bond Lengths

Rh(1)-P(1)	2.2612 (7)	Cl(2)-Al(1)	2.322 (1)	Al(1)-C(3)	1.956 (4)
Rh(1)-P(2)	2.2472 (6)	Cl(1*)-Al(2)	2.077 (1)	Al(1)-C(4)	1.936 (4)
Rh(1)-Al(2)	2.4581 (8)	Cl(2)-Al(2)	2.419 (1)	Al(2)-C(1)	2.085 (5)
Rh(1)-C(21)	2.234 (2)	P(1)-C(31)	1.820 (3)	Al(2)-C(2)	1.988 (2)
Rh(1)-C(22)	2.306 (3)	P(1)-C(32)	1.819 (3)	C(21)-C(22)	1.429 (4)
Rh(1)-C(23)	2.311 (3)	P(1)-C(33)	1.815 (3)	C(21)-C(25)	1.408 (4)
Rh(1)-C(24)	2.228 (2)	P(2)-C(41)	1.815 (3)	C(22)-C(23)	1.388 (4)
Rh(1)-C(25)	2.244 (2)	P(2)-C(42)	1.817 (3)	C(23)-C(24)	1.430 (4)
Cl(1)-Al(1)	2.182 (1)	P(2)-C(43)	1.819 (3)	C(24)-C(25)	1.399 (4)

Bond Angles

P(1)-Rh(1)-P(2)	98.24 (3)	C(32)-P(1)-C(33)	102.5 (1)	Cl(2)-Al(2)-C(1)	101.1 (2)
P(1)-Rh(1)-Al(2)	88.23 (3)	C(41)-P(2)-C(42)	102.6 (1)	Cl(2)-Al(2)-C(2)	95.36 (8)
P(2)-Rh(1)-Al(2)	90.69 (3)	C(41)-P(2)-C(43)	101.1 (1)	C(3)-Al(1)-C(4)	119.5 (2)
Al(1)-Cl(2)-Al(2)	113.60 (4)	C(42)-P(2)-C(43)	100.5 (1)	C(1)-Al(2)-C(2)	112.2 (2)
Rh(1)-P(1)-C(31)	112.66 (10)	Rh(1)-Al(2)-Cl(2)	107.99 (3)	C(22)-C(21)-C(25)	108.3 (2)
Rh(1)-P(1)-C(32)	123.11 (9)	Rh(1)-Al(2)-C(1)	110.4 (1)	C(21)-C(22)-C(23)	107.8 (3)
Rh(1)-P(1)-C(33)	113.60 (10)	Rh(1)-Al(2)-C(2)	125.57 (8)	C(22)-C(23)-C(24)	107.9 (3)
Rh(1)-P(2)-C(41)	122.31 (9)	Cl(1)-Al(1)-Cl(2)	100.57 (4)	C(23)-C(24)-C(25)	108.4 (2)
Rh(1)-P(2)-C(42)	115.75 (9)	Cl(1)-Al(1)-C(3)	109.4 (1)	C(21)-C(25)-C(24)	107.5 (2)
Rh(1)-P(2)-C(43)	111.53 (10)	Cl(1)-Al(1)-C(4)	111.0 (1)	Cl(1*)-Al(2)-Rh	110.7 (2)
C(31)-P(1)-C(32)	100.9 (1)	Cl(2)-Al(1)-C(3)	109.9 (1)	Cl(1*)-Al(2)-C(2)	111.9 (2)
C(31)-P(1)-C(33)	101.2 (1)	Cl(2)-Al(1)-C(4)	104.8 (1)	Cl(1*)-Al(2)-Cl(2)	101.1 (2)

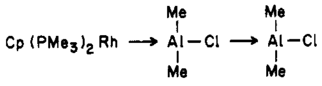
[a] The atoms C(1) and Cl(1*) are disordered in the site labeled C(1) in Figure 1, with an occupancy of 0.67 for C(1) and 0.33 for Cl(1*) and a separation of 0.014 Å.

Rh-P (2.212 (1)), Rh-C(olefinic) (average 2.09 (2)), C-C(olefinic) (1.45 (2))—and the overall geometry are quite similar to the structure of $(C_5Me_5)Rh(C_2H_4)(PPh_3)$[17] (structural data are given in the supplementary material).

One of the aluminum methyl groups in 7 (C(1)) is disordered and is occupied by roughly two-thirds CH_3 and one-third Cl. This occupancy has been found in data sets taken on two different crystals, as described in the Experimental Section. Halide and alkyl groups are rapidly scrambled among aluminum centers in solution,[19] so it is not difficult to accumulate an excess of chloride in the crystal. In fact, this disorder is fairly common in crystals containing alkylaluminum halide groups.[20] The disordered carbon and chlorine atoms could not be resolved in the least-squares analysis, and they refined to positions only 0.014 Å apart. Thus the Al(2)-C(1) and Al(2)-Cl(1*) bond lengths are distorted on the basis of related values in the structure.

