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Reactions of Aryl Isocyanates with Hydridotriosmium Carbonyl Cluster Compounds

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The reactions of aryl isocyanates with the cluster complexes $H_2Os_3(CO)_9L$ [I, L = CO; II, L = $P(CH_3)_2C_6H_5$] are described. The major products of the reaction of I with aryl isocyanates are complexes containing *N*-arylformamido ligands formed by the transfer of one hydride ligand to the carbon atom of the isocyanate molecule. An X-ray crystallographic analysis of the product $(\mu\text{-H})(\mu\text{-}p\text{-}CH_3C_6H_4NCHO)Os_3(CO)_{10}$ (III) was performed: space group $P\bar{1}$, $a = 7.925\ (2)$ Å, $b = 11.705\ (3)$ Å, $c = 13.928\ (4)$ Å, $\alpha = 66.71\ (2)°$, $\beta = 80.17\ (2)°$, $\gamma = 79.18\ (2)°$, $Z = 2$, $\rho_{\text{calcd}} = 2.83$ g/cm^3. For 3902 reflections, $R = 0.052$ and $R_w = 0.062$. III contains an *N*-*p*-tolylformamido ligand which is coordinated by its nitrogen and oxygen atoms across one edge of a triangular cluster of three osmium atoms. Reaction of III with dimethylphenylphosphine readily gives the monosubstitution product $(\mu\text{-H})(\mu\text{-}p\text{-}CH_3C_6H_4NCHO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (V). An X-ray crystallographic analysis of V was performed: space group $P\bar{1}$, $a = 10.690\ (1)$ Å, $b = 13.034\ (2)$ Å, $c = 13.200\ (4)$ Å, $\alpha = 109.78\ (2)°$, $\beta = 93.05\ (2)°$, $\gamma = 110.25\ (2)°$, $Z = 2$, $\rho_{\text{calcd}} = 2.28$ g/cm^3. For 3985 reflections, $R = 0.047$ and $R_w = 0.061$. V is similar to III except that it contains a dimethylphenylphosphine ligand coordinated in an equatorial position on the osmium atom coordinated to the oxygen atom of the bridging *N*-*p*-tolylformamido ligand. The major product of the reaction of II with *p*-tolyl isocyanate was an isomer of V which was characterized by spectroscopic and X-ray crystallographic methods as $(\mu\text{-H})(\mu\text{-}p\text{-}CH_3C_6H_4NHCO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (VI): space group $P2_1/c$, $a = 12.210\ (2)$ Å, $b = 14.337\ (4)$ Å, $c = 17.739\ (4)$ Å, $\beta = 104.49\ (2)°$. For reflections, $R = 0.034$ and $R_w = 0.032$. VI contains an *N*-hydrido-*N*-*p*-tolylcarboxamido ligand which is coordinated by its carbon and oxygen atoms across an edge of a triangular cluster of osmium atoms. This product was evidently formed by transfer of a hydrogen atom from the cluster to the nitrogen atom of the isocyanate. A minor product $(\mu\text{-H})(\mu\text{-}N\text{-}p\text{-}CH_3C_6H_4NHCO)Os_3(CO)_{10}$ (VII), which is similar to VI, was also isolated from the reaction of I with *p*-tolyl isocyanate. It was shown that III and VII cannot be interconverted under the reaction conditions. They are, thus, presumed to be formed by independent competing reactions. The changes in hydrogen transfer obtained when a carbonyl ligand is replaced with a dimethylphenylphosphine ligand are discussed.

Introduction

The transfer of hydrogen atoms from metal atoms to substrates is an integral component of any catalytic cycle involving metal–hydride intermediates.[1] Recently transition-metal cluster compounds have attracted considerable attention as a new source of homogeneous catalysts.[2] In an effort to delineate the nature of hydride transfers from cluster compounds to substrates, we have been investigating the reactivity of the hydridotriosmium carbonyl clusters $H_2Os_3(CO)_9L$ [I, L = CO; II, L = $P(CH_3)_2C_6H_5$] toward small unsaturated molecules.[3] These clusters are important because they are formally "electron deficient" and have been variously described as containing an osmium–osmium double bond[4] or an Os–H–Os–H four-center, four-electron bond.[5] As a result they readily react with donor molecules to form "electron saturated" 1:1 adducts.[6,10] If the donor is an unsaturated molecule, transfer of hydrogen from the cluster to the substrate becomes a viable process. In this regard, I has been shown to be a catalyst for the hydrogenation of terminal alkenes.[7] We have previously investigated the nature of hydrogen transfer from these clusters to heteronuclear unsaturated molecules although the processes were not catalytic.[3] Here, we report the results of our studies of the reactions of the clusters I and II with aryl isocyanates. A preliminary report of this work has been published.[8]

Experimental Section

General Information. Although the cluster complexes were generally air stable, reactions were routinely performed under a prepurified nitrogen atmosphere. Hexane was purified by distillation from sodium–benzophenone; other solvents were stored over 4-Å molecular sieves and degassed with a dispersed stream of nitrogen. Tolyl isocyanate was vacuum distilled and stored under nitrogen. Dimethylphenylphosphine and triethylamine were distilled from sodium metal and stored under nitrogen. Osmium carbonyl was obtained commercially (Strem) or prepared from OsO_4. Alumina for chromatography was Baker acid-washed aluminum oxide deactivated with 6% water, unless otherwise specified. $H_2Os_3(CO)_{10}$[9] and $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$[10] were prepared by published methods. Other reagents were used as received from commercial sources.

Melting points were determined in evacuated capillary tubes with a Thomas-Hoover and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer. Fourier transform ^1H NMR spectra were obtained at 270 MHz on a Bruker HX270. Mass spectra were obtained at 20 eV on a Hewlett-Packard 5985 GC/MS with use of a direct-inlet, electron-impact mode.

