

Oxidative Addition of Methyl Iodide to Monosubstituted and Disubstituted Derivatives of Osmium Pentacarbonyl

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Oxidative addition at room temperature of CH_3I to $\text{Os}(\text{CO})_4\text{L}$ or $\text{Os}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{PMe}_3$) gives complexes $[\text{Os}(\text{CO})_4\text{LCH}_3\text{I}]$ (**3**) or $[\text{Os}(\text{CO})_3\text{L}_2\text{CH}_3\text{I}]$ (**5**), respectively. Complexes **3** and **5** react at higher temperature ($50\text{--}70\text{ }^\circ\text{C}$) to give complexes $\text{Os}(\text{CO})_3\text{LCH}_3\text{I}$ (**7**) and $\text{Os}(\text{CO})_2\text{L}_2\text{CH}_3\text{I}$ (**9**), respectively. If this reaction is carried out in chloride-containing solvents, the formation of $\text{Os}(\text{CO})_3\text{L}(\text{CH}_3\text{CN})\text{Cl}$ (**8**) and $\text{Os}(\text{CO})_2\text{L}_2(\text{CH}_3\text{CN})\text{Cl}$ (**10**) is also observed. Chloride abstraction from solvent during the reaction suggests a radical mechanism for the oxidative addition reaction. During the purification of complexes **9** and **10** by HPLC with acetonitrile (CH_3CN) as eluent, complex $[\text{Os}(\text{CO})_3\text{L}(\text{CH}_3\text{CN})\text{CH}_3\text{I}]$ was obtained; it was transformed by reaction with NaBPh_4 to the complex $[\text{Os}(\text{CO})_3\text{L}(\text{CH}_3\text{CN})\text{CH}_3]\text{BPh}_4$ (**14**). The structures of complexes **14** and **9** have been solved by single-crystal X-ray diffraction methods. Complex **14** crystallizes in the monoclinic space group $P2_1/a$ with lattice parameters $a = 20.877(3)\text{ \AA}$, $b = 19.935(3)\text{ \AA}$, $c = 8.887(3)\text{ \AA}$, and $\beta = 98.92(2)^\circ$; it contains 4 molecules/cell. The structure has been solved by using 2729 observed reflections and refined to $R_w = 0.059$. Complex **9** crystallizes in the monoclinic space group $P2_1/a$ with lattice parameters $a = 13.979(3)\text{ \AA}$, $b = 9.124(2)\text{ \AA}$, $c = 13.950(3)\text{ \AA}$, and $\beta = 107.70(2)^\circ$; it contains 4 molecules/cell. The structure has been solved by using 1617 observed reflections and refined to $R_w = 0.043$.

Introduction

Many complexes of the type $\text{M}(\text{CO})_2\text{L}_2\text{RX}^{1,2}$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{X} = \text{halides}$; $\text{L} = \text{phosphine ligands}$) have been prepared via oxidative addition of alkyl halides to disubstituted complexes¹ of iron and ruthenium or by other methods.² Oxidative addition of alkyl halides was observed in only one case with the monosubstituted $\text{M}(\text{CO})_4\text{L}$ complexes.³ Extensive studies on the reactivity of these complexes have been carried out, with particular reference to the stereochemistry of CO ^{1c,2b,4-6} and isocyanide^{7,8} insertion.

$\text{R}_2\text{Os}(\text{CO})_4$ and $\text{RHOs}(\text{CO})_4$ are described in literature and were prepared by oxidative addition of MeI to the $\text{HOs}(\text{CO})_4^-$ anion.^{9,10} $\text{OsRX}(\text{CO})_4$ complexes were also obtained by electrophilic cleavage with X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) of $\text{R}_2\text{Os}(\text{CO})_4$,¹¹ via radical reaction¹² or via migratory insertion.¹³ Substituted derivatives with phosphine ligands cannot be obtained by direct

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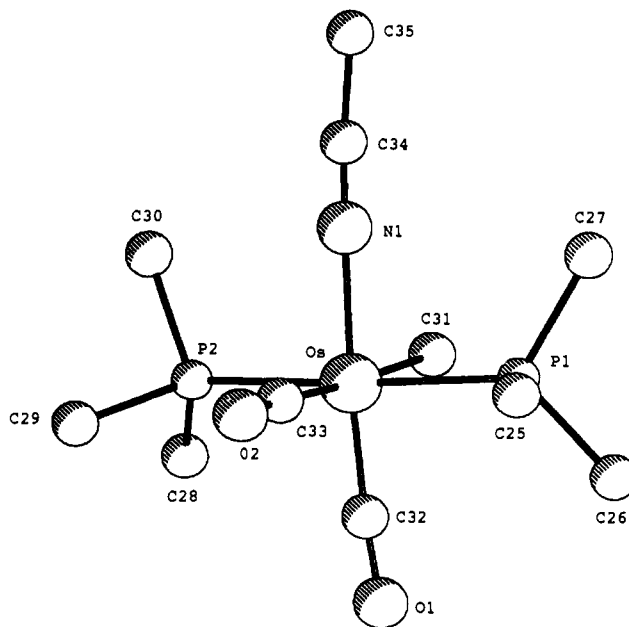


Figure 1. Molecular structure of the cation of complex **14**.

substitution with L because of reductive elimination.¹⁴ Rather, general oxidative addition methods^{13,15,16} must be used.

In this work we describe the preparation and the structural characterization of alkyl complexes of osmium obtained by oxidative addition of CH_3I to monosubstituted and disubstituted derivatives of osmium pentacarbonyl.

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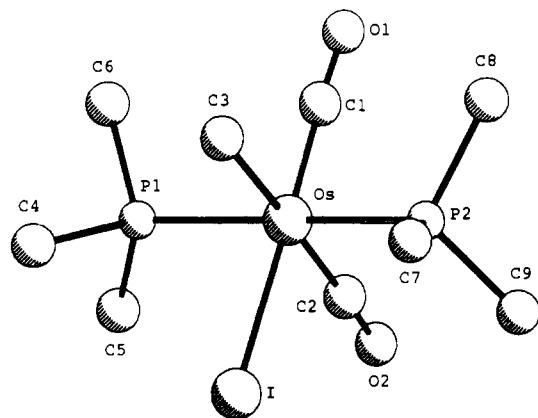


Figure 2. Molecular structure of complex 9.

Experimental Section

The solvents (benzene, toluene, CH_2Cl_2 , etc.) were dried by conventional methods¹⁷ and deaerated by bubbling with nitrogen. Tetrahydrofuran (THF) was purified as described in ref 18 and freshly distilled before use. Acetonitrile (ACN) and CH_3I were purified as described in refs 19 and 20, respectively. Trimethylphosphine was prepared following the method described by Schmidbaur.²¹ The other phosphine ligands were commercially obtained.