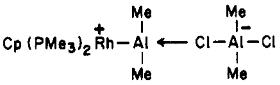
The rhodium-aluminum bond in 7 is the second crystallographically characterized unbridged transition metal-aluminum interaction. The bond length of 2.458 (1) Å is significantly shorter than the iron-aluminum bond in $[Cp(CO)_2Fe\text{-}AlPh_3]NEt_4$ (2.510 (2) Å),[7] especially considering that the radius of iron is smaller than that of rhodium[18] (the average Fe-C(Cp) distance in this complex is 0.17 Å shorter than the average Rh-C distance in 7). The Rh-Al bond is also shorter than the sum of the radii of rhodium and aluminum: 2.50 (using metallic radii) or 2.58 Å (covalent radii).[18]

The bridging chloride ion (Cl(2)) is asymmetrically located between the aluminum atoms, 0.1 Å farther from Al(2) than Al(1). The Al(2)-Cl(2) bond is at the long end of the known range of aluminum-bridging chloride distances.[21] This suggests that 7 is not fully described as a Lewis acid adduct (A) and that another valence bond structure (B)—a rhodium complex of $AlMe_2^+$ with a weakly associated $AlMe_2Cl_2^-$ counterion—is also important. An $AlMe_2^+$ complex would be expected to be close to planar at aluminum (by analogy with the structure of $Cp(CO)_3W\text{-}GaMe_2$[11]) and the geometry about Al(2) is distorted in this direction, the aluminum atom lying only 0.43 Å from the plane defined by Rh, C(1), and C(2). The sum of the angles around Al(2) involving these atoms is 348°, closer to planar (360°) than tetrahedral (328°).[22] The shortness of the rhodium-aluminum bond may also be related to the presence of resonance structure B, since a covalent Rh-Al bond (as in B) is expected to be shorter and stronger than a dative bond. A contribution from the zwitterion resonance form B may also explain the insolubility of 7 in aromatic solvents and its instability in polar solvents. An ionic compound similar to B has been prepared from $CpCo(PMe_3)_2$ and stannic chloride: $[Cp(PMe_3)_2CoSnCl_3^+][SnCl_5^-]$.[23]



$Cp(PMe_3)_2Rh \rightarrow AlMe_2\text{-}Cl \rightarrow AlMe_2\text{-}Cl$

A



$Cp(PMe_3)_2\overset{+}{Rh}\text{-}AlMe_2 \leftarrow Cl\text{-}\overset{-}{Al}Me_2\text{-}Cl$

B

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[22] A reviewer has pointed out that much of the distortion around Al(2) is due to the position of C(2), which may simply be caused by steric interactions with the phosphine methyl groups. However, these nonbonded contacts—C(2)···C(32) = 3.56 and C(2)···C(4) = 3.62 Å—are not short compared with the C(2)···C(1) and C(2)···Cl(2) contacts (3.38 and 3.28 Å). The H-H contacts are also not unusually short.

[23] Dey, K.; Werner, H. *Chem. Ber.* **1979**, *112*, 823-833.

Table III[a]

compound	k	T, K	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$CpRh(PMe_3)_2(AlMe_3)$ (1)	14	(274)			
	26	(278)			
	72	(287)			
	61	(288)	14.4	18	13
	137	(292)			
	232	(297)			
	600	(308)			
$CpRh(PMe_3)_2(AlEt_3)$ (2)	89	(274)	13.5		
$CpRh(PMe_2Ph)_2(AlMe_3)$ (3)	14	(242)			
	42	(250)	12.7	17	17
	200	(262)			
	1043	(274)			
$CpRh(PEt_3)_2(AlMe_3)$ (4)	60	(211)	10.5		
compd	K	T, K	ΔG	ΔH	ΔS
$CpRh(PMe_3)(C_2H_4)(AlMe_3)$ (5)	190	(191)	−2.0	−7	−27
	14	(222)			
$CpRh(PMe_2Ph)(C_2H_4)(AlMe_3)$	2.3	(191)	−0.3	−4	−17
	1.4	(201)			
	1.05	(210)			

[a] The kinetic parameters in the top half of the table refer to eq 9; the equilibrium parameters at the bottom refer to eq 11. Units: k, s^{-1}; K, $(M/L)^{-1/2}$; energies in kcal/mol; entropy in eu. Estimated errors are as follows: $\Delta G^{\ddagger}$, ΔG, ±0.5; $\Delta H^{\ddagger}$, ΔH, ±3; $\Delta S^{\ddagger}$, ±10; ΔS, ±15. All in toluene-d_8 solution.

NMR Studies. The proton NMR spectra of 1–4 suggest that they adopt geometries in solution similar to that found for 7 in the solid state. Prochiral groups on the phosphine ligands ($P\mathit{Me}_2Ph$ and $P(C\mathit{H}_2CH_3)_3$) are diastereotopic in the low-temperature proton NMR spectra, while the methylene hydrogen atoms in the triethylaluminum adduct 2 remain magnetically equivalent. No broadening of the cyclopentadienyl resonance is observed. These observations are consistent with a "three-legged-stool" geometry and inconsistent with the cyclopentadienyl ring being the site of metal basicity.

Low-temperture limiting ^1H NMR spectra for $CpRh(C_2H_4)PMe_3(AlMe_3)$ (5) and its dimethylphenylphosphine analogue have not been obtained because dissociation of trimethylaluminum is rapid on the NMR time scale at −80 °C (360 MHz). However, the resonances for the ethylene ligands in the starting materials and the adducts are similar, suggesting that the aluminum does not bind to the coordinated olefin.[24] The low-temperature proton spectrum of 8 is undecipherable, containing a cyclopentadienyl resonance and a number of broad complex multiplets. At ambient tempertures, the olefinic resonances of 5 and 8 are broad because olefin rotation is near the coalescence point. The ethylene ligands of the parent compounds are not fluxional, so Lewis acids appear to lower the activation barrier to olefin rotation. This is also observed in solutions of $CpRh(C_2H_4)PMe_3$, $CpRh(C_2H_4)_2$, and $CpIr(C_2H_4)_2$ containing dimethylaluminum chloride or diethylaluminum iodide and has been previously reported by Cramer for the mercuric chloride adduct of $CpRh(C_2H_4)_2$.[25] Ligand dissociation is not occurring under these conditions, since $^{13}C_2H_4$ is incorporated into 5 only slowly at 80 °C. More rapid olefin rotation is probably due both to the pseudooctahedral structures of the adducts that will have smaller preferences in the orientation of the ethylene ligand and to a reduction in the strength of π-back-bonding because of electron withdrawal by the Lewis acid.

