absorption coefficient and the orientation of the crystal during data collection, the maximum range of transmission factors was from 0.77 to 0.88).

Absences in $0k0$ of $k = 2n + 1$, and $h0l$, $l = 2n + 1$, uniquely defined the space group to be $P2_1/c$. The structure was solved by the straightforward application of the direct methods program MULTAN.[17] Several cycles of least-squares refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms afforded a reliability index of $R_1 = (|F_o| - |F_c|)/|F_o| = 0.18$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.12$. The 36 hydrogen atom positions were determined from a difference Fourier map, but their parameters were not refined. More cycles of refinement led to final values of $R_1 = 0.095$ and $R_2 = [w(|F_o| - |F_c|)^2/(F_o)^2]^{1/2} = 0.090$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.4 e/Å^3. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted.

Full-matrix, least-squares refinement was carried out by using the SHELX Library.[18] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for K, S, Al, C, and O were taken from Cromer and Waber;[19] those for H were from ref 20. The final values of the positional parameters are given in Table IV.[21]

X-ray Data Collection and Structure Determination for $K_2[Al_4Me_{12}SO_4]\cdot0.5$*p*-xylene, II. Data collection, structure solution, and refinement were carried out in the same manner as I. One independent quadrant of reflections was measured out to $2\theta = 36°$ resulting in 1300 observed (very little scattering was found beyond $2\theta = 36°$). R_1 with all non-hydrogen atoms refined isotropically was 0.108. Conversion to anisotopic thermal parameters and further refinement gave $R_1 = 0.069$.

All H atoms were located from a difference Fourier, but their parameters were not refined. Final refinement gave $R_1 = 0.055$ and $R_2 = 0.059$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviation. A final difference Fourier showed no feature greater than 0.3 e/Å^3. Unit weights were used and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)\lambda$ was noted. The final values of the positional parameters are given in Table V.[21]

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Registry No. I, 87861-92-5; II, 87861-93-6; K_2SO_4, 7778-80-5; $AlMe_3$, 75-24-1.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, complete bond lengths and angles, and structure factors for I and II (23 pages). Ordering information is given on any current masthead page.

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Halide, Hydride, and Alkyl Derivatives of (Pentamethylcyclopentadienyl)bis(trimethylphosphine)ruthenium[†]

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The reaction of ruthenium trichloride with pentamethylcyclopentadiene (C_5Me_5H), followed by PMe_3 gives $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$. Reaction of (pentamethylcyclopentadienyl)bis(trimethylphosphine)ruthenium chloride with the Grignard reagents RMgX affords alkyl derivatives (R = Me, Et, CH_2CMe_3, or CH_2SiMe_3) or the hydride $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ (R = *t*-Bu or *i*-Pr). The complexes $(\eta^5\text{-}C_5Me_5)_2Ru$, $(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$ (NBD = norbornadiene), and $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Br$ are also reported. Routes to the cationic species $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(CO)][PF_6]$ and $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2HCl][PF_6]$ are described.

Introduction

Attention is currently being drawn to the fact that more basic, electron-donating ligands significantly modify the chemistry of group 8 metals. This has been most amply demonstrated with the trimethylphosphine (PMe_3) and pentamethylcyclopentadienyl (C_5Me_5) ligands. One aspect of the change in reactivity in going to more electron-rich noble metal complexes appears to be the stabilization of higher formal oxidation states. Consequently, organometallic ruthenium(IV) derivatives such as $(\eta^5\text{-}C_5Me_4Et)Ru(CO)Br_3$[1] and $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2XCl][PF_6]$ (X = H and Cl)[2] have recently been characterized. In other cases, these electron-rich metal centers have allowed isolation of new types of ligand arrays, which are likely to be less stable in the presence of poorer, more labile donors