The IR spectra were obtained with a 1725X FTIR Perkin-Elmer spectrophotometer or with a 983 Perkin-Elmer conventional spectrophotometer. The ^1H , ^{13}C , and $^{31}\text{P}\{\text{H}\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer. The ^1H and ^{13}C NMR chemical shifts are relative to tetramethylsilane as internal reference, and the $^{31}\text{P}\{\text{H}\}$ NMR chemical shifts are relative to 85% H_3PO_4 in D_2O with a positive sign indicating a shift to lower field.

The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

The structures of the complexes are given in Figures 1 and 2; their IR and NMR characterization is given in Table I.

Preparation of $[\text{Os}(\text{CO})_4\text{PMe}_3]$ (1) and $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$ (2). $\text{Os}_3(\text{CO})_{12}$ (1 g) was dissolved in 70 mL of toluene, and the solution was reacted with a solution (30 mL) of PMe_3 in ethyl ether (molar ratio 5/1) in a Carius tube at 98 °C for 10 days. At the end of the reaction, the formation of $[\text{Os}(\text{CO})_4\text{PMe}_3]$, $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$, and $[\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3]$ was observed by the CO stretching bands. The solvent was removed under reduced pressure, and the solid residue was sublimed at $P \approx 10^{-2}$ mmHg. The complex $[\text{Os}(\text{CO})_4\text{PMe}_3]$ (0.65 g) was obtained at 40 °C. The complex $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$ (0.85 g) was obtained at 70 °C. The trisubstituted cluster $[\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3]$ remained in the residue and was identified by its CO stretching bands²² ($\nu_{\text{CO}} = 2020, 1866 \text{ cm}^{-1}$ in *n*-hexane).

$[\text{Os}(\text{CO})_4\text{PMe}_3]$ was characterized by analysis as $\text{C}_7\text{H}_9\text{O}_4\text{OsP}$. Anal. Found: C, 22.4; H, 2.35. Calcd: C, 22.22; H, 2.40. $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$ was characterized by analysis as $\text{C}_9\text{H}_{18}\text{O}_3\text{OsP}_2$. Anal. Found: C, 25.7; H, 4.40. Calcd: C, 25.30; H, 4.25.

The same reaction was also carried out with PMe_2Ph . In this case, the reaction was carried out at 65 °C using the ligand PMe_2Ph as solvent and $\text{Os}_3(\text{CO})_{12}$ (0.15 g). After 4 days the reaction was complete. The formation of $[\text{Os}(\text{CO})_4\text{PMe}_2\text{Ph}]$ ($\nu_{\text{CO}} = 2059, 1876$, and 1833 cm^{-1} , in CH_2Cl_2) and $[\text{Os}(\text{CO})_3(\text{PMe}_2\text{Ph})_2]$ ($\nu_{\text{CO}} = 1879 \text{ cm}^{-1}$, in CH_2Cl_2) was observed.

Preparation of $[\text{Os}(\text{CO})_4\text{PMe}_3(\text{CH}_3)]\text{I}$ (3) and $[\text{Os}(\text{CO})_4\text{PMe}_3(\text{CH}_3)]\text{BPh}_4$ (4). $[\text{Os}(\text{CO})_4\text{PMe}_3]$ (0.3 g) was added to CH_3I (5 mL), and the solution was cooled to -20 °C and stirred in a reactor under nitrogen. After 1 h the temperature was increased to +5 °C. The

formation of a white precipitate was observed. The reaction was complete after 2 days. The precipitate was filtered out and washed with CH_3I (yield 70%). The solid 3 was analyzed as $\text{C}_8\text{H}_{12}\text{IO}_4\text{Os}$. Anal. Found: C, 18.60; H, 2.25. Calcd: C, 18.47; H, 2.32. The solid 3 was dissolved in CH_3OH and precipitated with NaBPh_4 . Complex 4 was filtered out and analyzed as $\text{C}_{32}\text{H}_{32}\text{BO}_4\text{Os}$. Anal. Found: C, 54.2; H, 4.50. Calcd: C, 53.94; H, 4.53.

Preparation of $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2(\text{CH}_3)]\text{I}$ (5) and $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2(\text{CH}_3)]\text{BPh}_4$ (6). $[\text{Os}(\text{CO})_3(\text{PMe}_3)_2]$ (2) (1 g) was added to CH_3I (10 mL), and the mixture was cooled to -30 °C and stirred in a reactor under nitrogen. The formation of a white precipitate 5 was immediately observed. The solution was filtered. The CH_3I solution showed a series of bands in the following range of CO stretching: $\nu_{\text{CO}} = 2026, 2015, 2005, 1985, 1957, 1945$, and 1935 cm^{-1} . Also the ^1H and $^{31}\text{P}\{\text{H}\}$ NMR spectra in CD_2Cl_2 of the solid, obtained by removing CH_3I , showed a series of bands difficult to assign. In particular the $^{31}\text{P}\{\text{H}\}$ NMR spectrum indicates the presence of about 10 different chemical species.

The white solid 5 (0.82 g, yield 62%) was analyzed as $\text{C}_{10}\text{H}_{21}\text{IO}_3\text{P}_2\text{Os}$. Anal. Found: C, 21.3; H, 3.92. Calcd: C, 21.13; H, 3.72. Complex 5 was dissolved in CH_3OH and precipitated with NaBPh_4 . A white solid 6 (yield 90%) was obtained. Complex 6 was analyzed as $\text{C}_{34}\text{H}_{41}\text{BO}_3\text{P}_2\text{Os}$. Anal. Found: C, 53.3; H, 5.52. Calcd: C, 53.69; H, 5.43.

Reaction of Complex 5 in Chloride Solvents. The reaction was carried out in CH_2Cl_2 and 1,2-dichloroethane. The results were identical in the two solvents; the reaction was much slower in CH_2Cl_2 since the temperature could not be raised higher than 40 °C. Now we describe the reaction in 1,2-dichloroethane.

Complex 5 (1.9 g) was dissolved in 1,2-dichloroethane (50 mL), and the solution was deaerated and heated to 65 °C. The reaction was complete after 8 h. The reaction product remained stable for 3 days. Solvent was removed by evaporation under reduced pressure with an oil pump ($P \approx 10^{-2}$ mmHg). The solid residue was dissolved in *n*-hexane. The IR spectrum shows two CO stretching bands; accurate analyses of the IR form of the bands indicate the presence of other bands. This conclusion was confirmed by the ^1H NMR spectrum in CD_2Cl_2 , which showed two Os-CH₃ triplets and two PMe_3 triplets, indicating the presence of two complexes. Attempts to separate the two complexes by fractional crystallization were unsuccessful. A separation was obtained by HPLC, using an apolar C18 preparative column (Dynamax-60A) and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (90/10) as the eluent at room temperature.