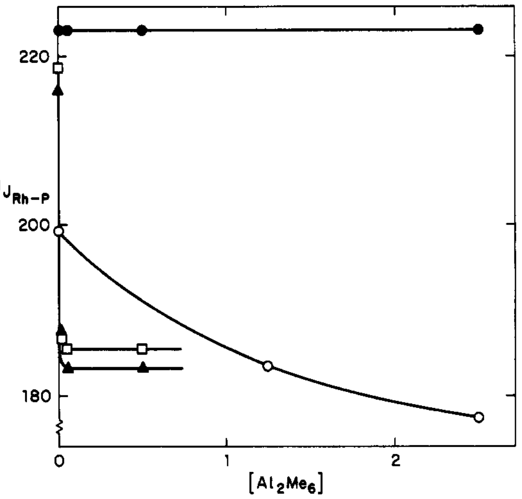

Figure 2. Graph of rhodium–phosphorus coupling constant (Hz) vs. concentration of Al_2Me_6 in benzene (M) for $CpRh(PPh_3)_2$ (●), $CpRh(PMe_2Ph)_2$ (□), $CpRh(PMe_3)_2$, (△), and $CpRh(C_2H_4)PMe_3$ (○).

The phosphorus NMR spectrum of 1 has a significantly smaller rhodium–phosphorus coupling constant than $CpRh(PMe_3)_2$: 183 vs. 216 Hz (see Figure 2). If less than 1 equiv of $AlMe_3$ per rhodium is present, a single doublet is observed with $^1J_{RhP}$ intermediate between the above values, indicating that the alkylaluminum group is rapidly exchanging between rhodium atoms at ambient temperatures. Addition of excess trialkylaluminum to 1, 2, or 3 does not further reduce the coupling constant, implying that the equilibrium in eq 7 lies far to the right. Data for

$$CpRhL_2 + {}^1/_2Al_2R_6 \rightleftharpoons CpRhL_2(AlR_3) \qquad (7)$$

compounds 4 and 5 suggest that they are primarily dissociated in solution. Addition of excess Al_2Me_6 to a solution of 5 shifts the equilibrium to the right, causing a gradual decrease in the apparent rhodium–phosphorus

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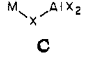
(24) Binding of the trimethylaluminum to the ethylene ligand would be expected to shift the olefin resonances upfield and significantly change the hydrogen–hydrogen coupling constants. These changes should be observable in the NMR spectrum even under the conditions where dissociation of $AlMe_3$ is rapid, as long as the adduct is the predominant species in solution. Attack of aluminum at a coordinated olefin might lead to a metallacycle like C (X = alkyl, halide). A structure of this type



C

has been observed by Kaminsky (Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 197–201). "Tebbe's reagent" (eq 1) is a four-membered ring analogue.[4a]

(25) Cramer, R.; Mrowca, J. J. *Inorg. Chim. Acta* **1971**, *5*, 528–530.

coupling constant (Figure 2). Compounds 1, 3, and 4, however, react further in concentrated solutions of trimethylaluminum, forming a number of (as yet uncharacterized) species that do not interconvert on the NMR time scale. The reduced rhodium phosphorus coupling constants for all of these adducts suggest partial oxidation of the rhodium atom by the Lewis acid since a rough inverse correlation exists between oxidation state and ${}^1J_{\mathrm{Rh-P}}$.[26] For example, ${}^1J_{\mathrm{Rh-P}}$ for 1 (183 Hz) is intermediate between those for $\mathrm{CpRh(PMe_3)_2}$ and $\mathrm{CpRh(PMe_3)_2H^+}$ (216 and 136 Hz).

For compounds 1–4, the degenerate equilibrium in eq 8 is rapid at ambient temperatures but slower than the NMR time scale at low temperatures. Rate constants and

$$\mathrm{CpRhL_2(AlR_3) + CpRhL_2 \rightleftharpoons CpRhL_2 + CpRhL_2(AlR_3)} \qquad (8)$$

activation parameters (Table III) have been determined by examining the cyclopentadienyl resonances in the proton NMR as a function of temperature; the values for 1 and 3 were obtained from a full line-shape analysis while those for 2 and 4 were estimated from the coalescence temperature using an approximate equation.[27] The rate constants were calculated with the assumption that the rate-determining step in the exchange process is unimolecular dissociation of Lewis acid (eq 9). The mechanism

$$\mathrm{CpRhL_2(AlR_3)} \xrightarrow{k} \mathrm{CpRhL_2 + AlR_3} \qquad (9)$$

$$\mathrm{AlR_3 + CpRhL_2} \xrightarrow{\text{fast}} \mathrm{CpRhL_2(AlR_3)} \qquad (10)$$

is completed by rapid scavenging of the alkylaluminum by uncomplexed rhodium compound. The calculated first-order rate constant is independent of the concentration of $\mathrm{CpRhL_2}$ in the $\mathrm{CpRh(PMe_3)_2/AlMe_3}$ system. Although the enthalpy of dissociation of alkylaluminum (eq 9) refers to a kinetic process, it should still be fairly close to the rhodium–aluminum bond dissociation energy[28] since the Lewis acid association reactions (eq 10) probably have small enthalpies of activation. Therefore, the $\mathrm{Cp(PMe_3)_2Rh{-}AlMe_3}$ bond strength is approximately 18 kcal/mol. To our knowledge, these are the first quantitative estimates of the strength of Lewis acid–transition metal interactions.

