As indicated previously, refluxing ethanol provides a much less favorable medium for the reaction. Formyl and hydride complex formation proceed as in *n*-butyl alcohol, but phosphine substitution is unfavorable. The additional energy provided by a higher boiling alcohol such as *n*-butyl alcohol apparently is essential for this step to proceed. Furthermore, substitution depends strongly on the nature of the counterion. We find that [PPN][$HFe(CO)_4$] reacts with PPh_3 in refluxing *n*-butyl alcohol to give, after 2 h, traces of *trans*-$Fe(CO)_3(PPh_3)_2$ and unreacted starting material. When the same experiment is carried out with Na[$HFe(CO)_4$], a 95% yield of the trans product is obtained. Moreover, the reaction of PPh_3 with [PPN][$Fe(CO)_4CHO$] gives only [PPN][$HFe(CO)_4$] while the reaction with Na[$Fe(CO)_4CHO$] produces an 87% yield of *trans*-$Fe(CO)_3(PPh_3)_2$ (Table II). This is consistent with Darensbourg's observation that Na[$HFe(CO)_4$] is much more reactive than [PPN][$HFe(CO)_4$] toward O_2 in THF.[6b,18] In addition, Ungvary and Wojcicki have shown that Na[$Co(CO)_4$] undergoes rapid substitution by phosphines while [PPN][$Co(CO)_4$] is unreactive, further underscoring the importance of the counterion in reactions involving organometallic carbonyl anions.[19]

In the course of elucidating the mechanism for the reaction of PR_3 with $Fe(CO)_5$ and $NaBH_4$, we have also discovered that *trans*-$Fe(CO)_3(PPh_3)_2$ may be prepared in high yield from the reaction of $Fe(CO)_5$, PPh_3, and NaOH. Furthermore, preliminary results suggest that the reaction of $HFe(CO)_3PR_3^-$ with PR'_3 provides a useful route to complexes containing two different phosphines. The generality of both of these reactions is now under investigation.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, Grant CHE-85-13021, for support of this research. We are grateful to the University of Illinois for the use of a 250-MHz NMR spectrometer. We thank Robert Newman for some of the initial experimental work.

Registry No. [PPN][$HFe(CO)_4$], 56791-54-9; [Et_4N][$HFe(CO)_3PPh_3$], 80612-33-5; $Fe(CO)_4PPh_3$, 35679-07-3; $Fe(CO)_5$, 13463-40-6; *trans*-$Fe(CO)_3(PPh_3)_2$, 21255-52-7; *trans*-$Fe(CO)_3[P(n\text{-}Bu)_3]_2$, 49655-14-3; $NaBH_4$, 16940-66-2; [PPN][$Fe(CO)_4CHO$], 41900-55-4; Na[$HFe(CO)_4$], 53558-55-7; K[$Fe_3(CO)_{11}$], 116466-60-5; *trans*-$Fe(CO)_3(PPh_2H)_2$, 40697-11-8; *trans*-fe$(CO)_3(PPh_2CH{=}CH_2)_2$, 87137-61-9; *trans*-$Fe(CO)_3(PPh_2CH_2CH_3)_2$, 36870-06-1; *trans*-$Fe(CO)_3(PPh_2Me)_2$, 40757-44-6; *trans*-$Fe(CO)_3[P(c\text{-}cy)_3]_2$, 40697-14-1.

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Oxidative Addition Reactions of Compounds of the Type (η^5-C_5Me_5)Os(CO)LR (L = CO, PMe_2Ph; R = Alkyl). The Role of Oxidized Intermediates in Electrophilic Cleavage Reactions of Osmium–Carbon σ-Bonds

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Received February 24, 1988

Compounds of the type Cp*Os(CO)LR (Cp* = η^5-C_5Me_5; L = CO, PMe_2Ph; R = Me, Et, *i*-Pr, CH_2Ph), most of them new, have been prepared and their reactions with the electrophiles CF_3CO_2H, Br_2, and $HgBr_2$ have been investigated. All of the electrophiles oxidatively add to give labile, formally osmium(IV) complexes of the type $[Cp^*Os(CO)(L)(R)(E)]^+X^-$, one of which, $[Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]^+$, has been isolated as the PF_6^- salt. In all cases, the osmium(IV) complexes decompose in solution to give the normal products of electrophilic cleavage.

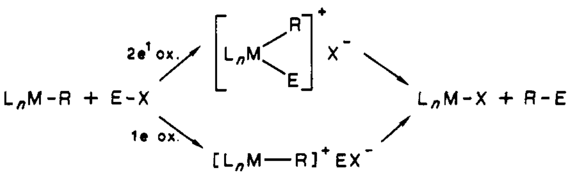
Introduction

Mechanisms of cleavage reactions of transition-metal–carbon bonds by electrophilic reagents have attracted considerable attention in recent years.[1,2] Reactions are generally of the form

$$L_nM\text{–}R + E\text{–}X \rightarrow L_nM\text{–}X + R\text{–}E \qquad (1)$$

M = transition metal; L = neutral, anionic ligands;
R = alkyl; EX = HX, X_2, CuX_2, HgX_2; X = halogen

Scheme I. S_E (Oxidative) Mechanisms



Many of the studies have involved a number of iron alkyl complexes of the type CpFe(CO)LR (L = CO, tertiary phosphine; R = alkyl),[3-9] but similar compounds of ru-

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Table I. Physical Data for the Compounds Cp*Os(CO)LX