Reaction of $H_2Os_3(CO)_{10}$ with *p*-$CH_3C_6H_4NCO$. A solution of $H_2Os_3(CO)_{10}$ (113 mg, 0.133 mmol) and *p*-$CH_3C_6H_4NCO$ (0.75 mL, ca. 5.3 mmol) in hexane (50 mL) was heated to reflux for 3 h and 45 min. All volatiles were removed in vacuo, and the oily yellow residue was dissolved in $CDCl_3$ and examined by ^1H NMR. This showed four metal hydride containing products (δ −11.26 (>90%); δ −11.46, −14.27, −20.18 (<5% each)). The mixture was chromatographed on alumina. The first yellow band was eluted with hexane/benzene (6/1 v/v), reduced to dryness, and crystallized from pentane at −20 °C to give $(\mu\text{-H})(\mu\text{-}p\text{-}CH_3C_6H_4NCHO)Os_3(CO)_{10}$ (III) as yellow crystals (89 mg, 68%). The second yellow band was eluted with benzene and dichloromethane and then reduced in vacuo and crystallized from

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Table I. Spectroscopic and Physical Data

compd	mp, °C	^{1}H NMR, δ	IR: ν(NH) and ν(CO), ±3 cm^{-1}
III, $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}$	128.5–130.0	7.65 s (1 H), 7.0 m (4 H), 2.34 s (3 H), −11.35 s (1 H)^a	2100 m, 2075 s, 2060 s, 2040 w, 2030 s, 2010 s, 2005 s, 1987 m, 1980 m^c
IV, $(\mu\text{-H})(\mu\text{-C}_6\text{H}_5\text{NCHO})\text{Os}_3(\text{CO})_{10}$	142–144	7.74 s (1 H), 7.27 m (5 H), −10.49 s (1 H)^a	2100 m, 2065 s, 2055 s, 1985 m, sh, 1965 w, sh^c
V, $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$	173–174	7.57 m (5 H), 7.44 (1 H), 7.08 d (2 H, $J = 8.5$ Hz), 6.44 d (2 H, $J = 7.3$ Hz), 2.35 s (3 H), 2.27 d (3 H, $^2J_{\text{PH}} = 9.8$ Hz), 2.25 d (3 H, $^2J_{\text{PH}} = 9.8$ Hz), −11.20 d (1 H, $^2J_{\text{PH}} = 13.4$ Hz)^b	2090 m, 2050 s, 2010 s, 1990 m, 1965 w, 1960 m, 1940 m^c
VI, $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$	182–184	7.52 m, 7.37 m (5 H), 7.23 br s (1 H), (4 H), 2.30 s (3 H), 2.05 d (3 H, $^2J_{\text{PH}} =$ 9.8 Hz), 2.03 d (3 H, $^2J_{\text{PH}} =$ 9.8 Hz), −13.92 d (1 H, $^2J_{\text{PH}} = 9.8$ Hz)^b	3440 w;^{b} 2090 m, 2050 s, 2010 vs, 2000 w, 1980 vw, 1975 w, 1955 w, 1940 w^c
VII, $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_{10}$	138–141	7.36 br s (1 H), 7.09 m (5 H), 2.30 s (3 H), −14.07 s (1 H)^b	3430 w;^{b} 2105 m, 2065 s, 2055 s, 2020 sh, 2010 vs, 1990 s, 1975 m^c

^{a} $(\text{CD}_3)_2\text{CO}$. ^{b} CDCl_3. ^{c} Hexane.

dichloromethane/hexane to give $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_{10}$ (VII) (1.5 mg, 1%) as yellow crystals. A mass spectrum of this compound showed a molecular ion (m/e 991 corresponding to $^{12}\text{C}_{18}{}^1\text{H}_9{}^{14}\text{N}^{16}\text{O}_{11}{}^{192}\text{Os}_3$) and fragment ions corresponding to the loss of each of nine carbonyl ligands, all with the expected complex isotope distribution pattern.

This reaction was performed similarily in a solvent consisting of 99/1 v/v hexane/triethylamine. There was no significant difference in the products or their ratios.

$\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_5\text{NCHO})(\text{CO})_{10}$ (IV) was similarly prepared from I and $\text{C}_6\text{H}_5\text{NCO}$. t-BuNCO does not react with I even after 19 h in refluxing hexane.

Reaction of $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}$ (III) with $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$. A solution of III (89 mg, 0.090 mmol) and dimethylphenylphosphine (0.3 mL, mmol) in heptane (40 mL) was heated to reflux for 3.5 h and then reduced to dryness in vacuo. A ^{1}H NMR spectrum of the crude product showed three osmium hydride species: δ −10.10 t (ca. 10%), −10.82 t (ca. 20%), −11.22 d (ca. 70%). Chromatography on alumina gave two major yellow bands, eluted with hexane/benzene (7/3 to 4/6, v/v) and benzene, respectively. Both were reduced to dryness in vacuo and crystallized from pentane at −20 °C. Band 1 produced yellow crystals of $(\mu\text{-H})(\mu\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (V) (50.3 mg, 51%). The second band produced 9.3 mg of a yellow solid which was evidently a phosphine disubstitution product (δ −10.79 t, $J_{\text{PH}} = 11.6$ Hz) and was not fully characterized.

Reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (II) with p-$\text{CH}_3\text{C}_6\text{H}_4\text{NCO}$. A solution of II (44.5 mg, 0.046 mmol) and p-tolyl isocyanate (0.1 mL, ca. 0.75 mmol) in hexane (20 mL) was heated to reflux for 22 h. The volatiles were removed in vacuo, and the oily residue was chromatographed on alumina. The major yellow band eluted with hexane/benzene (3/2, v/v) was shown by ^{1}H NMR to consist of major (δ −13.92 d, ca. 75%) and minor (δ −11.22, ca. 25%) products. Rechromatography on alumina (acid washed, 2.5% H_2O) gave a broad band which was collected in two portions. The front yellow portion was eluted with benzene/ethyl ether (4/1, v/v), and the orange tail was eluted with methanol. The first portion was reduced to dryness and crystallized from pentane at −20 °C to give yellow crystals of the major product $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (VI) (16.1 mg, 32%). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ gave yellow crystals of VI suitable for X-ray diffraction. The minor product (δ −11.22 d) was spectroscopically characterized as V.

Thermolyses of III and VII. Compound III (89.1 mg) was dissolved in 40 mL of heptane and heated to reflux for 4 h. The solvent was removed in vacuo, and the residue was dissolved in ca. 0.3 mL of CDCl_3. A ^{1}H NMR spectrum showed that the sample was unchanged. Compound VII was treated similarly and was also recovered unchanged.