The exchange of trimethylaluminum between molecules of $\mathrm{CpRh(C_2H_4)L}$ (L = $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$) is rapid even at −80 °C, preventing the determination of kinetic parameters. However, the equilibrium constant for eq 11 can be determined because separate resonances for rhodium-bound

$$\mathrm{CpRh(C_2H_4)L + {}^1/_2Al_2Me_6 \rightleftharpoons CpRh(C_2H_4)L(AlMe_3)} \qquad (11)$$

$\mathrm{AlMe_3}$ and free $\mathrm{Al_2Me_6}$ are observed below −60 °C. Thermodynamic parameters have been calculated from the equilibrium constants (Table III),[29] although the ΔH and ΔS values must be considered approximate (±3 kcal/mol, ±15 eu) because of the limited number of measurements and small temperature range. The derived values are at least consistent with the adducts being favored at low temperatures but predominantly dissociated at 25 °C. The strength of the Rh–Al bond can be approximated by adding the enthalpy of dimerization of trimethylaluminum (8 (±1) kcal/(mol of $\mathrm{AlMe_3}$)[30]) to the enthalpy of eq 13; this yields 15 (±4) kcal/mol for the rhodium–aluminum bond strength in 5.[28,29]

Reactions of Trimethylaluminum with Acidic Rhodium Complexes. The structure of 7 suggests that rhodium complexes of $\mathrm{AlMe_2^+}$ might be stable species. By analogy with the synthesis of $\mathrm{Cp(CO)_3W{-}GaMe_2}$ from trimethylgallium and the acidic tungsten hydride,[11] the reactions of acidic rhodium complexes with trimethylaluminum have been examined. $\mathrm{[CpRh(PMe_3)_2H]PF_6}$ and its cobalt analogue react with $\mathrm{Al_2Me_6}$ not by deprotonation but by methyl for hydride exchange (eq 12). The aluminum hydride is trapped by the methylene chloride

$$\mathrm{[CpM(PMe_3)_2H]PF_6 + {}^1/_2Al_2Me_6 \rightarrow [CpM(PMe_3)_2Me]PF_6 + \text{“}AlMe_2H\text{”}} \qquad (12)$$

$$\mathrm{M = Co, Rh}$$

solvent; $\mathrm{CD_2HCl}$ is the major product in $\mathrm{CD_2Cl_2}$ (by NMR). The isoelectronic neutral ruthenium hydride forms an adduct with trimethylaluminum (9, eq 13), which ap-

$$\mathrm{CpRu(PMe_3)_2H + {}^1/_2Al_2Me_6 \rightarrow \underset{\textbf{9}}{CpRu(PMe_3)_2H(AlMe_3)}} \qquad (13)$$

pears to have a Ru–H–Al bridge on the basis of a large change in the NMR chemical shift of the hydride ligand on complexation. The spectroscopic data are ambiguous, however, and this structural assignment must be considered tentative (see ref 8 and 9). A similar hydride-bridged species is probably an intermediate in the methyl for hydride exchange reactions (eq 12). Compound 9 is unchanged after 16 h at 80 °C in the presence of excess trimethylaluminum; as in the rhodium analogue, no methane is observed.

$\mathrm{[CpRh(C_2H_4)(PMe_3)H]BF_4}$ is much more acidic than the bis(phosphine) derivatives: it is deprotonated by fluoride and cyanide ions.[31] However, trimethylaluminum simply transfers methyl anion to the rhodium (10, eq 14), trapping

$$\mathrm{[CpRh(C_2H_4)(PMe_3)H]BF_4 + {}^1/_2Al_2Me_6 \rightarrow \underset{\textbf{10}}{CpRh(Me)(Et)(PMe_3)} + \text{“}AlMe_2BF_4\text{”}} \qquad (14)$$

the ethyl tautomer of the starting material (as chloride and bromide ions do[31]). The aluminum/boron coproduct is volatile enough to be removed with the benzene solvent and has not been isolated. It is surprising that trimethylaluminum does not deprotonate these acids, although proton-transfer reactions involving transition-metal complexes are often slow.[32] For example, the deprotonation of $\mathrm{Cp(CO)_3WH}$ by $\mathrm{Al_2Me_6}$ requires 20 h at 20 °C.[12]

Discussion

The synthesis of the trialkylaluminum adducts 1–6 is possible because of the strong basicity of the rhodium and cobalt complexes and the lack of ligand dissociation from the transition-metal center. The observation of $\mathrm{Me_3P{-}}$

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[26] Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag, New York, 1979; pp 16–28 and 110–114.

[27] Line-shape analysis was performed with a Nicolet NT200 spectrometer; lifetimes were converted to rate constants with the equations in ref 27a, which also contains approximate equations. Sandstrom, J. "Dynamic NMR Spectroscopy"; Academic Press: New York, 1982; pp 81–91.

[28] The values derived for the bond dissociation energy refer to the heterolytic cleavage of the Rh–Al bond, back to $\mathrm{CpRhL_2}$ and $\mathrm{AlR_3}$, since this is formally a dative bond. Homolytic cleavage, to $\mathrm{CpRhL_2^+}$ and $\mathrm{AlR_3^-}$, is probably much higher energy.