Four major and other less important fractions were obtained. After elution, solvent was evaporated from each and the remaining solid extracted with diethyl ether and dried with dehydrated MgSO_4 . The solution was filtered and the solvent removed by evaporation under reduced pressure.

Two of the fractions contained the two above mentioned complexes. They were purified by crystallization and obtained as light white needles. One of them was analyzed as $\text{C}_9\text{H}_{21}\text{IO}_2\text{P}_2\text{Os}$ (9). Anal. Found: C, 19.9; H, 3.95; I, 23.3; P, 11.3. Calcd: C, 20.01; H, 3.92; I, 23.49; P, 11.47. Molecular weight: found (osmometric method in benzene), 535 ± 10 ; calcd, 540.34. The other analyzed as $\text{C}_9\text{H}_{21}\text{ClO}_2\text{P}_2\text{Os}$ (10). Anal. Found: C, 23.8; H, 4.99; Cl, 8.1; P, 13.6. Calcd: C, 24.08; H, 4.72; Cl, 7.90; P, 13.80. Molecular weight: found (osmometric method in benzene), 440 ± 10 ; calcd, 448.88.

The two remaining fractions contained two new complexes, insoluble in apolar solvents. One of these gives the following IR bands: $\nu_{\text{CO}} = 2028$ and 1960 cm^{-1} in CH_2Cl_2 . The ^1H NMR spectrum in CD_2Cl_2 shows $\delta_{\text{CH}_3} = -0.14$ (t) ($^3J_{\text{HP}} = 8.4 \text{ Hz}$) and $\delta_{\text{PMe}_3} = 1.73$ (m) ($^2J_{\text{HP}} + ^4J_{\text{HP}} = 4.0 \text{ Hz}$); the $^{31}\text{P}\{\text{H}\}$ NMR spectrum in CD_2Cl_2 shows a singlet at $\delta = -37.9$ ppm. The other complex gives the following IR bands: $\nu_{\text{CO}} = 2029$ and 1963 cm^{-1} in CH_2Cl_2 . The ^1H NMR spectrum in CD_2Cl_2 shows $\delta_{\text{CH}_3} = -0.13$ (t) ($^3J_{\text{HP}} = 8.5 \text{ Hz}$) and $\delta_{\text{PMe}_3} = 1.75$ (m) ($^2J_{\text{HP}} + ^4J_{\text{HP}} = 4.1 \text{ Hz}$); the $^{31}\text{P}\{\text{H}\}$ NMR spectrum in CD_2Cl_2 shows a singlet at $\delta = -37.9$ ppm. These two complexes appear very similar.

Both these were dissolved in CH_3OH and precipitated with NaBPh_4 . An identical white solid complex was obtained (14), which analyzed as $\text{C}_{35}\text{H}_{44}\text{BNO}_2\text{P}_2\text{Os}$. Anal. Found: C, 54.6; H, 5.55; N, 1.75. Calcd: C, 54.33; H, 5.73; N, 1.81. The spectroscopic characterization of complex 14 is given in Table I. On the basis of this behavior compared to that of the previous insoluble complexes in apolar solvent, these compounds were attributed as having the same structure as that of 14, except with the anions Cl⁻ and I⁻: $[\text{Os}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3\text{CN})\text{CH}_3]\text{Cl}$ and $[\text{Os}(\text{CO})_2(\text{PMe}_3)_2(\text{CH}_3\text{CN})\text{CH}_3]\text{I}$, respectively.

The less important fractions, analyzed by IR and NMR (see Table

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Table I. IR and ¹H, ³¹P, and ¹³C NMR Spectral Data for the Complexes

complex	IR: ν _{CO} , cm ⁻¹	NMR: ^c δ, ppm, and J, Hz		
		¹ H	³¹ P{ ¹ H}	¹³ C
1 ^a	2061, 1981, 1939	δ _{PMe₃} = 1.85 d, ² J _{H-P} = 10.4	δ _P = -49.2 s, J _{P-Os} = 147, J _{P-Me} = 38.9, ² J _{P-CO} = 2.7	δ _{CO} = 189.8, δ _{CH₃} = 22.0 d, ¹ J _{C-P} = 38.9
2 ^a	1886	δ _{PMe₃} = 1.79 t, ² J _{H-P} + ⁴ J _{H-P} = 4.11	δ _P = -45.9 s	δ _{CH₃} = 23.5 t, ¹ J _{C-P} + ³ J _{C-P} = 36.2
3 ^b	2158 s, 2098 s, 2071 vs	δ _{CH₃} = 0.25 d, ³ J _{H-P} = 7.4, δ _{PMe₃} = 2.17 d, ² J _{H-P} = 11.0	δ _P = -45.5 s	
4 ^b	2161 s, 2100 s, 2080 vs	δ _{CH₃} = 0.21 d, ³ J _{H-P} = 7.4, δ _{PMe₃} = 1.57 d, ² J _{H-P} = 10.7	δ _P = -46.5 s	
5 ^b	2115 vw, 2034 s, 2023 sh	δ _{CH₃} = -0.08 t, ³ J _{H-P} = 7.6, δ _{PMe₃} = 1.95 t, ² J _{H-P} + ⁴ J _{H-P} = 8.6	δ _P = -47.5 s	
6 ^b	2115 vw, 2035 s, 2023 sh	δ _{CH₃} = -0.09 t, ³ J _{H-P} = 7.7, δ _{PMe₃} = 1.78 t, ² J _{H-P} + ⁴ J _{H-P} = 8.4	δ _P = -47.9 s	
7 ^a	2093 s, 2026 s, 1985 s	δ _{CH₃} = 0.51 d, ³ J _{H-P} = 8.6, δ _{PMe₃} = 1.82 d, ² J _{H-P} = 10.1	δ _P = -53.5 s	
8 ^a	2097 s, 2027 s, 1982 s	δ _{CH₃} = 0.32 d, ³ J _{H-P} = 8.6, δ _{PMe₃} = 1.68 d, ² J _{H-P} = 10.4	δ _P = -37.7 s	
9 ^a	2010 s, 1932 s	δ _{CH₃} = 0.17 t, ³ J _{H-P} = 8.6, δ _{PMe₃} = 1.77 t, ² J _{H-P} + ⁴ J _{H-P} = 7.8	δ _P = -50.5 s, ¹ J _{P-Os} = 165	δ _{CH₃} = -23.0 t, ² J _{C-P} = 8.26, δ _{PCH₃} = 17.1 t, ¹ J _{C-P} + ³ J _{C-P} = 36.6, δ _{CO} = 177.9
10 ^a	2007 s, 1934 s	δ _{CH₃} = -0.06 t, ³ J _{H-P} = 8.7, δ _{PMe₃} = 1.62, ² J _{H-P} + ⁴ J _{H-P} = 8.0	δ _P = -37.2 s, ¹ J _{P-Os} = 168	δ _{CH₃} = -13.6 t, ² J _{C-P} = 9.47, δ _{PCH₃} = 15.0 t, ¹ J _{C-P} + ³ J _{C-P} = 36.7, δ _{CO} = 179.8
11 ^a	2028 s, 1963 s	δ _{PMe₃} = 2.02 t, ² J _{H-P} + ⁴ J _{H-P} = 8.2	δ _P = -58.2 s, ¹ J _{P-Os} = 153	
12 ^a	2029 s, 1958 s	δ _{PMe₃} = 1.74 t, ² J _{H-P} + ⁴ J _{H-P} = 10.0	δ _P = -31.1 s	
13 ^a	2029 s, 1960 s	δ _{PMe₃} = 1.88 t, ² J _{H-P} + ⁴ J _{H-P} = 8.4	δ _P = -44.0 s, ¹ J _{P-Os} = 156	δ _{PCH₃} = 16.3 t, ¹ J _{C-P} + ³ J _{C-P} = 36.1
14 ^b	2032 s, 1969 s	δ _{CH₃} = -0.15 t, ³ J _{H-P} = 8.5, δ _{PMe₃} = 1.64, ² J _{H-P} + ⁴ J _{H-P} = 7.8, δ _{CN-CH₃} = 1.69 t, ² J _{H-P} = 1.7	δ _P = -38.3 s	