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Table I. ^{1}H and $^{31}P\{^{1}H\}$ NMR Data

compound	$^{1}H^{a}$				$^{31}P\{^{1}H\}^{b}$
	C_5Me_5 ^{c}	PMe_3 ^{d}	other assignts		
$(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$	1.32		NBD CH_2	1.13 (t, J = 1.7 Hz)	
			NBD olefinic	3.14 (m)	
			NBD CH	3.27 (m)	
			NBD CH	3.84 (m)	
			NBD olefinic	4.34 (m)	
$(\eta^5\text{-}C_5Me_5)_2Ru$	1.64				
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$	1.55 (1.6)	1.23 (8.2)			1.88
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Br$	1.59 (1.6)	1.26 (8.2)			0.41
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Me$	1.70 (1.4)	1.10 (7.5)	$RuCH_3$	−0.33 (t, $^{3}J_{PH}$ = 7.0 Hz)	8.70
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Et$	1.72 (1.4)	1.10 (7.4)	$RuC\mathit{H}_2CH_3$	0.58 (m)	8.77
			$RuCH_2C\mathit{H}_3$	1.50 (t, J_{HH} = 7.4 Hz)	
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2CMe_3$	1.62 (1.5)	1.16 (7.3)	$RuC\mathit{H}_2CMe_3$	1.00 (t, $^{3}J_{PH}$ = 5.8 Hz)	6.49
			$RuCH_2C\mathit{Me}_3$	1.28 (s)	
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2SiMe_3$	1.66 (1.5)	1.12 (7.3)	$RuC\mathit{H}_2SiMe_3$	−1.02 (t, $^{3}J_{PH}$ = 6.1 Hz)	5.25
			$RuCH_2Si\mathit{Me}_3$	0.34 (s)	
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$	1.95 (1.4, 0.6)^{e}	1.25 (7.7)	RuH	−13.8 (t, $^{2}J_{PH}$ = 38 Hz)	6.93
$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CO][PF_6]^{f}$	2.00 (1.8)	2.10 (9.6)			−0.21 (PMe_3) −58.7 (PF_6, heptet, J_{PF} = 708 Hz)
$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2HCl][PF_6]^{g}$	1.80 (1.5)	1.57 (11.0)	RuH	−10.4 (t, $^{2}J_{PH}$ = 35 Hz)	7.94 (PMe_3) −144.5 (PF_6, heptet, J_{PF} = 711 Hz)

^{a} Shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 90 MHz and 30 °C in C_6D_6. ^{b} Shifts are in ppm, referenced to 85% H_3PO_4 (δ 0.00) at 36.4 MHz and 30 °C in C_6D_6. All resonances are singlets unless otherwise noted. ^{c} Number in parentheses is $^{4}J_{PH}$, in Hz. ^{d} Number in parentheses is the separation between outer lines of the filled in doublet, $^{2}J_{PH} + {}^{4}J_{PH}$, in Hz. ^{e} Second number in parentheses is $^{4}J_{HH}$, in Hz. ^{f} Acetone-d_6, 30 °C. ^{g} CD_2Cl_2, 30 °C.

such as CO, PPh_3, and C_5H_5. Examples include the formyl hydride *cis*-$[Ir(PMe_3)_4H(CHO)][PF_6]$,[3] the hydroxymethyl $(\eta^5\text{-}C_5Me_5)Os(CO)_2CH_2OH$,[4] and the triple-methylene-bridged $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$.[5] Basic, electron-donating auxiliary ligands have also played key roles in the discovery of new reactivity patterns. Recently, hydrocarbon activation has been observed with species derived from $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)H_2$,[6] $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)H(aryl)$,[7] and $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[8] A rich and varied chemistry of rhodium and iridium has been developed by using pentamethylcyclopentadienyl as the key auxiliary ligand.[9]

In this context, we have sought to develop convenient, synthetic routes to complexes of ruthenium containing both C_5Me_5 and PMe_3 as ligands. In this report, we describe a route to $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and a number of complexes derived therefrom. Previous reports of peralkylated cyclopentadienyl derivatives of ruthenium are limited to $[(\eta\text{-}C_5Me_5)Ru(CO)_2]_2$,[10] $[(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2X]_2[PF_6]_1$,[1] $(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2X$ (X = Cl, Br, I),[1] $(\eta^5\text{-}C_5Me_4Et)Ru(CO)Br_3$,[1] $[(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2]_2$,[11] and $(\eta^5\text{-}C_5Me_4Et)Ru(CO)(PR_3)Br$ [PR_3 = $P(OPh)_3$, $P(OMe)_3$, and PPh_3].[12]

Results and Discussion

Initial attempts to prepare $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ by metathesis reactions met with little success. Thus, the dichloride *trans*-$RuCl_2(PMe_3)_4$[13] did not react with *n*-$Bu_3SnC_5Me_5$ in toluene (room temperature, 24 h) nor with LiC_5Me_5 in refluxing tetrahydrofuran (16 h). Reaction of $Li(C_5Me_5)$ with the norbornadiene complex $[Ru(NBD)Cl_2]_x$[14] did, however, lead to low yields (ca. 15%) of a dark orange compound formulated as $(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$.