[29] The equilibrium constant for eq 11 has units of $(\text{liter/mol})^{1/2}$, so the derived thermodynamic parameters are also concentration dependent. The concentration of $\mathrm{Al_2Me_6}$ was on the order of 5×10^{-3} M for measurements of K (L = $\mathrm{PMe_3}$) and 10^{-1} M for K (L = $\mathrm{PMe_2Ph}$). The rhodium complex concentrations were on the order of 10^{-2} M.

[30] (a) Hay, J. N.; Hooper, P. G.; Robb, J. C. *J. Organomet. Chem.* **1971**, *28*, 193–204. (b) Reference 19, pp 93–101.

[31] Feser, R.; Werner, H. *J. Organomet. Chem.* **1982**, *233*, 193–204.

[32] (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–63. (b) Pearson, R. G.; Ford, P. C. *Comm. Inorg. Chem.* **1982**, *1*, 279–292.

$AlMe_3$ in solutions of **6** is a reminder that in general Lewis acids will compete with a transition metal for ligands, which is perhaps the principal synthetic problem in this area of chemistry. In these simple reactions, where the binding of the acid is the only equilibrium in solution, kinetic and thermodynamic parameters can be determined.

The reactions of alkylaluminum halides are complicated by disproportionation (eq 15) and oligomerization through

$$2AlR_2X \rightleftharpoons AlR_3 + AlRX_2 \text{ etc.} \qquad (15)$$

the halogen atom.[1a,19] The structure of **7** is a good example of both of these problems. Because of these equilibria, the isolation of products like **7** or **8** is possible only when they are substantially less soluble than the other species in solution. For example, three products are formed on addition of dimethylaluminum chloride to a solution of $CpRh(PMe_3)_2$ (by ^{31}P NMR); only in the presence of excess $Al_2Me_4Cl_2$ does **7** precipitate in good yield.

The strength of trialkylaluminum/rhodium interaction varies in the order **1** > **2** > **3** > **4** ≈ **5** > $Cp(C_2H_4)(PMe_2Ph)Rh{\cdot}AlMe_3$ > $Cp(PPh_3)_2Rh{\cdot}AlMe_3$. Reducing the basicity of a rhodium compound by changing from a phosphine to an olefin ligand substantially lowers its affinity for a Lewis acid (compare **1** and **5**). The interaction is also weakened by increasing the steric bulk at rhodium (**1** vs. **4**) and weakened to a lesser extent by increasing the size of the aluminum alkyl (**1** vs. **2**). The consistency of this ordering supports the conclusion based on NMR spectra that the adducts are isostructural, with Rh–Al bonds as found for **7** in the solid state.

The rhodium–aluminum bond strength in **1** is roughly the same as that in $Ph_3P{\cdot}AlMe_3$ (18 kcal/mol) and weaker than $THF{\cdot}AlMe_3$ and $H_3N{\cdot}AlMe_3$ (23 and 28 kcal/mol).[19] The rhodium compounds are sterically hindered and more importantly very soft bases, preferring soft nucleophiles like zinc chloride or mercuric chloride. $HgCl_2$ binds very strongly even to $CpRh(C_2H_4)_2$,[25] which does not interact appreciably with trimethylaluminum. The rhodium complexes are also strong bases toward protic acids. For example, $CpRh(PMe_3)_2$ will deprotonate ammonium ions but will not abstract trimethylaluminum from $H_3N{\cdot}AlMe_3$. Thus the basicity of the metal is a strong function of Lewis acid.

The Lewis acid also determines the site of metal basicity in these compounds. Organoaluminum reagents seem to interact only with the transition metal, while trimethylsilyl cation reacts with the cyclopentadienyl ligand (eq 16).[5] It

$$CpRh(PMe_3)_2 + SiMe_3^+ \rightarrow (\eta^5\text{-}C_5H_4SiMe_3)Rh(PMe_3)_2H^+ \qquad (16)$$

is difficult to account for the difference in reactivity on the basis of steric effects or hard/soft acid–base arguments, because of the similarity of $AlMe_3$ and $SiMe_3^+$. Possibly, this difference results from the bond between a carbon nucleophile (like a Cp ligand) and $SiMe_3^+$ being stronger and more inert than a bond involving $AlMe_3$.

Experimental Section

Syntheses were performed in a continuous nitrogen flow glovebox or by standard vacuum line techniques. Benzene, toluene, and THF were purified by vacuum transfer from sodium/benzophenone, pentane by transfer from $LiAlH_4$, and methylene chloride by transfer from 4-Å molecular seives. Hexane was filtered through alumina before use. Proton NMR spectra were obtained by using Nicolet NT200, NT360, and Varian FT 80A spectrometers, ^{31}P spectra using a Nicolet NT200 spectrometer, and ^{13}C spectra using a Bruker WM400 spectrometer. The symbol "t*" is used to denote a non-first-order triplet pattern in the NMR spectra; the coupling constant reported is half the separation of the outer lines. A Perkin-Elmer 283B spectrophotometer was used to record IR spectra. Elemental analyses were performed by Mikroanalytisches Labor Pascher; rhodium analyses were consistently 1.2 times the calculated values and are not reported.

