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New Hydride, Alkyl, Aryl, Halide, Alkene, Alkyne, Acetylide, and Vinylidene Members of the $(\eta^5\text{-}C_5Me_5)Os(CO)(L)X$ Family. Crystal and Molecular Structures of $[(\eta^5\text{-}C_5Me_5)Os(CO)_3][BF_4]$ and $[(\eta^5\text{-}C_5Me_5)Os(CO)(PPh_3)(=C=C(t\text{-}Bu)H)][BF_4]$

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The photochemical reaction of $Cp^*Os(CO)_2I$ (1, $Cp^* = \eta^5\text{-}C_5Me_5$) with PMe_3 or PPh_3 under CO pressure gave substitution of I^- by PR_3 to form the salts $[Cp^*Os(CO)_2(PR_3)][I]$. Reaction of these salts with Me_3NO afforded the neutral complexes $Cp^*Os(CO)(PR_3)I$ (7, L = PMe_3, and 8, L = PPh_3) in good yield. The new alkyl complexes $Cp^*Os(CO)LR$ (L = CO, R = Me, 3; L = CO, R = Bu, 2; L = PMe_3, R = Me, 11) derived from reaction of 1 and 7 with the appropriate RLi reagent. Complex 11 was also obtained directly from $[Cp^*Os(CO)_2(PMe_3)]I$ by $NaBH_4$ reduction of a coordinated CO. The phenyl complex $Cp^*Os(CO)_2Ph$ was obtained by sequential treatment of 1 with $AgBF_4$ and PhLi or by photoassisted C–H activation of benzene with 3. Irradiation of $Cp^*Os(CO)_2CH_3$ in the presence of $CH_2{=}CH_2$ gave the new ethylene–methyl complex $Cp^*Os(CO)C_2H_4)(CH_3)$. Rotation of the C_2H_4 ligand in this complex was characterized by a variable-temperature NMR study. Treatment of $Cp^*Os(CO)(PPh_3)I$ with $AgBF_4$ followed by diphenylacetylene gave the η^2-alkyne complex $[Cp^*Os(CO)(PPh_3)(PhC{\equiv}CPh)][BF_4]$. When terminal alkynes were used in this latter reaction, the stable vinylidene complexes $[Cp^*Os(CO)(PPh_3)(=C=CHR)]^+BF_4$ (R = t-Bu, Ph) were obtained. The structure of $[Cp^*Os(CO)(PPh_3)(=C=C(t\text{-}Bu)H)][BF_4]$ (14) was confirmed by an X-ray diffraction study: $P\bar{1}$ with $a = 10.444$ (2) Å, $b = 12.091$ (2) Å, $c = 14.793$ (4) Å, $\alpha = 97.49$ (2)°, $\beta = 109.28$ (2)°, $\gamma = 101.64$ (2)°, $V = 1687.4$ (7) Å^3, $Z = 2$, $R = 3.42\%$, $R_w = 3.58\%$ for the 5595 reflections with $F_o \geqslant 2.5\sigma(F_o)$. In contrast, treatment of 1 with $AgBF_4$ followed by $HC{\equiv}C\text{-}t\text{-}Bu$ or other terminal alkynes gave a mixture of $[Cp^*Os(CO)_3][BF_4]$ (17) and another unidentified organometallic complex. Complex 17 was crystallographically characterized: $Pbcm$ with $a = 10.396$ (2) Å, $b = 13.008$ (3) Å, $c = 12.123$ (2) Å, $V = 1639.4$ (6) Å^3, $Z = 4$, $R = 5.44\%$, $R_w = 5.65\%$ for the 1521 reflections with $F_o \geqslant 3\sigma(F_o)$.

One of the most extensively investigated series of organometallic complexes are those that contain the CpFe(CO)(L) moiety. A large variety of organic ligands have been attached to the iron center in these derivatives, including alkyl,[1] acyl,[2] carbene,[3] vinylidene,[4] alkyne,[5] alkynyl,[6] alkene,[7] and vinyl[8] ligands. Many such complexes have found important synthetic applications, and noteworthy examples include the stereospecific cyclopropanation of olefins[3] and nucleophilic alkylation of coordinated acyls,[2] alkynes,[9] and vinylidenes.[10] Applications also extend into natural product syntheses with the recent preparations of 3-carbomethoxycarbapenam[11] and hydroazulene.[12]

In contrast to the chemistry of the CpFe(CO)(L)X complexes, the derivative chemistry of the corresponding ruthenium and osmium complexes has been little developed. This is in part due to the relative expense of the heavier elements but also is apparently a reflection of the lack of good synthetic methods for the desired precursor complexes. We have been particularly interested in $Cp^*Os(CO)(PMe_3)R$ ($Cp^* = C_5Me_5$) derivatives because of their potentially interesting photochemical properties. These complexes resemble the $Cp^*M(CO)L$ and $Cp^*Ir(H)_2L$ (M = Rh, Ir) complexes which have been demonstrated to activate carbon–hydrogen bonds in saturated hydrocarbons.[13,14] The related $Cp^*Os(CO)(PMe_3)R$ complexes could undergo similar reactions, and they have the added advantage of incorporating an additional alkyl or hydride ligand in the starting complex to possibly allow unique functionalization of the activated hydrocarbon.

Suitable synthetic procedures for the desired $Cp^*Os(CO)(L)X$ complexes were not available when we began these studies, and our first task was to develop them. Reported herein are the preparation and chemistry of a family of such complexes. Photochemical studies of these complexes will be separately described. At the beginning of these studies the only known Cp^*Os complexes were $Cp^*Os(CO)_2X$ (X = Br, I, H, and C_7H_7),[15] [Cp*Os-

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[1] Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 4, p 331.

[2] For a recent example see: Aktogu, N.; Felkin, H.; Baird, G. J.; Davies, S. G.; Watts, O. *J. Organomet. Chem.* **1984**, *262*, 49.

[3] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[4] Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628.

[5] Reger, D. L.; Coleman, C. J.; McElligot, P. J. *J. Organomet. Chem.* **1979**, *171*, 73.

[6] Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404.

[7] Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 4, p 377.

[8] Reger, D. L.; McElligot, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923.

[9] Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligot, P. J. *Organometallics* **1984**, *3*, 134.

[10] Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876.

[11] Berryhill, S. R.; Price, T.; Rosenblum, M. *J. Org. Chem.* **1983**, *48*, 158.

[12] Watkins, J. C.; Rosenblum, M. *Tetrahedron Lett.* **1984**, *25*, 2097.

[13] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

[14] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620.

[15] Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095.

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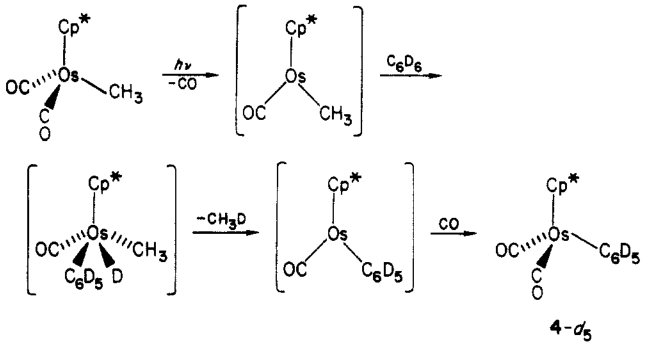
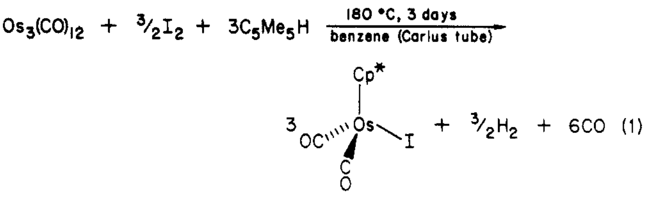
Scheme I



(CO)$_2$L]X (L = CO, H$_2$O, THF, C$_7$H$_8$; X = BF$_4^-$ or PF$_6^-$),[15] Cp*Os(CO)H$_3$,[16] [Cp*Os(CO)(μ-H)]$_2$,[16] Cp*$_2$Os$_2$(CO)(μ-H)$_2$,[16] and Cp*Os(CO)$_2$(CH$_2$OH),[17] but there were no known PR$_3$-substituted derivatives within the Cp*Os family.

Results and Discussion

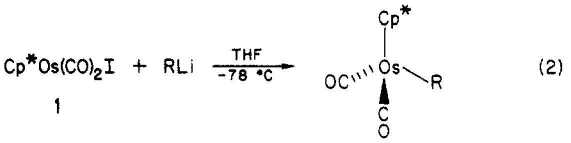
The syntheses which have been developed for the new Cp*Os complexes are described in the following paragraphs. The new complexes have been characterized by elemental analyses and mass, IR, ^{1}H NMR, and ^{31}P NMR spectra. Complete characterization details are given in the Experimental Section; only particularly significant data will be cited in the following paragraphs. The starting complex for all the syntheses described herein is Cp*Os(CO)$_2$I which we have found can be formed in 88% yield in a one-pot synthesis directly from Os$_3$(CO)$_{12}$ (eq 1).[18]



$$Os_3(CO)_{12} + {}^3/_2 I_2 + 3C_5Me_5H \xrightarrow[\text{benzene (Carius tube)}]{180\ °C,\ 3\ \text{days}} 3\,Cp^*Os(CO)_2I + {}^3/_2 H_2 + 6CO \quad (1)$$

1 (88%)

Synthesis of Cp*Os(CO)$_2$R Complexes. Treatment of complex 1 with MeLi and n-BuLi at low temperature gave the corresponding alkyl derivatives 2 and 3 in good yields (eq 2). The reaction temperature is important in these syntheses, and, for example, addition of n-BuLi at ambient temperature instead of −78 °C gave an approximately 1:1 mixture of the n-butyl complex 3 and the known[15] hydride complex Cp*Os(CO)$_2$H, the latter apparently formed via a β-hydride elimination process. Complexes 2 and 3 are white crystalline solids which are air-stable in the solid state and also in solution for several days.