^a IR spectra in *n*-Hexane. ^b IR spectra in CH₂Cl₂. ^c NMR spectra in CD₂Cl₂.

I) and elemental analyses, indicated the presence of [Os(CO)₂(PMe₃)₂I₂] (11), [Os(CO)₂(PMe₃)₂Cl₂] (12), and [Os(CO)₂(PMe₃)₂ICl] (13).

Preparation of [Os(CO)₂(PMe₃)₂(CH₃)I] (9). [Os(CO)₃(PMe₃)₂(CH₃)I] (5) (0.5 g) was reacted in THF at 50 °C, and the solution was vigorously stirred. The reaction was complete in 2 days. The solvent was removed under reduced pressure, and complex 9 was crystallized by *n*-hexane as white needles at -20 °C (yield 90%).

Preparation of [Os(CO)₂(PMe₃)₂(CH₃)Cl] (10). [Os(CO)₃(PMe₃)₂(CH₃)BPh₄] (6) (0.5 g) was reacted in THF at 50 °C with NBu₄Cl (0.5 g), and the solution was vigorously stirred. The reaction was complete in 2 days. The solvent was removed under reduced pressure, and complex 10 was crystallized by *n*-hexane as white needles at -20 °C (yield 85%).

Reaction of Complex 3 in Chloride Solvents. Complex 3 (0.5 g) was dissolved in deaerated 1,2-dichloroethane (100 mL) at 65 °C. The reaction was completed in 8 h. The IR and ¹H NMR spectra indicate the presence of two methyl complexes, as previously described for complex 5. Instead of carrying out the separation of the two complexes, they were prepared as described in the following sections.

Preparation of [Os(CO)₃PMe₃(CH₃)I] (7). [Os(CO)₄PMe₃(CH₃)I] (3) (0.5 g) was vigorously stirred in THF (100 mL) at 50 °C. The reaction was complete in 2 days. The solvent was removed under reduced pressure and the solid crystallized in *n*-hexane; white needles of complex 7 were obtained (0.4 g; yield 80%). The solid analyzed as C₇H₁₂IO₃POs. Anal. Found: C, 17.3; H, 2.65; I, 26.2; P, 6.45. Calcd: C, 17.08; H, 2.46; I, 25.78; P, 6.29.

Preparation of [Os(CO)₃PMe₃(CH₃)Cl] (8). [Os(CO)₄PMe₃(CH₃)BPh₄] (4) (0.5 g) was vigorously stirred at 50 °C with NBu₄Cl (0.5 g) in THF (100 mL). The reaction was complete in 3 days. The solvent was removed under reduced pressure and the solid extracted with *n*-hexane. The solution crystallized at -20 °C as white needles of complex 8 (0.3 g; yield 60%). The solid analyzed as C₇H₁₂ClO₃POs. Anal. Found: C, 21.1; H, 2.90; Cl, 8.60; P, 7.55. Calcd: C, 20.98; H, 3.02; Cl, 8.85; P, 7.73.

Reaction of [Os(CO)₃(PMe₃)₂(CH₃)BPh₄] (6) with I₂ or Halide Compounds. Complex 6 was reacted in THF at 50 °C with I₂. The reaction was followed by IR techniques. A fast reaction was observed with initial formation of complex 9; it reacted further with formation of another complex. This last reaction was complete in 1 h. The solvent was removed under reduced pressure and the solid residue extracted with *n*-hexane. Solid 11²³ was crystallized at -20 °C. It analyzed as C₈H₁₈I₂O₂P₂Os. Anal. Found: C, 14.5; H, 2.95. Calcd: C, 14.73; H, 2.78.

The reaction described with I₂ was also observed with CH₂I₂.

The reaction of 6 with CHCl₃ gave initial formation of complex 10, which then gave complex 12, which was analyzed and characterized²³ as the previous complex 11. No reaction was observed (10 days of reaction) when complex 6 was reacted with CH₂Cl₂ or 1,2-dichloroethane.

Reaction of Complex [Os(CO)₄PMe₃(CH₃)BPh₄] (4) with NBu₄I. Complex 4 (0.5 g) was reacted with NBu₄I (0.6 g) in THF (100 mL) at 50 °C. A fast reaction was observed with formation of complex 7. Complex 7 reacted further to give a complex which was characterized as Os(CO)₃PMe₃I₂ by its IR stretching CO bands.²⁴

Reaction of Complex [Os(CO)₃(PMe₃)₂(CH₃)BPh₄] (6) with NBu₄I. Complex 6 (0.5 g) reacted in THF (100 mL) with NBu₄I (0.6 g) at 50 °C. The first product of the reaction was complex 9, which could be isolated. If the reaction is not interrupted, complex 9 reacts further to give a methyl complex, which, to date, has not been characterized.

Collection of X-ray Diffraction Data. [Os(CO)₂(PMe₃)₂(NCCH₃)-(CH₃)BPh₄] (14). A white prismatic crystal of complex 14 was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer, equipped with graphite-monochromatized Mo Kα radiation. The crystals are monoclinic. The cell dimensions were determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 10 and 20°. The space group is P2₁/a (from systematic extinctions).

