Isocyanide Insertion Reactions and Their Role in the Cluster-Catalyzed Hydrogenation of Isocyanide Molecules

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Abstract: Studies of the reactions of $H_2Os_3(CO)_{10}$ with the isocyanide molecules, CNR, R = C_6H_5, CH_3, t-C_4H_9, are reported. The initial products are 1:1 adducts of the type $H(\mu$-$H)Os_3(CO)_{10}CNR$. A hydrogen atom can be transferred to the isocyanide ligand in two different ways depending on the reaction conditions. In strong donor solvents compounds of the type $(\mu$-$H)(\mu$-C=$N(H)R)Os_3(CO)_{10}$ are obtained apparently through a proton dissociation and readdition process. When heated in weak donor solvents a hydrogen atom is transferred to the carbon atom. This evidently occurs through an intramolecular insertion type process. The initial products, $(\mu$-$H)(\mu$-η^2-HC=$NR)Os_3(CO)_{10}$, R = C_6H_5, CH_3, contain a formimidoyl ligand bridging the edge of the cluster. With further heating these compounds lose CO, reversibly, to form the complexes $(\mu$-$H)(\mu_3$-η^2-HC=$NR)Os_3(CO)_9$, R = C_6H_5, CH_3, in which the formimidoyl ligand is bonded to the face of the cluster. An X-ray crystallographic analysis of the compound $(\mu$-$H)(\mu_3$-η^2-HC=$NC_6H_5)Os_3(CO)_9$ is reported. This compound reacts with $P(OCH_3)_3$ to form the adduct $(\mu$-$H)(\mu$-η^2-HC=$NC_6H_5)Os_3(CO)_9(P(OCH_3)_3)$ which contains an *edge*-bridging formimidoyl ligand. An X-ray crystallographic analysis of this compound is also reported. From the reaction solutions which have produced the formimidoyl-containing products, the compounds $(\mu$-$H)_2Os_3(CO)_9(CNR)$, R = C_6H_5, CH_3, t-C_4H_9, have been isolated. The possible role of these compounds in the formation of the formimidoyl-containing products is discussed.

Introduction

In recent years there has been a major effort to develop and exploit the catalytic properties of organometallic cluster compounds. Two principal interests are now apparent. (1) Cluster compounds may serve as crude models for metal surfaces. Thus their study might contribute to our understanding of the way in which small molecules bond and react in heterogeneous systems.[1-3] (2) Ligands bond to clusters in a great variety of coordination forms.[4] Thus they might produce a greater variability of ligand reactivity and promote a greater variety of reactions than mononuclear catalysts.

The recent reports by Muetterties that the cluster compounds $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ catalyze the hydrogenation of carbon monoxide are particularly noteworthy since they represent the first examples of this reaction being performed under homogeneous conditions.[5] Unfortunately, the reaction rates were so low that they precluded the possibility of mechanistic studies.[1] In the hope that we might gain some insight into the mechanistic detail of this interesting reaction we have elected to study a related system which utilizes isocyanide molecules and the cluster hydride, $H_2Os_3(CO)_{10}$. The utilization of $H_2Os_3(CO)_{10}$ is reasonable because it is a major product of the reaction of $Os_3(CO)_{12}$ with hydrogen[6] and readily forms adducts with a variety of donor ligands.[7] The close similarity of isocyanide molecules and carbon monoxide is also appealing. Here we wish to report the details of our studies of these reactions which constitute what we believe are the initial stages of the hydrogenation of isocyanide molecules by cluster hydride compounds. A preliminary report of this work has been published.[8]

Results

Formation of Isocyanide Adducts of $H_2Os_3(CO)_{10}$. As expected,[7] we have found that $H_2Os_3(CO)_{10}$ readily reacts with a variety of isocyanides to form adducts of the type $H_2O_3(CO)_{10}(CNR)$, R = C_6H_5, CH_3, and t-C_4H_9. The infrared spectra of all three adducts show absorptions in the region 2150–2250 cm^{-1} (Table I) which are characteristic of terminally coordinated isocyanide ligands. The low-temperature ^1H NMR spectra show resonances which indicate the presence of two isomers each of which has one bridging and one terminal hydride ligand. As the temperature is raised, the resonances broaden and collapse into the base line.[7a] This is indicative of rapid intramolecular scrambling and as is shown

below does occur through a nondissociative process. The molecular structure of these compounds has been verified by X-ray crystallographic methods.[9] An ORTEP diagram of the *tert*-butyl derivative is shown in Figure 1. A terminally coordinated isocyanide ligand is axially coordinated to the osmium atom Os(2). The hydride ligands were not observed crystallographically but the seemingly empty coordination site on atom Os(3) undoubtedly signifies the location of the terminal hydride ligand. The bridging hydride ligand probably straddles the Os(2)–Os(3) bond since this is the longest of the three metal–metal bonds. These molecules are structurally similar to $H_2Os_3(CO)_{11}$[10] and $H_2Os_3(CO)_{10}(P(C_6H_5)_3)$,[11] except that the latter has the triphenylphosphine ligand in an equatorial coordination site.

Since the reducing agent, H_2, and the prospective substrate, isocyanide, are both bonded to the cluster, it seemed reasonable to expect that perhaps by heating the two species could be induced to combine. They do, but we have found that the products obtained depend intimately on the donor ability of the reaction solvent.