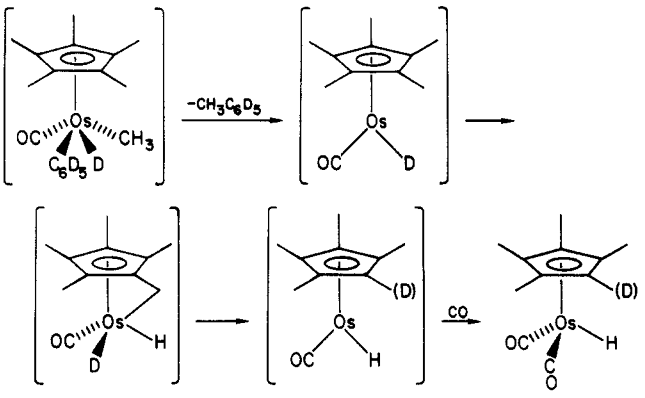


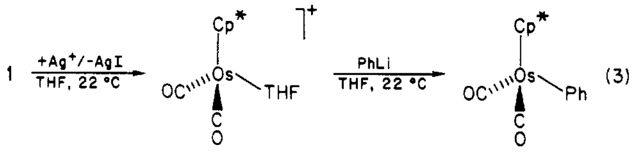
$$Cp^*Os(CO)_2I + RLi \xrightarrow[-78\ °C]{THF} Cp^*Os(CO)_2R \quad (2)$$

2, R = n-Bu (74%)
3, R = Me (61%)

In an attempt to prepare Cp*Os(CO)$_2$Ph by an analogous procedure, PhLi was added to 1 at −78 °C, but this gave instead a presently unidentified compound with a single strong ν(CO) band at 1891 cm^{-1} (THF). However, the phenyl derivative was obtained in good yield by addition of PhLi to [Cp*Os(CO)$_2$(THF)]$^+$,[15] prepared by addition of AgPF$_6$ to 1 in THF (eq 3).

Scheme II

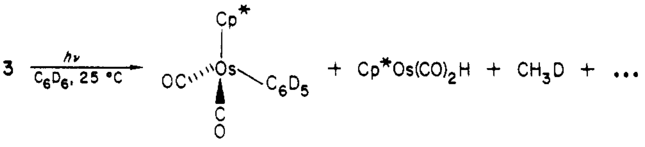




$$1 \xrightarrow[\text{THF, 22 °C}]{+Ag^+/-AgI} [Cp^*Os(CO)_2(THF)]^+ \xrightarrow[\text{THF, 22 °C}]{PhLi} Cp^*Os(CO)_2Ph \quad (3)$$

4 (63%)

Preparation of 4-d_5 via Photoinduced Arene C–H Bond Activation. The phenyl complex 4-d_5 was also obtained by irradiating complex 3 in C$_6$D$_6$ solution (eq 4).



$$3 \xrightarrow[C_6D_6,\ 25\ °C]{h\nu} Cp^*Os(CO)_2C_6D_5 + Cp^*Os(CO)_2H + CH_3D + \ldots \quad (4)$$

4-d_5 (17%)

Although isolated in modest yield, complex 4-d_5 was clearly the predominant photoproduct over the course of this reaction. The spectroscopic properties of 4-d_5 were identical with those of 4 except for the absence of phenyl resonances in the ^{1}H NMR spectrum, and a mass peak of 465 amu was observed for its parent ion. The formation of CH$_3$D was inferred from its characteristic 1:1:1 triplet at 0.14 ppm, and the known hydride complex Cp*Os(CO)$_2$H was identified by its characteristic hydride resonance at δ −13.47.[15] Another hydride complex with a resonance at δ −10.0 was evident, but this does not correspond to any of the known compounds. We have thus far been unable to isolate and characterize this latter species. Prolonged irradiation also gave small amounts of yet unidentified higher nuclearity clusters (M$^+$ 929, 684).

The most probable mechanism for reaction 4 involves activation of C–D bonds of the C$_6$D$_6$ solvent as outlined in Scheme I. It invokes extrusion of CO in the primary photochemical step followed by oxidative addition of one of the C–D bonds of C$_6$D$_6$ to the coordinatively unsaturated Os(II) center, reductive elimination of CH$_3$D, and finally scavenging of CO to give the observed products. The formation of Cp*Os(CO)$_2$H may result from reductive coupling of methyl and phenyl ligands in the proposed intermediate Cp*Os(CO)(H)(CH$_3$)(C$_6$D$_5$) to give toluene-d_5, followed by intramolecular scrambling of the label and CO capture of the resulting hydride complex (Scheme II).

Synthesis of [(η^5-C$_5$Me$_5$)Os(CO)$_2$L]I via Photoinduced Os–I Bond Cleavage. We initially wished to prepare Cp*Os(CO)(L)I with the expectation that nu-

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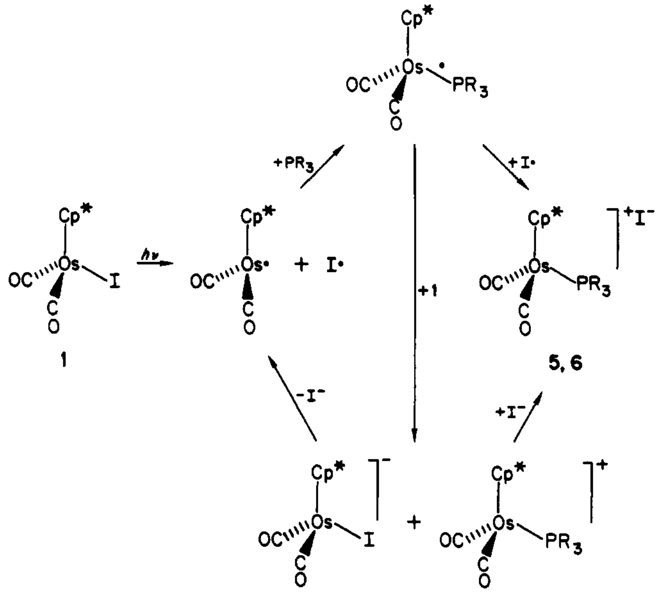
[16] Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722.

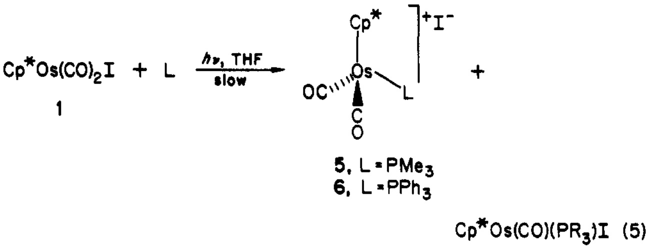
[17] May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49.

[18] See also: Rosenberg, S.; Herlinger, A. W.; Mahoney, W. S.; Geoffroy, G. L. *Inorg. Synth.*, submitted for publication.

Scheme III



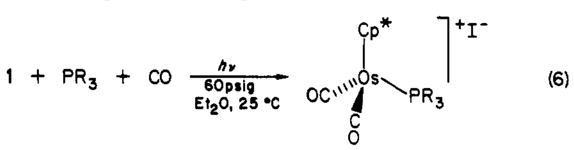
cleophilic displacement of the I⁻ ligand would lead to interesting Cp*Os(CO)(L)R complexes. The most logical approach to phosphine-substituted Cp*Os(CO)(L)I derivatives from 1 would be to photosubstitute the desired phosphine ligand for CO. However, this reaction does not readily occur. Instead, irradiation of 1 in the presence of excess PMe_3 or PPh_3 gives mainly unreacted 1 along with the salts $[Cp^*Os(CO)_2(PR_3)]I$ and a trace of the desired $Cp^*Os(CO)(PR_3)I$ complex. (eq 5). The yields of the salts



1

5, L = PMe₃
6, L = PPh₃

can be optimized by irradiating Et_2O solutions of 1 under 60–80 psig of CO in the presence of excess phosphine (eq 6). With PMe_3, the salt 5 precipitates from solution as

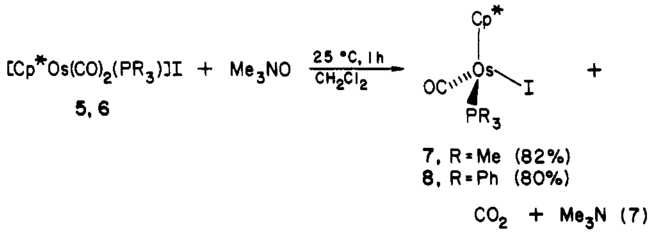


5 (92%)
6 (38%)

an off-white, air-stable powder, and the reaction is essentially complete within 15 min. The reaction with PPh_3 is much slower and requires several days for completion. As obtained, these salts are sufficiently pure for subsequent use.