Trimethylaluminum and dimethylaluminum chloride (Texas Alkyls) were vacuum transferred prior to use. A modification of Werner's procedure[5b] was used to prepare $CpRhL_2$ complexes (L = PMe_3, PMe_2Ph, PEt_3, PPh_3[33]), illustrated for $CpRh(PMe_3)_2$. A mixture of 0.82 g of PMe_3 (10.8 mmol) and 5 mL of THF was added to a solution of $[(C_2H_4)_2RhCl]_2$ (1.0 g, 5.14 mmol, Strem) in 20 mL of THF. After the solution was stirred for 20 min, TlCp (1.6 g, 5.99 mmol, Alfa) was slowly added and the stirring continued for another 1.5 h. Removal of the volatiles and recrystallization from hexane gave 1.28 g (78%) of $CpRh(PMe_3)_2$. $CpRh(PMe_2Ph)_2$ (63% yield): NMR (C_6D_6) δ 7.73 (m), 7.07 (m, $P(C_6H_5)Me_2$), 5.37 (m, C_5H_5), 1.29 (t*d, $P(CH_3)_2Ph$, J_{PH} = 4 Hz, J_{RhH} = 1 Hz). $CpRh(PEt_3)_2$ (67% yield): NMR δ (C_6D_6) 5.29 (m, C_5H_5), 1.1 (m, $P(CH_2CH_3)_3$).

$CpRh(PMe_3)_2(AlMe_3)$ (1). A solution of 125 mg of $CpRh(PMe_3)_2$ in 15 mL of pentane was filtered and 1 mL of $AlMe_3$ added at −80 °C. After the solution was warmed to 25 °C and filtered, the yellow solid was washed with pentane/$AlMe_3$, leaving 132 mg of **1** (86%): NMR (C_7D_8, −30 °C) δ 4.98 (s, C_5H_5), 0.97 (t*d, $P(CH_3)_3$, J_{PH} = 5, J_{RhH} = 1 Hz), −0.09 (s, $Al(CH_3)_3$). Anal. Calcd for $C_{14}H_{32}AlP_2Rh$: C, 42.87; H, 8.22; Al, 6.88. Found: C, 42.50; H, 8.22; Al, 7.05.

$CpRh(PMe_3)_2(AlEt_3)$ (2). A mixture of 43 mg of $AlEt_3$ and 1 mL of hexane was added dropwise to −50 °C solution of 0.10 g of $CpRh(PMe_3)_2$ in 5 mL of hexane. The suspension was stirred at 25 °C for 15 min, cooled to −50 °C, and filtered. The yellow solid was washed once with hexane to give 105 mg of **2** (77%): NMR (C_7D_8, −20 °C) δ 5.01 (s, C_5H_5), 1.75 (t, $Al(CH_2CH_3)_3$, J_{HH} = 8 Hz), 0.96 (t*, $P(CH_3)_3$, J_{PH} = 4 Hz) 0.41 (q, $Al(CH_2CH_3)_3$, J_{HH} = 8 Hz).

$CpRh(PMe_2Ph)_2(AlMe_3)$ (3) was prepared by the same procedure as **1**: A 122-mg sample of $CpRh(PMe_2Ph)_2$ gave 128 mg of yellow **3** (89%): NMR (C_7D_8, −80 °C) δ 4.94 (s, C_5H_5), 7.85 (m), 6.96 (m), 6.57 (m, $P(C_6H_5)Me_2$), 1.31 (br s, $P(CH_3)(CH_3')Ph$), 1.23 (br s, $P(CH_3)(CH_3')Ph$), 0.23 ($Al(CH_3)_3$). Anal. Calcd for $C_{24}H_{38}AlP_2Rh$: C, 55.82; H, 7.03; Al, 5.23. Found: C, 55.36; H, 7.20; Al, 5.17.

$CpRh(PEt_3)_2(AlMe_3)$ (4) was prepared by a procedure similar to that for **2** except that the solids were isolated by decantation at −50 °C. A 100-mg sample of $CpRh(PEt_3)_2$ plus 50 mg of $AlMe_3$ gave 72 mg (60%) of yellow solid roughly 75% **4** and 25% $CpRh(PEt_3)_2$: NMR (C_7D_8, −87 °C) δ 5.19 (s, C_5H_5), 1.47 (br s, $P(CHH'Me)_3$), 1.26 (br s, $P(CHH'Me)_3$), 0.65 (br t, $P(CH_2CH_3)_3$, J = 6 Hz), 0.18 (s, $Al(CH_3)_3$).

$CpRh(C_2H_4)(PMe_3)(AlMe_3)$ (5). $AlMe_3$ (2 mL) was added to a −80 °C solution of 0.28 g of $CpRh(C_2H_4)PMe_3$[15] in 15 mL of pentane. After the cold suspension was stirred for 10 min, filtration at −80 °C gave 0.18 g of yellow **5** (51%): NMR (C_6D_6, 25 °C) δ 5.10 (s, C_5H_5), 2.7, 1.6 (v br, C_2H_4), 0.78 (dd, $P(CH_3)_3$, J_{PH} = 9 Hz, J_{RhH} = 1 Hz), −0.34 (s, $Al(CH_3)_3$); IR 1370, 1190*, 1160, 1000, 940, 840, 800*, 775, 690*, 670 cm^{-1} (all bands except the ones with the asterisk appear at essentially the same frequency in the spectrum of $CpRh(C_2H_4)PMe_3$). Anal. Calcd for $C_{13}H_{27}AlPRh$: C, 45.36; H, 7.91; Al, 7.84; P, 9.00. Found: C, 44.82; H, 7.78; Al, 7.79; P, 9.07.

$CpCo(PMe_3)_2(AlMe_3)$ (6) was prepared from $CpCo(PMe_3)_2$[34] by the same procedure as **1**: NMR (C_7D_8, −80 °C) δ 4.31 (s, C_5H_5), 0.79 (br s, $P(CH_3)_3$), 0.12 (s, $Al(CH_3)_3$). Anal. Calcd for $C_{14}H_{32}AlCoP_2$: C, 48.28; H, 9.26; Al, 7.75; Co, 16.92. Found: C, 47.82; H, 8.98; Al, 7.75; Co, 16.9.