$$[Ru(NBD)Cl_2]_x + LiC_5Me_5 \xrightarrow{THF} (\eta^5\text{-}C_5Me_5)Ru(NBD)Cl + LiCl$$

The ^{1}H NMR spectrum reveals five sets of inequivalent protons for the NBD ligand, as expected for a species containing the chelating diolefin (see Table I). Although this compound is formed in low yield and is therefore of limited use as a starting material, it does provide a clean route to $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$. As monitored by ^{1}H NMR excess PMe_3 (ca. 10 equiv) reacts with $(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$ in C_6D_6 solution (within 12 h at 70 °C) to generate $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (vide infra) and free norbornadiene.

Direct reaction of cyclopentadiene with a group 8 metal complex is often a useful route to $(\eta^5\text{-}C_5H_5)ML_x$ species. The compound $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ is conveniently prepared by refluxing $RuCl_3{\cdot}nH_2O$, cyclopentadiene, and PPh_3 in ethanol.[15] In an attempt to prepare the pentamethycyclopentadienyl analogue, this reaction was repeated by using the permethylated diene in place of C_5H_6. The only product isolated, however, was $RuCl_2(PPh_3)_4$,[16] in high yield. Similarly, if $RuCl_3{\cdot}nH_2O$, C_5Me_5H, and PMe_3 are refluxed in ethanol, the major product is *trans*-

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Table II. $^{13}C\{^1H\}$ NMR Data

compound	C_5Me_5	PMe_3 [b]	C_5Me_5	other assignts	
$(\eta^5\text{-}C_5Me_5)_2Ru$	10.3 (s)		82.9 s		
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$	11.0 (s)	20.4 (26)	87.6 s		
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Me$	11.2 (s)	21.5 (24)	89.5 s	$RuCH_3$	−16.4 (t, $^2J_{PC}$ = 14 Hz)
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Et$	11.6 (s)	21.2 (24)	90.5 (t, $^2J_{PC}$ = 2.5 Hz)	$Ru\mathit{CH}_2CH_3$	−0.84 (t, $^2J_{PC}$ = 13 Hz)
				$RuCH_2\mathit{CH}_3$	22.8 (t, $^3J_{PC}$ = 7 Hz)
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2CMe_3$	12.1 (s)	22.7 (24)	90.0 (t, $^2J_{PC}$ = 2.6 Hz)	$Ru\mathit{CH}_2CMe_3$	19.6 (t, $^2J_{PC}$ = 13 Hz)
				$RuCH_2\mathit{C}Me_3$	35.2 (t, $^3J_{PC}$ = 3.0 Hz)
				$RuCH_2C\mathit{Me}_3$	36.3 (s)
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2SiMe_3$	11.9 (s)	21.9 (25)	89.7 (t, $^2J_{PC}$ = 2.6 Hz)	$Ru\mathit{CH}_2SiMe_3$	−22.8 (t, $^2J_{PC}$ = 11 Hz)
				$RuCH_2Si\mathit{Me}_3$	5.73 (s)
$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$	12.8 (s)	26.0 (26)	90.3 (s)		
$[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CO]PF_6$ [c]	10.9 (s)	20.7 (34)	100.6 (s)	RuCO	204.6 (*t*, $^2J_{PC}$ = 0.7 Hz)

[a] Shifts are in ppm, referenced to $SiMe_4$ (δ 0.00) at 22.6 MHz and 30 °C in C_6D_6. [b] Apparent triplet, number in parentheses is $^2J_{PC} + {^3J_{PC}}$, in Hz. [c] Acetone-d_6 30 °C.