These syntheses involve photosubstitution of PR_3 ligands for I⁻, but not for CO. There is little organometallic precedent for such a photosubstitution process. Products similar to 5 and 6 have been obtained in related $CpFe(CO)_2X$ systems,[19-21] but examples of photoinduced metal–halide bond cleavage in organometallic chemistry are rare.[22,23] The most reasonable mechanisms are (1) photodissociation of I⁻ followed by PR_3 addition and (2) the free radical chain path outlined in Scheme III. The latter is similar to the radical chain path proposed by Tyler and co-workers[24] for the photochemical disproportionation of $(MeCp)_2Mo_2(CO)_6$ in the presence of phosphine ligands and is consistent with the observed dependence of the rate of formation of the $[Cp^*Os(CO)_2L]I$ complexes on the nature of the entering ligand, PMe_3 >> PPh_3 >> CO.

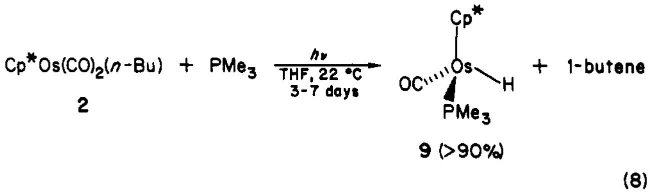
Synthesis of Cp*Os(CO)(L)I via Decarbonylation of [Cp*Os(CO)$_2$L]I. The phosphine-substituted neutral $Cp^*Os(CO)(PR_3)I$ complexes readily form from the salts 5 and 6 by Me_3NO- or PhIO-induced decarbonylation (eq 7). Complexes 7 and 8 are yellow-orange solids which are air-stable both in the solid state and in solution.



5, 6

7, R = Me (82%)
8, R = Ph (80%)

Synthesis of Cp*Os(CO)(PMe$_3$)H by Photolysis of Cp*Os(CO)$_2$Bu + PMe$_3$ Solutions. The hydride complex 9 readily forms upon photolysis of the *n*-butyl complex 2 in the presence of PMe_3 (eq 8). However, the



2

9 (>90%)

reaction is slow but it eventually goes to completion with 9 formed in >90% yield by ^1H NMR spectroscopy. However, if excess PMe_3 is used, the product is usually contaminated with small amounts (~5%) of the disubstituted complex $Cp^*Os(PMe_3)_2H$. These two complexes cannot be readily separated as both rapidly decompose upon chromatography, although flash chromatography on Al_2O_3 gave small quantities of essentially pure 9 as a pale yellow oil. Complex 9 was characterized by converting it to the bromo complex 10 (eq 9), which was fully characterized. The overall yield of 10 based on the amount of

$$\underset{\mathbf{9}}{\mathrm{Cp^*Os(CO)(PMe_3)H}} \xrightarrow[\mathrm{C_6H_6,\ room\ temp,}\ 5\ \mathrm{min}]{\mathrm{CHBr_3}} \underset{\mathbf{10}\ (>90\%)}{\mathrm{Cp^*Os(CO)(PMe_3)Br}} \quad (9)$$

$Cp^*Os(CO)_2Bu$ used to make 9 was 63%. If a phosphine ligand is not present during the photolysis of 2, the reaction gives quantitative yield of the known hydride complex $Cp^*Os(CO)_2H$[15] (eq 10).

$$\underset{\mathbf{2}}{\mathrm{Cp^*Os(CO)_2Bu}} \xrightarrow[\mathrm{N_2,\ THF}]{h\nu} \mathrm{Cp^*Os(CO)_2H} + \text{1-butene} \quad (10)$$

The synthesis of 9 presumably proceeds via photoinduced CO loss from 2, followed by β-hydride elimination to give a butene–hydride complex which then undergoes

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(19) Treichel, P. M.; Shubkin, R. L; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

(20) King, R. B.; Houk, L. W.; Pannell, K. H. *Inorg. Chem.* **1969**, *8*, 1042.

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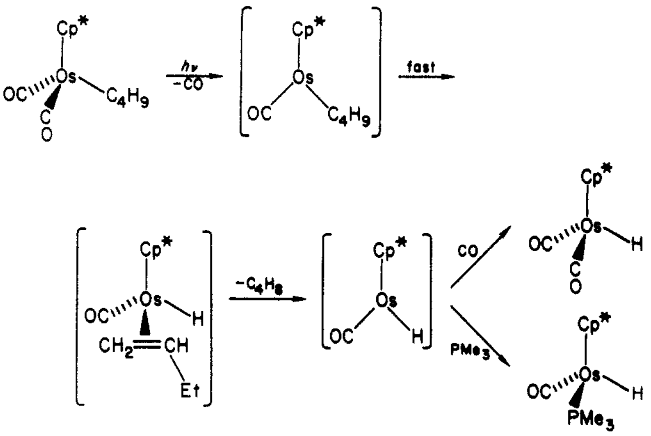
(22) Ali, L. H.; Cox, A.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1475.

(23) Allen, D. M.; Cox, A.; Kemp, T. J.; Ali, L. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1899.

(24) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066.

Scheme IV

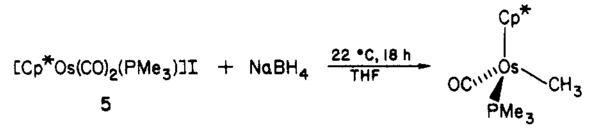


substitution of PMe_3 for butene (Scheme IV). If PMe_3 is not present, 1-butene is displaced by the initial photoreleased CO to give $Cp^*Os(CO)_2H$. Such reaction has considerable precedence in the photochemical reactions of $CpM(CO)_2R$ (M = Fe, Ru) complexes which have been clearly demonstrated to lose CO upon irradiation followed by β-hydride elimination where possible.[25]

Synthesis of $Cp^*Os(CO)(PMe_3)Me$ (11) via BH_4^- Reduction of a CO Ligand in 5. The title complex 11 can be obtained by iodide displacement from 7 with MeLi (eq 11). However, the most direct route to 11, which

$$\underset{7}{\text{Cp*Os(CO)(PMe}_3\text{)I}} + \text{MeLi} \xrightarrow[\text{THF}]{-78\ ^\circ\text{C}} \underset{11}{\text{Cp*Os(CO)(PMe}_3\text{)Me}} + \text{LiI} \quad (11)$$

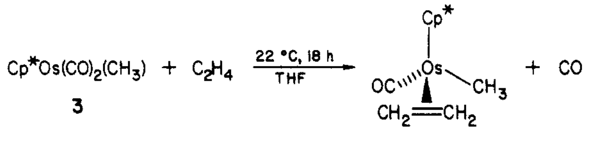
avoids isolation of the intermediate 7, is $NaBH_4$ reduction of a coordinated carbonyl in 5 (eq 12). This method has precedent in the recently reported reduction of $[Cp^*Fe(CO)_3]^+$ to $Cp^*Fe(CO)_2CH_3$ as well as in the BH_4^- reduction of other cationic carbonyl complexes.[26]



(12)

11 (93%)

Synthesis and Fluxional Properties of $Cp^*Os(CO)(C_2H_4)(CH_3)$. The methyl complex 3 is photosensitive and loses CO when irradiated under a flow of ethylene to cleanly give the ethylene–methyl complex 12 which can be isolated as a white, air-stable solid (eq 13).



(13)

12 (49%)

The yield of 12 increased with shorter irradiation times and a faster flow of ethylene. Slow decomposition occurred at longer irradiation times as evidenced by a darkening of the solution. Also, when pure 12 was allowed to stand in solution, it slowly decomposed back to 3, presumably by loss of ethylene and displacement of C_2H_4 by CO released from small amounts of 12 which undergo other decomposition paths.

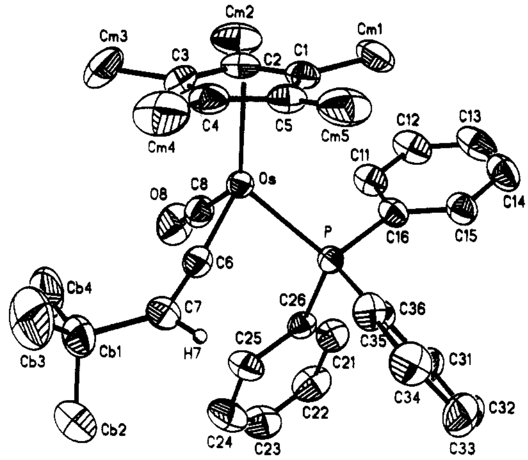
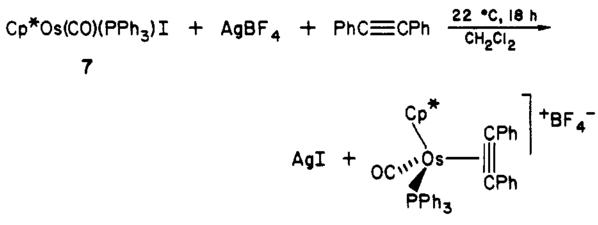


Figure 1. An ORTEP drawing of $[Cp^*Os(CO)(PPh_3)({=}C{=}C(t\text{-}Bu)H)]BF_4$ (14). Thermal ellipsoids are drawn at the 50% probability level.

