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Reaction Pathways for *fac*-$Os(CO)_3(MeCN)Me_2$ with Mono- and Bidentate Ligands

Matthew J. Overett,[†] Hong Su, and John R. Moss*

Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

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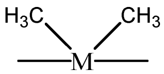
The reactions of *fac*-$Os(CO)_3(L)Me_2$ (**1a**, L = MeCN; **1b**, L = THF) with monodentate and bidentate ligands have been studied for the first time. Treatment of **1a** or **1b** with PPh_3 gives *fac*-$Os(CO)_3(PPh_3)Me_2$ (**2**), which may be further reacted with Me_3NO in acetonitrile to give the unexpected isomer *cis*-$Os(CO)_2(PPh_3)(MeCN)Me_2$ (**3**). Subsequent reaction of **3** with PPh_3 gives *cis,trans*-$Os(CO)_2(PPh_3)_2Me_2$ (**4**), with a further isomerization accompanying the ligand substitution. Oxidative decarbonylation of **4** with Me_3NO was found not to be possible. Treatment of **1a** or **1b** with bidentate ligands gives different reaction products, depending on the choice of ligand, the reaction conditions, and the stoichiometry. Reactions with small-bite-angle bidentate ligands (L-L) gave the compounds *cis*-$Os(CO)_2$(L-L)(COMe)Me (**5a**, L-L = dppm; **5b**, L-L = dppe; **5c**, L-L = 2,2′-bipy). These mixed methyl acetyl complexes are formed by displacement of the labile ligand and subsequent chelation, accompanied by methyl migration onto carbonyl. Reaction of **1a** with 1 equiv of dppp, however, resulted in a series of reactions which led to the formation of the decarbonylated product *cis*-$Os(CO)_2(dppp)Me_2$ (**7**). However, reaction of **1a** with 0.5 equiv of dppp gave the bimetallic dppp-bridged complex [*fac*-$Os(CO)_3Me_2]_2(\mu$-dppp) (**8**). In addition to characterization of all the new compounds by analytical and spectroscopic techniques, the molecular structures of **5a** and **8** have been determined by X-ray diffraction.

Introduction

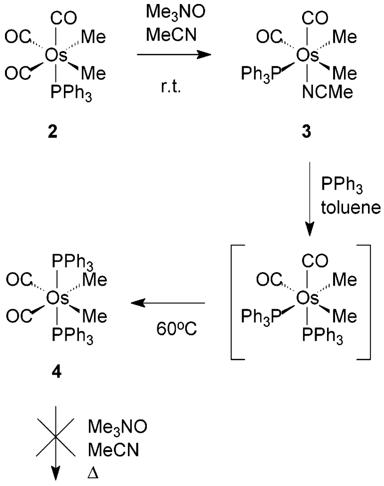
Although the reactions of metal carbonyl alkyls of the type $M(CO)_5R$ (M = Mn, Re) have been extensively studied,[1] relatively few reactions of metal carbonyl dialkyls such as *cis*-$Os(CO)_4R_2$ (R = Me, Et, etc.)[2] have been reported. Thermal decomposition of *cis*-$Os(CO)_4Me_2$ gives methane as the primary organic product, which is believed to form via a radical pathway.[3] Reactions with Br_2, HF, and CO have also been described, and these reactions yield $Os(CO)_4MeBr$,[2b] *cis*-$Os(CO)_4F_2$,[4] and $Os(CO)_5$,[2b] respectively. Little is known about the reactivity of such systems with monodentate or multidentate neutral ligands; the literature only describes the substitution of *cis*-$Os(CO)_4Me_2$ with PPh_3 by thermal[5] or oxidative[2a] decarbonylation to give *fac*-$Os(CO)_3(PPh_3)Me_2$. No carbonyl insertion reactions have been observed.

Since $LnOsMe_2$ (where Ln = other ligands) could be a model for



surface sites in heterogeneous catalysis, we have explored the reactions of $Os(CO)_3Me_2$ species. We have recently described the synthesis of *fac*-$Os(CO)_3(L)Me_2$ (**1a**, L = MeCN; **1b**, L = THF) and the reaction of these compounds with PPh_3 to give *fac*-$Os(CO)_3(PPh_3)Me_2$ (**2**).[6] The presence of a labile MeCN or THF ligand effectively activates the dialkylosmium carbonyl for substitution reactions. We report here a study of some of the rich coordination chemistry that results from the reactions of **1** or **2** with simple mono- and bidentate ligands.