Thermolysis of the Adducts in Poor Donor Solvents. Thermolyses of all three adducts in poor donor solvents such as hexanes, octane, or even *n*-butyl ether proceeded in the following way. The yellow solutions of the adducts initially turned red. During this time IR spectra showed the disappearance of the isocyanide absorption of the adduct and the formation of a new isocyanide absorption at ~30–50 cm^{-1} lower in energy. If thermolysis was terminated upon reaching the maximum red coloration,[12] chromatographic workup permitted the isolation of low yields of red compounds which contained this new isocyanide absorption. The combination of IR, ^1H NMR, elemental analyses, and X-ray crystallographic analyses[9] of the *tert*-butyl and phenyl analogues confirmed the formulation of these molecules as $(\mu$-$H)_2Os_3(CO)_9(CNR)$. The molecular structure of the *tert*-butyl analogue is shown in Figure 2. This compound is simply an isocyanide analogue of $(\mu$-$H)_2$-$Os_3(CO)_{10}$[13] and is formed by the elimination of 1 mol of CO from the original adduct. The ^1H NMR spectra show three hydride resonances (Table 1), two of which are of equal intensity. We interpret this as due to a mixture of two isomers. One isomer has the isocyanide ligand in an equatorial position as observed in the structure of the *tert*-butyl derivative while the second isomer has the isocyanide ligand in one of the four pseudo-axial ligand sites. This is the configuration as observed

Table I

compd	yield, %	mp, °C	anal. found (calcd) C	anal. found (calcd) H	anal. found (calcd) N	IR, cm⁻¹ (±3 cm⁻¹)	¹H NMR, δ ppm
$H_2Os_3(CO)_{10}(CN-t-C_4H_9)$	100	125.5–126.0	19.61 (19.25)	1.48 (1.18)	1.82 (1.50)	2200 m, 2096 s, 2065 vs,ᵃ 2048, vs, 2028 vs, 2000 vs, 1985 sh	−9.84 d, −19.73 d, J = 3.2 Hz, 1.54 s,ᵉ⁻ᵍ −10.12 d, −19.88 J = 4.0 Hz, 1.56 sʰ
$H_2Os_3(CO)_{10}(CNCH_3)$	96	118.5–119.5	16.62 (16.12)	0.77 (0.56)	1.83 (1.57)	2237 sh, 2232 m, 2100 sᵃ 2070 vs, 2050 vs, 2027 vs, 2005 vs, 1983 m	−9.88 d, −19.76 d, = 3.0 Hz, 3.93ᵉ⁻ᵍ −10.14 d, −19.84 d, J = 4.3 Hz, 3.94ʰ
$H_2Os_3(CO)_{10}(CNC_6H_5)$	76	97–102	21.75 (21.36)	0.98 (0.74)	1.30 (1.46)	2185 m, 2100 s, 2070 vs,ᵈ 2052 vs, 2032 vs, 2005 vs, 1982 s, 1967 m	−9.76 d, −19.57 d, J = 3.8 Hzᵉ⁻ᵍ −10.07 d, −19.67 d, J = 3.8 Hz, 7.6 m
$H_2Os_3(CO)_9(CN-t-C_4H_9)$	22	109–110	19.24 (18.52)	1.69 (1.22)	1.52 (1.54)	2165 m, 2080 s, 2053 vs,ᵇ 2027 vs, 2010 vs, 1995 s, 1978 s, 1965 m	−11.32 s, 1.69 s;ᵉ·ᵍ −11.21 s, −12.66 s, 1.58 sʰ; −10.89 s, −11.07 s, 1.45 sⁱ
$H_2Os_3(CO)_9(CNCH_3)$	16	97–114	15.53 (15.26)	0.79 (0.58)	1.72 (1.62)	2196 m, 2092 s, 2052 vs,ᵇ 2030 vs, 2014 vs, 2000 s, 1984 s, 1967 m	−11.30 s, 3.77 s;ᵉ·ᵍ −11.19 s, −12.74 s, 3.73 s;ʰ −10.93 s, −11.06 s, 3.69 sⁱ
$H_2Os_3(CO)_9(CNC_6H_5)$	26	113.5–115.0	21.09 (20.71)	1.08 (0.76)	1.28 (1.51)	2152 m, 2089 s, 2057 vs,ᵇ 2030 vs, 2014 vs, 2000 s, 1986 s, 1973 m	−11.24 s;ᶜ·ᵍ −11.07 s, −12.165; s;ʰ 7.5 m
$(\mu-H)(\mu-\eta^2-HC=NC_6H_5)Os_3(CO)_{10}$	64	131–133	21.82 (21.36)	0.79 (0.74)	1.59 (1.46)	2103 m, 2064 vs, 2055 vs,ᵇ 2022 vs, 2010 vs, 1995 vs, 1975 m	−15.15 s, 11.25 sᵉ 7.4 m
$(\mu-H)(\mu-\eta^2-HC=NCH_3)Os_3(CO)_{10}$	9	215–216	16.58 (16.12)	0.77 (0.56)	1.85 (1.57)	2105 m, 2063 vs, 2054 vs,ᵇ·ʲ 2021 s, 2008 vs, 1992 vs, 1975 m	−15.16 s,ᵉ 10.33 s, 3.56 s
$(\mu-H)(\mu_3-\eta^2-HC=NCH_3)Os_3(CO)_9$	18	178–183 dec	15.70 (15.26)	0.64 (0.58)	1.67 (1.62)	2095 m, 2067 vs, 2040 vs,ᵇ·ʲ 2013 vs, 2000 s, 1995 vs, 1970 m	−17.82 sᵉ·ʲ 10.15 s, 3.91 s
$(\mu-H)(\mu_3-\eta^2-HC=NC_6H_5)Os_3(CO)_9$	65		k			2097 m, 2067 vs, 2040 vs,ᵇ 2015 vs, 2005 s, 2000 vs, 1977 m, 1971 m	−17.45 s,ᵉ 10.69 s 7.3 m
$(\mu-H)(\mu-\eta^2-HC=NC_6H_5)Os_3(CO)_9(P(OCH_3)_3)$	17	110–112	k			2087 s, 2048 vs, 2012 vs,ᵇ 1996 vs, 1972 m, 1964 m	−14.95 d, J_{P-H} = 9.7 Hzᵉ 10.99 d, J_{P-H} 8.9 Hz, 3.81 d, J_{P-CH_3} = 12.2 Hz 7.2 m
$(\mu-H)(\mu-\eta^1-C=N(H)(t-C_4H_9))Os_3(CO)_{10}$	60	134–136	19.56 (19.25)	1.50 (1.18)	1.60 (1.50)	3295 m, 2098 m, 2057 vs,ᶜ 2050 vs, 2015 vs, 2002 sh, 1980 s	−16.85 s, 1.51 sᵉ
$(\mu-H)(\mu-\eta^1-C=N(H)(CH_3))Os_3(CO)_{10}$	34	138–141	15.79 (16.12)	1.08 (0.56)	1.71 (1.57)	3327 m, 2100 m, 2060 vs,ᶜ 2052 vs, 2020 vs, 2003 s, 1990 s, 1557 m	−16.67 s, 10.45 s, 3.67 d,ᵉ J = 4.6 Hz
$(\mu-H)(\mu-\eta^1-C=N(H)C_6H_5)Os_3(CO)_{10}$	l	l	l			3300 m, 2087 m, 2050 vs,ᵈ 2042 s, 2008 vs, 1996 s, 1974 s, 1582 m	−16.21 d, J = 2.7 Hzᵉ 12.52 br (N–H) 7.2 m
$Os_3(CO)_{11}(CN-t-C_4H_9)$	12	141–145	20.26 (19.98)	1.27 (0.94)	1.57 (1.46)	2180 s, 2100 m, 2052 s, 2040 s,ᵃ 2020 m, 2005 s, 1980 m	1.58 sᵉ