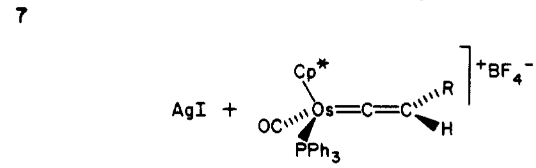
The ^1H NMR spectrum of 12 at −80 °C shows four distinct resonances at 2.19, 1.42, 1.29, and 0.88 ppm due to the four inequivalent ethylene hydrogens. The low-field signal of this ABCD pattern appears as a doublet of doublets with J_{cis}, J_{trans} = 8 and 11 Hz. The upfield resonances are less well-resolved, appearing as pseudotriplets with $J_{cis,trans}$ = 10 Hz. These resonances coalesce into the base line when the sample is warmed to −35 °C. From these data, an activation energy of 47 kJ/mol for ethylene rotation can be estimated, which is larger than those reported for the analogous $CpM(CO)(C_2H_4)(CH_3)$ (M = Fe, Ru) complexes (41.3 and 34.6 kJ/mol, respectively).[27] The higher barrier to olefin rotation in $Cp^*Os(CO)(C_2H_4)(CH_3)$ may be attributed to the greater steric bulk of the permethylated Cp ring and to increased Os–(C_2H_4) back-electron donation due to the greater electron-releasing ability of Cp*.

Synthesis of η^2-Alkyne and Vinylidene Complexes. Treatment of 7 with $AgBF_4$ in the presence of PhC≡CPh gave the orange η^2-alkyne complex 13 in excellent yield (eq 14). However, similar reactions with the terminal alkynes PhC≡CH and t-BuC≡CH gave instead the vinylidene complexes 14 and 15 (eq 15). Complex 14 has been fully characterized by an X-ray diffraction study, the results of



(14)

13 (89%)



(15)

14, R=t-Bu (95%)
15, R=Ph (>90%, by IR)

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[25] (a) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* 1982, *1*, 602. (b) Pourreau, D. B.; Geoffroy, G. L. G. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: Orlando, 1985; Vol. 24, p 249.

[26] Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* 1983, 430 and references therein.

[27] Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* 1985, 1365.

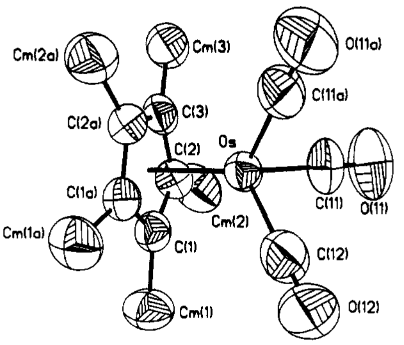
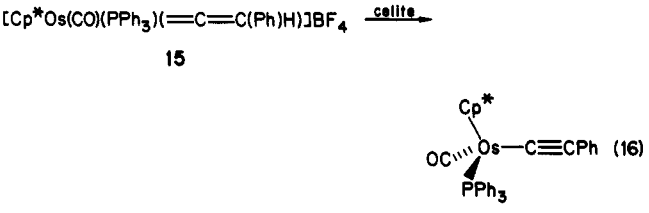


Figure 2. An ORTEP drawing of [Cp*Os(CO)$_3$]BF$_4$ (17). Thermal ellipsoids are drawn at the 40% probability level.

which are shown in Figure 1; see below. Each of these complexes showed characteristic vinylidene ν(C=C) stretches in the 1650–1700 cm^{-1} region and characteristic ^{13}C NMR chemical shifts for the vinylidene α- and β-carbons. Rearrangement of terminal alkynes to vinylidene ligands is a well-precedented reaction.[28]

The vinylidene complex 15 is easily deprotonated to give the acetylide complex 16 (eq 16). This reaction occurs



$$[Cp^*Os(CO)(PPh_3)(=C=C(Ph)H)]BF_4 \xrightarrow{\text{celite}} Cp^*(OC)(PPh_3)Os-C\equiv CPh \quad (16)$$

15

16

simply upon filtering solutions of the vinylidene complex through celite in air. In contrast, the t-BuC≡CH-derived vinylidene complex 14 survives this workup and is recovered unchanged. The acetylide complex 16 shows a characteristic ν(C≡C) stretch at 2095 cm^{-1}.

In contrast to the above reactions, treatment of Cp*Os(CO)$_2$I with AgBF$_4$ in the presence of terminal alkynes did not yield a vinylidene complex but instead a mixture of the known salt [Cp*Os(CO)$_3$][BF$_4$] (17) and a yet unidentified organometallic compound. Complex 17 has been fully defined by an X-ray diffraction study (Figure 2); see below.

Table I. Selected Bond Distances and Angles for [Cp*Os(CO)(PPh$_3$)(=C=C(t-Bu)H)]BF$_4$ (14)

	Bond Distances (Å)		
Os-P	2.353 (1)	Os-C(6)	1.879 (6)
Os-CTR[a]	1.943 (6)	C(8)-O(8)	1.138 (7)
Os-C(8)	1.879 (5)	C(6)-C(7)	1.282 (10)
C(7)-H(7)	0.898 (62)	C(7)-Cb(1)	1.557 (12)
	Bond Angles (deg)		
P-Os-CTR[a]	129.5 (2)	C(6)-Os-C(8)	94.0 (3)
C(6)-Os-CTR	122.1 (2)	C(6)-C(7)-Cb(1)	128.5 (7)
C(8)-Os-CTR	124.2 (2)	Os-C(6)-C(7)	175.0 (5)
P-Os-C(6)	90.7 (2)	Os-C(8)-O(8)	177.2 (6)
P-Os-C(8)	85.4 (2)	Cb(1)-C(7)-H(7)	127 (4)
C(6)-C(7)-H(7)	104 (4)	C(6)-C(7)-Cb(1)	128.5 (7)

[a] CTR = centroid of Cp* ring.

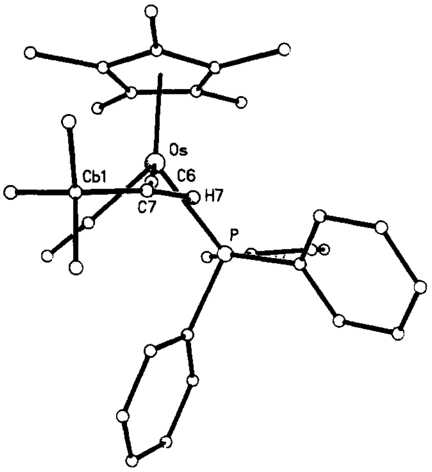


Figure 3. View of [Cp*Os(CO)(PPh$_3$)(=C=C(t-Bu)H]BF$_4$ (14) showing the orientation of the Cb(1)-C(7)-H(7) plane.

Crystal and Molecular Structure of [Cp*Os(CO)(PPh$_3$)(=C=C(t-Bu)H)]BF$_4$ (14). An ORTEP drawing of complex 14 is shown in Figure 1. Selected bond distances and angles are listed in Table I. Of special interest are the structural features relevant to the vinylidene ligand. The latter is essentially linear with an Os–C6–C7 angle of 175.0° and has near perfect trigonal-planar geometry about the β-carbon C7. Also, the maximum deviation from planarity for the entire Os=C6=C7-(Cb1)H7 unit is 0.0121 Å for C7. The structures of [CpRe(NO)(PPh$_3$)(=CHR)]$^+$ complexes[29] and related calculations[29,30] suggest that the α-carbon substituents in carbene complexes should align themselves in a plane that contains the better π-acceptor ligand and the metal. Since the substituents on the β-carbon of a vinylidene ligand should be rotated 90° from those on the α-carbon of a carbene ligand, they should then align themselves with the *worst* π-acceptor ligand, in this case PPh$_3$. However, as Figure 3 illustrates, the plane of the vinylidene β-carbon and its substituents is *not aligned with any metal ligand plane of the molecule.* We suspect this is due primarily to steric repulsion between the vinylidene *tert*-butyl group and the Cp* ring.