L	X (mp, °C)	ν_{CO},[a] cm^{-1}	^{1}H NMR,[b] δ
CO	Me (118–120)	1983, 1914	1.99 (s, 15 H, Cp*), 0.26 (s, 3 H, Me)
CO	Et (76–78)	1990, 1930	1.98 (s, 15 H, Cp*), 1.64 (t, J = 7.5 Hz, 3 H, CH_3), 1.25 (q, J = 7.5 Hz, 2 H, CH_2)
CO	*i*-Pr (84–86)	1978, 1910	2.00 (s, 15 H, Cp*), 1.7–1.6 (m, 1 H, CH), 1.62 (d, J = 4.6 Hz, 6 H, CH_3)
CO	CH_2Ph (88–90)	1985, 1920	7.4–6.8 (m, 5 H, Ph), 2.64 (s, 2 H, CH_2), 2.03 (s, 15 H, Cp*)
PMe_2Ph	Br (166–168)	1909	7.6–7.5 (m, 5 H, Ph), 1.96 (d, J = 9.8 Hz, 3 H, P–Me), 1.92 (d, J = 9.7 Hz, 3 H, P–Me), 1.66 (d, J = 1.2 Hz, 15 H, Cp*)
PMe_2Ph	Me (94–95)	1870	7.5–7.4 (m, 5 H, Ph), 1.73 (d, J = 9.2 Hz, 3 H, P–Me), 1.66 (d, J = 1.1 Hz, 15 H, Cp*), 1.62 (d, J = 8.9 Hz, 3 H, P–Me), 0.13 (d, J = 6.0 Hz, 3 H, Os–Me)
PMe_2Ph	Et (83–84)	1870	7.6–7.3 (m, 5 H, Ph), 1.76 (d, J = 9.1 Hz, 3 H, P–Me), 1.68 (d, J = 1.2 Hz, 15 H, Cp*), 1.62 (d, J = 8.8 Hz, 3 H, P–Me), 1.47 (m, 3 H, CH_3), 1.41, 0.81 (m, 2 H, CH_2)
PMe_2Ph	*i*-Pr (83–84)	1873	7.3–7.3 (m, 5 H, Ph), 2.12 (m, J = 6.0 Hz, 1 H, CH), 1.79 (d, J = 8.7 Hz, 3 H, P–Me), 1.74 (d, 3 H, P–Me), 1.72 (d, J = 1.2 Hz, 15 H, Cp*), 1.43 (d, J = 7.2 Hz, 3 H, CH_3), 1.37 (d, J = 7.3 Hz, 3 H, CH_3)
PMe_2Ph	CH_2Ph	1877	7.5–7.0 (m, 10 H, Ph), 2.86 (t, $J_{HH} = J_{PH}$ = 10.3 Hz, 1 H, CH_2), 2.44 (dd, J_{HH} = 10.3 Hz, J_{PH} = 3.3 Hz, 1 H, CH_2), 1.68 (d, J = 7.8 Hz, 3 H, P–Me), 1.65 (d, J = 8.2 Hz, 3 H, P–Me), 1.57 (d, J = 1.2 Hz, 15 H, Cp*)
PMe_2Ph	$OCOCF_3$	1923[c]	7.5–7.4 (m, 5 H, Ph), 1.85 (d, J = 9.8 Hz, 3 H, P–Me), 1.72 (d, J = 9.7 Hz, 3 H, P–Me), 1.62 (d, J = 1.3 Hz, 15 H, Cp*)

[a] CH_2Cl_2 was solvent. [b] CD_2Cl_2 was solvent. [c] $\nu_{C=O}$ = 1718 cm^{-4} (in hexane).

Table II. ^{13}C and ^{31}P NMR Data for the Compounds Cp*Os(CO)LX

L	X	^{13}C NMR,[a,b] δ	^{31}P NMR,[c] δ
CO	Me	186.6 (s, CO), 97.4 (s, $\mathit{C}_5\mathrm{Me}_5$), 9.8 (s, $\mathrm{C}_5\mathit{Me}_5$), −38.7 (s, Os–Me)	
CO	Et	187.6 (s, CO), 97.4 (s, $\mathit{C}_5\mathrm{Me}_5$), 24.4 (s, CH_3), 9.7 (s, $\mathrm{C}_5\mathit{Me}_5$), −17.2 (s, CH_2)	
CO	*i*-Pr	187.4 (s, CO), 97.8 (s, $\mathit{C}_5\mathrm{Me}_5$), 35.3 (s, CH_3), 9.8 (s, $\mathrm{C}_5\mathit{Me}_5$), −2.4 (s, CH)	
CO	CH_2Ph	186.5 (s, CO), 155–122 (Ph), 97.3 (s, $\mathit{C}_5\mathrm{Me}_5$), 9.8 (s, $\mathrm{C}_5\mathit{Me}_5$), −4.6 (s, CH_2)	
PMe_2Ph	Br	188.6 (d, J = 11 Hz, CO), 137–128 (Ph), 92.8 (s, $\mathrm{C}_5\mathrm{Me}_5$), 20.0 (d, J = 41 Hz, P–Me), 14.8 (d, J = 36 Hz, P–Me), 9.8 (s, $\mathrm{C}_5\mathit{Me}_5$)	−24.5
PMe_2Ph	Me	191.6 (d, J = 12 Hz, CO), 139–128 (Ph), 92.1 (s, $\mathit{C}_5\mathrm{Me}_5$), 19.1 (d, J = 39 Hz, P–Me), 12.6 (d, J = 33 Hz, P–Me), 9.4 (s, $\mathrm{C}_5\mathit{Me}_5$), −37.0 (d, J = 7 Hz, Os–Me)	−20.3
PMe_2Ph	Et	192.1 (d, J = 11 Hz, CO), 139–128 (Ph), 92.9 (s, $\mathit{C}_5\mathrm{Me}_5$), 24.3 (s, CH_3), 9.7 (s, $\mathrm{C}_5\mathit{Me}_5$), 19.2 (d, J = 40 Hz, P–Me), 12.6 (d, J = 33 Hz, P–Me), −19.3 (d, J = 7 Hz, CH_2)	−19.3
PMe_2Ph	*i*-Pr	190.6 (d, J = 11 Hz, CO), 140–128 (Ph), 93.8 (s, $\mathit{C}_5\mathrm{Me}_5$), 33.8 (s, CH_3), 32.0 (s, CH_3), 19.3 (d, J = 36 Hz, P–Me), 15.8 (d, J = 30 Hz, P–Me), 10.1 (s, $\mathrm{C}_5\mathit{Me}_5$), −11.4 (d, J = 6 Hz, CH)	−22.1
PMe_2Ph	CH_2Ph	191.6 (d, J = 11 Hz, CO), 157–122 (Ph), 92.9 (s, $\mathit{C}_5\mathrm{Me}_5$), 19.4 (d, J = 39 Hz, P–Me), 12.5 (d, J = 32 Hz, P–Me), 9.6 (s, $\mathrm{C}_5\mathit{Me}_5$), −6.4 (d, J = 6 Hz, CH_2)	−22.3
PMe_2Ph	CF_3CO_2	188.6 (CO), 163.5 (q, J = 34 Hz, O*C*O),[d] 136–128 (Ph), 113.2 (q, J = 291 Hz, CF_3),[d] 92.2 (s, $\mathit{C}_5\mathrm{Me}_5$), 9.6 (s, $\mathrm{C}_5\mathit{Me}_5$), 17.8 (d, J = 40 Hz, P–Me), 15.4 (d, J = 33 Hz, P–Me)	−20.0

[a] Solvent was CD_2Cl_2. [b] Coupling is to phosphorus. [c] Solvent was 80:20 CH_2Cl_2/20 CD_2Cl_2. [d] Coupling is to ^{19}F.

thenium[10] and rhenium[11] have also been studied. Much of the evidence obtained to date has led to the conclusion that reactions as in (1) do not proceed via classical S_E2 processes but rather via one- and/or two-electron transfer reactions and oxidized intermediates as shown in Scheme I.