Crystallographic Analyses. Crystals of III, V and VI suitable for diffraction measurements were obtained from hexane solutions by cooling to −20 °C. All crystals were mounted in thin-walled glass capillaries. All diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least-squares routines. The space groups were determined from the systematic absences observed during data collection. In the triclinic cases the space groups $P\bar{1}$ were assumed and were confirmed by the successful solution and refinement of the structures. Crystal data and data collections parameters are listed in Table VIII. All data processing was performed on a Digital PDP 11/45 computer with use of the Enraf-Nonius SDP program library. Absorption corrections of a Gaussian integration type were done for all structures. Neutral-atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied for all nonhydrogen atoms.[11b] All structures were solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were either obtained from difference Fourier syntheses or calculated on the basis of geometric considerations. Hydrogen atom contributions were included in structure factor calculations, but their positions were not refined. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_{\text{obsd}}| - |F_{\text{calcd}}|)^2$ where $w = 1/(\sigma(F))^2$, $\sigma(F) = (F_{\text{obsd}}{}^2)/2F_{\text{obsd}}$ and $\sigma(F_{\text{obsd}}{}^2) = [(\sigma(I_{\text{raw}}))^2 + (PF_{\text{obsd}}{}^2)^2]^{1/2}/Lp$. Structure III was refined by using unit weights for all reflections. All atoms heavier than oxygen were refined with anisotropic temperature factors. All other atoms were refined with isotropic temperature factors only. Final fractional atomic coordinates, thermal parameters, and structure factor amplitudes are available for all structures (see supplementary material). Ineratomic distances and angles with errors obtained from the inverse matrix calculated on the final cycle of least-squares refinement are listed in Tables II–VII. The Os(1)–C(2) bond length of 1.64 (1) Å in V is anomalously short. The C(2)–O(2) at 1.23 (1) Å is a little long. It seems atom C(2) may be slightly incorrectly positioned in this structure. In spite of the final refinement, we feel that these distances should not be taken too seriously.

Results

The Formamido Complexes. The principal products isolated from the reaction of I with aryl isocyanates are the complexes $(\mu\text{-H})(\mu\text{-ArNCHO})\text{Os}_3(\text{CO})_{10}$, which contain formamido ligands. These complexes were formed by an addition of one isocyanate molecule to the cluster, which was accompanied by a transfer of one hydrogen atom from the cluster to the carbon atom of the isocyanate. The presence of the hydrogen atom on the carbon atom was indicated by the ^{1}H NMR

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[11] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149–150.

Table II. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}$ (III)

Os(1)–Os(2)	2.903 (1)	C(11)–C(12)	1.40 (1)
Os(1)–Os(3)	2.909 (1)	C(12)–C(13)	1.39 (1)
Os(2)–Os(3)	2.888 (1)	C(13)–C(14)	1.36 (2)
Os(1)–C(5)	1.912 (9)	C(14)–C(15)	1.39 (2)
Os(1)–C(6)	1.898 (9)	C(15)–C(16)	1.41 (1)
Os(1)–C(7)	1.910 (8)	C(16)–C(11)	1.39 (1)
Os(1)–N	2.156 (6)	C(14)–C(18)	1.56 (2)
Os(2)–C(1)	1.963 (8)	C(1)–O(1)	1.13 (1)
Os(2)–C(2)	1.948 (9)	C(2)–O(2)	1.15 (1)
Os(2)–C(3)	1.901 (8)	C(3)–O(3)	1.15 (1)
Os(2)–C(4)	1.924 (10)	C(4)–O(4)	1.17 (1)
Os(3)–C(8)	1.902 (10)	C(5)–O(5)	1.13 (1)
Os(3)–C(9)	1.889 (9)	C(6)–O(6)	1.17 (1)
Os(3)–C(10)	1.903 (11)	C(7)–O(7)	1.14 (1)
Os(3)–O(11)	2.145 (6)	C(8)–O(8)	1.18 (1)
C(17)–O(11)	1.27 (1)	C(9)–O(9)	1.16 (1)
C(17)–N	1.33 (1)	C(10)–O(10)	1.16 (1)
N–C(11)	1.45 (1)		

Table III. Interatomic Angles (Deg) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}$ (III)

Os(1)–Os(2)–Os(3)	60.31 (1)	Os(2)–Os(3)–O(11)	89.8 (1)
Os(2)–Os(1)–Os(3)	59.60 (1)	Os(2)–Os(3)–C(8)	88.4 (3)
Os(1)–Os(3)–Os(2)	60.09 (1)	Os(2)–Os(3)–C(9)	91.0 (3)
Os(2)–Os(1)–N	92.8 (2)	Os(2)–Os(3)–C(10)	177.1 (3)
Os(2)–Os(1)–C(5)	90.0 (3)	O(11)–Os(3)–C(8)	93.3 (3)
Os(2)–Os(1)–C(6)	179.5 (3)	O(11)–Os(3)–C(9)	177.1 (3)
Os(2)–Os(1)–C(7)	84.7 (3)	O(11)–Os(3)–C(10)	87.9 (4)
Os(3)–Os(1)–N	82.0 (2)	C(8)–Os(3)–C(9)	89.5 (4)
Os(3)–Os(1)–C(5)	93.5 (3)	C(8)–Os(3)–C(10)	93.5 (4)
Os(3)–Os(1)–C(6)	120.0 (3)	C(9)–Os(3)–C(10)	91.3 (4)
Os(3)–Os(1)–C(7)	144.0 (3)	Os(1)–N–C(11)	119.0 (5)
N–Os(1)–C(5)	172.6 (3)	Os(1)–N–C(17)	124.2 (5)
N–Os(1)–C(6)	87.5 (3)	Os(3)–O(11)–C(17)	126.1 (6)
N–Os(1)–C(7)	96.5 (3)	O(11)–C(17)–N	124.8 (8)
C(5)–Os(1)–C(6)	89.7 (4)	C(17)–N–C(11)	115.2 (7)
C(5)–Os(1)–C(7)	90.7 (4)	N–C(11)–C(12)	121.8 (8)
C(6)–Os(1)–C(7)	95.8 (4)	N–C(11)–C(16)	118.8 (8)
Os(1)–Os(2)–C(1)	87.0 (2)	C(16)–C(11)–C(12)	119.3 (9)
Os(1)–Os(2)–C(2)	90.0 (3)	C(11)–C(12)–C(13)	120.1 (9)
Os(1)–Os(2)–C(3)	99.9 (3)	C(12)–C(13)–C(14)	120.9 (11)
Os(1)–Os(2)–C(4)	158.9 (3)	C(13)–C(14)–C(15)	118.8 (12)
Os(3)–Os(2)–C(1)	88.1 (2)	C(14)–C(15)–C(16)	121.5 (12)
Os(3)–Os(2)–C(2)	90.2 (3)	C(15)–C(16)–C(11)	118.9 (10)
Os(3)–Os(2)–C(3)	160.1 (3)	C(13)–C(14)–C(18)	119.7 (13)
Os(3)–Os(2)–C(4)	98.6 (3)	C(15)–C(14)–C(18)	121.4 (13)
C(1)–Os(2)–C(2)	177.0 (4)	Os(1)–C(5)–O(5)	178.6 (8)
C(1)–Os(2)–C(3)	89.2 (3)	Os(1)–C(6)–O(6)	175.9 (8)
C(1)–Os(2)–C(4)	92.6 (4)	Os(1)–C(7)–O(7)	177.1 (8)
C(2)–Os(2)–C(3)	91.6 (4)	Os(2)–C(1)–O(1)	172.8 (7)
C(2)–Os(2)–C(4)	90.1 (4)	Os(2)–C(2)–O(2)	175.5 (8)
C(3)–Os(2)–C(4)	101.2 (4)	Os(2)–C(3)–O(3)	176.8 (8)
Os(1)–Os(3)–O(11)	81.7 (2)	Os(2)–C(4)–O(4)	177.8 (8)
Os(1)–Os(3)–C(8)	147.9 (3)	Os(3)–C(8)–O(8)	177.3 (8)
Os(1)–Os(3)–C(9)	96.3 (3)	Os(3)–C(9)–O(9)	173.8 (8)
Os(1)–Os(3)–C(10)	117.8 (3)	Os(3)–C(10)–O(10)	177.5 (9)