Crystal and Molecular Structure of [Cp*Os(CO)$_3$]BF$_4$ (17). An ORTEP drawing of complex 17 is shown in Figure 2. Selected bond distances and angles are listed in Table II. The structure is unexceptional but can be compared to the established structures of CpMn(CO)$_3$,[31] CpRe(CO)$_3$,[32] and [CpFe(CO)$_3$]PF$_6$.[33] Several theoretical studies of CpM(CO)$_3$ complexes have addressed the relative energetics of the staggered (A) and eclipsed (B) conformations of the Cp ring and the CO ligands, as well as the effect of these conformations on the bonding within the Cp ring.[34] The calculations indicate little energy difference between conformations A and B, with a small barrier (0.002 kcal/mol) to rotation of the Cp ring.[34a] Thus the conformation in the solid state is likely dictated by

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Table II. Selected Bond Distances and Angles for $[Cp^*Os(CO)_3]BF_4$ (17)

	Bond Distances (Å)		
Os–CTR[a]	1.96 (2)	C(11)–O(11)	1.14 (2)
Os–C(11)	1.95 (2)	C(12)–O(12)	1.15 (2)[b]
Os–C(12)	1.96 (2)[b]	C(2)–C(3)	1.40 (2)
C(1)–C(2)	1.38 (2)	C(3)–C(2a)	1.40 (2)
C(1a)–C(2a)	1.38 (2)	C(1)–C(1a)	1.44 (3)
	Bond Angles (deg)		
CTR[a]–Os–C(11)	123.0 (7)	C(11)–Os–C(12)	93.0 (7)
CTR–Os–C(12)	123.6 (7)	Os–C(11)–O(11)	179 (1)
C(11)–Os–C(11a)	92.7 (10)	Os–C(12)–O(12)	179 (2)
C(12)–Os–C(11a)	93.0 (7)		

[a] CTR = centroid of Cp* ring. [b] These bond distances constrained (see text).

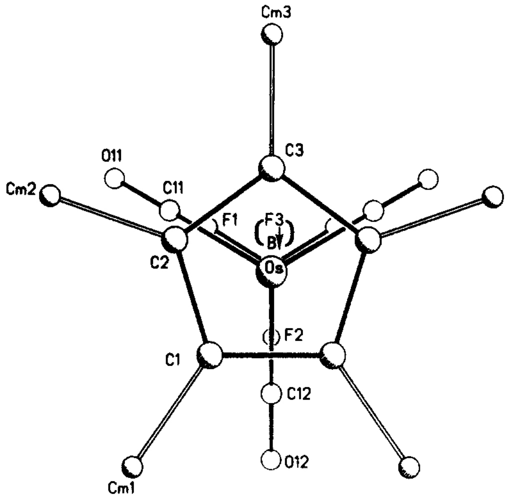

Figure 4. View of $[Cp^*Os(CO)_3]BF_4$ (17) along the Cp* centroid–Os axis showing the staggered conformation of the carbonyls and the three basal fluorine atoms of the BF_4^- counterion.

crystal packing forces. Figure 4 shows that complex 17 adopts a staggered conformation in the solid state, as do $CpMn(CO)_3$[31] and $CpRe(CO)_3$,[32] whereas $[CpFe(CO)_3]^+$ is eclipsed.[33] The effect of permethylation of the Cp ring as in 17 has not been previously addressed in this particular regard, and it is possible that the conformation of 17 is in fact dictated by *intramolecular* steric and/or electronic forces.

Other theoretical results indicate that C–C bonds within the Cp ring that are eclipsed by carbonyls should be longer than uneclipsed bonds.[34c] Distortions in accord with this theory were noted in the crystal structures of $CpMn(CO)_3$[31] and $CpRe(CO)_3$[32] as well as in the related $Cp^*Co(CO)_2$ complex.[35] However, the bond length variation of $[CpFe(CO)_3]^+$ is opposite to that expected,[33] but this has been attributed to an effect of the PF_6^- counterion located in proximity to the Cp ring.[34c] The C–C bond lengths of 17 are identical within the uncertainties given in Table II, but the trend is in the direction predicted by the theoretical results. Note that in 17, the BF_4^- counterion is located opposite the ring along the Cp* centroid–Os axis with no contact less than 3.5 Å and seems to have no effect on the ring C–C distances (Figure 5).

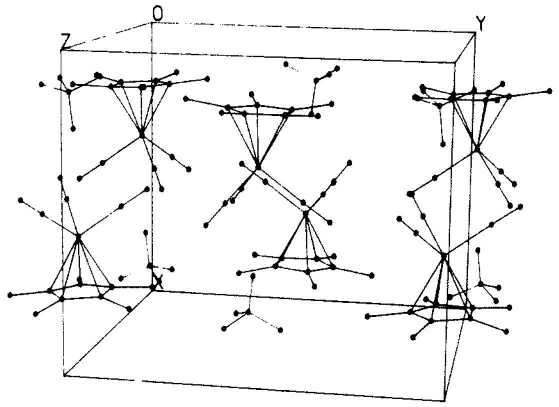

Figure 5. View of the lattice cell of $[Cp^*Os(CO)_3]BF_4$ (17) showing the location of the BF_4^- counterion.

Experimental Section

General Data. PMe_3 (Strem), PPh_3 (Alfa), $AgPF_6$, $AgBF_4$, PhLi, MeLi, *n*-BuLi, Me_3NO, HC≡C-*t*-Bu, HC≡CPh, PhC≡CPh (Aldrich), C_2H_4, and CO (Linde) were used as received without further purification. The terminal alkynes were distilled from CaH_2 under N_2 and stored under N_2. Unless otherwise specified, all operations were performed under a prepurified N_2 atmosphere using rigorously dried and deoxygenated solvents and standard Schlenk techniques. The spectroscopic instruments employed in this research have been previously described.[36] Field desorption (FD) mass spectra were recorded by Guy Steinmetz and Robert Hale at the Tennessee Eastman Co., Kingsport, TN. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY.

Photochemical experiments performed under a flow of gas were conducted in a fume hood with broad-band irradiation from a 100-W Blak Ray B100 A lamp filtered through Pyrex ($\lambda > 300$ nm) or a Pyrex-filtered 450-W Hanovia medium-pressure Hg vapor lamp.

Preparation of (η^5-C_5Me_5)$Os(CO)_2I$ (1).[18] A 300-mL Carius tube was charged with $Os_3(CO)_{12}$ (1.0 g, 1.1 mmol), I_2 (0.42 g, 1.1 mol), and 50 mL of benzene. The purple suspension was degassed by one freeze–pump–thaw cycle and heated under vacuum at 175–180 °C for 24 h. The resulting yellow solution was treated with C_5Me_5H (0.50 m, 0.435 g, 3.20 mmol), degassed by one freeze–pump–thaw cycle, and heated 3 days at 165 °C. The cloudy yellow solution was filtered through Celite in air and evaporated to dryness to give a yellow-orange solid. Recrystallization from CH_2Cl_2/hexanes gave 1.58 g (89%) of $Cp^*Os(CO)_2I$. IR (hexanes): 2020 s, 1968 vs cm^{-1} (lit.[15] 2020 s, 1968 vs cm^{-1}).

Preparation of (η^5-C_5Me_5)$Os(CO)_2$(*n*-Bu) (2). Tetrahydrofuran (THF, 60 mL) was vacuum transferred into a 100-mL Schlenk flask containing $Cp^*Os(CO)_2I$ (1.0 g, 1.97 mmol), and the yellow solution was cooled to −78 °C in a dry ice/2-propanol bath. A 1.1 equiv of *n*-BuLi (1.5 M solution in hexanes) was added dropwise over a 5-min period after which the IR spectrum showed that most of the starting $Cp^*Os(CO)_2I$ was consumed. The resulting brownish yellow solution was treated with 5 mL of saturated aqueous NH_4Cl followed by 2.0 g of Kieselgel and evaporated to dryness in vacuo. The residue was added to a 2 × 20 cm column of silica gel (Kieselgel; Merck) and eluted with pentane in air. The first 400 mL of eluent contained only $Cp^*Os(CO)_2$(*n*-Bu) (2) and this was followed by $Cp^*Os(CO)_2H$ (<1%) and 1, respectively. Evaporation of the solvent gave 636 mg (74%) of analytically pure 2 as a colorless, low-melting solid (mp 51.5–52.5 °C). Anal. Calcd for $C_{16}H_{24}O_2Os$: C, 43.82; H, 5.52. Found: C, 43.89; H, 5.77. IR (pentane): ν_{CO} (rel abs) 1989 (50), 1931 (100) cm^{-1}. MS: *m/e* 440 (M^+), 411 (M^+ − CO), 383 (M^+ − 2CO, M^+ − Bu), 352 (M^+ − Bu − CO), 320 (M^+ − Bu − 2CO). ^1H NMR (C_6D_6): δ 2.08 (p, *J* = 8.5 Hz, $OsCH_2CH_2CH_2CH_3$), 1.58 (s, C_5Me_5), 1.60–1.39 (m, $OsCH_2CH_2CH_2CH_3$), 1.05 (t, *J* = 7 Hz, $OsCH_2CH_2CH_2CH_3$). ^1H NMR (C_6D_{12}): δ 1.94 (s, C_5Me_5), 1.73–1.65 (m, $OsCH_2CH_2CH_2CH_3$), 1.32–1.17 (m, $OsCH_2CH_2CH_2CH_3$), 0.89 (t, *J* = 7 Hz, $OsCH_2CH_2CH_2CH_3$).