The intensities of ±*h*, *k*, *l* reflections were collected up to 2θ = 44°. A total of 4850 reflections were measured. A total of 2121 having *I* < 3σ(*I*) were considered as "unobserved" and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variations in intensity during data collection. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North et al.²⁵

The structure was solved by Patterson method and refined by the full-matrix least-squares method of the SHELX-76²⁶ program package.

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Table II. Atomic Parameters for the Structure of Complex 14^a

atom ^b	x	y	z
Os	3178.0 (3)	5423.4 (3)	1532.0 (8)
P1	3170 (2)	4401 (2)	146 (6)
P2	3124 (2)	6497 (2)	2701 (6)
C1	119 (5)	2150 (3)	2752 (11)
C2	269 (5)	1638 (3)	1795 (11)
C3	234 (5)	970 (33)	2238 (11)
C4	48 (5)	813 (3)	3639 (11)
C5	-102 (5)	1325 (3)	4596 (11)
C6	-66 (5)	1994 (3)	4153 (11)
C7	-339 (5)	3472 (5)	2880 (13)
C8	-951 (5)	3216 (5)	3438 (13)
C9	-1425 (5)	3635 (5)	3438 (13)
C10	-1287 (5)	4310 (5)	3753 (13)
C11	-675 (5)	4566 (5)	3631 (13)
C12	-201 (5)	4147 (5)	3194 (13)
C13	-127 (5)	3080 (5)	373 (8)
C14	-398 (5)	2780 (5)	-544 (8)
C15	-522 (5)	2922 (5)	-2099 (8)
C16	-121 (5)	3364 (5)	-2737 (8)
C17	404 (5)	3664 (5)	1820 (8)
C18	528 (5)	3522 (5)	265 (8)
C19	1002 (4)	3125 (6)	3052 (13)
C20	1160 (4)	3505 (6)	4375 (13)
C21	1808 (4)	3592 (6)	5017 (13)
C22	2298 (4)	3299 (6)	4336 (13)
C23	2139 (4)	2919 (6)	3013 (13)
C24	1491 (4)	2832 (6)	2371 (13)
C25	3463 (9)	3654 (9)	1288 (21)
C26	3668 (13)	4356 (12)	1354 (30)
C27	2342 (11)	4123 (11)	-712 (27)
C28	3756 (11)	7100 (11)	2323 (25)
C29	3239 (10)	6480 (11)	4804 (25)
C30	2330 (13)	6931 (14)	2280 (29)
C31	2982 (9)	5944 (9)	-672 (20)
C32	4047 (7)	5517 (7)	1591 (18)
O1	4613 (6)	5620 (6)	1532 (14)
C33	3296 (8)	4968 (9)	3464 (21)
O2	3396 (7)	4712 (8)	4610 (19)
N	2164 (7)	5380 (7)	1301 (16)
C34	1604 (9)	5371 (8)	1089 (20)
C35	883 (10)	5398 (10)	762 (24)
B	230 (9)	2962 (9)	2269 (21)

^a Standard deviations in parentheses refer to the last digit. ^b Coordinates multiplied by 10 000.

Table III. Atomic Parameters for the Structure of Complex 9^a

atom ^b	x	y	z
Os	1346.8 (7)	248 (1)	2418.3 (7)
I	663 (1)	2445 (1)	3435 (1)
P1	1933 (3)	2111 (5)	1559 (3)
P2	899 (3)	-1475 (4)	3482 (3)
C1	1829 (11)	-1178 (20)	1795 (13)
O1	2114 (11)	-2122 (18)	1405 (12)
C2	39 (12)	221 (16)	1484 (12)
O2	-762 (12)	254 (16)	857 (13)
C3	2811 (11)	333 (16)	3551 (12)
C4	2645 (14)	3608 (21)	2334 (14)
C5	973 (14)	3144 (20)	609 (15)
C6	2771 (14)	1441 (23)	885 (15)
C7	1354 (15)	-1094 (25)	4853 (16)
C8	1483 (17)	-3283 (25)	3459 (19)
C9	-456 (18)	-1782 (26)	3250 (19)

^a Standard deviations in parentheses refer to the last digit. ^b Coordinates multiplied by 10 000.

Anisotropic thermal parameters were refined for Os and P atoms. The phenyl groups were refined as rigid groups, assuming a perfect hexagonal geometry (C-C bond length = 1.395 Å). The hydrogen atoms were included at the calculated positions (C-H = 1.08 Å) and refined with an overall temperature factor, $U = 0.12 \text{ \AA}^2$.

The refinement converged at $R = R(\text{unweighted}) = 0.054$ and $R_w = R(\text{weighted}) = 0.059$ for 137 parameters and 2729 observed reflections

Table IV. Crystallographic Data for Complexes 14 and 9

	14	9
chem formula	C ₁₁ H ₂₄ NO ₂ P ₂ O ₈ ·C ₂₄ H ₂₀ B	C ₉ H ₂₁ IO ₂ P ₂ O ₈
<i>a</i> (esd), Å	20.877 (3)	13.979 (3)
<i>b</i> (esd), Å	19.935 (3)	9.124 (2)
<i>c</i> (esd), Å	8.887 (3)	13.950 (3)
β (esd), deg	98.92 (2)	107.70 (2)
<i>V</i> , Å ³	3653.9	1695.0
<i>Z</i>	4	4
fw	762	540
space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>T</i> , °C	20	20
λ , Å	0.710 69	0.710 69
ρ_{calcd} , g cm ⁻³	1.395	2.115
μ , cm ⁻¹	66.93	33.3
transm coeff	0.73–0.99	0.90–0.99
$R(F_o)^a$	0.054	0.041
$R_w(F_o)^a$	0.059	0.043

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = \sum (\sqrt{w}(|F_o| - |F_c|)) / \sum \sqrt{w}|F_o|.$$

Table V. Relevant Bond Lengths (Å) and Angles (deg) in Complex 14^a

Bond Lengths			
Os–P(1)	2.381 (4)	Os–N(1)	2.097 (14)
Os–P(2)	2.390 (4)	O(1)–C(32)	1.208 (16)
Os–C(31)	2.198 (17)	O(2)–C(33)	1.129 (18)
Os–C(32)	1.817 (14)	N(1)–C(34)	1.154 (19)
Os–C(33)	1.924 (18)		
Angles			
P(1)–Os–P(2)	174.3 (2)	Os–N(1)–C(34)	176.0 (13)
P(1)–Os–C(31)	87.6 (4)	N(1)–C(34)–C(35)	176.4 (18)
P(1)–Os–C(32)	91.7 (5)	Os–C(32)–O(1)	174.4 (13)
P(1)–Os–C(33)	92.7 (5)	Os–C(33)–O(2)	176.6 (16)
P(1)–Os–N(1)	89.3 (4)	C(31)–Os–C(32)	91.4 (6)
P(2)–Os–C(31)	87.1 (4)	C(32)–Os–C(33)	91.9 (7)
P(2)–Os–C(32)	90.5 (5)	C(33)–Os–N(1)	93.2 (6)
P(2)–Os–C(33)	92.5 (5)	N(1)–Os–C(31)	83.5 (6)
P(2)–Os–N(1)	88.0 (4)	C(32)–Os–N(1)	174.7 (6)

^a Standard deviations in parentheses refer to the last digit.