Table IV. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (V)

Os(1)–Os(2)	2.940 (1)	C(15)–C(16)	1.41 (1)
Os(1)–Os(3)	2.911 (1)	C(16)–C(11)	1.41 (1)
Os(2)–Os(3)	2.897 (1)	C(14)–C(17)	1.55 (1)
Os(1)–C(1)	1.80 (1)	P–C(31)	1.78 (1)
Os(1)–C(2)	1.64 (1)	P–C(32)	1.81 (1)
Os(1)–C(3)	1.90 (1)	P–C(21)	1.82 (1)
Os(1)–N	2.162 (6)	C(21)–C(22)	1.44 (1)
Os(2)–C(4)	1.83 (1)	C(22)–C(23)	1.38 (1)
Os(2)–C(5)	1.92 (1)	C(23)–C(24)	1.38 (1)
Os(2)–O(10)	2.134 (5)	C(24)–C(25)	1.30 (2)
Os(2)–P	2.343 (2)	C(25)–C(26)	1.48 (2)
Os(3)–C(6)	1.95 (1)	C(26)–C(21)	1.38 (1)
Os(3)–C(7)	1.87 (1)	C(1)–O(1)	1.20 (1)
Os(3)–C(3)	1.91 (1)	C(2)–O(2)	1.23 (1)
Os(3)–C(9)	1.90 (1)	C(3)–O(3)	1.15 (1)
C(10)–O(10)	1.31 (1)	C(4)–O(4)	1.16 (1)
C(10)–N	1.31 (1)	C(5)–O(5)	1.16 (1)
N–C(11)	1.44 (1)	C(6)–O(6)	1.13 (1)
C(11)–C(12)	1.39 (1)	C(7)–O(7)	1.17 (1)
C(12)–C(13)	1.41 (1)	C(8)–O(8)	1.15 (1)
C(13)–C(14)	1.40 (1)	C(9)–O(9)	1.17 (1)
C(14)–C(15)	1.38 (1)		

Table V. Interatomic Angles (Deg) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_9[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]$ (V)

Os(2)–Os(1)–Os(3)	59.35 (1)	C(6)–Os(3)–C(9)	90.6 (4)
Os(1)–Os(2)–Os(3)	59.84 (1)	C(7)–Os(3)–C(8)	91.7 (5)
Os(1)–Os(3)–Os(2)	60.81 (1)	C(7)–Os(3)–C(9)	103.3 (5)
Os(2)–Os(1)–N	81.3 (2)	C(8)–Os(3)–C(9)	93.4 (4)
Os(2)–Os(1)–C(1)	94.3 (4)	Os(1)–N–C(10)	125.8 (6)
Os(2)–Os(1)–C(2)	142.2 (4)	Os(1)–N–C(11)	122.1 (6)
Os(2)–Os(1)–C(3)	121.0 (3)	N–C(10)–C(10)	124.5 (8)
Os(3)–Os(1)–N	94.8 (2)	C(10)–N–C(11)	112.1 (7)
Os(3)–Os(1)–C(1)	85.4 (3)	N–C(11)–C(12)	121.2 (8)
Os(3)–Os(1)–C(2)	83.8 (4)	N–C(11)–C(16)	117.5 (8)
Os(3)–Os(1)–C(3)	177.5 (3)	C(16)–C(11)–C(12)	121.0 (8)
N–Os(1)–C(1)	174.6 (4)	C(11)–C(12)–C(13)	119.1 (9)
N–Os(1)–C(2)	94.7 (4)	C(12)–C(13)–C(14)	121.1 (10)
N–Os(1)–C(3)	87.7 (3)	C(13)–C(14)–C(15)	118.5 (10)
C(1)–Os(1)–C(2)	90.7 (5)	C(14)–C(15)–C(16)	122.2 (9)
C(1)–Os(1)–C(3)	92.1 (4)	C(15)–C(16)–C(11)	118.0 (9)
C(2)–Os(1)–C(3)	96.2 (5)	C(13)–C(14)–C(17)	117.5 (10)
Os(1)–Os(2)–O(10)	81.9 (2)	C(15)–C(14)–C(17)	123.8 (9)
Os(1)–Os(2)–P	114.14 (7)	Os(2)–P–C(31)	111.7 (4)
Os(1)–Os(2)–C(4)	99.9 (3)	Os(2)–P–C(32)	117.1 (4)
Os(1)–Os(2)–C(5)	150.5 (3)	Os(2)–P–C(21)	114.6 (3)
Os(3)–Os(2)–O(10)	92.2 (2)	C(31)–P–C(32)	105.4 (6)
Os(3)–Os(2)–P	170.59 (6)	C(31)–P–C(21)	103.0 (5)
Os(3)–Os(2)–C(4)	94.7 (3)	C(32)–P–C(21)	103.7 (5)
Os(3)–Os(2)–C(5)	92.2 (3)	P–C(21)–C(22)	118.5 (7)
O(10)–Os(2)–P	79.4 (2)	P–C(21)–C(26)	122.5 (8)
O(10)–Os(2)–C(4)	172.9 (3)	C(26)–C(21)–C(22)	118.9 (9)
O(10)–Os(2)–C(5)	90.6 (3)	C(21)–C(22)–C(23)	121.0 (9)
P–Os(2)–C(4)	93.6 (3)	C(22)–C(23)–C(24)	118.8 (12)
P–Os(2)–C(5)	92.2 (3)	C(23)–C(24)–C(25)	122.7 (13)
C(4)–Os(2)–C(5)	91.1 (4)	C(24)–C(25)–C(26)	121.7 (11)
Os(1)–Os(3)–C(6)	84.7 (3)	C(25)–C(26)–C(21)	116.8 (11)
Os(1)–Os(3)–C(7)	154.3 (3)	Os(1)–C(1)–O(1)	171.0 (9)
Os(1)–Os(3)–C(8)	93.0 (3)	Os(1)–C(2)–O(2)	177.2 (9)
Os(1)–Os(3)–C(9)	101.6 (3)	Os(1)–C(3)–O(3)	176.7 (10)
Os(2)–Os(3)–C(6)	91.0 (3)	Os(2)–C(4)–O(4)	174.6 (9)
Os(2)–Os(3)–C(7)	94.5 (3)	Os(2)–C(5)–O(5)	179.2 (10)
Os(2)–Os(3)–C(8)	84.7 (3)	Os(3)–C(6)–O(6)	177.5 (9)
Os(2)–Os(3)–C(9)	162.1 (3)	Os(3)–C(7)–O(7)	177.4 (10)
C(6)–Os(3)–C(7)	88.9 (4)	Os(3)–C(8)–O(8)	174.8 (9)
C(6)–Os(3)–C(8)	175.7 (4)	Os(3)–C(9)–O(9)	176.5 (8)