Preparation of (η-C_5Me_5)$Os(CO)_2Me$ (3). To a cold solution of 1 (500 mg, 1.0 mmol) in THF (50 mL), prepared as described above, was added via syringe 5 equiv of MeLi in Et_2O. The resulting brownish solution was treated with 5 mL of saturated aqueous NH_4Cl and silica gel, and the solvent was removed in

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Table III. Crystallographic Details for [Cp*Os(CO)(PPh$_3$)(=C=C(*t*-Bu)H)]BF$_4$, (14) and [Cp*Os(CO)$_3$]BF$_4$ (17)

	14	17
formula	$C_{35}H_{40}OPOsBF_4$	$C_{13}H_{15}O_3OsBF_4$
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbcm*
cryst size, mm	0.36 × 0.36 × 0.25	0.31 × 0.21 × 0.17
a, Å	10.444 (2)	10.396 (2)
b, Å	12.091 (2)	13.008 (3)
c, Å	14.793 (4)	12.123 (2)
α, deg	97.49 (2)	90
β, deg	109.28 (2)	90
γ, deg	101.64 (2)	90
V, Å^3	1687.4 (7)	1639.4 (6)
Z	2	4
abs coeff, cm^{-1}	41.0	82.9
max/min transm	0.161/0.121	0.011/0.005
diffractometer	Nicolet R3	
radiatn	Mo Kα (λ = 0.71073 Å)	
monochromator	graphite crystal	
temp, °C	24	24
scan technique	ω	ω
scan speed, deg min^{-1}	variable, 5–20	variable, 5–20
2θ scan range, deg	4–50	4–50
data collected	$\pm h,\pm k,+l$	$+h,+k,+l$
unique data	6209	1521
unique data obsd	5595 with $F_o \geq 2.5\sigma(F_o)$	1189 with $F_o \geq 3.0\sigma(F_o)$
R(int)	2.11%	(no redundt data)
std reflctns	3 std/197 rflns	3 std/197 rflns
g^a	0.00029	0.00080
R_F, R_{wF}, GOF^a	3.42%, 3.58%, 1.695	5.44%, 5.65%, 1.632
mean shift/esd max, final cycle	0.136	0.037
highest peak, final diff map, e/Å^3	1.15 (within BF$_4^-$)	1.35 (0.88 Å from Os)

$^a w^{-1} = \sigma^2(F_o) + |g|(F_o)^2$; $R_F = \sum[|F_o| - |F_c|]/\sum|F_o|$; $R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; GOF $= [\sum w(F_o - F_c)^2/(N_{obsd} - N_p)]^{1/2}$.

vacuo. Chromatography of the resulting powder on SiO$_2$ with pentane as eluent gave 236 mg (61%) of analytically pure **3** as a white, air-stable solid. Anal. Calcd for $C_{13}H_{18}O_2Os$: C, 39.37; H, 4.58. Found: C, 39.55; H, 4.68. IR (pentane): ν_{CO} (rel abs): 1995 (85), 1935 (100) cm^{-1}. MS: *m/e* 398 (M$^+$), 383 (M$^+$ − CH$_3$), 370 (M$^+$ − CO), 355 (M$^+$ − CH$_3$ − CO). ^{1}H NMR (C_6D_6): δ 1.56 (s, C$_5$*Me*$_5$), 0.65 (s, OsC*H*$_3$).

Preparation of (η^5-C_5Me_5)Os(CO)$_2$Ph (4). A 100-mL Schlenk flask was charged in the drybox with **1** (500 mg, 1.0 mmol) and AgPF$_6$ (500 mg, 2.0 mmol). THF (50 mL) was vacuum transferred into the flask to give a yellow solution of the known cationic salt [Cp*Os(CO)$_2$(THF)]PF$_6$.[15] Five equivalents of PhLi in Et$_2$O were then added at room temperature followed by the usual workup (aqueous NH$_4$Cl and chromatography on SiO$_2$). Elution with a 15% mixture of CH$_2$Cl$_2$ in pentane gave 284 mg (63%) of analytically pure **4** as a white, air-stable solid. Anal. Calcd for $C_{18}H_{20}O_2Os$: C, 47.15; H, 4.40. Found: C, 47.01; H, 4.36. IR (pentane): ν_{CO} (rel abs) 2002 (89), 1945 (100) cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.62–7.57 (m, Os*Ph*), 7.11–7.05 (m, Os*Ph*), 1.52 (s, C$_5$*Me*$_5$). MS: *m/e* 460 (M$^+$), 432 (M$^+$ − CO), 404 (M$^+$ − 2CO), 354 (M$^+$ − CO − Ph).

Preparation of (η^5-C_5Me_5)Os(CO)$_2$(Ph-d_5) (4-d_5). Complex **3** (30 mg, 0.075 mmol) was irradiated in C_6D_6 for 24 h under vacuum in a sealed NMR tube. The resulting yellow mixture was separated by thin-layer chromatography on SiO$_2$ and gave 6 mg of complex **4**-d_5 (17%) as an off-white air-stable solid. IR (pentane): ν_{CO} (rel abs) 2002 (96), 1945 (100) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.52 (s, C$_5$*Me*$_5$). MS: *m/e* 465 (M$^+$), 437 (M$^+$ − CO), 409 (M$^+$ − 2CO), 354 (M$^+$ − CO − (Ph-d_5)).

Preparation of [(η^5-C_5Me_5)Os(CO)$_2$(PMe$_3$)][I] (5). Freshly distilled Et$_2$O (approximately 50 mL) was transferred via cannula to a Fisher-Porter bottle containing **1** (1.00 g, 1.97 mmol). The yellow solution was purged with CO by pressurizing the bottle to 60 psig and releasing the pressure. PMe$_3$ (0.5 mL, 7.9 mmol) was then added via spyringe and the solution placed under 70 psig of CO. Irradiation caused the cationic complex **5** to precipitate as it formed as a white solid. After 15-min irradiation, the pressure was released, the suspension was filtered in air on a medium porosity frit, and the off-white powder was washed with Et$_2$O. The yield of **5** was 1.06 g (92%) and was pure enough for most purposes. An analytically pure sample was obtained by recrystallization from CH$_2$Cl$_2$/hexanes. Anal. Calcd for $C_{15}H_{24}IO_2OsP$: C, 30.83; H, 4.14. Found: C, 30.86; H, 4.12. IR (CH$_2$Cl$_2$): ν_{CO} (rel abs) 2039 (85), 1985 (100) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 2.18 (d, J_{P-H} = 1.4 Hz, C$_5$*Me*$_5$), 1.95 (d, J_{P-H} = 10.9 Hz, P*Me*$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −38.92.

Preparation of [(η^5-C_5Me_5)Os(CO)$_2$(PPh$_3$)][I] (6). A mixture of complex **1** (250 mg, 0.49 mmol), PPh$_3$ (500 mg, 1.91 mmol), and CO was irradiated in diethyl ether as described for compound **5**. Workup as described above gave **6** in 38% yield as an off-white air-stable powder. Anal. Calcd for $C_{30}H_{30}IO_2OsP$: C, 46.76; H, 3.92. Found: C, 47.03; H, 3.97. IR (CH$_2$Cl$_2$): ν_{CO} (rel abs) 2041 (87), 1989 (100) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.61–7.25 (m, P*Ph*$_3$), 1.99 (d, J_{P-H} = 1.4 Hz, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 7.03.

Preparation of (η^5-C_5Me_5)Os(CO)(PMe$_3$)I (7). A 100-mL Schlenk flask containing **5** (500 mg, 0.86 mmol) was charged with Me$_3$NO (100 mg, 1.33 mmol) inside a drybox. CH$_2$Cl$_2$ (~50 mL) was vacuum distilled onto the mixture resulting in an immediate color change from colorless to yellow-orange. The solution was allowed to stir at room temperature for 1 h and the solvent removed by rotary evaporation. The residue was extracted with 200 mL of pentane to give a bright yellow solution which was filtered through Celite and evaporated to dryness. The yield of **7** was 389 mg (82%). An analytically pure sample of **7** was obtained by recrystallization from pentane. Anal. Calcd for $C_{14}H_{24}IOOsP$: C, 30.22; H, 4.35. Found: C, 30.33; H, 4.23. IR (pentane): ν_{CO} 1931 s. MS: *m/e* 558 (M$^+$), 530 (M$^+$ − CO), 452 (M$^+$ − CO − PMe$_3$). ^{1}H NMR (C_6D_6): δ 1.71 (d, J_{P-H} = 0.9 Hz, C$_5$*Me*$_5$), 1.40 (d, J_{P-H} = 9.8 Hz, P*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ −42.78.

Preparation of (η^5-C_5Me_5)Os(CO)(PPh$_3$)I (8). The cation **6** (250 mg, 0.34 mmol) was treated with Me$_3$NO (30 mg, 0.40 mmol) in CH$_2$Cl$_2$ as described above. Complex **8** was obtained in pure form by filtering the reaction mixture through a plug of alumina, followed by recrystallization from CH$_2$Cl$_2$/pentane. Complex **8** was obtained in 80% yield (192 mg) as a bright yellow air-stable powder. Anal. Calcd for $C_{29}H_{30}IOOsP$: C, 46.90; H, 4.07. Found: C, 47.04; H, 4.07. IR (CH$_2$Cl$_2$): ν_{CO} 1914 cm^{-1}. MS: *m/e* 744 (M$^+$), 716 (M$^+$ − CO), 482 (M$^+$ − PPh$_3$), 454 (M$^+$ − CO − PPh$_3$). ^{1}H NMR (C_6D_6): δ 7.93–6.92 (m, P*Ph*$_3$), 1.54 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ 10.18.