$CpRh(PMe_3)_2(Al_2Me_4Cl_2)$ (7). A 1:3 mixture of $AlMe_2Cl$/benzene was added dropwise to a solution of 53 mg of $CpRh(PMe_3)_2$ in 2 mL of benzene. After four drops an orange oil appeared and another 1 mL of benzene was added. After another drop of $AlMe_2Cl/C_6H_6$ solid started to form; 12 h later the solution was decanted, leaving large yellow crystals of **7** (55 mg, 66%). **7** is insoluble in aromatic solvents and reactive with polar solvents. Anal. Calcd for $C_{15}H_{35}Al_2Cl_2P_2Rh$: C, 35.66; H, 6.98; Al, 10.68; Cl, 14.04. Found: C, 35.09; H, 6.78; Al, 10.5; Cl, 13.62.

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(33) Yamazaki, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2260–1.

(34) Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481–3493.

$CpIr(C_2H_4)_2$ has been prepared by Thorn[35] by bubbling ethylene through a solution of $[(C_8H_{14})_2IrCl]_2$[36] (1.0 g, 2.23 mmol of Ir) in 25 mL of THF for 30 min, followed by addition of TlCp (0.62 g, 2.30 mmol) and another 15 min of stirring. After filtration, the solvent was removed from the filtrate and white $CpIr(C_2H_4)_2$ was sublimed for the residue (60 °C, 10^{-3} torr): yield 0.7 g (100%); NMR (C_6D_6, 25 °C) δ 4.74 (s, C_5H_5), 2.71 (m), 0.81 (m, $Ir(C_2H_4)_2$).

$CpIr(C_2H_4)_2(AlEt_2I)$ (8). A mixture of 95 mg of $AlEt_2I$ (Texas Alkyls) and 1 mL of hexane was added to a −50 °C solution of $CpIr(C_2H_4)_2$ (140 mg) in 5 mL of hexane. The off-white precipitate was isolated by filtration: 190 mg of 8 (81%); NMR (C_6D_6, 25 °C) δ 4.71 (C_5H_5), 2.6 (br s), 0.9 (br s, 4 H each, $Ir(C_2H_2H'_2)_2$), 1.27 (t, $Al(CH_2CH_3)_2$, J_{HH} = 8 Hz), 0.54 (q, $Al(CH_2CH_3)_2$, J_{HH} = 8 Hz). Compound 8 has not been isolated in pure form because of its instability in solution.

$[CpRh(PMe_3)_2H]PF_6$ and $[CpCo(PMe_3)_2H]PF_6$ were prepared by literature methods.[5b,34] Reactions with Al_2Me_6 (either stoichiometric or excess) in methylene chloride gave $[CpM(PMe_3)_2Me]PF_6$, identified by comparison with published NMR spectra.[5b,34] The CD_2HCl byproduct was prepared independently from $[Cp_2ZrHCl]_x$ (Aldrich) and CD_2Cl_2.

$CpRu(PMe_3)_2H$ was prepared by the method used for the triphenylphosphine analogue:[37] a solution of 0.10 g of NaOMe and 0.20 g of $CpRu(PMe_3)_2Cl$[38] in 10 mL of 2-propanol was refluxed for 40 min. After the volatiles were removed, the yellow residue was dissolved in benzene, filtered, and stripped to dryness, leaving 83 mg (46%): NMR (C_6D_6, 25 °C) δ 4.68 (s, C_5H_5), 1.24 (t*, $P(CH_3)_3$, J_{PH} = 4 Hz), −13.30 (t, RuH, J_{PH} = 37 Hz); IR 1900 (Ru–H), 1280, 955, 935 cm^{-1}. Anal. Calcd for $C_{11}H_{24}P_2Ru$: C, 41.37; H, 7.58. Found: C, 41.53; H, 7.59.

$CpRu(PMe_3)_2H(AlMe_3)$ (9). A solution of 20 mg of Al_2Me_6 in 1 mL of hexane was added to $CpRu(PMe_3)_2H$ (40 mg) in 2 Ml of hexane. Removal of the volatiles left 36 mg of white powder (73%). This solid has less than a stoichiometric amount of trimethylaluminum; spectroscopic data were obtained by adding small amounts of Al_2Me_6 to this solid: NMR (C_6D_6, 25 °C) δ 4.39 (s, C_5H_5), 1.03 (t*, $[P(CH_3)_3]$, J_{PH} = 4 Hz), −0.13 (s, $Al(CH_3)_3$), −16.30 (t, Ru–H–Al, J_{PH} = 27 Hz); IR 1920 cm^{-1} (v br, RuHAl).

$CpRh(Me)(C_2H_5)(PMe_3)$ (10). Al_2Me_6 (91 mg) was added dropwise to a suspension of $[CpRh(PMe_3)(C_2H_4)H]BF_4$[15] (105 mg) in 3 mL of benzene. After the solution was stirred for 0.5 h, the volatiles were removed to yield essentially pure **10** as an orange oil: ^1H NMR (C_6D_6, 25 °C) δ 5.01 (dd, C_5H_5, J_{PH} = 1.4, J_{RhH} = 0.4 Hz), 1.54 (m, $RhCHH'CH_3$), 1.34 (m, $RhCHH'CH_3$), 0.89 (dd, $P(CH_3)_3$, J_{PH} = 10, J_{RhH} = 1 Hz), 0.46 (dd, $RhCH_3$, J_{PH}, J_{Rh} = 5.1, 2.6 Hz); ^{13}C NMR (C_6D_6, 25 °C) δ 90.54 (C_5H_5, $^1J_{CH}$ = 172, J_{PC} = 2, J_{RhC} = 2 Hz), 17.94 ($P(CH_3)_3$, $^1J_{CH}$ = 128, J_{PC} = 30 Hz), −17.49 ($RhCH_3$, $^1J_{CH}$ = 130, J_{PC}, J_{RhC} = 15, 30 Hz), 3.89 ($RhCH_2CH_3$, $^1J_{CH}$ = 130, J_{PC}, J_{RhC} = 13, 27 Hz), 24.33 ($RhCH_2CH_3$, J_{CH} = 123 Hz); ^{31}P NMR (C_6D_6, 25 °C) δ 16.3 (d, J_{RhP} = 180 Hz).