Direct evidence for the mechanisms proposed in Scheme I has been difficult to obtain for the iron and ruthenium systems, as previous studies of electrophilic cleavage reactions of complexes of the type CpMLL′R (M = Fe, Ru; L, L′ = CO, PPh_3; R = alkyl) failed to detect any evidence for oxidized intermediates.[8,10] We have therefore initiated an investigation into the oxidative cleavage of osmium–alkyl bonds in complexes of the type Cp*Os(CO)LR, (Cp* = η^5-C_5Me_5; L = CO, PMe_2Ph; R = Me, Et, *i*-Pr, CH_2Ph). It was anticipated that metal–ligand bond dissociation energies of compounds of the third-row transition-metal osmium would be generally greater than those of the lighter counterparts[12] and that evidence for the proposed oxidized intermediates in these reactions might be obtained. Also, the pentamethylcyclopentadienyl (Cp*) ligand was chosen so as to make the metal center more electron-rich[13] and, hopefully, easier to oxidize.

At the time this research was started, there were several reports of ruthenium(IV) and osmium(IV) complexes in the literature,[14–18] suggesting that oxidized Os(IV) species formed during the electrophilic cleavage of the osmium–

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alkyl bonds might be stable. For example, $Cp^*Os(CO)H_3$[17] and $[CpOs(H)_2(PPh_3)_2]^+X^-$ (X = Cl, Br, I, I_3, BPh_4)[18] are isolable osmium(IV) complexes. A preliminary report of this research has appeared.[19]

Experimental Section

Instrumentation. Infrared spectra were recorded on a Bruker IFS-85 FT IR spectrophotometer. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM 400 spectrometer at 400, 100.6, and 162.0 MHz, respectively. Chemical shifts are reported in δ relative to an internal standard of tetramethylsilane for ^1H and ^{13}C and relative to external 85% H_3PO_4 for ^{31}P NMR spectra; positive shifts are reported downfield of the reference. IR and NMR data for all compounds are listed in Tables I and II.

High-pressure reactions were carried out in a 300-mL Finnan superpressure microseries reaction assembly. Photochemical reactions were carried out by irradiating a solution through a water-cooled quartz finger. A Hanovia lamp was used, and the solution was stirred throughout irradiation. Melting points of samples sealed under a nitrogen atmosphere were determined on a Gallenkamp melting point apparatus. Elemental analyses were carried out by Canadian Microanalytical Service Ltd., New Westminster, B.C.

The compounds $Os(CO)_4Br_2$,[20] $Cp^*Os(CO)_2Br$,[21] $Cp^*Os(CO)_2Me$,[22,23] Cp^*H,[24] CuBr,[25] and CF_3CO_2H[26] were prepared by literature methods. Solutions of Grignard reagents were prepared[27] and used immediately. All preparations and reactions were carried out with freshly distilled dry solvents and in a nitrogen atmosphere.

$Cp^*Os(CO)_2R$, (R = Et, *i*-Pr, CH_2Ph). These new compounds were all prepared in the same manner, analogous to the preparation of the methyl compound of Sturgeoff and Graham.[23] To 0.94 g (6.5 mmol) of CuBr in 90 mL of THF, cooled to −78 °C in a 2-propanol/dry ice bath, was added 3.25 mmol of the appropriate Grignard solution. The mixture was stirred for 15 min, and a solution of 0.60 g (1.3 mmol) of $Cp^*Os(CO)_2Br$ in 50 mL of THF was added in portions. The Dewar flask surrounding the reaction flask was then packed with dry ice, and the reaction mixture was left to warm to room temperature over 10–12 h. The solution was then hydrolyzed with 20–30 mL of H_2O and filtered. The solvent was removed under vacuum, and the residue was extracted with hexanes (200–250 mL), dried over $MgSO_4$, and pumped to dryness. With the exception of the benzyl compound, the alkyl compounds were normally of sufficient purity for elemental analyses at this stage. After the hexane solution of $Cp^*Os(CO)_2CH_2Ph$ was dried, the products were separated on an alumina column. Bibenzyl was eluted with hexane, and the organometallic product was eluted with 2:1 hexane/CH_2Cl_2. Yields of the alkyl compounds were on the order of 50–60%, based on $Cp^*Os(CO)_2Br$. Calcd for R = Et: C, 40.96; H, 4.91. Found: C, 40.65; H, 4.91. Calcd for R = *i*-Pr: C, 42.44; H, 5.22. Found: C, 42.48; H, 5.16. Calcd for R = CH_2Ph: C, 48.29; H, 4.69. Found: C, 48.75; H, 4.70.

$Cp^*Os(CO)(PMe_2Ph)Br$. This compound was prepared in two ways. A solution of 0.50 g of $Cp^*Os(CO)_2Br$ and 0.3 mL of PMe_2Ph in 200 mL of 30/60 petroleum ether was photolyzed with a Hanovia lamp for 12–24 h. Alternatively, $Cp^*Os(CO)_2Br$ (0.50 g, 1.1 mmol), Me_3NO (0.20 g, 2.2 mmol), and PMe_2Ph (0.30 mL, 2.2 mmol) were refluxed in CH_2Cl_2 (75 mL) for 24 h. In both preparations the reaction solution was pumped to dryness and the residue was dissolved in 4:1 hexane (or 30/60 petroleum ether)/CH_2Cl_2 and put on an alumina column. Elution with about 200–250 mL of the same solvent mixture removed any excess phosphine, and elution with 2:1 CH_2Cl_2/hexane removed the product as a bright yellow band. Removal of the solvent in vacuo gave a bright yellow solid. Yields for the photolysis preparation were about 50% while the second method gave yields of 80%. Anal. Calcd: C, 39.93; H, 4.59. Found: C, 39.78; H, 4.50.

$Cp^*Os(CO)(PMe_2Ph)Me$. Photolysis of a solution of 0.50 g (1.26 mmol) of $Cp^*Os(CO)_2Me$ and 0.3 mL (2 mmol) of PMe_2Ph in 30/60 petroleum ether gave the substituted compound $Cp^*Os(CO)(PMe_2Ph)Me$ after 24–36 h. The product was purified by column chromatography on an alumina column, the starting material and excess phosphine being eluted with 30/60 petroleum ether and the product with a 2:1 mixture of 30/60 petroleum ether/CH_2Cl_2. The solvent was removed in vacuo, leaving a cream solid in a yield of 45–50%. Anal. Calcd: C, 47.42; H, 5.55. Found: C, 47.37; H, 5.73.