$RuCl_2(PMe_3)_4$, with no C_5Me_5-containing compounds compounds being isolated. However, in the absence of phosphine, $RuCl_3{\cdot}nH_2O$ and C_5Me_5H react in boiling ethanol or methanol to produce decamethylruthenocene, $(\eta^5\text{-}C_5Me_5)_2Ru$ (10%), and a brown-red complex containing the C_5Me_5 ligand. The latter material is paramagnetic and gives an analysis consistent with the empirical formula $[(\eta^5\text{-}C_5Me_5)RuCl_2]_x$.[17] On this formulation, the yield of the brown-red compound is *ca.* 80%. The reaction of $RhCl_3{\cdot}3H_2O$ and C_5Me_5H in refluxing methanol gives $[(\eta^5\text{-}C_5Me_5)RhCl_2)]_2$.[18]

The addition of excess PMe_3 to a dichloromethane solution of the paramagnetic complex produces the diamagnetic ruthenium(II) species $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and *trans*-$RuCl_2(PMe_3)_4$ in 50 and 20% isolated yields, respectively. These two products are readily separated by taking advantage of their different solubility properties (see Experimental Section). It is not yet clear how the dichloride is formed in this reaction. The ^1H NMR spectrum of the orange $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ consists of a triplet for the C_5Me_5 ligand [δ 1.55 ($^4J_{PH}$ = 1.6 Hz)] as well as a filled in doublet ("virtual triplet") for the PMe_3 protons at δ 1.23. The related $(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl$ has been reported previously.[19]

Primary alkyl derivatives of the $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2]$ unit are formed by reaction of the chloride with the Grignard reagents RMgCl (R = Me, CH_2CMe_3, and CH_2SiMe_3) and EtMgBr in diethyl ether or toluene.

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl + RMgX \rightarrow (\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2R + MgXCl$$

The yields range from 73 to 84%. The complexes were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, as well as by elemental analysis. All are yellow and quite soluble in saturated hydrocarbons, from which they can be crystallized at low temperature. While the methyl and ethyl derivatives do not survive brief exposure to air, compounds of the bulkier CH_2CMe_3 and CH_2SiMe_3 groups are stable in air for hours in the solid state. Recently, Lehmkuhl has reported some analogous alkyls $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2R$ (R = primary alkyl).[20] The alkyls $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2R$ (R = Me and CH_2Ph) were reported earlier by Stone et al.[21]

Attempts to prepare secondary or tertiary alkyls from RMgCl (R = *i*-Pr and *t*-Bu) have led to isolation of the hydride.

$$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl + RMgCl \rightarrow (\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H + MgCl_2 + \text{alkene}$$

For the reaction involving *t*-BuMgCl, isobutene, the product of β-H elimination, was observed in the reaction solution (by GC). This hydride complex, which can also be obtained in lower yield by reaction of the chloride with lithium aluminum hydride, shows a typical ν_{RuH} in its infrared spectrum (1877 cm^{-1}). The ^1H NMR spectrum reveals coupling between the protons of C_5Me_5 and the hydride ligand, as demonstrated by decoupling experiments. The resonance for the C_5Me_5 group appears as a triplet of doublets (δ 1.95 ($^4J_{PH}$ = 1.4 Hz, $^4J_{HH}$ = 0.6 Hz)) and that of the hydride ligand as a broadened triplet (δ −13.8 ($^2J_{PH}$ = 38 Hz)). The compound is quite air sensitive and very soluble in hydrocarbons, ethers, acetone, and methanol.

Since the product of ethylene insertion into the Ru–H bond is a stable compound, $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Et$, this reaction was attempted. After the solution of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ in toluene was stirred for 3 days under an ethylene pressure of 12 atm, only the hydride was recovered from the reaction solution (by ^1H NMR). The failure of this reaction is undoubtedly due to the inability of ethylene to coordinate, as the PMe_3 ligands are expected to be very tightly bound.

In some cases, use of bromide Grignard reagents led to much slower reaction times compared to the corresponding chlorides. For instance, use of Me_3CCH_2MgBr produced only 26% of the alkyl after 1 week (diethyl ether, room temperature), with a significant amount of the bromide $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Br$ being formed (35%). Similar results were obtained for the reaction of *i*-PrMgBr and $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ in diethyl ether. Characterization of the bromide was made by comparison to spectral properties of an authentic sample, prepared by reaction of the chloride and KBr in refluxing ethanol. This observation is related to that of Stone et al.,[21] who observed that $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ reacted with MeMgI by halogen exchange, but with MeLi to give the methyl derivative.