ᵃ CHCl₃. ᵇ Hexanes. ᶜ CDCl₃. ᵈ n-Butyl ether. ᵉ Acetone-d₆. ᶠ Al −70 °C. ᵍ Isomer 1. ʰ Isomer 2. ⁱ Possibly third isomer. ʲ Essentially identical with compound of same formula prepared by a different method, ref 16. ᵏ Confirmed by X-ray crystal structure analysis. ˡ Characterized spectroscopically only.

in the phenyl derivative.[9] In this latter isomer the two bridging hydride ligands are inequivalent. It has recently been reported that phosphine addition to $(\mu-H)_2Os_3(CO)_{10}$ produces the compounds $(\mu-H)_2Os_3(CO)_9(PR_3)$ through loss of CO.[14]

With continued heating, the second isocyanide absorption subsequently disappeared from reaction solutions of the methyl and phenyl isocyanide adducts, but not for the *tert*-butyl analogue. Upon disappearance of the isocyanide absorption the reaction solutions returned to yellow and no prominent infrared absorptions due to isocyanide ligands were evident. At this stage either of two types of compounds could be chromatographically isolated. One type has the formula $(\mu-H)(\mu-\eta^2-HC=NR)Os_3(CO)_{10}$, R = C_6H_5, CH_3, which was obtained on the basis of IR, ¹H NMR, mass spectra, and elemental analyses. The mass spectra of these compounds show the appropriate parent ion and ions corresponding to the loss of each of ten carbonyl groups. The second type have the formula $(\mu-H)(\mu_3-\eta^2-HC=NR)Os_3(CO)_9$, R = C_6H_5, CH_3, which was obtained on the basis of IR, ¹H NMR, elemental analyses, and an X-ray crystallographic analysis of the phenyl derivative (vide infra). The latter compound is obtained at the
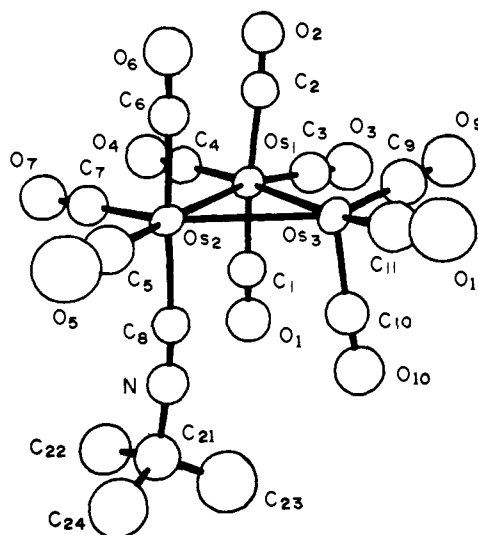

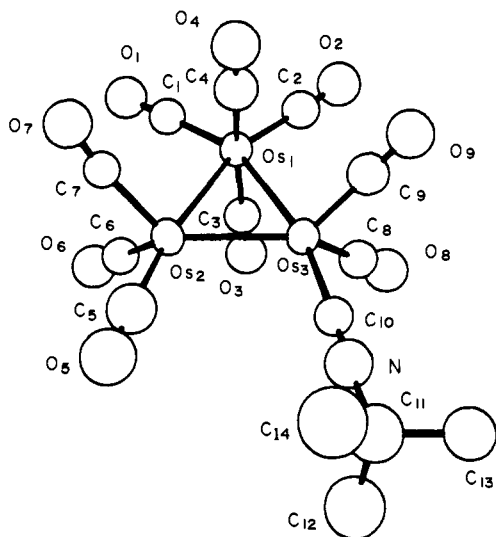Figure 1. An ORTEP diagram of $H_2Os_3(CO)_{10}(CN-t-C_4H_9)$ showing 50% probability ellipsoids.

Figure 2. An ORTEP diagram of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$ showing 50% probability ellipsoids.

Figure 3. An ORTEP diagram of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}{=}\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$ showing 50% probability ellipsoids.