spectra, which showed very low-field resonances (δ 8–9), characteristic of formamido and related ligands,[12] and indirectly supported by an X-ray crystallographic analysis of the *p*-tolyl derivative.

An ORTEP drawing of the molecular structure of $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}$ (III) is shown in Figure 1. The formamido hydrogen atom was not observed crystallographically, but it is shown in an idealized position in the figure. Interatomic distances and angles are listed in Tables II and III. The molecule consists of a triangular cluster of three osmium atoms. The three osmium–osmium bond distances range from 2.888 (1) to 2.909 (1) Å and are only slightly longer than the osmium–osmium bond distance (2.877 (1) Å) found in $\text{Os}_3(\text{CO})_{12}$.[13] The formamido ligand is bonded in a "diaxial" coordination arrangement (i.e., in two coordination positions perpendicular to the Os_3 plane) and bridges the Os(1)–Os(3) edge of the cluster. The oxygen atom O(11)

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(12) (a) Sahajpal, A.; Robinson, S. D. *Inorg. Chem.* **1979**, *18*, 3572. (b) Robinson, S. D.; Sahajpal, A. *Ibid.* **1977**, *16*, 2722. (c) Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Ibid.* **1977**, *16*, 2728.

(13) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Table VI. Interatomic Distances (Å) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4NHCO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (VI)

Os(1)–Os(2)	2.945 (1)	C(15)–C(16)	1.393 (10)
Os(1)–Os(3)	2.859 (1)	C(16)–C(11)	1.342 (9)
Os(2)–Os(3)	2.893 (1)	C(14)–C(17)	1.515 (12)
Os(1)–P	2.359 (2)	P–C(27)	1.828 (9)
Os(1)–C(1)	1.827 (8)	P–C(28)	1.842 (8)
Os(1)–C(2)	1.867 (9)	P–C(21)	1.816 (8)
Os(1)–O(10)	2.141 (4)	C(21)–C(22)	1.376 (9)
Os(2)–C(3)	1.890 (9)	C(22)–C(23)	1.446 (11)
Os(2)–C(4)	1.925 (9)	C(23)–C(24)	1.375 (12)
Os(2)–C(5)	1.866 (10)	C(24)–C(25)	1.331 (11)
Os(2)–C(10)	2.121 (7)	C(25)–C(26)	1.407 (11)
Os(3)–C(6)	1.899 (10)	C(26)–C(21)	1.402 (10)
Os(3)–C(7)	1.859 (11)	C(1)–O(1)	1.197 (8)
Os(3)–C(8)	1.948 (9)	C(2)–O(2)	1.192 (9)
Os(3)–C(9)	1.898 (9)	C(3)–O(3)	1.153 (9)
C(10)–O(10)	1.254 (9)	C(4)–O(4)	1.160 (9)
C(10)–N	1.345 (8)	C(5)–O(5)	1.193 (11)
N–C(11)	1.442 (8)	C(6)–O(6)	1.187 (10)
C(11)–C(12)	1.370 (11)	C(7)–O(7)	1.199 (11)
C(12)–C(13)	1.403 (12)	C(8)–O(8)	1.164 (9)
C(13)–C(14)	1.371 (10)	C(9)–O(9)	1.162 (9)
C(14)–C(15)	1.360 (10)		

Table VII. Interatomic Angles (Deg) with Esd's for $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4NHCO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (VI)