Scheme 1



Results and Discussion

Oxidative decarbonylation of **2** using Me_3NO was found to be possible under mild conditions (Scheme 1). Thus, treatment of **2** with excess Me_3NO in acetonitrile gives a single new

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* To whom correspondence should be addreseed. E-mail: John.Moss@science.uct.ac.za. Fax: +27 (0)21 689 7499. Tel: +27(0)21 650 2535.

[†] Present address: Sasol Technology R&D, 1 Klasie Havenga Rd., Sasolburg 1947, South Africa.

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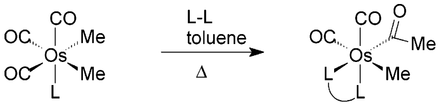
Scheme 2



1a: L = MeCN
1b: L = THF

5a: L-L = dppm
5b: L-L = dppe
5c: L-L = bipy

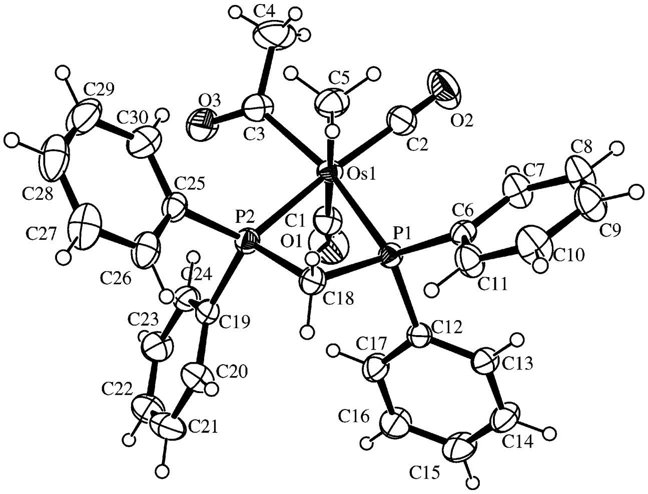


Figure 1. Molecular structure of *cis*-Os(CO)$_2$(dppm)(COMe)Me (**5a**). Thermal ellipsoids are drawn at the 35% probability level. Selected interatomic distances (Å) and angles (deg): Os1−C1, 1.901(3); Os1−C2, 1.884(3); Os1−C3, 2.104(3); Os1−C5, 2.218(3); Os1−P1, 2.4094(7); Os1−P2, 2.4156(7); C1−O1, 1.138(3); C2−O2, 1.147(3); C3−O3, 1.209(3); C3−C4, 1.531(4); P1−Os1−P2, 69.98(2); P1−C18−P2, 97.4(1); Os1−C3−C4, 120.2(2).

carbonyl compound, which was identified by IR and NMR spectroscopy as *cis*-Os(CO)$_2$(PPh$_3$)(MeCN)Me$_2$ (**3**). Interestingly, decarbonylation and phosphine coordination is accompanied by rearrangement, presumably through loss of octahedral configuration in the pentacoordinate transition state. The tertiary phosphine ligand shifts to a trans,cis orientation with respect to the methyls and the labile MeCN substituent coordinates cis to both methyls (Scheme 1). This may be deduced from the ^3J(PH) couplings for the methyl peaks in the ^{1}H NMR: the methyl trans to phosphine, located upfield (0.49 ppm) from the cis methyl (1.25 ppm), has a significantly greater ^3J(PH) coupling (8 Hz vs 4 Hz). Compound **3** is moderately thermally unstable, both as an isolated solid and in solution, due to the lability of the acetonitrile ligand.

Reaction of **3** with triphenylphosphine gives, as expected, Os(CO)$_2$(PPh$_3$)$_2$Me$_2$, although the ligand displacement reaction is again accompanied by a selective isomerization. This may be observed by monitoring the reaction in situ using IR spectroscopy. After reaction of **3** with 1 equiv of PPh$_3$ for 1 h at 60 °C in toluene, new bands characteristic of a *cis*-dicarbonyl species were observed at 2006 and 1915 cm^{-1}; however, before complete conversion of **3**, a further set of bands attributable to another *cis*-discarbonyl species appeared at 1985 and 1912 cm^{-1}. After 16 h, complete conversion to this new product was apparent. After isolation, the compound was identified as *cis,trans*-Os(CO)$_2$(PPh$_3$)$_2$Me$_2$ (**4**) by NMR spectroscopy (Scheme 1). The IR-observed intermediate is presumably the kinetically favored *cis,cis*-Os(CO)$_2$(PPh$_3$)$_2$Me$_2$, formed by direct displacement of MeCN by PPh$_3$. The subsequent isomerization to the thermodynamically favored product is due to steric repulsion of the bulky phosphines (Scheme 1).