Figure 4. An ORTEP diagram of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}{=}\text{NC}_6\text{H}_5)\text{Os}_3$ $(\text{CO})_9(\text{P(OCH}_3)_3)$ showing 50% probability ellipsoids.

expense of the former giving in the limit none of the former. The difference between the compounds is simply the thermolytic removal of 1 mol of carbon monoxide. Indeed, isolated samples of the decacarbonyls can be quantitatively converted into the nonacarbonyls. What was somewhat surprising was the fact that the reaction was fully reversible and solutions of the nonacarbonyl under 1 atm of carbon monoxide can be quantitatively converted back into the decacarbonyls. In addition, the nonacarbonyl readily forms a mono adduct with trimethyl phosphite. The ^{1}H NMR spectra of these compounds show resonances in the regions δ 10–12 and -15 to -18 ppm. The latter we attribute to bridging metal hydride ligands while the former we interpret as due to hydrogen atoms of formimidoyl ligands.[15] As is described below, crystal structure analyses show that the nonacarbonyl complexes contain $\mu_3\text{-}\eta^2\text{-HC}{=}\text{NR},$ *face*-bridged, formimidoyl ligands while the decacarbonyl and phosphite adduct complexes contain $\mu_2\text{-}\eta^2\text{-HC}{=}\text{NR},$ *edge*-bridged, formimidoyl ligands.

The *tert*-butyl isocyanide complexes could not be converted into complexes containing formimidoyl ligands. Instead, we isolated small amounts of the compound $\text{Os}_3(\text{CO})_{11}(\text{CN-}t\text{-}\text{C}_4\text{H}_9)$ from the thermolysis solutions which contained much $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-}\text{C}_4\text{H}_9)$. We believe that this is due to a competitive loss of H_2 from the original isocyanide adducts followed by the addition of carbon monoxide. Trace amounts of $\text{Os}_3(\text{CO})_{11}(\text{CNCH}_3)$ were isolated from the thermolysis reactions of the methyl isocyanide adducts. It is notable that the yields of formimidoyl-containing products from the methyl isocyanide adduct are substantially smaller than those from the phenyl isocyanide adduct. Interestingly, Deeming et al. have recently reported the syntheses of these *N*-methylformimidoyl compounds through the reaction of trimethylamine with $\text{Os}_3(\text{CO})_{12}$.[16]

Description of the Structure of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}{=}\text{N-}\text{C}_6\text{H}_5)\text{Os}_3(\text{CO})_9$. The molecular structure of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}{=}\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$ is shown in Figure 3. The compound contains a regular triangle of three osmium atoms. Bond distances and angles are listed in Tables IV and V. Three linear terminal carbonyl ligands are bonded to each osmium atom. The gross carbonyl arrangement is such that three ligands lie oriented perpendicular to the osmium triangle while the remaining six lie more or less in the plane of the triangle. On the remaining face of the cluster is bonded a η^2-formimidoyl ligand which is attached to all three osmium atoms through the iminyl function, $\text{C}(10)\text{-N}$. Osmium atom $\text{Os}(1)$ is bonded solely to the carbon, $\text{Os}(1)\text{-C}(10) = 2.032$ (10) Å, and $\text{Os}(2)$ is bonded solely to the nitrogen, $\text{Os}(2)\text{-N} = 2.121$ (9) Å. Os-
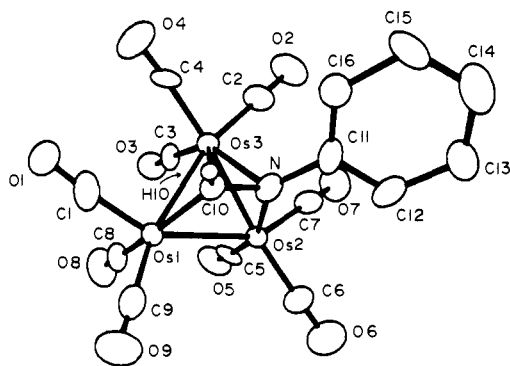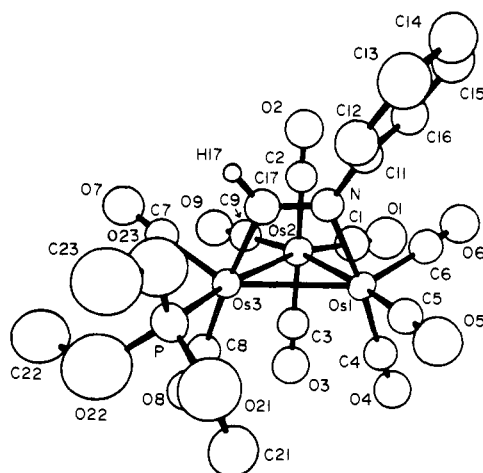
mium atom $\text{Os}(3)$ is bonded to both the carbon and the nitrogen atoms, $\text{Os}(3)\text{-C}(10) = 2.266$ (10) Å; $\text{Os}(3)\text{-N} = 2.219$ (9) Å. The basic structure is very similar to that of the compound $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-CH}_3\text{C}{=}\text{NH})\text{Fe}_3(\text{CO})_9$ which was recently reported by Kaesz.[17] The iminyl bond distance, $\text{C}(10)\text{-N}$, is very long at 1.415 (11) Å, and approaches that of a C–N single bond (1.47 Å). η^2-Iminyl ligands show much shorter C–N bond distances when bonded to only one, 1.232 (6)[18] and 1.30 (1) Å,[19] and two metal atom groupings, 1.278 (10[20] and 1.32 (1) Å.[21] It is also substantially longer than the C–N distance of 1.344 (2) Å found in the complex $(\mu\text{-H})\text{-}(\mu_3\text{-}\eta^2\text{-CH}_3\text{C}{=}\text{NH})\text{Fe}_3(\text{CO})_9$[17] where the iminyl group is bonded to three iron atoms. The formimidoyl hydrogen atom, $\text{H}(10)$, was located, as shown, in difference Fourier maps, but no attempts to refine its position were made. The bridging hydride ligand was not observed crystallographically but is assumed to occupy a position across the $\text{Os}(1)\text{-Os}(2)$ bond analogous to that in the iron complex.[17] Pertinent atomic planes are listed in Table VI.