Table VI. Relevant Bond Lengths (Å) and Angles (deg) in Complex 9^a

Bond Lengths			
Os–P(1)	2.365 (4)	Os–C(3)	2.174 (15)
Os–P(2)	2.373 (4)	Os–I	2.787 (1)
Os–C(1)	1.806 (19)	C(1)–O(1)	1.153 (21)
Os–C(2)	1.895 (16)	C(2)–O(2)	1.193 (20)
Angles			
P(1)–Os–P(2)	172.3 (2)	P(2)–Os–I	87.8 (1)
P(1)–Os–C(1)	92.1 (6)	Os–C(1)–O(1)	177.7 (17)
P(1)–Os–C(2)	94.1 (5)	Os–C(2)–O(2)	176.0 (15)
P(1)–Os–C(3)	87.0 (4)	C(1)–Os–I	178.0 (5)
P(1)–Os–I	88.1 (1)	C(1)–Os–C(2)	94.7 (7)
P(2)–Os–C(1)	91.8 (6)	C(1)–Os–C(3)	88.2 (7)
P(2)–Os–C(2)	92.2 (5)	C(2)–Os–I	87.2 (5)
P(2)–Os–C(3)	86.5 (4)	C(3)–Os–I	89.8 (4)

^a Standard deviations in parentheses refer to the last digit.

($w = (\sigma^2(F_o) + 0.0018F_o^2)^{-1}$). The atomic scattering factors were taken from ref 27 for P, O, C, N, B, H, and Os; the correction for anomalous dispersion was included.

The atomic coordinates are listed in Table II. Thermal parameters are given in the supplementary material.

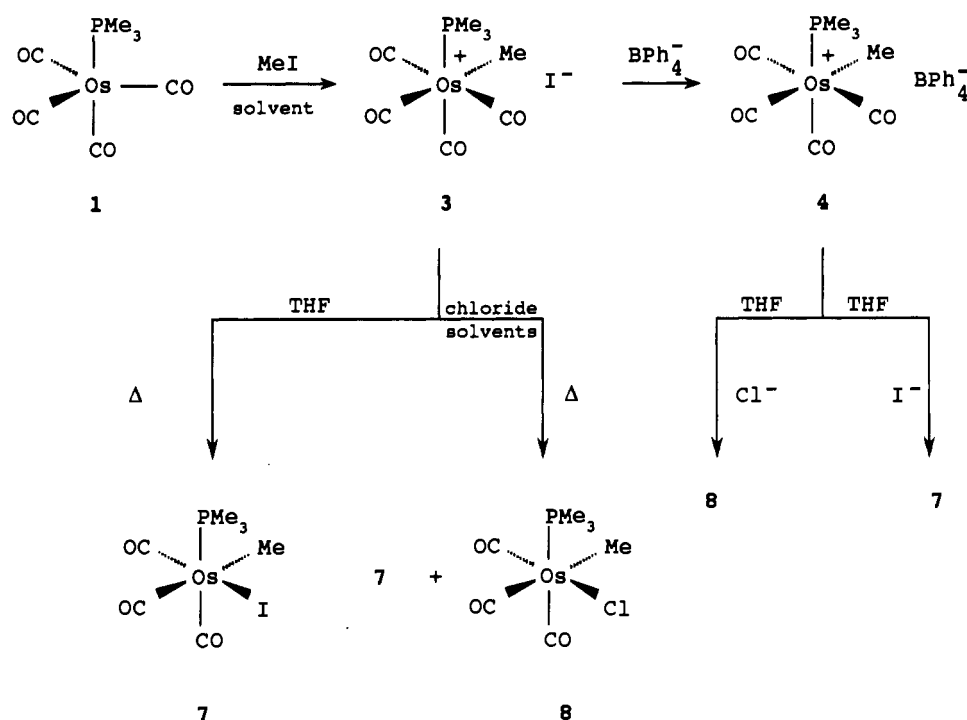
[Os(CO)₂(PMe₃)₂(CH₃)I] (9). A crystal of complex 9 was mounted on the above mentioned diffractometer. The crystals were monoclinic, space group *P*2₁/*a*. The cell dimensions were determined as for complex 14.

The intensity data of 5580 \pm *h, k, l* and \pm *h, -k, l* reflections were measured

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Scheme I



as for complex 14 up to $2\theta = 50^\circ$. The data were treated as described previously and then merged to give 1617 unique "observed" reflections ($R_{\text{eq}} = 0.06$).

The structure was resolved and refined as for complex 14, with anisotropic thermal parameters for Os, I, and P atoms. The final R was 0.041, and $R_w = 0.043$, with $w = ((\sigma^2(F_o) + 0.0083F_o^2)^{-1})$ for 81 parameters.

The atomic coordinates are given in Table III. Tables of thermal parameters are given in the supplementary material.

Results

The results of the structure studies of complexes 14 and 9 are presented in Table IV. The salient bond distances and angles for complexes 14 and 9 are reported in Tables V and VI, respectively. The IR and NMR characterization of the complexes is given in Table I. The transformations observed in this work are summarized in Scheme I, for the oxidative addition of Os(CO)₄L₂, and in Scheme II, for the oxidative addition of Os(CO)₃L₂.

Discussion

(a) **Description of the Molecular Structure of [Os(CO)₂(PMe₃)₂(NCCH₃)(CH₃)BPh₄] (14).** The cation of 14 shows an octahedral structure with two trans PMe₃ ligands (P(1)–Os–P(2) = 174.3 (0.2)°) and two cis CO ligands (C(32)–Os–C(33) = 91.9 (0.7)°) (Table V). The last two positions are occupied by an acetonitrile and a methyl ligand. The acetonitrile ligand shows a near-linear structure (N(1)–C(34)–C(35) = 176.4 (1.8)° and Os–N(1)–C(34) = 176.0 (1.3)°). The bond lengths Os–P(1) (2.381 (0.004) Å) and Os–P(2) (2.390 (0.004) Å) are almost equal within the limit of the experimental error.