The alkyllithium reagents *t*-BuLi and Me_3CCH_2Li also proved less suitable for preparation of pure compounds from $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$. Although low yields of the respective products $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ and $(\eta^5\text{-}C_5Me_2)Ru(PMe_3)_2CH_2CMe_3$ were obtained, the major

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product appeared to contain the metalated CH_2PMe_2 group.[22]

Further aspects of the reactivity of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ resemble those of $(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl$. The carbonyl cation $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(CO)][PF_6]$ is prepared by reaction of the chloride in refluxing methanol under an atmosphere of CO and in the presence of KPF_6. The infrared absorption of the carbonyl ligand (ν_{CO} = 1935 cm^{-1} in Nujol) is somewhat lower than those reported for $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(CO)][PF_6]$ (1980 cm^{-1} in CH_2Cl_2[19a] and 1961 cm^{-1} in Nujol[19b]). This difference reflects the greater electron-donating ability of the pentamethylcyclopentadienyl ligand. In the $^{13}C\{^1H\}$ spectrum, the shift of the carbonyl carbon was located at δ 204.6 (t, $^2J_{PC}$ = 0.7 Hz). The shift of the carbonyl carbon atom in the $^{13}C\{^1H\}$ spectrum of $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2(CO)][PF_6]$ was not reported.

Likewise, the basicity of the chloride complex allows isolation of cationic hydrides via protonation. In refluxing tetrahydrofuran, it is protonated at the metal by NH_4PF_6, generating the ruthenium(IV) hydride $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2HCl][PF_6]$. Bruce et al. have reported the protonation of $(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl$ by the stronger acid $HPF_6\cdot OEt_2$.[19b] As in the case of $[(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2HCl][PF_6]$, the diagonal isomer, with equivalent phosphines, is the only one observed.

We are presently studying further aspects of the reactivities of the above compounds and will report these results shortly.

Experimental Section

General Data. All manipulations were conducted under an inert-atmosphere of nitrogen. Methanol, ethanol, and dichloromethane were distilled from activated 4-Å molecular sieves. Aliphatic and ethereal solvents were distilled from sodium benzophenone ketal.

Elemental analyses were performed by Galbraith or Dornis and Kolbe microanalytical laboratories. The nuclear magnetic resonance spectra were recorded on JEOL FX-90Q or Bruker HX-90E spectrometers. Infrared spectra were recorded on Beckman 4240 or Perkin-Elmer 1430 spectrometers.

$(\eta^5\text{-}C_5Me_5)Ru(NBD)Cl$. Tetrahydrofuran (20 mL), LiC_5Me_5 (0.17 g, 1.2 mmol), and $(Ru(NBD)Cl_2)_x$[13] (0.31 g, 1.2 mmol) were placed in a flask and stirred for 36 h. The tetrahydrofuran was removed under vacuum and the solid residue extracted with pentane (2 × 40 mL). These extracts were combined; concentration and cooling afforded the light brown complex in 15% yield. Anal. Calcd for $C_{17}ClH_{23}Ru$: C, 56.1; H, 6.37. Found: C, 55.9; H, 6.23.