Description of the Structure of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}{=}\text{N-}\text{C}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$. The molecular structure of the compound $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}{=}\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$ formed by the addition of $\text{P(OCH}_3)_3$ to the above *face*-bridged compound is shown in Figure 4. Bond distances and angles are listed in Tables VIII and IX. This compound also contains a regular triangle of three osmium atoms. Nine linear terminal carbonyl ligands are distributed such that $\text{Os}(1)$ contains three, $\text{Os}(2)$ contains four, and $\text{Os}(3)$ contains only two. This indicates that a carbonyl shift between metal atoms has accompanied the incorporation of $\text{P(OCH}_3)_3$ into the cluster unit since each osmium atom in the *face*-bridged compound contained three carbonyl ligands.

Table II. Crystallographic Data for the X-ray Diffraction Structural Analyses of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=NC_6H_5)Os_3(CO)_9$ and $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=NC_6H_5)Os_3(CO)_9(P(OCH_3)_3)$

	$(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=NC_6H_5)$-$Os_3(CO)_9$	$(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=NC_6H_5)$-$Os_3(CO)_9(P(OCH_3)_3)$
A. Crystal Parameters at 25 °C		
space group	$P2_1/n$	$P\bar{1}$
a	8.518 (3) Å	9.345 (4) Å
b	8.095 (2) Å	12.323 (3) Å
c	30.141 (4) Å	12.609 (4) Å
α	90.0°	75.88 (2)°
β	93.85 (2)°	81.32 (3)°
γ	90.0°	82.58 (3)°
Z	4	2
ρ_{calcd}, g/cm³	2.97	2.52
B. Measurement of Intensity Data		
detector aperture horizontal: $A + B \tan\theta$	A = 3.0 mm B = 1.0 mm	A = 2.6 mm B = 1.2 mm
vertical	4 mm	4 mm
crystal–detector distance	330 mm	330 mm
reflections measured	$+h, +k, \pm l$	$+h, \pm k, \pm l$
max 2θ	50°	50°
scan type	moving crystal–stationary counter	moving crystal–stationary counter
θ scan width, deg	$0.70 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
background	¼ additional scan at each end of scan	¼ additional scan at each end of scan
θ scan rate (variable)	max 10.0°/min min 1.1°/min	max 10.0°/min min 1.25°/min
no. reflections used $(F^2 > 3.0\sigma(F)^2)$	2468	3548
C. Treatment of Data		
absorption coeff μ	195.5 cm⁻¹	147.1 cm⁻¹
grid	$10 \times 8 \times 10$	$14 \times 6 \times 8$
transmission factors	max 0.268 min 0.022	max 0.338 min 0.131
ignorance factor p	0.02	0.03
D. Solution and Refinement Data		
R	0.034	0.045
R_w	0.040	0.054
max shift/error (final cycle)	0.16	0.35
peak max final diff Four. e/Å³	1.88	2.35
error obsd unit weight	2.23	3.17
hydrogen atom positions	calcd (not refined) (excluding metal hydride)	calcd (not refined) (excluding methyl groups and metal hydride)
thermal parameters anisotropic isotropic	all nonhydrogen atoms	osmium and phosphorus atoms all remaining atoms

Table III. Final Fractional Atomic Coordinates for $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=NC_6H_5)Os_3(CO)_9$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Os(1)	1.025 38 (7)	0.149 40 (9)	0.181 89 (2)	C(12)	0.697 (2)	0.495 (2)	0.0626 (5)
Os(2)	0.925 90 (7)	0.124 96 (9)	0.086 26 (2)	C(13)	0.586 (2)	0.607 (2)	0.0448 (5)
Os(3)	0.721 47 (7)	0.057 94 (8)	0.150 34 (2)	C(14)	0.453 (2)	0.635 (2)	0.0647 (5)
O(2)	0.409 (1)	0.016 (2)	0.0943 (4)	C(15)	0.423 (2)	0.556 (3)	0.1030 (6)
O(3)	0.836 (1)	−0.297 (2)	0.1602 (4)	C(16)	0.534 (2)	0.443 (2)	0.1214 (5)
O(4)	0.552 (2)	0.072 (2)	0.2360 (4)	C(2)	0.527 (2)	0.024 (2)	0.1145 (5)
O(5)	1.079 (2)	−0.207 (2)	0.0687 (5)	C(3)	0.788 (2)	−0.165 (2)	0.1571 (4)
O(6)	1.122 (2)	0.338 (2)	0.0273 (4)	C(4)	0.608 (2)	0.070 (2)	0.2038 (5)
O(7)	0.670 (2)	0.047 (2)	0.0125 (4)	C(5)	1.028 (2)	−0.079 (3)	0.0745 (5)
O(8)	1.224 (2)	−0.173 (2)	0.1873 (4)	C(6)	1.052 (2)	0.260 (3)	0.0499 (4)
O(9)	1.283 (2)	0.402 (2)	0.2049 (4)	C(7)	0.764 (2)	0.080 (2)	0.0399 (5)
O(1)	0.932 (1)	0.134 (2)	0.2779 (3)	C(8)	1.152 (2)	−0.052 (3)	0.1865 (5)
N	0.787 (1)	0.296 (2)	0.1198 (3)	C(9)	1.189 (2)	0.304 (3)	0.1957 (5)
C(10)	0.842 (2)	0.303 (2)	0.1650 (4)	C(1)	0.973 (2)	0.142 (2)	0.2421 (5)
C(11)	0.667 (2)	0.413 (2)	0.1011 (4)				