Os(1)–Os(2)–Os(3)	58.63 (1)	C(6)–Os(3)–C(9)	91.1 (4)
Os(1)–Os(3)–Os(2)	61.59 (1)	C(7)–Os(3)–C(8)	95.0 (4)
Os(2)–Os(1)–Os(3)	59.78 (1)	C(7)–Os(3)–C(9)	100.7 (4)
Os(2)–Os(1)–P	109.53 (5)	C(8)–Os(3)–C(9)	92.4 (4)
Os(2)–Os(1)–C(1)	112.5 (3)	Os(2)–C(10)–O(10)	117.5 (5)
Os(2)–Os(1)–C(2)	144.8 (3)	Os(2)–C(10)–N	125.4 (5)
Os(2)–Os(1)–O(10)	68.0 (1)	Os(1)–O(10)–C(10)	109.3 (4)
Os(3)–Os(1)–P	168.99 (5)	C(10)–N–C(11)	125.1 (6)
Os(3)–Os(1)–C(1)	92.5 (3)	N–C(11)–C(12)	120.2 (7)
Os(3)–Os(1)–C(2)	92.9 (3)	N–C(11)–C(16)	119.7 (7)
Os(3)–Os(1)–O(10)	90.3 (1)	C(16)–C(11)–C(12)	120.0 (8)
P–Os(1)–C(1)	94.4 (3)	C(11)–C(12)–C(13)	118.2 (8)
P–Os(1)–C(2)	95.8 (3)	C(12)–C(13)–C(14)	122.3 (9)
P–Os(1)–O(10)	82.6 (1)	C(13)–C(14)–C(15)	117.5 (8)
C(1)–Os(1)–C(2)	88.6 (4)	C(14)–C(15)–C(16)	120.8 (8)
C(1)–Os(1)–O(10)	176.9 (3)	C(15)–C(16)–C(11)	121.2 (8)
C(2)–Os(1)–O(10)	92.5 (3)	C(13)–C(14)–C(17)	120.5 (9)
Os(1)–Os(2)–C(3)	118.3 (3)	C(15)–C(14)–C(17)	122.0 (8)
Os(1)–Os(2)–C(4)	107.3 (3)	Os(1)–P–C(27)	117.3 (3)
Os(1)–Os(2)–C(5)	137.5 (3)	Os(1)–P–C(28)	114.7 (3)
Os(1)–Os(2)–C(10)	65.2 (2)	Os(1)–P–C(21)	113.3 (3)
Os(3)–Os(2)–C(3)	176.7 (3)	C(27)–P–C(28)	101.6 (4)
Os(3)–Os(2)–C(4)	91.6 (2)	C(27)–P–C(21)	104.5 (4)
Os(3)–Os(2)–C(5)	84.3 (3)	C(28)–P–C(21)	103.8 (4)
Os(3)–Os(2)–C(10)	87.9 (2)	P–C(21)–C(22)	120.6 (6)
C(3)–Os(2)–C(4)	90.7 (4)	P–C(21)–C(26)	119.7 (6)
C(3)–Os(2)–C(5)	98.0 (4)	C(26)–C(21)–C(22)	119.6 (7)
C(3)–Os(2)–C(10)	89.5 (3)	C(21)–C(22)–C(23)	119.5 (8)
C(4)–Os(2)–C(5)	92.7 (4)	C(22)–C(23)–C(24)	118.6 (8)
C(4)–Os(2)–C(10)	171.3 (3)	C(23)–C(24)–C(25)	121.9 (9)
C(5)–Os(2)–C(10)	95.9 (3)	C(24)–C(25)–C(26)	120.9 (9)
Os(1)–Os(3)–C(6)	86.7 (3)	C(25)–C(26)–C(21)	119.4 (8)
Os(1)–Os(3)–C(7)	161.2 (3)	Os(1)–C(1)–O(1)	176.2 (7)
Os(1)–Os(3)–C(8)	85.0 (3)	Os(1)–C(2)–O(2)	177.3 (7)
Os(1)–Os(3)–C(9)	98.2 (3)	Os(2)–C(3)–O(3)	176.3 (8)
Os(2)–Os(3)–C(6)	85.2 (3)	Os(2)–C(4)–O(4)	174.9 (7)
Os(2)–Os(3)–C(7)	99.6 (3)	Os(2)–C(5)–O(5)	174.2 (9)
Os(2)–Os(3)–C(8)	88.8 (3)	Os(3)–C(6)–O(6)	176.9 (9)
Os(2)–Os(3)–C(9)	159.5 (3)	Os(3)–C(7)–O(7)	175.9 (9)
C(6)–Os(3)–C(7)	92.2 (4)	Os(3)–C(8)–O(8)	175.1 (8)
C(6)–Os(3)–C(8)	171.4 (4)	Os(3)–C(9)–O(9)	179.4 (9)

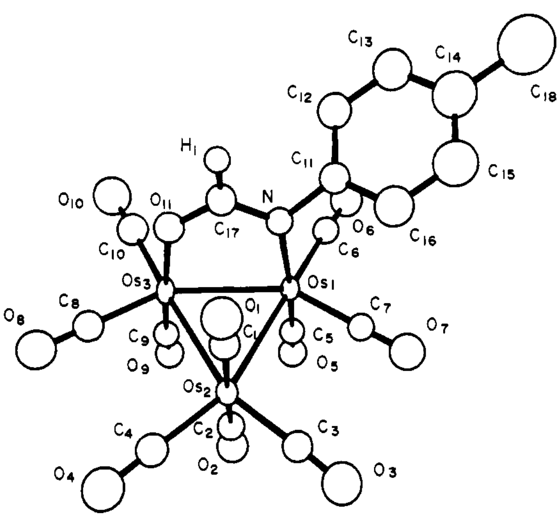

Figure 1. ORTEP diagram of $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4HNCHO)Os_3(CO)_{10}$ (III) showing 50% probability ellipsoids. The hydrogen atom H_1 is shown in an idealized position.

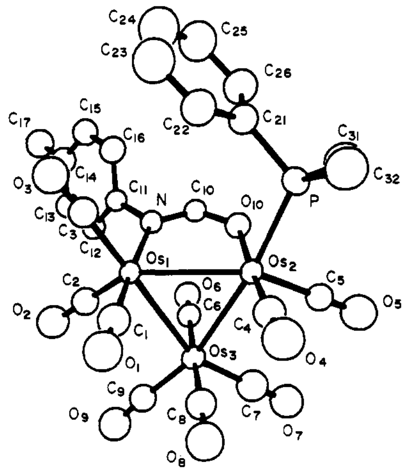

Figure 2. ORTEP diagram of $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4NCHO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (V) showing 50% probability ellipsoids.

is bonded solely to Os(3) while the nitrogen atom is bonded solely to Os(1). The C(17)–O(11) and C(17)–N bond lengths at 1.27 (1) and 1.33 (1) Å, respectively, are intermediate between single- and double-bond lengths and indicate significant electron delocalization across the N–C–O unit. A hydride ligand indicated by its ^{1}H NMR resonance δ −11.35 was not observed crystallographically but is believed to occupy a bridging position across the Os(1)–Os(3) bond. This is supported by a bending away of the carbonyl ligands C(6)–O(6) and C(10)–O(10) as characterized by the large angles Os(3)–Os(1)–C(6) (120.0 (3)°) and Os(1)–Os(3)–C(10) (117.8 (3)°) from the Os(1)–Os(3) bond. The complex contains ten linear terminal carbonyl ligands. Six lie essentially in the plane of the Os_3 triangle while four are perpendicular to it.