Preparation of (η^5-C_5Me_5)Os(CO)(PMe$_3$)H (9). THF (apprxomimately 50 mL) was vacuum distilled onto 250 mg (0.572 mmol) of complex **2** and 5 equiv of PMe$_3$ added via syringe under an N_2 purge. The resulting solution was irradiated ($\lambda > 300$ nm) for several days until the IR spectrum showed only a strong band at 1904 cm^{-1} and no **2** remaining. The solvent was removed in vacuo, and the yellow oily residue was dissolved in 3 mL of a mixture of pentane and THF (5:1, v/v). This solution was transferred via syringe to a 3 × 4 cm plug of neutral alumina on a 60-mL Schlenk frit and rapidly eluted with the same solvent mixture into a 100-mL Schlenk flask. Removal of the solvent in vacuo gave **9** as an air-sensitive yellow oil which did not solidify upon standing for several days at −20 °C. IR (pentane): ν_{Os-H} (rel abs) 2023 (10) br, ν_{CO} (rel abs) 1906 (100) cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.08 (s, C_5M_5), 1.40 (d, J_{P-H} = 9.5 Hz, PMe_3), ^{1}H NMR (C_6D_{12}): δ 2.06 (d, J_{P-H} = 0.81 Hz, C_5Me_5), 1.51 (d, J_{P-H} = 9.5 Hz, PMe_3), −15.25 (d, J_{P-H} = 32.2 Hz, Os–H). MS: m/e 432 (M^+). $^{31}P\{^1H\}$ NMR (C_6H_6): δ −41.12. ^{31}P NMR (C_6H_6): δ −40.70 to −41.55 (m, $J_{P-Hydride}$ = 32 Hz, J_{P-CH_3} = 8 Hz).

Preparation of $(\eta^5\text{-}C_5Me_5)Os(CO)(PMe_3)Br$ (10). Complex **9** was converted to the corresponding bromide derivative **10** by addition of 1.1 equiv of $CHBr_3$ to a benzene solution of **9** at room temperature to give 183 mg (63% from **2**) of $Cp^*Os(CO)(PMe_3)Br$ (**10**) as a yellow, air-stable solid. Anal. Calcd for $C_{14}H_{24}BrOOsP$: C, 33.01; H, 4.75. Found: C, 32.98; H, 5.00. IR (pentane): ν_{CO} 1927 cm^{-1}. MS: m/e 510 (M^+), 482 (M^+ − CO), 406 (M^+ − CO − PMe_3). ^{1}H NMR (C_6D_6): δ 1.64 (d, J_{P-H} = 1 Hz, C_5Me_5), 1.32 (d, J_{P-H} = 9.8 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −37.97. ^{31}P NMR (C_6D_6): −37.62 to −38.21 (m, J_{P-H} = 9.6 Hz).

Preparation of $(\eta^5\text{-}C_5Me_5)Os(CO)(PMe_3)(CH_3)$ (11). THF (50 mL) was vacuum transferred onto a mixture of **5** (300 mg, 0.514 mmol) and $NaBH_4$ (20 mg, 0.529 mmol). The suspension was stirred for 18 h at room temperature during which time most *of the solid dissolved and the solution became pale yellow.* The solvent was removed in vacuo and the residue extracted with 100 mL of pentane. The pale yellow solution was filtered through Celite in air and evaporated to dryness to give 213 mg of **11** (93%) as a microcrystalline solid stable in air for short periods of time. Anal. Calcd for $C_{15}H_{27}OOsP$: C, 40.53; H, 6.12. Found: C, 39.80; H, 6.10. IR (pentane): ν_{CO} 1900 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.72 (s, C_5Me_5), 1.16 (d, J_{P-H} = 8.9 Hz, PMe_3), 0.43 (d, J_{P-H} = 7.2 Hz, $OsCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −37.48.

Preparation of $(\eta^5\text{-}C_5Me_5)Os(CO)(C_2H_4)(CH_3)$ (12). THF (100 mL) was vacuum transferred into a Schlenk tube containing 100 mg of **3**. The solution was irradiated for 24 h under a flow of ethylene. The resulting solution was filtered through Celite and evaporated to dryness. Chromatography of the brownish residue on silica gel with pentane gave first unreacted **3** immediately followed by **12** as colorless bands. Evaporation of solvent from these fractions gave 16 mg of **3** and 47 mg (56% with respect to unreacted **3**) of **12** as white air-stable crystalline solids. Anal. Calcd for $C_{14}H_{22}OOs$: C, 42.41; H, 5.59. Found: C, 42.60; H, 5.59. IR (pentane): ν_{CO} 1937 cm^{-1}. MS: m/e 398 (M^+), 383 ($M^+ - CH_3$), 370 (M^+ − CO/$M^+ - C_2H_4$). ^{1}H NMR (CH_2Cl_2, 298 K: δ 1.75 (s, C_5Me_5), 1.48 (s, C_2H_4; see text), 1.45 (s, C_2H_4; see text), 0.58 (s, CH_3). ^{1}H NMR (CH_2Cl_2, 192 K): δ 2.19 (dd, J_{cis} = 8 Hz, J_{trans} = 10 Hz), 1.67 (s, C_5Me_5), 1.43 (t, $J_{cis} = J_{trans}$ = 6 Hz), 1.29 (t, $J_{cis} = J_{trans}$ = 5 Hz), 0.87 (t, $J_{cis} = J_{trans}$ = 6 Hz), 0.48 (s, CH_3).

Preparation of $[(\eta^5\text{-}C_5Me_5)Os(CO)(PPh_3)(PhC{\equiv}CPh)][BF_4]$ (13). A mixture of **8** (200 mg, 0.27 mmol) and $PhC{\equiv}CPh$ (48 mg, 0.27 mmol) was treated with $AgBF_4$ (53 mg, 0.27 mmol) in a glovebox. CH_2Cl_2 (~20 mL) was transferred onto this mixture by cannula, and the resulting suspension was stirred for 5 h at ambient temperature. The AgI produced was removed by filtration through Celite. Concentration of the filtrate to ~10 mL followed by addition of Et_2O (~100 mL) gave 210 mg of **13** (89%) as a bright orange air-stable solid. IR (CH_2Cl_2): ν_{CO} 1970 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.66–6.59 (m, Ph), 1.79 (d, J_{P-H} = 1.3 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.91.

Preparation of $[(\eta^5\text{-}C_5Me_5)Os(CO)(PPh_3)({=}C{=}C(t\text{-}Bu)H)][BF_4]$ (14). A mixture of **8** (200 mg, 0.27 mmol) and $AgBF_4$ (53 mg, 0.27 mmol) was treated with freshly distilled CH_2Cl_2 (~20 mL) and $HC{\equiv}C\text{-}t\text{-}Bu$ (35 μ, 0.29 mmol). The resulting suspension was stirred for 5 h at ambient temperature and worked up as for **13**. Complex **14** was isolated as a tan air-stable solid in 95% (213 *mg) yield.* IR (CH_2Cl_2): ν_{CO} 1995 cm^{-1}, $\nu_{C=C}$ 1684 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.58–7.28 (m, pPh_3), 2.77 (d, J_{P-H} = 3 Hz, ${=}C{=}C(t\text{-}Bu)H$), 1.89 (d, J_{P-H} = 1.2 Hz, C_5Me_5), 1.11 (s, ${=}C{=}C(t\text{-}Bu)H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.54. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 321.16 (d, J_{P-C} = 8.4 Hz, ${=}C{=}C(t\text{-}Bu)H$), 180.92 (d, J_{P-C} = 2.7 Hz, CO), 134.08–127.97 (m, PPh_3), 123.22 (s, ${=}C{=}C(t\text{-}Bu)H$), 103.79 (s, C_5Me_5), 31.71 (s, ${=}C{=}C(t\text{-}Bu)H$), 29.80 (s, ${=}C{=}C(t\text{-}Bu)H$), 9.30 (s, C_5Me_5).