By contrast, the bond lengths Os–C(32) (1.817 (0.014) Å) and Os–C(33) (1.924 (0.018) Å) are appreciably different and reflect the effect of the ligand in the trans position as observed in other complexes.^{8b,28} The bond length Os–C(31) (2.198 (0.017) Å) is in agreement with the bond length observed for the osmium–sp³ carbon bond in alkyl derivatives, which change in the range

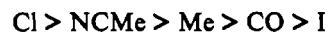
2.10–2.21 Å.^{29–31} The acetonitrile ligand is cis to the methyl ligand, as observed in the isoelectronic iron complexes.³² The structure and the metal bond length of the acetonitrile ligand are in agreement with the literature data.^{33,34}

(b) **Description of the Molecular Structure of [Os(CO)₂(PMe₃)₂(CH₃)I] (9).** Complex 9 shows an octahedral structure with two trans PMe₃ ligands (P(1)–Os–P(2) = 172.3 (0.2)°) and two cis CO ligands (C(1)–Os–C(2) = 94.7 (0.7)°) (Table VI). The last two positions are occupied by the methyl and the iodide ligands. The Os–C(3) bond length (2.174 (0.015) Å) is in agreement with the other Os–sp³ carbon characterized bond length.^{29–31}

(c) **NMR Spectra.** The ³¹P{H} NMR spectra of the disubstituted complexes of osmium d⁶ Os(CO)₂L₂XY show a strong substituent effect. If the effect of the X and Y substituents is supposed to be additive, the chemical shift can be expressed as

$$\delta = a + \delta_X + \delta_Y$$

in which a is the contribution of the constant moiety Os(CO)₂L₂, which can be fixed at zero. In this case the contributions of the substituents are in ppm: $\delta_I = -29$; $\delta_{\text{Cl}} = -15.5$; $\delta_{\text{Me}} = -21.5$; $\delta_{\text{NCMe}} = -16.8$; $\delta_{\text{CO}} = -26.4$. This gives the following order for the substituent effect:



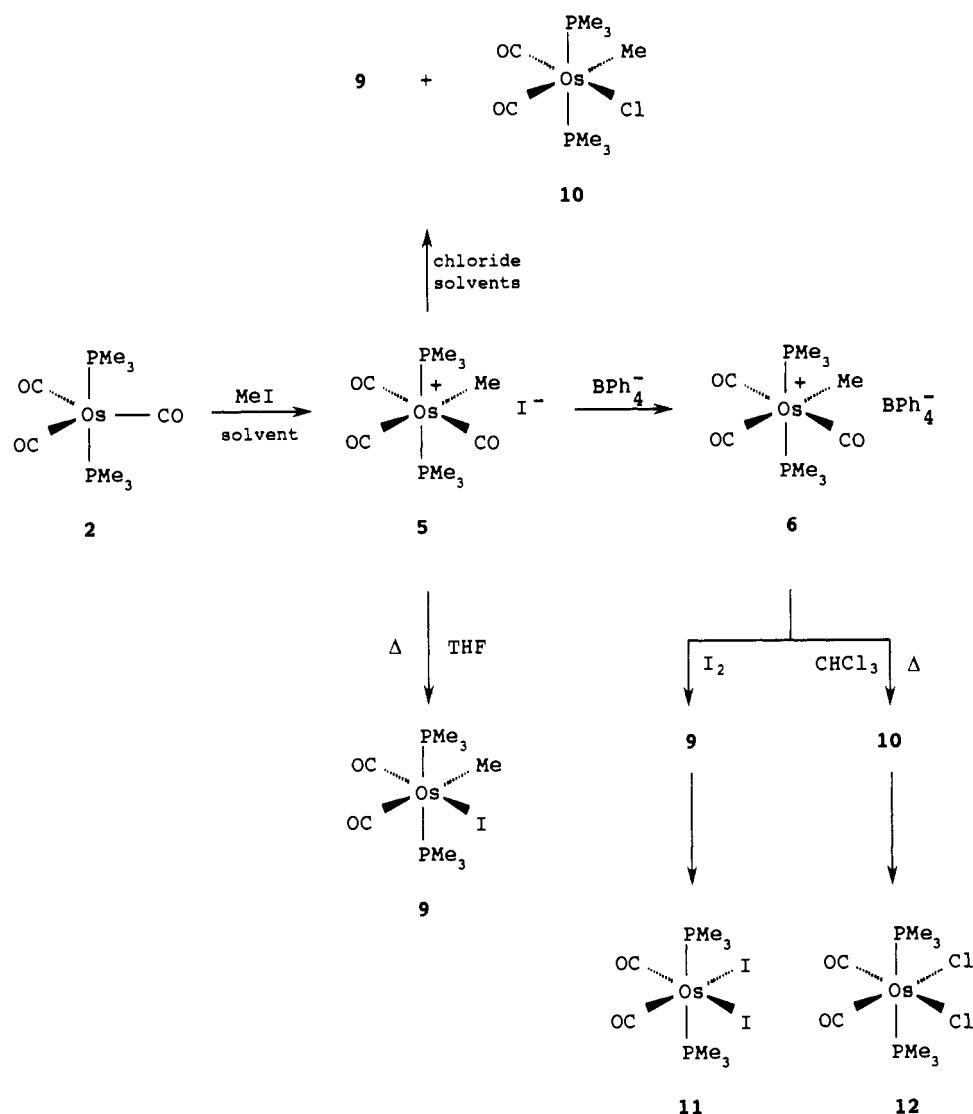
The extension to the monosubstituted derivatives is not possible since a sufficient number of substituents are not available.

In the ³¹P{H} NMR spectra, a few complexes (1, 9, 10, 11, 13) show satellite peaks assigned to the complex containing the ¹⁸⁷Os isotope ($I = 1/2$, natural abundance 1.64%). The ¹J_{P–Os} coupling

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Scheme II



constants (Table I) are in agreement with the literature values for similar complexes.³⁵ They are slightly sensitive to substituent (range 153–168 Hz) and to the oxidation state of osmium complexes (complex **1**, $^1J_{\text{P-Os}} = 147$ Hz, oxidation state zero; complex **11**, $^1J_{\text{P-Os}} = 153$ Hz, oxidation state +2). When we compare our results with the literature values,^{36,37} the $^1J_{\text{P-Os}}$ coupling constants are, on the contrary, very sensitive to the stereochemical structure of the complexes, changing between 30–80 Hz for $[\text{M}_2\text{Os}_3(\text{CO})_{13}\text{PR}]$ cluster complexes³⁶ to 300–400 Hz for $[(\eta^5\text{-Cp})\text{RL}_2\text{Os}]$ complexes³⁷ through $[\text{Os}(\text{CO})_2\text{L}_2\text{XY}]$ and $[\text{OsH}_4\text{L}_3]$ ³⁵ complexes, which show 140–170-Hz values.