Complex III reacts with dimethlphenylphosphine in refluxing heptane to give the monosubstituted product $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4NCHO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (V) in 51% yield. This complex was also analyzed crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2. Interatomic distances and angles are listed in Tables IV and V. Like III, V also contains a triangular cluster of osmium atoms. The osmium–osmium bond distances are slightly longer than those found in III. The increase is similar to the 0.02 Å increase in metal–metal bond lengths, which was observed when a phosphite ligand was substituted for a carbonyl ligand in $Os_3(CO)_{12}$.[14] The *p*-tolylformamido ligand shows a diaxial coordination and bridges an edge of the cluster. The formamido hydrogen and hydride ligands were not observed crystallographically but were confirmed spectroscopically. The hydride ligand probably bridges the Os(1)–Os(2) bond. The dimethylphenylphosphine ligand occupies an equatorial coordination site on Os(2) approximately trans to

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(14) Benfield, R. E.; Johnson, B. F. G.; Raithby, P. R.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 666.

Table VIII

	III	V	VI
	(A) Crystallographic Data for X-ray Diffraction Studies		
formula	$Os_3O_{11}NC_{18}H_9$	$Os_3PO_{10}NC_{25}H_{20}$	$Os_3PO_{10}NC_{25}H_{20}$
temp, °C (±5 °C)	27	27	27
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	7.295 (2)	10.690 (1)	12.210 (2)
b, Å	11.705 (3)	13.034 (2)	14.337 (4)
c, Å	13.928 (4)	13.200 (4)	17.739 (4)
α, deg	66.71 (2)	109.78 (2)	90.0
β, deg	80.17 (2)	93.05 (2)	104.49 (2)
γ, deg	79.18 (2)	110.25 (2)	90.0
V, $Å^3$	1158.9 (5)	1593 (1)	3006 (2)
mol wt	985.9	1096.0	1096.0
ρ_{calcd}, g/cm^3	2.83	2.28	2.42
	(B) Measurement of Intensity Data		
radiation	Mo K$\bar{\alpha}$ (0.710 73 Å)^a		
monochromator	graphite^a		
detector aperture, mm			
horizontal ($A + B$ tan θ): *A*, *B*	3.0, 1.0	3.0, 1.0	3.0, 1.0
vertical	4.0	4.0	4.0
cryst faces	$11\bar{1}$, $\bar{1}\bar{1}1$, $0\bar{1}0$, 010, $10\bar{1}$, $\bar{1}01$, $\bar{1}1\bar{2}$, $1\bar{1}2$, $1\bar{2}4$, $\bar{1}24$	$12\bar{2}$, $\bar{1}\bar{2}2$, 120, $\bar{1}\bar{2}0$, $2\bar{1}0$, $\bar{2}10$	100, $\bar{1}00$, $1\bar{1}\bar{1}$, $\bar{1}11$, 001, $00\bar{1}$, $11\bar{1}$, $\bar{1}\bar{1}1$
cryst size, mm	0.15 × 0.18 × 0.25	0.10 × 0.08 × 0.23	0.11 × 0.24 × 0.16
cryst orientation: direction; deg from φ axis	*c**; 30.0	normal to $2\bar{1}0$; 8.5	[010]; 4.3
reflctn measd	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, \pm l$
max 2θ, deg	54.0	50.0	48.0
scan type	moving crystal–stationary counter^a		
ω-scan width (A + 0.347 tan θ): *A*, deg	1.05	0.8	0.8
background	¹/₄ additional scan at each end of scan^a		
ω-scan rate (variable), deg/min: max, min	10.0, 1.4	10.0, 1.2	6.7, 1.2
no. of reflctns measd	4930	5546	5101
data used [$F^2 \geqslant 3.0(\sigma(F))^2$]	3902	3985	3286
	(C) Treatment of Data		
decay cor: max, min	none	1.10, 0.99	none
absorption cor			
coeff, cm^{-1}	175.1	127.9	135.6
grid	8 × 8 × 10	10 × 6 × 12	6 × 16 × 10
transmission coeff: max, min	0.18, 0.03	0.44, 0.09	0.30, 0.03
P factor		0.005	0.01
final residuals: *R*, R_w	0.052, 0.062	0.047, 0.061	0.034, 0.032
esd of unit wt	3.74	6.31	2.66
largest shift/error value on final cycle	0.09	0.21	0.11

^{a} For all three compounds.

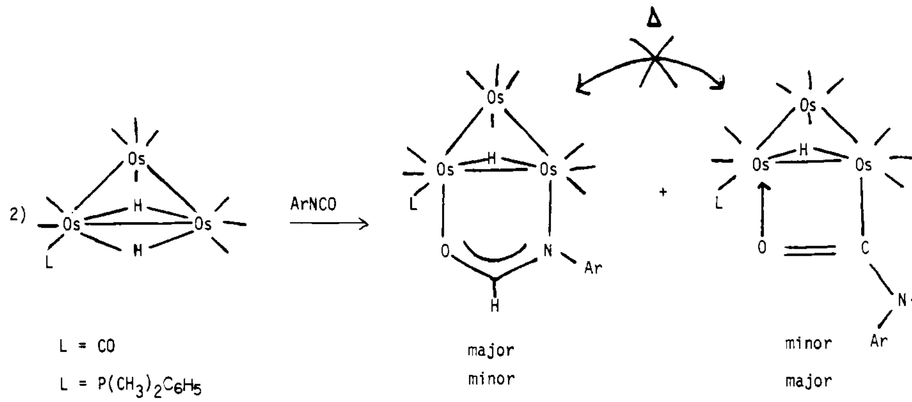
the Os(2)–Os(3) bond. There are nine linear terminal carbonyl ligands.

The Carboxamido Complexes. The major product (isolated in 32% yield) obtained from the reaction of II with *p*-tolyl isocyanate has the formula (μ-H)(μ-*p*-$CH_3C_6H_4NHCO$)$Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (VI). This complex was characterized spectroscopically and by an X-ray crystallographic analysis. The infrared spectrum of VI shows an absorption at 3440 cm^{-1}, which can be attributed to an N–H stretching vibration while a broad resonance at δ 7.23 in the ^{1}H NMR spectrum can be assigned to an N–H hydrogen atom. A hydride resonance was observed at −13.92 ppm.