Further reaction of **4** with Me$_3$NO proved impossible, even under harsh conditions (large excess of Me$_3$NO, in refluxing acetonitrile). This is in agreement with the "rule of thumb" that only metal carbonyls with CO stretches above 2000 cm^{-1} are susceptible to oxidative carbonylation using Me$_3$NO.[7]

Having thus established the limit of substitution for monodentate ligands achievable by oxidative decarbonylation, our attention now turned to the reaction of **1** with bidentate ligands (L-L). Since only one labile ligand is available for substitution, a number of different reactions are possible after the initial displacement of MeCN (or THF). Possible reactions include decarbonylation and chelation to form Os(CO)$_2$(L-L)Me$_2$, methyl migration onto carbonyl (alternatively carbonyl insertion into Os−Me) and chelation to form Os(CO)$_2$(L-L)(COMe)Me, and formation of bimetallic compounds of the form [Os(CO)$_3$Me$_2$]$_2$(μ-L-L). Our investigations show that all of these reactions can take place, depending on the choice of ligand, the reaction conditions, and the stoichiometry. Thus, reaction of **1a** or **1b** with bidentate ligands such as bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), and 2,2′-bipyridyl (bipy) under mild conditions gave in each case a single new compound in high yield (Scheme 2). In these reactions, displacement of the labile ligand and subsequent chelation was accompanied by a methyl migration onto an adjacent carbonyl to give compounds of the type *cis*-Os(CO)$_2$(L-L)(COMe)Me (**5a**, L-L = dppm; **5b**, L-L = dppe; **5c,** L-L = bipy).

These products were fully characterized by spectroscopic and analytical techniques, and in addition, the structure of **5a** was determined by X-ray diffraction (Figure 1).

Compound **5a** crystallizes as a racemate in the monoclinic crystal system with a *C*2/*c* space group and eight repeating units per unit cell (four of each mirror image). The molecular structure has a distorted-octahedral geometry, with the bite angle of dppm being 69.98°. The acyl C−O bond length of 1.209 Å is, as expected, greater than the carbonyl C−O bond lengths (1.138 and 1.147 Å).

To the best of our knowledge, compounds **5a**−**c** are the first isolated and structurally characterized osmium complexes with both acyl and alkyl groups. Decomposition of such acetyl methyl compounds could lead to useful organic products.

The bidentate ligands thus far employed were all characterized by relatively small bite angles and a tendency toward chelation. Our attention now turned to bidentate ligands with larger bite angles with the potential to coordinate in a bridging mode across a bimetallic system. Such a ligand is 1,3-bis(diphenylphosphino)propane (dppp). Thus, treatment of **1a** with 1 equiv of dppp in toluene at 70 °C led to the formation of a new product (Scheme 3), identified as *fac*-Os(CO)$_3$(dppp)Me$_2$ (**6**). Although **6** was not isolated, its structure as a *fac*-tricarbonyl species with monodentate phosphine substitution (and therefore a pendant free phosphine as well) may be deduced by comparison of the IR spectrum with that of **2** (ν_{CO} 2068, 1993, and 1960 cm^{-1}; cf. 2068, 1994, and 1960 cm^{-1} for **2**). Monitoring the reaction by NMR in C$_6$D$_6$ is also instructive. The formation of **6** is indicated by the presence of singlets at −6.5 ppm (coordinated phosphine) and −17.4 ppm (free phosphine) in the ^{31}P NMR spectrum. After a prolonged reaction time at 70 °C, formation of *cis*-Os(CO)$_2$(dppp)(COMe)Me (**5d**) is apparent (Scheme 3), by both IR spectrocopy (ν_{CO} 2013 and 1949 cm^{-1}; cf. 2005 and 1940 cm^{-1} for **5b**) and in situ ^{31}P NMR spectroscopy (doublets at −24.0 and −24.8 ppm). However, under the forcing conditions required to drive the reaction to completion (110 °C),

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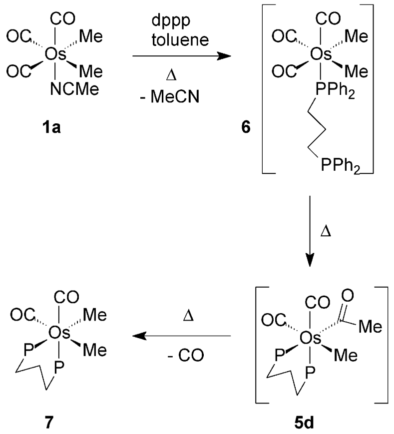
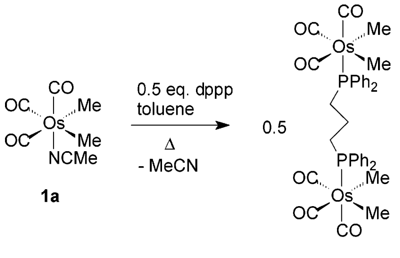
Scheme 3