$Cp^*Os(CO)(PMe_2Ph)R$ (R = Et, *i*-Pr, CH_2Ph). These compounds were prepared in a method analogous to that of the dicarbonyl alkyl compounds. A suspension of 0.47 g of CuBr in 50 mL of THF was cooled to −78 °C in a dry ice bath and then treated with first 1.63 mmol of the appropriate Grignard solution and then, after 15 min, a cooled solution of 0.35 g of $Cp^*Os(CO)(PMe_2Ph)Br$ in 25 mL of THF. The solution was allowed to warm to room temperature overnight (10–12 h), and the workup of the reaction solution was carried out in the same way as for the dicarbonyl alkyl compounds discussed above. About 10–15 mL of water was added to the reaction solutions, which were then filtered and taken to dryness in vacuo. The residues were extracted with hexane, and, after being dried over $MgSO_4$, the solutions were filtered and the hexane was removed in vacuo to leave the alkyl complexes. The ethyl and isopropyl complexes were cream (or very pale yellow) solids, and the benzyl complex was a very pale yellow oil. As with the dicarbonyl analogue, $Cp^*Os(CO)(PMe_2Ph)CH_2Ph$ was always contaminated wth bibenzyl and column chromatography was necessary to separate the bibenzyl from the organometallic product. The benzyl complex was dissolved in hexane and poured onto an alumina column. After eluting with 200–300 mL of hexane, $Cp^*Os(CO)(PMe_2Ph)CH_2Ph$ was eluted with 2:1 hexane/CH_2Cl_2. The solvent was then removed in vacuo to leave a yellow oil. Yields were generally slightly lower than for the dicarbonyl analogues. Anal. Calcd for R = Et: C, 48.45; H, 6.00. Found: C, 48.67; H, 5.95. Calcd for R = *i*-Pr: C, 49.42; H, 6.22. Found: C, 49.96; H, 6.30. Calcd for R = CH_2Ph: C, 53.59; H, 5.71. Found: C, 54.26; H, 5.71.

$Cp^*Os(CO)(PMe_2Ph)(OCOCF_3)$. $Cp^*Os(CO)(PMe_2Ph)R$ (R = Me, Et, *i*-Pr) (0.20 g, 0.4 mmol, for R = Me) was dissolved in CH_2Cl_2. To the almost colorless solution was added a molar excess of CF_3COOH (40 μL, 0.5 mmol, for R = Me). The solution immediately turned a bright yellow color, and in all cases the IR (CH_2Cl_2) spectrum showed a band at 1923 cm^{-1}. The solutions were pumped to dryness, and the residues were dissolved in hexane and poured onto an alumina column. The complex was then eluted as a yellow band with 2:1 hexane/diethyl ether. Concentration of this solution yielded a yellow oil which, when dissolved in several milliliters of hexane and cooled in an ice/NaCl bath, yielded a yellow precipitate in 70–75% yield. Anal. Calcd: C, 41.72; H, 4.33. Found: C, 42.03; H, 4.35.

$[Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]PF_6$. Isolation of this complex was carried out by dissolving $Cp^*Os(CO)(PMe_2Ph)Me$ (0.1 g, 0.2 mmol) in methanol (20 mL) and adding a molar equivalent of $HgBr_2$ (0.72 g, 0.2 mmol). After the solution was stirred for 5 min, the color of the solution had turned from almost colorless to a bright yellow color. Excess $NaPF_6$ in methanol was then added to the stirred solution, resulting in the precipitation of a pale yellow solid. This solid was filtered off, was washed with methanol, and, after drying in vacuo, was of sufficient purity for elemental analysis. Anal. Calcd: C, 25.77; H, 3.14. Found: C, 25.43; H, 3.14. (IR (CH_2Cl_2) 1986 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.5–7.4 (m, 5 H, Ph), 2.05 (d, J_{PH} = 9.5 Hz, 3 H, P–Me), 2.04 (d, J_{PH} = 9.5 Hz, 3 H, P–Me), 1.98 (d + satellites, J_{PH} = 1.0 Hz, J_{HgH} = 21.3 Hz, 15 H, Cp*), 0.94 (d + satellites, J_{PH} = 9.3 Hz, J_{HgH} = 35.4 Hz, 3 H, Os–Me); ^{13}C NMR (CD_2Cl_2) δ ~180 (CO), 137.9–129.5 (Ph), 99.8 (s, $C_5(CH_3)_5$), 18.8 (d, J = 40 Hz, P–Me),

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Table III. NMR and IR Data for Intermediates Observed during Cleavage Reactions of Cp*Os(CO)LR with Electrophilic Reagents EX

L	R	EX	IR,[a] cm^{-1}	^{1}H NMR,[b] δ	^{31}P NMR,[c] δ
PMe$_2$Ph	Me	CF$_3$CO$_2$H		1.81 (s, Cp*), 0.61 (d, J = 9.7 Hz, Os–Me), 1.96 (d, J = 9.6, P–Me), 1.87 (d, J = 9.5 Hz, P–Me), −12.28 (d, J = 80 Hz, Os–H)	
CO	Me	HgBr$_2$	2040[d]	2.11 (s, Cp*), 1.01 (s, Os–Me)	
CO	Et	HgBr$_2$		2.02 (s, Cp*), 1.68 (t, J = 7.3 Hz, CH) 1.53 (q, J = 7.3 Hz, CH$_2$)	
PMe$_2$Ph	Me	Br$_2$	2043	2.10 (d, J = 10.4 Hz, P–Me),[e] 1.95 (d, J = 1.0 Hz, Cp*), 1.28 (d, J = 9.7 Hz, Os–Me)	−37.2
PMe$_2$Ph	Me	I$_2$	2030		−46.2
PMe$_2$Ph	Me	HgBr$_2$	2002	2.10 (d, J = 9.4 Hz, P–Me), 1.97 (s, Cp*), 1.94 (d, J = 9.8 Hz, P–Me), 0.86 (d, J = 9.1 Hz, Os–Me)	−45.7[g]
PMe$_2$Ph	Et	HgBr$_2$	1991	2.01 (d, J = 1.0 Hz, Cp*), 1.94 (d, J = 9.3 Hz, P–Me)[e,f]	−43.5[h]

[a] Solvent CH$_2$Cl$_2$ unless otherwise stated. [b] Solvent CD$_2$Cl$_2$ unless otherwise stated. [c] Solvent 4:1 CH$_2$Cl$_2$/CD$_2$Cl$_2$. [d] Solvent was acetone. [e] Other PMe$_2$Ph methyl doublet obscured by Cp* resonance. [f] CH$_2$ and CH$_3$ resonances obscured. [g] $^2J_{HgP}$ = 720 Hz. [h] $^2J_{HgP}$ = 734 Hz.

18.2 (d, J = 40 Hz, P–Me), 10.5 (C$_5$(CH$_3$)$_5$), −17.7 (d, J = 11 Hz, Os–Me); ^{31}P NMR (80:20 CH$_2$Cl$_2$/CD$_2$Cl$_2$) δ −46.0 (t, $^2J_{HgP}$ = 688 Hz, *P*Me$_2$Ph), −143.9 (septet, $^1J_{FP}$ = 710 Hz, *P*F$_6^-$)).