$(\eta^5\text{-}C_5Me_5)_2Ru$. To a filtered solution of $RuCl_3\cdot nH_2O$ (2.0 g, 7.7 mmol) in methanol (50 mL) was added pentamethylcyclopentadiene (2.4 g, 18 mmol). Refluxing the solution for 3 h resulted in the separation of brown-red microcrystals. The reaction mixture was cooled to −50 °C and after 10 h, filtered. The brown-red and beige crystals were dried under vacuum and extracted with hexane (2 × 30 mL). The combined extracts were concentrated to 8 mL under vacuum and cooled to −50 °C to obtain off-white needles of $(\eta^5\text{-}C_5Me_5)_2Ru$ (0.29 g, 10% yield). Recrystallization from hexane yielded pure white crystals of the air-stable compound (mp >250 °C dec): IR (Nujol) 1426 (w), 1072 (m), 1027 (s), 433 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{30}Ru$: C, 64.7; H, 8.14. Found: C, 64.7; H, 8.02.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$. The brown-red solid obtained in the above preparation was dissolved in dichloromethane (50 mL). To this solution was added trimethylphosphine (2.0 mL, 21 mmol). The solution was stirred for 12 h, and the volatiles were removed under vacuum. Addition of hexane (100 mL) gave an orange solution, which was filtered, concentrated to ca. 60 mL, and cooled (−50 °C). The orange needles were collected and dried under vacuum. The yield was ca. 50% based on $RuCl_3\cdot 3H_2O$. This crystalline sample contained ca. 4% *trans*-$RuCl_2(PMe_3)_4$ (by ^1H and $^{31}P\{^1H\}$ spectroscopy) and was further purified by recrystallization (mp 238–239 °C). Further extraction of the residue with toluene (25 mL) allowed isolation of *trans*-$RuCl_2(PMe_3)_4$ (ca. 20% yield) by crystallization (8 mL, −50 °C): IR (Nujol) 1422 (w), 1300 (m), 1282 (s), 1270 (w sh), 1149 (w), 1066 (m), 1025 (m), 929 (s), 851 (m), 716 (s), 663 (m), 608 (w) cm^{-1}. Anal. Calcd for $C_{16}ClH_{33}P_2Ru$: C, 45.3; Cl, 8.36; H, 7.85; P, 14.6. Found: C, 45.1; Cl, 8.56; H, 7.70; P, 14.4.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Me$. The Grignard MeMgCl in tetrahydrofuran (0.52 mL, 1.5 mmol) was added to a cold (0 °C) solution of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (0.59 g, 1.4 mmol) in diethyl ether (30 mL). After 30 min, the solution was slowly warmed to room temperature and stirred for 6 h. After evaporation of solvents, the yellow residue was extracted with hexane (50 mL). This hexane solution was concentrated to 4 mL and cooled to −70 °C. The yellow prisms (mp 225–226 °C) that formed were collected and dried under vacuum. The yield was 0.40 g (84%): IR (Nujol) 1426 (w), 1294 (w sh), 1289 (m), 1273 (m), 1177 (w), 1064 (w), 1024 (m), 936 (s), 843 (s), 700 (s), 666 (w sh), 657 (s), 609 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{36}P_2Ru$: C, 50.6; H, 8.99; P, 15.4. Found: C, 50.5; H, 8.93; P, 15.2.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Et$. The complex was prepared by the same method used for the methyl derivative, but with the Grignard EtMgBr (diethyl ether solution). The yield of yellow prisms (mp 197–198 °C) was 78% (0.35 g): IR (Nujol) 1414 (w), 1289 (m), 1269 (m), 1219 (m), 1160 (m), 1062 (w), 1021 (m), 946 (m sh), 931 (s), 840 (s), 694 (s), 657 (s), 608 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{38}P_2Ru$: C, 51.8; H, 9.17; P, 14.8. Found: C, 51.7; H, 9.15; P, 14.7.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2CMe_3$. The preparation is analogous to that for $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Me$, using Me_3CCH_2MgCl (diethyl ether solution). The yellow prisms (mp 184–185 °C dec) were isolated in 76% yield (0.41 g): IR (Nujol) 1412 (w), 1287 (w), 1268 (m), 1227 (w), 1017 (m), 941 (s), 927 (s), 840 (s), 694 (m), 649 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{44}P_2Ru$: C, 54.9; H, 9.65; P, 13.5. Found: C, 54.8; H, 9.58; P, 13.4.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2CH_2SiMe_3$. To the chloride $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (0.45 g, 1.1 mmol) in toluene (10 mL) was added a diethyl ether solution of Me_3SiCH_2MgCl (1.0 mL, 1.1 mmol) at room temperature. After 12 h of stirring, the solvents were removed and the yellow residue was extracted with hexane (50 and 30 mL). The combined extracts were concentrated to 5 mL and cooled to −70 °C, affording yellow prisms (mp 209–210 °C dec) of the compound in 73% yield (0.38 g): IR (Nujol) 1411 (w), 1286 (m), 1266 (s), 1223 (s), 1058 (m), 1018 (m), 941 (w sh), 920 (s), 839 (s), 810 (s), 731 (w), 720 (m), 697 (s), 657 (s), 602 (w), 370 (s), 365 (m), 263 (w) cm^{-1}. Anal. Calcd for $C_{20}H_{44}P_2RuSi$: C, 50.5; H, 9.32; P, 13.0. Found: C, 50.4; H, 9.28; P, 12.9.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ (from *t*-BuMgCl). To $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (0.38 g, 0.90 mmol) dissolved in cold (0 °C) diethyl ether (30 mL) was added the Grignard *t*-BuMgCl (1.12 mL of a 0.80 M solution in diethyl ether, 0.90 mmol). The reaction mixture was warmed slowly to room temperature and stirred for 17 h. After removal of the volatile components under vacuum, the residue was extracted with pentane (30 mL). This extract was concentrated to ca. 10 mL and cooled (−70 °C) to obtain yellow prisms (mp 56–57 °C). Further concentration and cooling resulted in crystallization of more product and an overall yield of 65%: IR (Nujol) 1877 (s), 1421 (w), 1285 (w), 1270 (m), 1015 (w), 946 (m sh), 924 (s), 841 (m), 693 (m), 659 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{34}P_2Ru$: C, 49.3; H, 8.80; P, 15.9. Found: C, 49.2; H, 8.74; P, 16.0.