Scheme 4



a further transformation taking place simultaneously was indicated by IR spectroscopy (ν_{CO} 2005 and 1929 cm^{-1}). After prolonged reflux to allow completion of the reaction, a new product, identified as *cis*-Os(CO)$_2$(dppp)Me$_2$ (**7**), was isolated in low yield (Scheme 3). Compound **7** is formed by decarbonylation of the acyl moiety in **5d** under the high-temperature conditions required to drive the chelation of the dppp ligand to the osmium. Similar thermally mediated decarbonylation reactions have been observed for other organometallic acyl species.[8]

Given the high stability of **6** against chelation, the formation of a bimetallic species with bridging dppp was accessible. Thus, reaction of **1a** with 0.5 equiv of dppp under mild conditions gave the expected bimetallic product [*fac*-Os(CO)$_3$Me$_2$]$_2$(μ-dppp) (**8**) in good yield (Scheme 4).

The bimetallic nature of **8** and its stereochemistry was confirmed by an X-ray crystal structure determination (Figure 2).

Compound **8** crystallizes in the monoclinic crystal system with a $P2_1/c$ space group and four repeating units per unit cell. The coordination geometry around the two osmium atoms is that of an irregular octahedron. Bimetallic metal carbonyl compounds with bridging dppp ligands have been reported with several metals, including tungsten,[9] molybdenum,[9a,10] chromium,[9a,10] and rhenium;[11] however, to the best of our knowledge, **8** is the first example of a bimetallic osmium compound with a bridging diphosphine ligand and is certainly the only example of a bimetallic dimethylosmium compound.

Conclusions

In conclusion, we have explored the reactivity of dimethyl osmium carbonyl compounds with a range of simple mono- and bidentate ligands. The "activated" compound *fac*-Os(CO)$_3$(MeCN)Me$_2$ (**1a**) was found to be a convenient point of departure. A maximum of two substitutions by triphenylphosphine can be performed on this system by further oxidative decarbonylation with Me$_3$NO. Thus, *cis*,*trans*-Os(CO)$_2$(PPh$_3$)$_2$Me$_2$ (**4**) was prepared in three steps from **1a**, and further reaction with Me$_3$NO could not be achieved. Treatment of **1a** with bidentate ligands (L-L) resulted in a variety of different reactions, depending on the choice of ligand, the reaction conditions, and the stoichiometry employed. These include new examples of several classical organometallic reactions, including methyl migration to carbonyl and acyl decarbonylation. Thus, compounds of the form *cis*-Os(CO)$_2$(L-L)(COMe)Me (**5a**−**d**), *fac*-Os(CO)$_3$(L-L)Me$_2$ (**6**), *cis*-Os(CO)$_2$(L-L)Me$_2$ (**7**), and [*fac*-Os(CO)$_3$Me$_2$]$_2$(μ−L-L) (**8**) could all be prepared and identified.

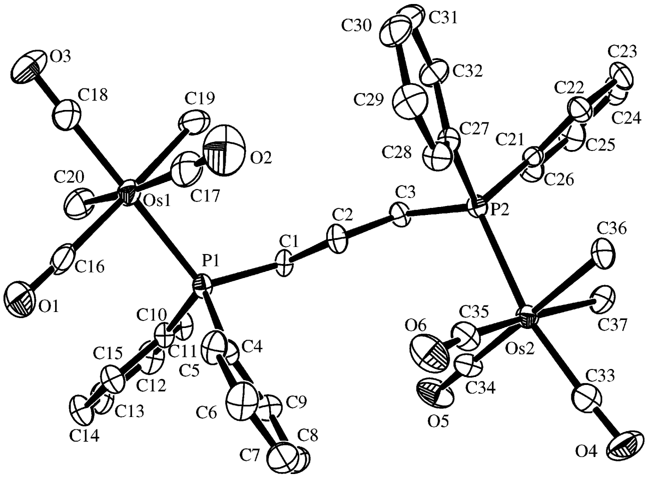


Figure 2. Molecular structure of [*fac*-Os(CO)$_3$Me$_2$]$_2$(μ-dppp) (**8**). Thermal ellipsoids are drawn at the 35% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Os1−C16, 1.922(5); Os1−C17, 1.935(5); Os1−C18, 1.904(5); Os1−C19, 2.196(4); Os1−C20, 2.199(4); Os1−P1, 2.410(1); Os1−P1−C1, 117.0(1); Os1−P1−P2−Os2, 139.8(6).