Chemical Cleavage Reactions. These reactions were monitored by IR and ^{1}H NMR spectroscopy, the yields of the reactions being determined by the integrations of the appropriate resonances in the ^{1}H NMR spectra of the reaction mixtures relative to the integrals of the starting material and an internal standard of 1,4-dioxane. The ^{1}H NMR data of the products were in agreement with literature data.[28-33]

CF$_3$CO$_2$H Cleavage Reactions. Addition of CF$_3$CO$_2$H to Cp*Os(CO)(PMe$_2$Ph)Me in CD$_2$Cl$_2$ at −60 °C was monitored by ^{1}H NMR spectroscopy. In addition to resonances of the starting material and the product Cp*Os(CO)(PMe$_2$Ph)OCOCF$_3$, a new set of resonances, listed in Table III, was observed. This set of resonances disappeared as the sample was warmed to room temperature, and a new resonance at δ 0.21 (s) grew in along with the resonances of the organometallic product.

Bromine Cleavage Reactions. To monitor these reactions by IR spectroscopy, a spectrum of a stirred solution of the alkyl compound was run. Small additions of bromine (<1 μL) were then made, an IR spectrum being run following each addition. The reactions of all the alkyl complexes with bromine were immediate, the near colorless solutions of the alkyl complexes turning yellow. Addition of excess bromine (>1 molar equiv) gave rise to further reactions, and solutions became much darker in color.

NMR monitoring of the reactions was done in much the same way. The alkyl compounds were weighed accurately (10–50 mg) into NMR tubes under N$_2$, and 0.5 mL of CD$_2$Cl$_2$ and 2–5 μL of 1,4-dioxane were added. The ^{1}H NMR spectrum of the solution was run, and then approximately 1 molar equiv of Br$_2$ was syringed into the NMR tube. The resulting solutions were normally blue-green in color. The ^{1}H NMR spectra were collected, and the yields were calculated relative to the *p*-dioxane standard. In some cases, excess bromine was also added; the resultant NMR spectra contained very broad resonances and yields of the organometallic bromo complexes, if these resonances were observed, were generally lowered.

Mercuric Bromide Cleavage Reactions. IR scale reactions were performed by adding an excess of HgBr$_2$ to a stirred dichloromethane solution of the alkyl compound. A color change was usually seen upon addition, i.e. from an almost colorless to a yellow solution. These heterogeneous reactions were monitored by running IR spectra of the solutions at regular intervals. When the alkyl group was methyl and ethyl, new carbonyl bands were observed to higher frequency after HgBr$_2$ addition, but these bands had disappeared by the time the reaction had gone to completion. The reactions generally proceeded cleanly and within 12–24 h with vigorous stirring. The reaction of Cp*Os(CO)$_2$CH$_2$Ph with HgBr$_2$ was extremely slow, taking approximately 3 days, with vigorous stirring, to go to completion.

Table IV. Electrophilic Cleavage Reactions[a]

expt	L	R	EX	products (% yield)
1	CO	Me	Br$_2$	Cp*Os(CO)$_2$Br (66), MeBr (53)
2	CO	Et	Br$_2$	Cp*Os(CO)$_2$Br (64), EtBr (39)
3	CO	*i*-Pr	Br$_2$	Cp*Os(CO)$_2$Br (75), -*PrBr* (39), Cp*Os(CO)$_2$*i*-Pr (6), propene (6)
4	CO	CH$_2$Ph	Br$_2$	Cp*Os(CO)$_2$Br (69), PhCH$_2$Br (65)
5	PMe$_2$Ph	Me	Br$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (59), MeBr (21), Cp*Os(CO)(PMe$_2$Ph)Me (4)
6	PMe$_i$Ph	Et	Br$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (78), EtBr (65)
7	PMe$_2$Ph	*i*-Pr	Br$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (77), *i*-PrBr (50), propylene (9)
8	PMe$_2$Ph	CH$_2$Ph	Br$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (77), PhCH$_2$Br (83)
9	CO	Me	HgBr$_2$	Cp*Os(CO)$_2$Br (67), MeHgBr (70)
10	CO	Et	HgBr$_2$	Cp*Os(CO)$_2$Br (96), EtHgBr (60)
11	CO	*i*-Pr	HgBr$_2$	Cp*Os(CO)$_2$Br (77), *i*-PrBr (11), *i*-PrHgBr (61)
12	CO	CH$_2$Ph	HgBr$_2$	Cp*Os(CO)$_2$Br (24), PhCH$_2$Br (30), Cp*Os(CO)$_2$CH$_2$Ph (25), PhCH$_2$HgBr (14)[b]
13	PMe$_2$Ph	Me	HgBr$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (74), MeHgBr (58)
14	PMe$_2$Ph	Et	HgBr$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (74), EtHgBr (67)
15	PMe$_2$Ph	*i*-Pr	HgBr$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (73), *i*-PrHgBr (60), Cp*Os(CO)(PMe$_2$Ph)*i*-Pr (11)
16	PMe$_2$Ph	CH$_2$Ph	HgBr$_2$	Cp*Os(CO)(PMe$_2$Ph)Br (92), PhCH$_2$HgBr (88)

[a] Solvent CD$_2$Cl$_2$. [b] Yields calculated after 3 days although the reaction had not gone to completion.

Reactions monitored by NMR spectroscopy were carried out in CD$_2$Cl$_2$, in which some were initially heterogeneous. The alkyl compounds were weighed accurately into NMR tubes, and then the solvent and *p*-dioxane were added and the ^{1}H NMR spectrum of the solution of the alkyl compound was run. A known amount of HgBr$_2$ was then added to the NMR solution, and the reaction was monitored by ^{1}H NMR spectroscopy until it had gone to completion. The time required was usually several hours, although the reactions of Cp*Os(CO)$_2$CH$_2$Ph and Cp*Os(CO)(PMe$_2$Ph)Me required 3 days or more before they had gone to completion. The yields were again calculated from the *p*-dioxane internal standard. See Table III for IR and NMR data for observed intermediates and Table IV for the ultimate products and their yields.

Results and Discussion

Syntheses and Characterization of the Osmium–Alkyl Compounds. For the preparation of complexes of the type Cp*Os(CO)$_2$R (R = alkyl), a general method first proposed by Graham et al.[22,29] for the syntheses of alkyl compounds of rhenium and osmium was used. This involved treatment of Cp*Os(CO)$_2$Br with an excess of the corresponding alkylcopper(I) compound, CuR, and normally proceeded in yields of 50–60%. For the preparation

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of the complex Cp*Os(CO)(PMe_2Ph)Me, photochemical decarbonylation of the dicarbonyl methyl complex in the presence of PMe_2Ph was carried out. As this method was not applicable to the preparation of Cp*Os(CO)(PMe_2Ph)R (R = Et, *i*-Pr, CH_2Ph), an extension of the method used to prepare the dicarbonyl alkyl complexes, involving treatment of Cp*Os(CO)(PMe_2Ph)Br with CuR, was used instead. Cp*Os(CO)(PMe_2Ph)Br was prepared by decarbonylation of Cp*Os$(CO)_2$Br, effected by photolysis or by the presence of Me_3NO, in the presence of PMe_2Ph.