X-ray Data Collection and Structure Solution and Refinement. Crystals of 7 were obtained from the reaction mixture. The crystal chosen was sealed in a capillary under nitrogen and placed on a Syntex R3 diffractometer equipped with a Mo Kα source, graphite monochromator, and LT-1 low-temperature attachment. All measurements were made at −100 °C. Initial scans through several peaks indicated only slight broadening with a half-width of 0.25° for a typical ω scan. The preliminary diffractometer routines indicated a monoclinic system with a = 15.696 (2), b = 12.664 (2), and c = 12.544 (2) Å and β = 108.32 (1)° verified by axial photographs on the diffractometer. The systematic absences were consistent with space group $P2_1/n$. Data were collected in the usual ω scan mode with a scan rate which varied from 4 to 10°/min depending on the intensity of the peak. A total of 5665 reflections were collected from $4 < 2\theta < 55°$ of which 4297 with $I > 2\sigma(I)$ were used for the structure determination and refinement. The data were later corrected for absorption using the Gaussian integration method. With μ = 11.786 cm^{-1} the transmission factors for the blocklike crystal with faces, ±[111, 0.125; $10\bar{1}$, 0.130; $1\bar{1}1$, 0.135 mm] varied from 0.743 to 0.793. The structure was readily solved from the Patterson function and subsequent Fourier maps and refined by using isotropic temperature factors to R = 0.079. At this stage it was noted that the temperature factor of atom C(1) was negative and consistent with a scattering power equivalent to a fluorine atom. Refinement was continued with anisotropic thermal parameters using the fluorine scattering factor for atom C(1) and included calculated positions for the hydrogen atoms with all C–H distances set to 0.95 Å. A difference electron density map at this stage clearly revealed (R = 0.027, R_w = 0.033) three hydrogens around the anomalous C(1), indicating a probable mixture of carbon and chlorine at this site. A refinement of the multiplicity factors assuming a C/Cl mixture indicated a chlorine occupancy of 0.32 (2), with a slightly improved fit (R = 0.026, R_w = 0.032). For $RhCl_{2.333}P_2Al_2Cl_{4.667}H_{32}$ the calculated density is 1.431 g/cm^3. A complete data set was recollected on a second crystal with exactly the same results. This type of disorder has been noted previously for related compounds.[20] For the final refinement series, both C(1) and its associated chlorine Cl(1*) were allowed to vary independently on alternate cycles with multiplicities fixed at 0.667 and 0.333. The refinement included terms for the anomalous scattering of Rh, P, and Cl and idealized hydrogen coordinates as fixed atom contributors with B_{iso} set to 4.5 Å^2. The refinement converged with R = 0.025 and R_w = 0.029, and the esd of an observation at unit weight is 1.20. The largest residuals on a final difference map were peaks of 0.39 e/Å^3 near the terminal Cl(1). All calculations were performed on a DEC VAX 11/780 using programs written by J.C.C. The absorption program was written by Coppens, and plots were made with the ORTEP program (Johnson).

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Registry No. 1, 90413-10-8; 2, 90413-11-9; 3, 90413-12-0; 4, 90413-13-1; 5, 90413-14-2; 6, 90413-15-3; 7, 90413-16-4; 8, 90413-17-5; 9, 90413-18-6; 10, 90413-19-7; $CpRh(PMe_2Ph)(C_2H_4)(AlMe_3)$, 90413-25-5; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; $CpRh(PMe_3)_2$, 69178-15-0; $CpRh(PMe_2Ph)_2$, 90413-20-0; $CpRh(PEt_3)_2$, 90413-21-1; $CpRh(C_2H_4)PMe_3$, 69178-16-1; $CpCo(PMe_3)_2$, 63413-01-4; $CpIr(C_2H_4)_2$, 88411-52-3; $[(C_8H_{14})_2IrCl]_2$, 12246-51-4; $[CpRh(PMe_3)_2H]PF_6$, 70483-21-5; $[CpCo(PMe_3)_2H]PF_6$, 64508-16-3; $[CpRh(PMe_3)_2Me]PF_6$, 70496-20-7; $[CpCo(PMe_3)_2Me]PF_6$, 90413-23-3; $CpRu(PMe_3)_2Cl$, 74558-74-0; $CpRu(PMe_3)_2H$, 90413-24-4; $[CpRh(PMe_3)(C_2H_4)H]BF_4$, 69178-20-7; $AlMe_2Cl$, 1184-58-3.

Supplementary Material Available: For the structure of 7, tables of non-hydrogen atom thermal parameters (Table IV), hydrogen atom positions (Table V), and observed and calculated structure amplitudes (Table VI) and for $CpRh(C_2H_4)PMe_3$, an ORTEP drawing (Figure 3), tables of fractional coordinates and (hydrogen) isotopic thermal parameters (Table VII), anisotropic thermal parameters (Table VIII), bond distances and bond angles (Tables IX and X), and observed and calculated structure amplitudes (Table XI) (33 pages). Ordering information is given on any current masthead page.

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