In the future, we plan to explore the reactions of other dialkylosmium compounds with a wider range of ligands, to determine the underlying reasons for the selective isomerization reactions and to explore the thermal decomposition of the acyl alkyl complexes.

Experimental Section

General Considerations. All reactions were carried out under nitrogen or argon using standard Schlenk techniques. *fac*-Os(CO)$_3$(MeCN)Me$_2$ (**1a**), *fac*-Os(CO)$_3$(THF)Me$_2$ (**1b**), and *fac*-Os(CO)$_3$(PPh$_3$)Me$_2$ (**2**) were prepared as described previously.[6] Me$_3$NO•2H$_2$O was purified by sublimation under vacuum at 60 °C onto a dry ice cooled finger. All other reagents were obtained from Sigma-Aldrich and used without purification. Toluene was dried and purified by distillation from sodium. Acetonitrile and dichloromethane were dried and purified by distillation from calcium hydride. Melting points were recorded on a Kofler hotstage microscope (Reichert Thermovar) and are uncorrected. Microanalysis data were obtained from the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer as solutions in cells with NaCl windows. NMR spectra were recorded on a Varian Unity-400

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spectrometer (^{1}H, ^{13}C) or a Varian Mercury-300 spectrometer (^{1}H, ^{13}C, ^{31}P). Mass spectrometry was carried out using electron impact (EI) or fast atom bombardment (FAB) ionization by Dr. Phillip Boshoff of the Cape Technikon, and the reported *m*/*z* value corresponds to the most abundant isotopes for each element. In each case the observed isotopic distribution corresponds to the theoretical distribution. The X-ray diffraction data were collected at room temperature on a Nonius Kappa CCD diffractometer with 1.5 kW graphite-monochromated Mo radiation.

***cis*-Os(CO)$_2$(PPh$_3$)(MeCN)Me$_2$ (3).** A stirred solution of **2** (100 mg, 0.177 mmol) in acetonitrile (5 mL) was treated with Me$_3$NO·2H$_2$O (76 mg, 0.68 mmol) in acetonitrile (2 mL), added in 0.5 mL aliquots over 48 h, after which the reaction was judged to be complete by IR spectroscopy. After removal of the volatiles in vacuo and column chromatography (silica, 40% dichloromethane in hexane, $R_f = 0.24$), **3** was obtained as a white crystalline material which decomposes slowly in solution or as an isolated solid (yield 69 mg, 67%). Mp: 133−136 °C. IR (ν_{max}/cm^{-1}; dichloromethane): 1992 s, 1921 s. ^{1}H NMR (δ; 300 MHz, C$_6$D$_6$): 7.68−6.95 (15H, m, *H*$_{aryl}$), 1.25 (3H, d,^3J(PC) = 4 Hz, Os−*Me* trans to CO), 0.49 (3H, d, ^3J(PC) = 8 Hz, Os−*Me* trans to PPh$_3$), 0.26 (3H, d, ^4J(PC) = 1.5 Hz, −NC*Me*). ^{31}P{^{1}H} NMR (δ; 120 MHz, C$_6$D$_6$): 9.38. MS (*m*/*z*; FAB): 582 (M$^+$ + H, 3%), 542 (M$^+$ + 2H − MeCN, 11%), 526 (M$^+$ + H − MeCN − Me, 10%).

***cis,trans*-Os(CO)$_2$(PPh$_3$)$_2$Me$_2$ (4).** A stirred mixture of **3** (82 mg, 0.14 mmol) and PPh$_3$ (48 mg, 0.18 mmol) in toluene (15 mL) was heated to 60 °C. The reaction was monitored by IR spectroscopy. After 1 h, the bands at 1993 and 1926 cm^{-1} (**3**) were replaced by new bands at 2006 and 1915 cm^{-1}, along with a minor band at 1985 cm^{-1}. After 3 h, bands at bands at 1985 and 1912 cm^{-1} were dominant, with the band at 2006 cm^{-1} still evident. After 16 h, only bands at 1985 and 1911 cm^{-1} were apparent. The volatiles were removed in vacuo, and after column chromatography (silica, 25% dichloromethane in hexane, $R_f = 0.27$) and recrystallization (dichloromethane/hexane), **4** was obtained as a white crystalline solid (yield 68 mg, 60%). Mp: 222−224 °C. Anal. Found: C, 60.2; H, 4.3. Calcd for C$_{40}$H$_{36}$O$_2$P$_2$Os: C, 60.0; H, 4.5. IR (ν_{max}(CO)/cm^{-1}; dichloromethane): 1985 s, 1909 s. ^{1}H NMR (δ; 400 MHz, CDCl$_3$): 7.56−7.34 (30H, m, *H*$_{aryl}$), −0.65 (6H, t, ^3J(PH) = 8 Hz, Os−*Me*). ^{13}C{^{1}H} NMR (δ; 100 MHz, CDCl$_3$): 183.6 (t, ^2J(PC) = 8 Hz, *C*O), 134.2 (*C*$_{aryl}$), 132.8 (*C*$_{aryl}$), 129.8 (*C*$_{aryl}$), 127.8 (*C*$_{aryl}$), −13.8 (t, ^2J(PC) = 8 Hz, Os−*Me*). ^{31}P{^{1}H} NMR (δ; 120 MHz, CDCl$_3$): 5.84 (s).