Table IV. Bond Distances for $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=NC_6H_5)Os_3(CO)_9$

atoms	distance, Å	atoms	distance, Å
Os(1)–Os(2)	2.956 (1)	C(10)–N	1.415 (11)
Os(1)–Os(3)	2.797 (1)	N–C(11)	1.478 (13)
Os(2)–Os(3)	2.740 (1)	C(11)–C(12)	1.377 (13)
Os(1)–C(10)	2.032 (10)	C(12)–C(13)	1.390 (16)
Os(1)–C(1)	1.897 (11)	C(13)–C(14)	1.333 (17)
Os(1)–C(8)	1.954 (16)	C(14)–C(15)	1.357 (17)
Os(1)–C(9)	1.901 (15)	C(15)–C(16)	1.403 (15)
Os(2)–N	2.121 (9)	C(16)–C(11)	1.345 (15)
Os(2)–C(5)	1.911 (14)	C(1)–O(1)	1.161 (12)
Os(2)–C(6)	1.924 (12)	C(2)–O(2)	1.144 (13)
Os(2)–C(7)	1.933 (12)	C(3)–O(3)	1.149 (14)
Os(3)–C(10)	2.266 (10)	C(4)–O(4)	1.108 (11)
Os(3)–N	2.219 (9)	C(5)–O(5)	1.142 (15)
Os(3)–C(2)	1.936 (12)	C(6)–O(6)	1.127 (14)
Os(3)–C(3)	1.897 (13)	C(7)–O(7)	1.138 (13)
Os(3)–C(4)	1.937 (10)	C(8)–O(8)	1.155 (16)
		C(9)–O(9)	1.141 (15)

Table V. Bond Angles for $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=NC_6H_5)Os_3(CO)_9$

atoms	angle, deg	atoms	angle, deg
Os(1)–Os(2)–Os(3)	58.67 (1)	Os(2)–Os(3)–C(10)	70.3 (2)
Os(2)–Os(1)–Os(3)	56.81 (1)	Os(2)–Os(3)–C(2)	101.3 (3)
Os(1)–Os(3)–Os(2)	64.52 (1)	Os(2)–Os(3)–C(3)	96.6 (3)
Os(2)–Os(1)–C(10)	68.4 (2)	Os(2)–Os(3)–C(4)	162.4 (4)
Os(2)–Os(1)–C(1)	149.3 (4)	N–Os(3)–C(10)	36.8 (3)
Os(2)–Os(1)–C(8)	97.7 (3)	N–Os(3)–C(2)	97.0 (4)
Os(2)–Os(1)–C(9)	114.6 (3)	N–Os(3)–C(3)	141.9 (4)
Os(3)–Os(1)–C(10)	53.1 (3)	N–Os(3)–C(4)	117.1 (5)
Os(3)–Os(1)–C(1)	92.7 (4)	C(10)–Os(3)–C(2)	126.5 (5)
Os(3)–Os(1)–C(8)	107.3 (4)	C(10)–Os(3)–C(3)	133.0 (4)
Os(3)–Os(1)–C(9)	153.9 (4)	C(10)–Os(3)–C(4)	92.3 (4)
C(10)–Os(1)–C(1)	91.9 (4)	C(2)–Os(3)–C(3)	99.4 (5)
C(10)–Os(1)–C(8)	159.9 (5)	C(2)–Os(3)–C(4)	90.8 (5)
C(10)–Os(1)–C(9)	100.9 (5)	C(3)–Os(3)–C(4)	96.9 (5)
C(1)–Os(1)–C(8)	94.0 (5)	Os(1)–C(1)–O(1)	175.6 (11)
C(1)–Os(1)–C(9)	90.8 (4)	Os(1)–C(8)–O(8)	176.9 (10)
C(8)–Os(1)–C(9)	98.1 (6)	Os(1)–C(9)–O(9)	177.0 (12)
Os(1)–Os(2)–N	68.0 (2)	Os(2)–C(5)–O(5)	174.6 (12)
Os(1)–Os(2)–C(5)	97.7 (3)	Os(2)–C(6)–O(6)	177.3 (11)
Os(1)–Os(2)–C(6)	112.5 (3)	Os(2)–C(7)–O(7)	177.0 (13)
Os(1)–Os(2)–C(7)	149.6 (3)	Os(3)–C(2)–O(2)	174.6 (12)
Os(3)–Os(2)–N	52.5 (2)	Os(3)–C(3)–O(3)	176.2 (11)
Os(3)–Os(2)–C(5)	106.2 (4)	Os(3)–C(4)–O(4)	175.0 (11)
Os(3)–Os(2)–C(6)	156.8 (4)	C(10)–N–C(11)	121.2 (8)
Os(3)–Os(2)–C(7)	90.9 (3)	N–C(11)–C(12)	118.0 (10)
N–Os(2)–C(5)	158.1 (4)	N–C(11)–C(16)	121.5 (9)
N–Os(2)–C(6)	104.7 (5)	C(12)–C(11)–C(16)	120.4 (10)
N–Os(2)–C(7)	94.1 (4)	C(11)–C(12)–C(13)	118.6 (10)
C(5)–Os(2)–C(6)	96.0 (6)	C(12)–C(13)–C(14)	121.0 (11)
C(5)–Os(2)–C(7)	90.9 (5)	C(13)–C(14)–C(15)	120.9 (11)
C(6)–Os(2)–C(7)	95.4 (5)	C(14)–C(15)–C(16)	119.0 (11)
Os(1)–Os(3)–N	70.1 (2)	C(15)–C(16)–C(11)	120.0 (10)
Os(1)–Os(3)–C(10)	45.9 (2)	Os(1)–C(10)–N	114.6 (7)
Os(1)–Os(3)–C(2)	164.9 (4)	Os(1)–C(10)–Os(3)	81.0 (4)
Os(1)–Os(3)–C(3)	87.2 (4)	Os(2)–N–C(10)	109.0 (7)
Os(1)–Os(3)–C(4)	102.0 (3)	Os(2)–N–Os(3)	78.3 (3)
Os(2)–Os(3)–N	49.3 (2)	Os(3)–N–C(10)	73.4 (5)
		Os(3)–C(10)–N	69.8 (5)