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2H$ (from *i*-PrMgCl). A solution of the Grignard *i*-PrMgCl (0.14 mL of a 3.33 M diethyl ether solution, 0.47 mmol) was added to a toluene (20 mL) solution of $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (0.17 g, 0.40 mmol) at room temperature. The solution was stirred for 4 h and then evacuated to dryness. The hydride complex was extracted from the residue with hexane (2 × 40 mL) and crystallized (ca. 1 mL, −70 °C). The yield was 0.06 g (39%).

$(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Br$. The chloride $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ (0.20 g, 0.47 mmol) and KBr (1.41 g, 11.8 mmol) were refluxed in dry ethanol (20 mL) for 40 h. After removal of solvent,

---

[22] The compound appears to be $(\eta^5\text{-}C_5Me_5)Ru(CH_2PMe_2)(PMe_3)$: $^{31}P\{^1H\}$ NMR (C_6D_6, 30 °C) δ −2.26 (d, $^2J_{PP}$ = 35 Hz), −39.3 (d, $^2J_{PP}$ = 35 Hz); ^1H (C_6D_6, 30 °C) δ −0.55 (m) and −0.22 (m), assigned as the $RuCH_2P$ protons. The other resonances were obscured by other products.

the bromide complex was dissolved in hexane (60 mL) and crystallized (from ca. 20 mL of solvent, −25 °C). The orange plates (mp >280 °C) were collected and dried under vacuum: IR (Nujol) 1410 (w), 1289 (m), 1271 (m), 1060 (w), 1016 (m), 929 (s), 840 (m), 708 (m), 660 (m) cm^{-1}. Anal. Calcd for $BrC_{16}H_{33}P_2Ru$: Br, 17.1; C, 41.0; H, 7.10; P, 13.2. Found: Br, 17.1; C, 41.0; H, 7.07; P, 13.3.

[(η^5-C_5Me_5)Ru(PMe_3)$_2$(CO)][PF_6]. Carbon monoxide was bubbled through a refluxing methanol solution (25 mL) of (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl (0.18 g, 0.42 mmol) and KPF_6 (0.08 g, 0.43 mmol). After 6 h, the volatile components were removed under vacuum, and the residue was extracted with methylene chloride (20 mL). This solution was concentrated to ca. 6 mL and diethyl ether (35 mL) was added, depositing white microcrystals. Cooling to −70 °C caused further crystallization. The yield of isolated material (mp >280 °C) was 0.20 g (85%): IR (Nujol) 1935 (s), 1281 (w), 949 (s), 820 (s), 721 (w), 666 (w) cm^{-1}. Anal. Calcd for $C_{17}F_6H_{33}OP_3Ru$: C, 36.4; H, 5.99; P, 16.5. Found: C, 36.5; H, 6.04; P, 16.4.

[(η^5-C_5Me_5)Ru(PMe_3)$_2$HCl][PF_6]. A flask was charged with (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl (0.24 g, 0.57 mmol), NH_4PF_6 (0.10 g, 0.61 mmol), and tetrahydrofuran (20 mL). The solution was refluxed for 17 h, after which the solvent was evaporated and methylene chloride (20 mL) added. After filtration, this solution was evaporated to ca. 12 mL and diethyl ether (10 mL) was added. Cooling (−25 °C) afforded yellow crystals (mp 208–213 °C dec). Further crystallization from the mother liquors resulted in an overall yield of 54%: IR (Nujol) 2012 (w), 1300 (w), 1284 (m), 1274 (w sh), 1069 (w), 1013 (w), 940 (s), 830 (s), 734 (m), 705 (m), 672 (m), 673 (m), 550 (m), 356 cm^{-1}. Anal. Calcd for $C_{16}ClF_6H_{34}P_3Ru$: C, 33.7; H, 6.01. Found: C, 33.8; H, 6.05.