***cis*-Os(CO)$_2$(dppm)(COMe)Me (5a).** A stirred mixture of **1a** (78 mg, 0.22 mmol) and dppm (86 mg, 0.22 mmol) in toluene (5 mL) was heated to 70 °C. The reaction was monitored by IR spectroscopy and was judged to be complete after 3 days. The volatiles were removed in vacuo, and after recrystallization from dichloromethane/hexane, **5a** was obtained as a white crystalline solid (yield 142 mg, 91%). X-ray-quality crystals were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of **5a**. Mp: 186−189 °C. Anal. Found: C, 52.6; H, 3.8. Calcd for C$_{30}$H$_{28}$P$_2$O$_3$Os: C, 52.3; H, 4.1. IR (ν_{max}/cm^{-1}; dichloromethane): 2003 s (CO), 1939 s (CO), 1588 w (COMe). ^{1}H NMR (δ; 300 MHz, CDCl$_3$): 7.81−7.31 (20H, m, H$_{aryl}$), 4.7 (2H, m, PC*H*$_2$P), 2.58 (3H, s, CO*Me*), −0.15 (3H, t, ^3J(PH) = 20 Hz, Os−*Me*). ^{13}C{^{1}H} NMR (δ; 75 MHz, CDCl$_3$) 186.9 (*C*O), 185.6 (d, ^2J(PC) = 7 Hz, *C*O), 182.9 (d, ^2J(PC) = 8 Hz, *C*OMe), 135.7−127.9 (*C*$_{aryl}$), 52.9 (d, ^3J(PC) = 19 Hz, −CO*Me*), 43.3 (dd, ^1J(PC) = 29 Hz, ^1J(PC) = 24 Hz, P*C*H$_2$P), −20.6 (dd, ^2J(PC) = 9 Hz, ^2J(PC) = 6 Hz, Os−*Me*). ^{31}P{^{1}H} NMR (δ; 75 MHz, CDCl$_3$): −48.2 (d, ^2J(PP) = 10 Hz), −54.3 (d, ^2J(PP) = 10 Hz).

***cis*-Os(CO)$_2$(dppe)(COMe)Me (5b).** A stirred mixture of **1a** (71 mg, 0.21 mmol) and dppe (83 mg, 0.21 mmol) in toluene (5 mL) was heated to 70 °C. The reaction was monitored by IR spectroscopy and was judged to be complete after 3 days. The volatiles were removed in vacuo, and after recrystallization from dichloromethane/hexane, **5b** was obtained as a white crystalline solid (yield 118 mg, 81%). Mp: 184−187 °C. Anal. Found: C, 53.2; H, 4.0. Calcd for C$_{31}$H$_{30}$O$_3$P$_2$Os: C, 53.0; H, 4.3. IR (ν_{max}/cm^{-1}; dichloromethane): 2005 s (CO), 1940 s (CO), 1588 w (COMe). ^{1}H NMR (δ; 300 MHz, CDCl$_3$): 7.94−7.31 (20H, m, H$_{aryl}$), 2.78 (2H, m, PC*H*$_2$CH$_2$P), 2.49 (3H, s, CO*Me*), 2.41 (2H, m, PCH$_2$C*H*$_2$P), −0.65 (3H, dd, ^3J(PH) = 9 Hz, ^3J(PH) = 9 Hz, Os−*Me*). ^{13}C{^{1}H} NMR (δ; 75 MHz, CDCl$_3$); 186.8 (dd, $^2J_{trans}$(PC) = 5 Hz, $^2J_{cis}$(PC) = 4 Hz, *C*OMe), 185.6 (dd, $^2J_{trans}$(PC) = 5 Hz, $^2J_{cis}$(PC) = 4 Hz, *C*O trans to PPh$_2$), 181.8 (t, $^2J_{cis}$(PC) = 4 Hz, *C*O trans to Me), 135.7−127.8 (*C*$_{aryl}$), 53.0 (d, $^3J_{trans}$(PC) = 18 Hz, CO*Me*), 28.2 (dd, ^1J(PC) = 33 Hz, ^2J(PC) = 16 Hz, P*C*H$_2$CH$_2$P), 27.5 (dd, ^1J(PC) = 28 Hz, ^2J(PC) = 10 Hz, PCH$_2$*C*H$_2$P), −19.7 (dd, ^2J(PC) = 14 Hz, ^2J(PC) = 9 Hz). MS (*m*/*z*; FAB): 705 (M$^+$ + H, 5%), 689 (M$^+$ − Me, 69%)