A normal trimethyl phosphite ligand is bonded to osmium atom Os(3). The most interesting feature is the formimidoyl ligand which now occupies a bridging position on the *edge* of the cluster along the Os(1)–Os(3) bond. The formimidoyl C–N distance is 1.32 (1) Å, nearly 0.1 Å shorter than the distance found in the *face*-bridged compound. Overall, this compound is very similar to $(\mu\text{-H})(\mu\text{-}\eta^2\text{-}(C_6H_5)C=NCH_3)Os_3(CO)_{10}$ which contains an *edge*-bridging iminyl group.[20] In this latter compound the iminyl C–N distance was 1.278 (10) Å. The osmium–carbon, 2.075 (9) Å, and osmium–nitrogen, 2.150 (6) Å, distances are very similar to those observed in the iminyl complex.[20] Least-squares planes of several atomic groupings are listed in Table VI.

The formimidoyl ligand has now been structurally characterized in compounds where it is coordinated to one,[15c] two, and three metal atoms. In the complex $Ru(O_2CCH_3)(\eta^1\text{-}HC=N(p\text{-}CH_3C_6H_4))(CO)(P(C_6H_5)_3)_2$ the C–N distance for the η^1-C-coordinated formimidoyl ligand was found to be 1.24 (1) Å. This distance lengthens to 1.32 (1) Å in the η^2-*edge*-bridging ligand as found in our phosphite cluster and lengthens further to 1.415 (11) Å when bonded to three metal atoms as found in our *face*-bridged cluster. This trend vividly demonstrates the notion emphasized by Muetterties[4] that polynuclear coordinations produce greater reducing effects upon unsaturated ligands than mononuclear coordination.

Thermolysis of the Adducts in Strong Donor Solvents. When thermolysis of the isocyanide adducts was performed in strong donor solvents such as THF, none of the previously described compounds was obtained. Instead, we have isolated a series of compounds which have been formulated as $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}=N(H)R)Os_3(CO)_{10}$ on the basis of IR, ^{1}H NMR, mass spectra, elemental analyses and an X-ray crystallographic analysis of the *tert*-butyl analogue.[9] These compounds are not especially stable. Although all three compounds $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}=N(H)R)Os_3(CO)_{10}$, R = C_6H_5, CH_3, and $t\text{-}C_4H_9$, were readily prepared and characterized spectroscopically, the phenyl derivative resisted isolation owing to decomposition processes and was not completely characterized. These compounds are similar to the compound $(\mu\text{-H})(\mu\text{-C}=N\text{-}(CH_3)_2)Ru_3(CO)_{10}$ which has also been analyzed structurally.[22] The $\mu\text{-}\eta^1$-iminyl ligand is bonded to the cluster through the carbon atom only and bridges two osmium atoms. The nitrogen atom contains the R substituent and a hydrogen atom, $\nu(\text{N-H}) = 3250\text{-}3350$ cm^{-1}. The same products can be obtained in nondonor solvents upon addition of trace amounts of mild bases such as triethylamine. For example, the original isocyanide adducts are stable for several hours in chloroform solutions; however, the addition of catalytic quantities of triethylamine produced rapid (5–10 min depending on the

complex) conversion to the $\mu\text{-}\eta^1$-iminyl complexes at room temperature. Spectroscopically, the conversion appears to be quantitative.

Although the $\mu\text{-}\eta^1$-iminyl compounds do decompose, we were unable to prepare any of the formimidoyl-containing compounds from them even under prolonged and forcing thermolytic treatment. Likewise, we were unable to prepare the $\mu\text{-}\eta^1$-iminyl compounds from thermolyses of the formimidoyl compounds.

Discussion

In the scheme is presented a summary of our results. $H_2Os_3(CO)_{10}$ reacts smoothly and cleanly with isocyanide molecules to form 1:1 adducts, A. These adducts exist in solution as a mixture of two isomers which contain terminally coordinated isocyanide ligands. Bridging and terminal hydride ligands are rapidly equilibrating at room temperature.[7a] In the presence of mild base or strong donor solvents, the adducts are readily converted into the N-hydridoiminyl compounds, E. Because this reaction is base catalyzed, we believe that the mechanism involves deprotonation and formation of a transient anion, $(\text{H})Os_3(CO)_{10}CNR^-$. In the anionic form the isocyanide ligand moves into a bridging position whereupon lone-pair character develops on the nitrogen atom. The proton is then returned to the anion at the nitrogen atom to complete formation of the product. This last step is formally analogous to the protonation of the anion $(\mu\text{-H})(\mu\text{-CO})Fe_3(CO)_{10}^-$ on the oxygen atom of the bridging carbonyl ligand.[23] Furthermore, since this dissociative process is very slow in nondonor solvents, this indicates that the rapid interconversion of the