In all cases, the new compounds were characterized by their IR and NMR spectroscopic data. See Tables I and II.

CF_3CO_2H Cleavage Reactions. The reaction of Cp*Os(CO)(PMe_2Ph)Me with 1 molar equiv of CF_3CO_2H was performed at −60 °C and was monitored by ^1H NMR spectroscopy. Immediately after the addition of the acid to the CD_2Cl_2 solution of Cp*Os(CO)(PMe_2Ph)Me, the ^1H NMR spectrum exhibited two new sets of resonances as well as, in some experiments, the resonances due to the starting methyl complex. One set of these resonances was identified as those of the product of the reaction, Cp*Os(CO)(PMe_2Ph)($OCOCF_3$) (Tables I and II), while the other set of new resonances, listed in Table III, was only observed at low temperatures. As the NMR sample was warmed to room temperature, the latter set of resonances disappeared, leaving only the resonances due to the organometallic product Cp*Os(CO)(PMe_2Ph)($OCOCF_3$) and a singlet at δ 0.2 (CD_2Cl_2) which is attributed to methane.[34]

The deshielding of the Cp* and methyl resonances of the species seen at −60 °C, relative to those of Cp*Os(CO)(PMe_2Ph)Me, are consistent with oxidation of the osmium, and the fact that the methyl and hydride resonances showed coupling to the phosphorus atom indicated that all three ligands (Me, H, and PMe_2Ph) were bonded to the osmium atom in the intermediate. We note also that the hydride resonance at δ −12.3 is comparable in chemical shift with the hydride resonances of osmium(IV) hydrides[17,18] but is downfield of the hydride resonance of a very similar osmium(II) complex, Cp*Os(CO)(PMe_3)H.[35] The well-resolved ^1H NMR spectrum, even at low temperature, points to this species being diamagnetic, and the observation that the resonances of this unidentified species disappeared (and the product resonances appeared) as the sample was warmed suggested that the intermediate was the hydrido complex in the reaction shown in eq 2. Thus

$$\mathrm{Cp^*Os(CO)(PMe_2Ph)Me} \xrightarrow{CF_3CO_2H} [\mathrm{Cp^*Os(CO)(PMe_2Ph)(Me)H}](CF_3CO_2) \rightarrow \mathrm{Cp^*Os(CO)(PMe_2Ph)(OCOCF_3)} + CH_4 \quad (2)$$

the intermediate can be considered to result from oxidative addition of the acid to the osmium(II) alkyl complex. This type of intermediate has been proposed for acid cleavage of metal–carbon bonds of analogous compounds of iron,[36-38] but no prior evidence for it has been documented. Reductive elimination of RH, in this case methane, from the proposed intermediate followed by coordination of the acetate anion would give the observed organometallic product.

Bromine Cleavage Reactions. From Table IV, it can be seen that the reactions of bromine with the osmium complexes generally proceeded as in eq 3, although the yields of the organometallic products Cp*Os$(CO)_2$Br and Cp*Os(CO)(PMe_2Ph)Br and of the organic products RBr (R = Me, Et, *i*-Pr, CH_2Ph) were lower than anticipated on the basis of the stoichiometry of eq 3.

$$\mathrm{Cp^*Os(CO)(L)R} + Br_2 \rightarrow \mathrm{Cp^*Os(CO)(L)Br} + \mathrm{RBr} \quad (3)$$

The low yields of methyl and ethyl bromides were likely a result, in part, at least, of the volatility of these compounds, which could result in their partial volatilization into the head space of the NMR tube. However, in at least some of the experiments (experiments 5, 11, 12), the NMR spectra also suggested the presence of unidentified products. The low yields of the organometallic products Cp*Os$(CO)_2$Br and Cp*Os(CO)(PMe_2Ph)Br can also be rationalized on the basis of secondary reactions, as addition of bromine to a solution of Cp*Os$(CO)_2$Br (ν_{CO} = 2016, 1957 cm^{-1}) led to disappearance of these two ν_{CO} bands in the IR spectrum and to the appearance of a number of bands at higher wavenumbers (ν_{CO} = 2133 w, 2097 w, 2041 m, 2025 s, 1968 s cm^{-1}). Over 24 h, the weak bands at 2133 and 2097 cm^{-1} disappeared, but the other bands remained. IR monitoring of reactions of Cp*Os$(CO)_2$R (R = Et, *i*-Pr) with several molar equivalents of Br_2 resulted in observation of the same two bands at 2025 and 1968 cm^{-1}, as well as of a number of weak bands in the region from 2050 to 1900 cm^{-1}. Cp*Os(CO)(PMe_2Ph)Br (ν_{CO} = 1909 cm^{-1}) also reacted with bromine, as addition of several molar equivalents of bromine to a solution of this compound gave rise to several new bands (ν_{CO} = 2069, 2036, 1984 cm^{-1}). These same IR bands were seen after several additions of bromine to a solution of Cp*Os(CO)(PMe_2Ph)*i*-Pr.

The exact nature of the products from the reactions of Cp*Os$(CO)_2$Br and Cp*Os(CO)(PMe_2Ph)Br with bromine and giving rise to the ν_{CO} bands at higher frequencies was not determined, although the broad resonances seen in the ^1H NMR spectra of reactions of the osmium alkyl complexes with excess bromine suggested the presence of paramagnetic materials. Successive additions of Br_2 to solutions of these alkyl complexes indicated that the product of the addition of 1 molar equiv of Br_2 was the bromo complex, which then reacted with any excess bromine.

An unanticipated result during the bromine cleavage reactions of both Cp*Os$(CO)_2$*i*-Pr and Cp*Os(CO)(PMe_2Ph)*i*-Pr was the observation of small amounts of propylene. Propylene would be not be produced directly during the bromine cleavage reactions but was probably formed via reductive elimination from the possibly stereochemically nonrigid osmium(IV) intermediates. Although no osmium hydrides were detected as products of these reactions, any hydrides formed would certainly react with bromine to give the observed bromo product.

Monitoring of the reaction of Cp*Os(CO)(PMe_2Ph)Me and bromine by ^1H NMR spectroscopy revealed a new set of resonances (Table III) which were downfield of the corresponding resonances of the starting methyl complex. The ^{31}P NMR spectrum of this reaction mixture exhibited a new resonance at δ −37.2 (Table III), significantly downfield of the ^{31}P NMR resonances of the osmium(II) bromo and alkyl complexes (Table II), while the IR spectrum exhibited a new ν_{CO} at 2043 cm^{-1}.