(d) **Oxidative Addition.** $\text{Os}_3(\text{CO})_{12}$ reacts with phosphine ligands L (L = PMe_3 , PMe_2Ph), giving a mixture of monosubstituted complex $[\text{Os}(\text{CO})_4\text{L}]$, disubstituted complex $[\text{Os}(\text{CO})_3\text{L}_2]$, and symmetric trisubstituted cluster $[(\text{Os}(\text{CO})_3\text{L}_3)]_3$.³⁸ The relative rates depend on temperature and concentration of L.³⁹

The monosubstituted complexes $\text{Os}(\text{CO})_4\text{L}$ react with CH_3I at 5 °C giving ionic methyl complex **3** according to the reaction of Scheme I.

The structure of complex **3** is assigned on the basis of the CO stretching bands.⁴⁰ Complex **3** shows three CO stretching bands of comparable intensity (Table I). The alternative structure with PMe_3 and CH_3 in the trans position (point group C_{4v}) should give two IR-active CO stretching bands of A_1 and E_1 symmetry.

The disubstituted complexes $[\text{Os}(\text{CO})_3\text{L}_2]$ (L = PMe_3 , PMe_2Ph) react instantaneously with CH_3I at –30 °C giving the ionic complex **5** according to the reaction of Scheme II.

The IR spectrum of complex **5** is very similar to those of the corresponding complexes of Fe³² and Ru.^{1e} Both Fe and Ru complexes showed two CO stretching bands, one very weak and the other very strong. This supports an equatorial structure of these CO ligands. The IR spectrum of complex **5** shows a similar pattern with a very strong degenerate band. The ^1H and ^{31}P NMR spectra of **5** confirm the structure: in fact the ^1H NMR spectrum for the methyl bonded to Os shows a triplet due to the coupling with two equivalent phosphorus atoms and a triplet for the methyl bonded to phosphorus atoms (triplet by virtual coupling⁴¹). The $^{31}\text{P}\{\text{H}\}$ NMR spectrum indicates a single band and shows two equivalent phosphine ligands. A facial structure, which should give three IR CO stretching bands of comparable intensity,⁴⁰ is excluded.

Complexes **3** and **5**, dissolved in non-halide solvents, react

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slowly, giving the neutral alkyl complexes with structures 7 and 9, respectively. Structure 7 has been assigned on the basis of IR and NMR information. In fact, in the IR it shows three CO stretching bands of comparable intensities in agreement with a facial structure. Structure 7 was also observed in the Ru(CO)₃PMe₃CH₃I complex.³

The structure of complex 9 in the solid state was established by X-ray diffractometric analysis and discussed previously in this work. In solution structure 9 is maintained as indicated by the spectroscopic information, which indicates two CO ligands in the cis position (two CO stretching bands of comparable intensities),⁴⁰ two equivalent phosphine ligands (an apparent triplet by virtual coupling for the methyl bonded to phosphorus (X_nAA'X'_n structure),⁴¹ and a triplet for the methyl bonded to osmium in ¹H NMR spectrum). The structure of complex 9 is also observed for the corresponding Fe^{1a,b} and Ru² complexes.

In a summary of the results of the Experimental Section, the following observations can be made: (a) The cation [Os(CO)₃(PMe₃)₂CH₃]BPh₄ reacts with I₂, CH₂I₂ or, CHCl₃, giving as the first product the complexes Os(CO)₂(PMe₃)₂CH₃X. Further reaction gives Os(CO)₂(PMe₃)₂X₂ by cleavage of the Os-CH₃ bond. (b) The complex [Os(CO)₃(PMe₃)₂CH₃]I (5) reacts at 60 °C in THF giving Os(CO)₂(PMe₃)₂CH₃I (3). If the reaction is carried out in chloride-containing solvents, the formation of nearly equimolar amount of the corresponding chloride complex (10) is observed. (c) In order for reaction b to occur, the iodide ion is required; the reaction is not observed if the anion is BPh₄⁻. (d) During the oxidative addition of Os(CO)₃L₂ with CH₃I, the ionic complex 5 precipitates from the solution. In CH₃I solution, the formation of many complexes (up to 10) is observed. Although the structure of these complexes was not ascertained, IR and NMR information indicates a general structure Os(CO)₂L₂XY (X, Y = I, CH₃, H, or other σ ligands).

Observation a is explained by halogenolysis of the complexes.⁴² Observations b-d cannot be explained only by reaction of the cation, since the reaction should occur also with complex 4 containing BPh₄⁻. The observed behavior indicates the importance of the I⁻ anion in order for the reaction observed in b to occur.

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Moreover the formation of a large number of complexes (point d) suggests a radical mechanism. A possibility is the formation, during the oxidative addition of Os(CO)₃L₂ with CH₃I, of a caged radical pair,^{43,44} [Os(CO)₃(PMe₃)₂CH₃·, I·]. The caged radical pair can diffuse in the solution, and the two radicals obtained abstract H·, CH₃·, and I· from the solvent and give Os(CO)₂L₂-XY complexes.⁴³ Simultaneously, the caged radical pair can give by a further electron transfer⁴⁵ the ionic complex [Os(CO)₃(PMe₃)₂CH₃]I, which separates by precipitation. In the presence of chloride-containing solvents the intermediate radicals can extract Cl· to give the chloride derivatives. Although a mechanism of this type was not observed previously, its single steps (caged radicals pair⁴⁴ with further electron transfer to give ionic derivatives⁴⁵) were observed.

The same reaction is also observed with the monosubstituted Os(CO)₄L, for which the oxidative addition is slower, in agreement with a lower electronic density in the metal for the monosubstituted complex.⁴⁶

The inclination of osmium complexes to react by radical mechanism has been ascertained in the literature.^{14,47} More studies are necessary to support this reaction mechanism.

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Supplementary Material Available: A paragraph of text describing the structure solution, a summary of crystal data and intensity collection for complexes 14 and 9 (Table SI), unrefined hydrogen atom coordinates for complex 14 (Table SII), thermal parameters for complexes 14 (Table SIII) and 9 (Table SIV), and bond distances and angles for complexes 14 (Table SV) and 9 (Table SVI) (7 pages). Ordering information is given on any current masthead page.

- (43) Tyler, D. R. *Progress in Inorganic Chemistry*; Wiley Interscience: New York, 1988; Vol. 36, pp 125-194.
 (44) Klabunde, K. J.; Roberts, J. S. *J. Organomet. Chem.* **1977**, *137*, 113-130.
 (45) Wine, P. H.; Mauldin, R. L.; Thorn, R. P. *J. Phys. Chem.* **1988**, *92*, 1156-1162.
 (46) Collmann, J. R.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 279-354.
 (47) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55-66.