***cis*-Os(CO)$_2$(2,2′-bipy)(COMe)Me (5c). From 1a.** A stirred mixture of **1a** (52 mg, 0.15 mmol) and 2,2′-bipyridyl (27 mg, 0.17 mmol) in toluene (5 mL) was heated to 50 °C for 5 days. A bright orange color developed in the solution, and the reaction was monitored by IR spectroscopy. The volatiles were removed in vacuo, and after purification by preparative TLC (alumina, ethyl acetate, $R_f = 0.56$), **5c** was obtained as an orange crystalline solid (yield 61 mg, 87%). Mp: 169−172 °C. Anal. Found: C, 39.0; H, 3.0; N, 6.1. Calcd for C$_{15}$H$_{14}$N$_2$O$_3$Os: C, 39.1; H, 3.1; N, 6.1%. IR (ν_{max}/cm^{-1}; toluene): 1992 s (CO), 1916 s (CO), 1584 w (COMe). ^{1}H NMR (δ; 300 MHz, C$_6$D$_6$): 10.34 (1H, m, bipy), 8.61 (1H, m, bipy), 7.06 (2H, m, bipy), 6.87 (2H, m, bipy), 6.58 (1H, m, bipy), 6.27 (1H, m, bipy), 3.15 (3H, s, −CO*Me*), −0.01 (3H, s, Os−*Me*). ^{13}C{^{1}H} NMR (δ; 75 MHz, CDCl$_3$): 190.5 (*C*OMe), 188.8 (*C*O), 181.7 (*C*O), 155.7 (1-*C*$_{bipy}$), 154.9 (1′-*C*$_{bipy}$), 153.7 (3-*C*$_{bipy}$), 153.4 (3′-*C*$_{bipy}$), 137.8 (5-*C*$_{bipy}$), 137.2 (5′-*C*$_{bipy}$), 126.0 (*C*$_{bipy}$), 125.8 (*C*$_{bipy}$), 122.6 (*C*$_{bipy}$), 122.3 (*C*$_{bipy}$), 53.9 (CO*Me*), 1.9 (Os-*Me*). MS (*m*/*z*; EI): 907 (2M$^+$ − Me, 10%), 879 (2M$^+$ − Me − CO, 7%), 461 (M$^+$ − H, 3%) 447 (M$^+$ − Me, 40%), 419 (M$^+$ − Me − CO, 100%), 391 (M$^+$ − Me − 2CO, 27%).

From 1b. A solution of **1b** was prepared by treatment of *cis*-Os(CO)$_4$Me$_2$ (50 mg, 0.15 mmol) with excess Me$_3$NO·2H$_2$O in THF and filtration through silica after completion of the reaction.[6] 2,2′-Bipyridyl (24 mg, 0.15 mmol) was added, and the mixture was refluxed for 48 h. A dark orange color formed in solution. The reaction was monitored by IR spectroscopy. After removal of the volatiles in vacuo and purification by preparative TLC (alumina, dichloromethane) an orange crystalline solid was recovered and identified as **5c** by comparison of its IR and NMR spectra with those of an authentic sample (yield 44 mg, 64%).