The IR band and the ^1H and ^{31}P NMR resonances of this new species all decreased in intensity over time as the bromo complex Cp*Os(CO)(PMe_2Ph)Br was produced, suggesting that the species was an intermediate in the cleavage reaction. The intermediate had many charac-

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teristics similar to those of the intermediate observed at −60 °C during the reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ and CF_3CO_2H. The Cp* and Os–Me resonances of both intermediates were shifted downfield in the ^1H NMR spectrum from the Cp* and Os–Me resonances of the osmium(II) starting methyl complex. Furthermore, in the reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ with bromine, the shift of the ν_{CO} band of the intermediate to higher frequency was also indicative of oxidation of the osmium.

It is thus concluded that the intermediate in the reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ and bromine was the osmium(IV) complex $[Cp^*Os(CO)(PMe_2Ph)(Me)Br]Br$, formed via the oxidative addition of bromine to the osmium(II) methyl complex as in eq 4. As with the reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ with CF_3CO_2H, this type of intermediate has been previously proposed for reactions of analogous iron and ruthenium compounds[6,7] but not detected. Previous stereochemical studies, assuming that this type of oxidized intermediate was formed, have also concluded that it must subsequently react to form the products via nucleophilic attack by free halide ion on the α-carbon atom; the divalent metal product would be the leaving group.[3,4,6–8]

$$Cp^*Os(CO)(PMe_2Ph)Me + Br_2 \rightarrow [Cp^*Os(CO)(PMe_2Ph)(Me)Br]Br \rightarrow Cp^*Os(CO)(PMe_2Ph)Br + MeBr \quad (4)$$

Mercury(II) Bromide Cleavage Reactions. The mercury(II) bromide cleavage reactions generally proceeded as in eq 5. The yields of the bromo osmium complex and of the alkyl mercuric halides, as recorded in Table IV, were generally high, two exceptions being the products of reactions of the complexes $Cp^*Os(CO)_2$*i*-Pr and $Cp^*Os(CO)_2CH_2Ph$. In addition to the products anticipated on the basis of eq 5, alkyl bromides and an unidentified Cp*-containing product (having a resonance at δ(Cp*) 2.25 in the ^1H NMR spectrum) were also produced in the two anomalous reactions. An investigation of the reactions of similar complexes of the type $CpFe(CO)_2R$ with mercury(II) halides revealed the occurrence of the pathway shown in eq 6.

$$Cp^*Os(CO)(L)R + HgBr_2 \rightarrow Cp^*Os(CO)(L)Br + RHgBr \quad (5)$$

$$L = CO, PMe_2Ph$$

$$CpFe(CO)_2R + HgX_2 \rightarrow CpFe(CO)_2HgX + RX \quad (6)$$

If the formation of *i*-PrBr and $PhCH_2Br$ in the mercury(II) bromide cleavage reactions of $Cp^*Os(CO)_2R$ (R = *i*-Pr, CH_2Ph) resulted from a reaction proceeding as in (6), then the unidentified Cp* resonances (δ 2.25) observed in the ^1H NMR spectra of these two reaction mixtures may possibly be attributed to $Cp^*Os(CO)_2HgBr$. This compound has not been previously reported, but consideration of the NMR spectral properties of the iron complexes shows that the Cp proton resonances of $CpFe(CO)_2Cl$[39] and the $CpFe(CO)_2HgCl$[40] do not differ greatly, being δ 4.98 and δ 5.03, respectively. The resonance at δ 2.25 is somewhat shifted from the Cp* resonance of $Cp^*Os(CO)_2Br$ at δ 2.05, but the direction of the shift, downfield, is in the direction predicted by comparison with the iron complexes.

The reactions of $Cp^*Os(CO)_2R$ (R = Me, Et) with $HgBr_2$ proceeded via intermediates, the resonances of which were observed at room temperature in the ^1H NMR spectra of the reaction mixtures (Table III). The resonances of the intermediates disappeared over a period of several hours while the resonances of the products $Cp^*Os(CO)_2Br$ and RHgBr gained in intensity. For R = Me, the ^1H NMR resonances of the intermediate were downfield of the ^1H NMR resonances of the starting methyl complex; a new ν_{CO} at 2040 cm^{-1} was also observed immediately following the addition of $HgBr_2$ to a solution of $Cp^*Os(CO)_2Me$. For R = Et, the new resonances in the ^1H NMR spectrum were also deshielded relative to the corresponding resonances of the starting material. The sharp resonances of both of the intermediates in the ^1H NMR spectra indicated that these species were diamagnetic, and thus, by analogy with the arguments presented above, the intermediates were most likely complexes of the type $[Cp^*Os(CO)_2(R)(HgBr)]^+Br^-$ resulting from the oxidative addition of $HgBr_2$ to $Cp^*Os(CO)_2R$ (eq 7).

$$Cp^*Os(CO)_2R + HgBr_2 \rightarrow [Cp^*Os(CO)_2(R)(HgBr)]^+Br^- \rightarrow Cp^*Os(CO)_2Br + RHgBr \quad (7)$$

The reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ and $HgBr_2$ resulted in the formation of an intermediate with ν_{CO} = 2002 cm^{-1} and resonances in the ^1H NMR spectrum at δ 1.97 (Cp*) and 0.86 (Os–Me). This species thus also exhibited the characteristics expected for an osmium(IV) intermediate. The ^{31}P NMR spectrum of the reaction mixture showed a new resonance at δ −45.7, which was shifted from the ^{31}P resonance of the starting methyl complex at δ −20.3 and which had the appearance of an approximately 1:8:1 triplet, indicating spin–spin coupling to a ^{199}Hg nucleus. The coupling constant (J = 720 Hz) was consistent with a two-bond coupling, as the ^{31}P NMR spectrum of $[cis\text{-}RuMe(PMe_3)_4]_2Hg$[41] exhibits $^2J_{HgP}$ of 780 Hz (trans) and 341 Hz (cis). One-bond ^{199}Hg–^{31}P coupling constants are much larger: for example, $^1J_{HgP}$ for $(Et_2PhP)_2Hg_2Br_2$ is 6627 Hz.[42] On the basis of the spectral data, the intermediate may be identified as an osmium(IV) species formed by oxidative addition of $HgBr_2$ to the starting osmium(II) methyl complex, as shown in eq 8.

$$Cp^*Os(CO)(PMe_2Ph)Me + HgBr_2 \rightarrow Cp^*Os(CO)[(PMe_2Ph)(Me)(HgBr)]Br \rightarrow Cp^*Os(CO)(PMe_2Ph)Br + MeHgBr \quad (8)$$

This intermediate converted slowly to the products $Cp^*Os(CO)(PMe_2Ph)Br$ and MeHgBr over a period of 1–2 days. The reaction of $Cp^*Os(CO)(PMe_2Ph)Et$ with $HgBr_2$ resulted in the formation of a similar species (Table III), which also converted to Products $Cp^*Os(CP)(PMe_2Ph)Br$ and EtHgBr after 10 h.