An ORTEP diagram of VI is shown in Figure 3. Interatomic distances and angles are given in Tables VI and VII. This complex also contains a triangular cluster of three osmium atoms. There are nine linear terminal carbonyl ligands. A dimethylphenylphosphine ligand is coordinated in an equatorial coordination site to Os(1). The most interesting ligand is a carboxamido ligand which bridges the Os(1)–Os(2) edge of the cluster in a diaxial coordination arrangement. It is bonded to the cluster through the carbon atom C(10) to Os(2) and the oxygen atom O(10) to Os(1). The C(10)–O(10) distance at 1.254 (8) Å and the C(10)–N distance at 1.345 (8) Å indicate multiple-bond character in the form of a delocalization through the N–C–O unit. A hydrogen arom is believed to be bonded to the nitrogen atom, but this was not observed crystallographically. The hydride ligand was not observed crystallographically, but it is believed to bridge the Os(1)–Os(2) edge of the cluster as in III and V. V was also obtained in the reaction of II with *p*-tolyl isocyanate. It was difficult to separate pure V from VI, but, spectroscopically, the ratio of V/VI was approximately 1/3.

A minor product (1% yield) was also isolated from the reaction of I with *p*-$CH_3C_6H_4NCO$. Its infrared spectrum showed an N–H stretching vibration at 3430 cm^{-1} and a carbonyl absorption pattern which resembled that of III. Its ^{1}H NMR spectrum showed a broad resonance at δ 7.36 (N–H) and a high-field singlet at −14.07 ppm which can be attributed to a bridging hydride ligand. The mass spectrum showed a parent ion at *m*/*e* 991 (^{192}Os) and ions corresponding to the loss of each of nine carbonyl ligands. Accordingly, we formulate this product as (μ-H)(μ-*p*-$CH_3C_6H_4NHCO$)$Os_3(CO)_{10}$

Scheme I



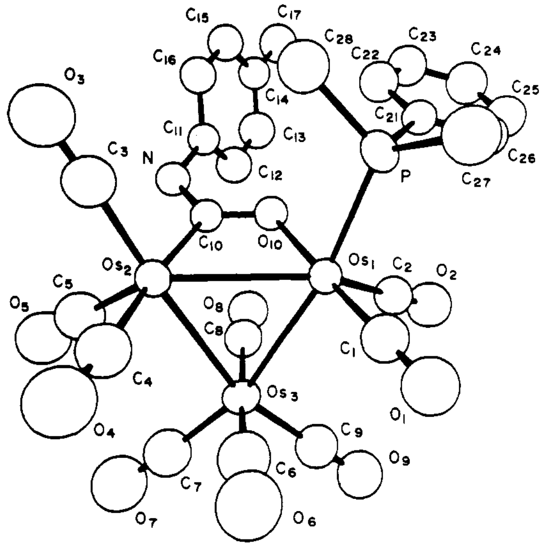


Figure 3. ORTEP diagram of $(\mu\text{-H})(\mu\text{-}p\text{-CH}_3C_6H_4NHCO)Os_3(CO)_9[P(CH_3)_2C_6H_5]$ (VI) showing 50% probability ellipsoids.

(VII), which we believe is a decacarbonyl analogue of **VI**.

Allowing that VII might have been formed from III or vice versa, we thermolyzed pure samples of III and VII independently. III could not be converted into VII and vice versa even under conditions more severe than those of their formation. Similar results were obtained for V and VI.

Discussion

Mononuclear transition metal hydride complexes react with isocyanates by hydrogen transfer, producing either chelating formamido complexes[12a] or C-coordinated carboxamido complexes.[15] The latter products are formed in base-promoted reactions and are believed to proceed via a proton abstraction from the metal hydride and readdition to a metal isocyanate adduct.[15]

The reaction of I with aryl isocyanates is exemplified in Scheme I. Hydride transfer to either the carbon or nitrogen atom of the isocyanate can occur, although transfer to the carbon is by far the preferred route. Both the formamido and carboxamido ligands bridge an edge of the cluster. Since III and VII cannot be interconverted, it appears that they must have been formed in independent, competing reactions. While we have shown previously that intramolecular and dissociative hydrogen-transfer processes can produce different products,[3a] this does not appear to be an explanation of the difference in this case since the same products in the same ratios were obtained in both hexane and triethylamine/hexane solvents. Whether or not an adduct between I and the isocyanate molecule is formed prior to hydrogen transfer remains to be established. Although we have not observed any such adducts, we believe the reactions most probably do proceed via such intermediates.[6] Carboxamido complexes similar to VII have been formed through the reaction of primary amines with $Os_3(CO)_{12}$.[16]

The molecular structure of II[17] is similar to that of $(H)_2Os_3(CO)_9P(C_6H_5)_3$[18] and $(H)_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$,[19] having the phosphine ligand in an equatorial coordination site with the bridging hydride ligands along the adjacent "unsaturated" osmium–osmium bond. In contrast to the reaction of I, the reaction of II with *p*-tolyl isocyanate proceeds predominantly with transfer of hydrogen to the *nitrogen atom* with formation of the carboxamido complex VI. The arrangement of ligands in the product suggests that the isocyanate molecule has entered the cluster at the hydrogen-bridged osmium–osmium bond, the presumed site of highest reactivity.[20] Why hydrogen transfer from II occurs preferentially to the nitrogen atom while the opposite was true for I has not been revealed by this work. Steric bulk introduced by the phosphine and an increase in electron density on the metal atoms caused by the more highly donating phosphine ligand are reasonable explanations; however, in either case the result is clear. *Changing the ligand structure of the cluster has caused a pronounced change in the regioselectivity of the hydrogen transfer.* Such effects could play an important role in product control in some cases of cluster catalysis.

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Registry No. I, 41766-80-7; II, 61260-84-2; III, 70545-10-7; IV, 70545-09-4; V, 76402-97-6; VI, 76402-98-7; VII, 76402-99-8; $p\text{-CH}_3C_6H_4NCO$, 622-58-2; C_6H_5NCO, 103-71-9.

Supplementary Material Available: Final fractional atomic coordinates, thermal parameters, and structure factor amplitudes for all three structures (75 pages). Ordering information is given on any current masthead page.

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