***cis*-Os(CO)$_2$(dppp)Me$_2$ (7).** A stirred mixture of **1a** (101 mg, 0.292 mmol) and dppp (121 mg, 0.292 mmol) in toluene (10 mL) was heated to 70 °C. The reaction was monitored by IR spectroscopy. After 16 h, **1a** was consumed, and new bands at 2068, 1993, and 1960 cm^{-1} indicated formation of a new *fac*-tricarbonyl species, assigned as the pendant η^2-dppp intermediate **6**. Simultaneously, new bands at 2013 and 1949 cm^{-1}, which grew in strength relative to the bands at 2068, 1994, and 1960 cm^{-1}, indicated formation of a dicarbonyl species, assigned as **5d**. After 72 h the reaction was still incomplete, and the mixture was refluxed for 24 h. Significant decomposition was observed, and IR spectroscopy indicated formation of a third product, a dicarbonyl species with bands at 2005 and 1930 cm^{-1}, present in solution with both **6** and **5d**. After additional reflux for 72 h, the reaction was judged to be complete. The volatiles were removed in vacuo, the residue was taken up in dichloromethane, and this solution was filtered through silica. After removal of the volatiles in vacuo and two recrystallizations from dichloromethane/hexane, a white crystalline solid was recovered and identified as **7** (yield 55 mg, 27%). Mp: 242−245 °C. Anal. Found: C, 54.2; H, 4.5. Calcd for C$_{31}$H$_{32}$O$_2$P$_2$Os: C, 54.1; H, 4.7%. IR (ν_{max}(CO)/cm^{-1}; dichloromethane): 2001 s, 1924 s. ^{1}H NMR (δ; 300 MHz, CDCl$_3$): 7.52−7.20 (20H, m, *H*$_{aryl}$), 2.74−1.58 (6H, m, PCH_2CH_2CH_2P), −0.14 (3H, dd, $^3J_{cis}$(PC) = 8 Hz, $^3J_{cis}$(PC) = 7 Hz, Me *trans* to CO), −0.29 (3H, dd, $^3J_{trans}$(PC) = 8 Hz, $^3J_{cis}$(PC) = 4 Hz, Me *trans* to P). ^{13}C{^{1}H} NMR (δ; 75 MHz, $CDCl_3$): 186.4 (t, ^2J(PP) = 7 Hz, *C*O trans to Me), 185.3 (m, *C*O trans to P), 136.9−127.5 (C_{aryl}), 24.3 (d, ^1J(PC) = 26 Hz, P*C*H_2−), 23.4 (dd, ^1J(PC) = 30 Hz, ^3J(PC) = 4 Hz, P*C*H_2−), 19.5 (m, PCH_2*C*H_2-CH_2P), −20.1 (dd, $^2J_{cis}$(PC) = 10 Hz, $^2J_{cis}$(PC) = 6 Hz, Me trans to CO), −23.5 (dd, $^2J_{trans}$(PC) = 42 Hz, $^2J_{cis}$(PC) = 8 Hz, Me trans to P). ^{31}P{^{1}H} NMR (δ; 120 MHz; $CDCl_3$): −16.7 (d, ^2J(PP) = 24 Hz), −24.1 (d, ^2J(PP) = 24 Hz). MS (*m*/*z*; FAB): 689 (M^+ − H, 6%), 675 (M^+ − Me, 11%), 658 (M^+ − H − 2Me, 100%), 631 (M^+ − H − 2Me − CO, 34%).

[*fac*-Os(CO)$_3$Me$_2$]$_2$(μ-dppp) (8). A stirred mixture of **1a** (117 mg, 0.339 mmol) and dppp (68 mg, 0.17 mmol) in toluene (10 mL) was heated to 70 °C. A brown color indicated some decomposition in solution. The reaction was monitored by infrared spectroscopy and was judged complete after 72 h. After removal of the volatiles in vacuo, purification by column chromatography (silica, 25% dichloromethane in hexane, R_f = 0.30), and recrystallization (dichloromethane/hexane), **8** was obtained as a white crystalline material (yield 73 mg, 43%), X-ray-quality crystals were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of **8**. Mp: 205−208 °C. Anal. Found: C, 43.7; H, 3.6. Calcd for $C_{37}H_{38}O_6P_2Os_2$: C, 43.5; H, 3.8. IR (ν_{max}(CO)/cm^{-1}; toluene): 2069 vs, 1993 s, 1961 s. ^{1}H NMR: (δ; 300 MHz, $CDCl_3$): 7.38−7.27 (20H, m, H_{aryl}), 2.38 (4H, m, PCH_2CH$_2$CH_2P), 1.01 (2H, m, PCH$_2$CH_2CH$_2$P), −0.46 (12H, d, ^3J(PH) = 8 Hz, Os−*Me*). ^{31}P{^{1}H} NMR (δ; 120 MHz, $CDCl_3$): −7.8 (s). MS (*m*/*z*; FAB): 1023 (M^+ + H, 20%).

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Supporting Information Available: CIF files giving full details of the crystal structure analyses for compounds **5a** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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