The intermediate that was formed during the reaction of $Cp^*Os(CO)(PMe_2Ph)Me$ with $HgBr_2$ was isolated as the hexafluorophosphate salt by the addition of $NaPF_6$ to a solution of the intermediate $[Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]Br$. The ^1H NMR spectrum of the recrystallized hexafluorophosphate salt was more easily interpreted in detail than that of the bromide salt, as resonances of the latter were somewhat obscured by other resonances during the course of the reaction. Thus the IR spectrum of the hexafluorophosphate salt exhibited one ν_{CO} band (1986 cm^{-1}), at higher frequency than the ν_{CO} band of $Cp^*Os(CO)(PMe_2Ph)Me$ (1870 cm^{-1}) but at a lower frequency than the ν_{CO} band (2002 cm^{-1}) of $[Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]^+Br^-$. In the ^1H NMR spectrum, the Cp* (δ 1.98 (J_{PH} = 1.0 Hz, J_{HgH} = 21.3 Hz)) and Os–Me

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(δ 0.94 (J_{PH} = 9.3 Hz, J_{HgH} = 35.4 Hz)) resonances were coupled to phosphorus as well as to mercury, showing that all of the ligands were still bonded to the osmium (see Experimental Section for full details).

The ^1H NMR and IR data were consistent, by the same arguments that were used to identify the previous intermediates, with the species being of osmium(IV). The isolation of this intermediate has shown that electrophilic cleavage of the osmium–carbon bond of the complex Cp*Os(CO)(PMe_2Ph)Me with $HgBr_2$ proceeds via oxidative addition of $HgBr_2$ to the osmium(II) methyl complex to form the osmium(IV) complex (eq 9). The intermediate, of a type previously proposed for mercuric halide cleavages of complexes of the type $CpFe(CO)_2R$ (R = alkyl),[6,7] has thus been confirmed, and by comparison with this isolated intermediate, the intermediates identified spectroscopically for other electrophilic cleavages of these osmium alkyl complexes are of the same type (osmium(IV) species).

$$\mathrm{Cp^*Os(CO)(PMe_2Ph)Me + HgBr_2 \rightarrow [Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]^+Br^- \rightarrow Cp^*Os(CO)(PMe_2Ph)Br + MeHgBr} \quad (9)$$

Summary and Conclusions. With few exceptions, reactions of osmium alkyl complexes of the type Cp*Os(CO)LR (L = CO, PMe_2Ph; R = Me, Et, *i*-Pr, CH_2Ph) with the electrophiles CF_3CO_2H, Br_2, and $HgBr_2$ all proceed as expected by comparison to previous work done on similar systems.[6–10,38,40] In most cases, spectroscopic evidence for the intermediates, previously proposed for these reactions but not identified, was found. The reactions all proceed via two-electron oxidation processes to give formally osmium(IV) intermediates of the type $[Cp^*Os(CO)L(R)(E)]^+X^-$, where the electrophile is represented as EX. In addition, for the reaction of Cp*Os(CO)(PMe_2Ph)Me with $HgBr_2$, the intermediate was isolated.

In general, the oxidized intermediates were more stable when L = PMe_2Ph than when L = CO and when R = Me or Et than when R = *i*-Pr or CH_2Ph. It is perhaps not surprising that the phosphine-substituted osmium(IV) complexes are the more stable, as the better electron-donating phosphine should more readily stabilize the higher oxidation state. However, the intermediates that would be formed during cleavage of the isopropyl and benzyl complexes were not observed in any of the reactions. Thus it would seem that the intermediates for R = *i*-Pr and CH_2Ph were not as stable as those of the methyl and ethyl analogues, perhaps because of lower osmium–carbon bond energies.[43]

Acknowledgment. This research was made possible by financial assistance from the Natural Sciences and Engineering Research Council of Canada in the form of scholarships to L.J.J. and operating grants to M.C.B. We are also indebted to the International Nickel Co. and Johnson Matthew for loans of osmium salts and to L. G. Sturgeoff and W. A. G. Graham for information concerning unpublished synthetic procedures.

Registry No. $Cp^*Os(CO)_2Br$, 81554-89-4; $Cp^*Os(CO)_2Me$, 102149-67-7; $Cp^*Os(CO)_2Et$, 116669-97-7; $Cp^*Os(CO)_2$(*i*-Pr), 116669-98-8; $Cp^*Os(CO)_2CH_2Ph$, 116669-99-9; Cp*Os(CO)(PMe_2Ph)Br, 107087-80-9; Cp*Os(CO)(PMe_2Ph)Me, 107087-79-6; Cp*Os(CO)(PMe_2Ph)Et, 116670-00-9; Cp*Os(CO)(PMe_2Ph)(*i*-Pr), 116670-01-0; Cp*Os(CO)(PMe_2Ph)CH_2Ph, 116670-02-1; Cp*Os(CO)(PMe_2Ph)($OCOCF_3$), 116670-03-2; [Cp*Os(CO)(PMe_2Ph)(Me)(HgBr)]PF_6, 107087-83-2; [Cp*Os(CO)(PMe_2Ph)(Me)H](CF_3CO_2), 116670-05-4; [Cp*Os(CO)(PMe_2Ph)(Me)Br]Br, 107333-51-7; [$Cp^*Os(CO)_2$(Me)(HgBr)]Br, 116670-06-5; [$Cp^*Os(CO)_2$(Et)(HgBr)]Br, 116724-45-9; [Cp*Os(CO)(PMe_2Ph)(Me)(HgBr)]Br, 107087-81-0; [Cp*Os(CO)(PMe_2Ph)(Et)(HgBr)]Br, 116670-07-6.

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Mechanism of Carbonyl "Insertion" Reactions of the Compounds *cis*-$MMeX(CO)_2(PMe_3)_2$ (M = Fe, Ru; X = I, CN). Stereochemistry at the Metal Centers

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Received March 8, 1988

Reactions of the compounds *cis*-$MMeX(CO)_2(PMe_3)_2$ (M = Fe, Ru; X = I, CN) with ^{13}CO, of the compounds *cis*-$MMeX(^{13}CO)_2(PMe_3)_2$ with ^{12}CO, and of selectively labeled compounds *cis*-$MMeX(^{12}CO)(^{13}CO)(PMe_3)_2$ with ^{13}CO are monitored by IR and variable-temperature ^{13}C NMR spectroscopy. In all cases, analyses of the reaction products indicate that the reactions involve a "migratory insertion" process in which the methyl group migrates to a cis carbonyl group. There is no evidence for a mechanism involving formal carbon monoxide migration to the methyl site.

Introduction

The mechanism of carbon monoxide insertion into the metal–carbon σ-bond (eq 1) has been extensively studied,

$$\mathrm{MR(CO)L}_n + \mathrm{L'} \rightarrow \mathrm{M(COR)L}_n\mathrm{L'} \quad (1)$$

as the reaction constitutes a key step in many catalytic processes.[1,2] Many studies of the stereochemistry at the α-carbon atom of the alkyl group R have been carried out, and it has been found that reactions as in (1) generally

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