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $[Cp^*Os(CO)(PPh_3)({=}C{=}C(t\text{-}Bu)H)]BF_4$ (14)

atom	x	y	z	U_{iso}[a]
Os	10871 (1)	2099 (1)	7397 (1)	40 (1)
C(1)	11614 (6)	1707 (5)	8969 (4)	55 (2)
C(2)	11714 (6)	827 (5)	8310 (4)	60 (3)
C(3)	12712 (7)	1341 (7)	7893 (5)	67 (3)
C(4)	13186 (6)	2536 (6)	8334 (5)	63 (3)
C(5)	12489 (6)	2782 (5)	8962 (4)	58 (2)
Cm(1)	10882 (8)	1579 (8)	9689 (5)	81 (4)
Cm(2)	11043 (9)	−440 (6)	8158 (6)	97 (4)
Cm(3)	13249 (10)	667 (9)	7224 (7)	116 (6)
Cm(4)	14337 (7)	3394 (8)	8192 (7)	106 (5)
Cm(5)	12839 (9)	3926 (7)	9664 (5)	96 (4)
C(11)	7556 (6)	669 (6)	7868 (4)	61 (3)
C(12)	6927 (7)	65 (7)	8412 (5)	74 (3)
C(13)	6700 (7)	649 (7)	9185 (5)	82 (3)
C(14)	7118 (7)	1845 (8)	9431 (5)	77 (3)
C(15)	7746 (6)	2462 (6)	8882 (4)	59 (3)
C(16)	7959 (5)	1873 (5)	8095 (4)	48 (2)
C(21)	6027 (6)	1648 (5)	5950 (5)	61 (2)
C(22)	5006 (7)	1427 (7)	5010 (6)	80 (3)
C(23)	5364 (8)	1752 (7)	4257 (5)	82 (3)
C(24)	6721 (9)	2281 (7)	4409 (5)	81 (3)
C(25)	7746 (7)	2493 (6)	5339 (4)	62 (3)
C(26)	7400 (5)	2202 (5)	6125 (4)	46 (2)
C(31)	7659 (6)	4481 (5)	7570 (5)	56 (3)
C(32)	7688 (8)	5628 (6)	7782 (5)	73 (3)
C(33)	8949 (9)	6449 (6)	8114 (5)	79 (4)
C(34)	10173 (8)	6141 (5)	8235 (5)	72 (3)
C(35)	10154 (6)	4975 (5)	8029 (4)	55 (2)
C(36)	8884 (6)	4131 (4)	7690 (4)	45 (2)
P	8791 (1)	2605 (1)	7347 (1)	38 (1)
C(6)	11243 (5)	3215 (5)	6680 (4)	49 (2)
C(7)	11609 (7)	3972 (6)	6219 (5)	56 (3)
Cb(1)	12091 (8)	3805 (7)	5331 (6)	76 (3)
Cb(2)	11165 (11)	4278 (10)	4523 (7)	115 (6)
Cb(3)	13624 (10)	4424 (10)	5613 (9)	131 (6)
Cb(4)	11891 (12)	2526 (7)	4960 (7)	118 (6)
C(8)	9711 (6)	957 (5)	6275 (4)	56 (2)
O(8)	9049 (6)	240 (4)	5605 (4)	86 (2)
B	5625 (1)	2711 (1)	1496 (1)	80 (4)
F(1)	4817 (5)	2909 (4)	1974 (4)	165 (5)
F(2)	4869 (6)	1986 (5)	664 (3)	258 (8)
F(3)	6222 (6)	3677 (4)	1326 (5)	192 (6)
F(4)	6588 (5)	2269 (6)	2015 (4)	254 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Preparation of $[(\eta^5\text{-}C_5Me_5)Os(CO)(PPh_3)({=}C{=}CPhH)][BF_4]$ (15) and $[(\eta^5\text{-}C_5Me_5)Os(CO)(PPh_3)(C{\equiv}C(Ph))][BF_4]$ (16). Complex **8** (50 mg, 0.07 mmol) reacts with $PhC{\equiv}CH$ (7.5 μL, 0.07 mmol) in the presence of $AgBF_4$ (14 mg, 0.07 mmol) in CH_2Cl_2 solution to give the phenylvinylidene **15**. IR (CH_2Cl_2): ν_{CO} 1999 cm^{-1}; $\nu_{C=C}$ 1671 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.66–6.90 (m, PPh_3 and ${=}C{=}C(Ph)H$), 4.03 (d, J_{P-H} = 2.9 Hz, ${=}C{=}C(Ph)H$), 1.90 (d, J_{P-H} = 0.9 Hz, C_5Me_5). However, workup as described above gave a mixture of **15** and the acetylide complex **16**. IR (CH_2Cl_2): $\nu_{C\equiv C}$ 2095 cm^{-1}, ν_{CO} 1914 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.47–6.90 (m, PPh_3 and $C{\equiv}CPh$), 1.76 (d, J_{P-H} = 1.0 Hz, C_5Me_5). Complex **15** was separated by addition of Et_2O (~25 mL) to a solution of the above mixture in CH_2Cl_2 (~2 mL) and filtered. The filtrate was shown by IR to contain only **16**.

Reaction of 1 with $AgBF_4$ and $HC{\equiv}C\text{-}t\text{-}Bu$. Sequential treatment of **1** with $AgBF_4$ followed by HCC-t-Bu as described for **14** gave an approximately 1:1 mixture of the known complex $[Cp^*Os(CO)_3][BF_4]$ and a yet unidentified organometallic complex (IR (CH_2Cl_2): ν_{CO} 2024 s, 1983 s, 1969 sh cm^{-1}). The two compounds were separated by fractional crystallization from CH_2Cl_2/Et_2O.

Crystal Structure Determinations of $[Cp^*Os(CO)(PMe_3)({=}C{=}C(t\text{-}Bu)H)]BF_4$ (14) and $[Cp^*Os(CO)_3]BF_4$ (17).

Table V. Atom Coordinates (×10^4) and Temperature Factors ($Å^2$ × 10^3) for [Cp*Os$(CO)_3$]BF_4 (17)

atom	*x*	*y*	*z*	U_{iso}[a]
Os	3751 (1)	283 (1)	2500	73 (1)
C(1)	1996 (11)	−506 (9)	1906 (10)	74 (4)
C(2)	1943 (12)	504 (9)	1566 (11)	76 (4)
C(3)	1916 (15)	1133 (13)	2500	75 (6)
C(11)	4691 (13)	950 (15)	1337 (14)	110 (7)
O(11)	5248 (12)	1329 (15)	656 (14)	176 (8)
C(12)	4799 (19)	−938 (13)	2500	143 (14)
O(12)	5392 (17)	−1665 (12)	2500	194 (14)
Cm(1)	1870 (16)	−1474 (12)	1179 (12)	110 (6)
Cm(2)	1765 (18)	876 (15)	378 (14)	128 (8)
Cm(3)	1694 (19)	2282 (16)	2500	105 (9)
B	8386 (10)	515 (9)	2500	114 (13)
F(1)	8711 (14)	1020 (8)	1632 (7)	217 (9)
F(2)	8909 (20)	−374 (11)	2500	234 (19)
F(3)	7214 (12)	397 (20)	2500	406 (33)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Collection of Diffraction Data. Data collection parameters are summarized in Table III. Crystals of both complexes were attached to fine glass fibers with epoxy cement. Complex **17** crystallizes in the orthorhombic space group *Pbcm*. The noncentrosymmetric alternative $Pbc2_1$ (nonstandard setting of $Pca2_1$) was rejected, initially by statistics and finally by the well-behaved solution and refinement of the structure. Unit-cell dimensions were derived from the least-squares fit of the angular setting of 25 reflections with 20° ≤ 2θ ≤ 30° for each crystal. A profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections. Data were corrected for absorption by an empirical procedure that employs six refined parameters to define a pseudoellipsoid used to calculate the corrections. No decay occurred in three standard reflections for either complex.

Solution and Refinement of the Structures. Both structures were solved by using the direct methods program Solv which located the Os atom in each case. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Additionally, the hydrogen atom at C(7) in **14** was located and refined isotropically. With all non-hydrogen atoms refined anisotropically and employing idealized hydrogen atom positions (d(C–H) = 0.96 Å) and thermal parameters equal 1.2 times the isotropic equivalent for the carbon atom to which it was attached), the final residuals R_F = 3.42% and R_{wF} = 3.58% were obtained for complex **14**, while final residuals of R_F = 5.44% and R_{wF} = 5.65% were obtained for **17**. For both **14** and **17** the BF_4^- anion was constrained to a tetrahedron, with B–F distances tied to a common variable. For **14** the average B–F distance is 1.304 (2) Å and is 1.291 (9) Å for **17**. During refinement of **17**, the Os–C(12) distance became unreasonably short while the C(12)–O(12) distance lengthened proportionately; prior to constraint the Os–C(12) distance was 1.83 Å and the C(12)–O(12) distance was 1.27 Å. The Os–C(12) bond was, therefore, constrained to a distance of 1.95 (1) Å and the C(12)–O(12) bond to 1.14 (1) Å. The final difference Fourier syntheses showed only diffuse backgrounds (maximum 1.15 e/$Å^3$, **14**; maximum 1.35 e/$Å^3$, **17**). An inspection of F_o vs. F_c values and trends based upon sin θ, Miller index, or parity group failed to reveal any systematic errors in the data for either structure. Atomic positional parameters for **14** and **17** are listed in Tables IV and V, respectively. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3, SHELXTL (version 4.1), and XP.

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Registry No. **1**, 81554-98-5; **2**, 102149-66-6; **3**, 102149-67-7; **4**, 102149-68-8; **4**-d_5, 102149-85-9; **5**, 102149-69-9; **6**, 102149-70-2; **7**, 102149-71-3; **8**, 102149-72-4; **9**, 102149-73-5; **10**, 102149-74-6; **11**, 102149-75-7; **12**, 102149-76-8; **13**, 102149-78-0; **14**, 102149-80-4; **15**, 102149-82-6; **16**, 102149-84-8; **17**, 81554-87-2; $Os_3(CO)_{12}$, 15696-40-9; C_5Me_5H, 41539-64-4.

Supplementary Material Available: Tables of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for **14** and **17** (49 pages). Ordering information is given on any current masthead page.