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Registry No. (η^5-C_5Me_5)Ru(NBD)Cl, 87640-46-8; (η^5-C_5Me_5)$_2$Ru, 84821-53-4; (η^5-C_5Me_5)Ru(PMe_3)$_2$Cl, 87640-47-9; (η^5-C_5Me_5)Ru(PMe_3)$_2$Br, 87640-48-0; (η^5-C_5Me_5)Ru(PMe_3)$_2$Me, 87640-49-1; (η^5-C_5Me_5)Ru(PMe_3)$_2$Et, 87640-50-4; (η^5-C_5Me_5)Ru(PMe_3)$_2$$CH_2CMe_3$, 87640-51-5; ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$$CH_2SiMe_3$, 87640-52-6; ($\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$H, 87640-53-7; [$\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$Co][$PF_6$], 87640-55-9; [$\eta^5$-$C_5Me_5$)Ru($PMe_3$)$_2$HCl][$PF_6$], 87640-57-1; (Ru(NBD)$Cl_2$)$_x$, 42740-82-9; *trans*-$RuCl_2(PMe_3)_4$, 71936-64-6.

Reactivity of Bis(pentamethylcyclopentadienyl)zirconium Hydrides with Group 8 Transition-Metal Carbonyls[†]

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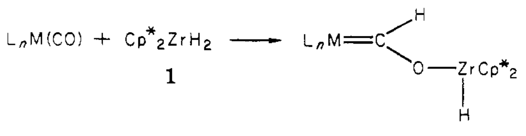
The reactions of $Cp^*_2ZrH_2$ ($Cp^* \equiv \eta^5$-C_5Me_5) with cyclopentadienyl carbonyl complexes of Co, Rh, Fe, and Ru have been carried out in order to explore the generality of Zr–H addition across the C–O bond of transition-metal carbonyls to form the corresponding zirconoxycarbene complexes. These reactions have been observed to follow two different reaction pathways. The first proceeds by interaction of a carbonyl group with the zirconium center, reductive elimination of H_2, and rearrangement to afford carbonyl-bridged "early" and "late" mixed-metal dimers. Thus CpM(μ-CO)(μ-η^1,η^2-CO)ZrCp^*_2 ($Cp \equiv \eta^5$-C_5H_5; M = Co, Rh) and Cp(H)Ru(μ-CO)(μ-η^1,η^2-CO)ZrCp^*_2 are obtained by treatment of CpM$(CO)_2$ (M = Co, Rh) or CpRu$(CO)_2$(H) with $Cp^*_2ZrH_2$. The second reaction pathway involves CO reduction by Zr–H, giving the corresponding group 8 metal zirconoxycarbene complex, or products arising from zirconoxycarbene intermediates. Thus Cp(CO)M=CHOZr(X)Cp^*_2 (M = Co, Rh; X = Cl, F) are obtained by treatment of CpM$(CO)_2$ with Cp^*_2Zr(H)(X) (X = Cl, F). The reaction between CpM(CO)(PMe_3)(H) (M = Fe, Ru), $Cp^*_2ZrH_2$, and PMe_3 yields Cp$(PMe_3)_2$M–CH_2O–Zr(H)Cp^*_2, whereas CpM$(CO)_2$(CH_3) (M = Fe, Ru), $Cp^*_2ZrH_2$, and PMe_3 afford Cp^*_2Zr(H)(OCH=CH_2) and CpM(CO)(PMe_3)H.

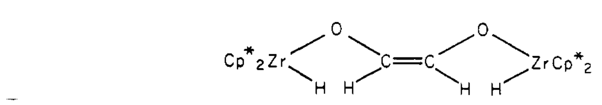
Introduction

In view of the ease with which $Cp^*_2ZrH_2$ (1) ($Cp^* \equiv \eta^5$-C_5Me_5) reduces group 5 and 6 transition-metal carbonyls to the corresponding oxycarbene complexes,[1] the reactions of 1 and related hydrides with other metal carbonyls have been investigated to explore the generality of Zr–H reduction of coordinated CO. Prior to this work $Cp^*_2Zr(CO)_2$ was the only transition-metal dicarbonyl complex observed to give a clean product, *cis*-$(Cp^*_2ZrH)_2$(μ-OCH=CHO–),[1b,2] upon treatment with $Cp^*_2ZrH_2$ (eq 2). Unfortunately, no intermediates could be identified during the course of this reaction to provide information as to the mechanism of this unique transformation. The reactivity of 1 with other



(1)

$L_nM = Cp_2Cr, Cp_2Mo, Cp_2W, Cp_2NbR;\ Cp \equiv \eta^5\text{-}C_5H_5$



(2)

[†] Contribution No. 6874.

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