+ CNR   R = C₆H₅, CH₃, t-C₄H₉

A   E

$Os_3(CO)_{11}CNR$ $\xleftarrow[+CO]{-H_2}$ BASE

+ CO ‖ − CO

B   C   D

2 ↓ + CO   2 ↑ reorrange   ↓ + P(OCH₃)₃

*   *

F   P(OCH₃)₃

$\ast$ not observed
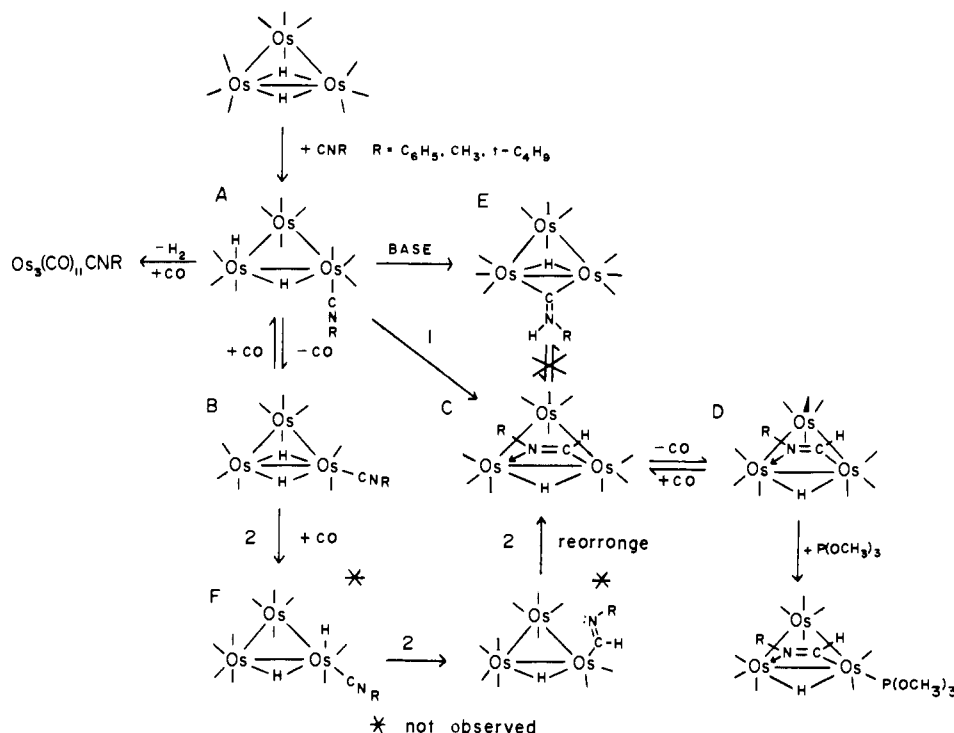
bridging and terminal hydride ligands as seen by NMR in the original adducts must be due to a nondissociative process.

When heated in poor donor solvents, a reaction occurs in which the adducts initially lose 1 mol of carbon monoxide to form the red-colored products, $(\mu\text{-H})_2Os_3(CO)_9(CNR)$, B, which are analogues of the original starting material, $(\mu\text{-H})_2Os_3(CO)_{10}$.

With continued heating, the methyl and phenyl isocyanide products again add carbon monoxide and are converted into the products, C, which contain *edge*-bridging formimidoyl ligands. We have found that under mild conditions the addition of carbon monoxide to the compounds, B, quantitatively regenerates the original adducts, A (i.e., the A → B conversion is fully reversible.). The mechanism whereby the compounds, A, are converted into the products, C, is not clear at this time but we shall discuss two possibilities. Let us point out firstly, however, that, since the A → E conversion is apparently a dissociative process, and since the products C and E cannot be interconverted, we believe that the conversion of A to C is almost certainly an intramolecular, insertion-type, process.

One possible mechanism is a direct conversion of A into C, mechanism 1. The mechanism suffers from the fact that only the bridging hydrogen atom is physically capable of participating in the insertion. Because that hydrogen atom is bonded to two metal atoms, we believe that its tendency to engage in such a reaction will be reduced. The nature of intermediates which might be traversed in going from A to C is unclear and would be difficult to describe, but it is fairly clear that A will not be smoothly transformed into C in a one-step process.

Alternatively, one could imagine the addition of CO to B to produce an intermediate F (mechanism 2), in which the hydrogen atom has been shifted to a terminal position on the osmium atom containing the isocyanide ligand. Although no other products were observed in the reaction medium if F were only 2–3 kcal less stable than A it would probably go unnoticed. In fact one could imagine an equilibrium of the type A ⇌ B ⇌ F via the intermediate B. If F were formed, an intramolecular insertion rearrangement could very likely proceed by utilizing the terminal hydride ligand. Similar insertions have been reported on previous occasions.[15a-d] Following the insertion, the lone pair on the nitrogen atom need only attack an adjacent osmium atom and induce a carbonyl shift to form C.

Thermolysis of the compounds C produces further loss of 1 mol of carbon monoxide. The formimidoyl ligand then rolls onto the face of the cluster, D. This transformation is also fully reversible and under 1 atm of CO the compounds C are quantitatively regenerated. The addition of phosphite to D is similar and produces an *edge*-bridging formimidoyl ligand. Interestingly, the addition of phosphite to the cluster has induced a carbonyl shift between osmium atoms.

It is notable that the *tert*-butyl isocyanide compounds could not be converted into formimidoyl-containing complexes. We think that this simply reflects the lower tendency of the *tert*-butyl isocyanide ligand to engage in insertion reactions.[24] From thermolysis solutions of the *tert*-butyl isocyanide adduct we have obtained the compounds $(\mu\text{-H})_2Os_3(CO)_9(CN\text{-}t\text{-}C_4H_9)$ and $Os_3(CO)_{11}(CN\text{-}t\text{-}C_4H_9)$. The formation of the latter compound suggests that the adducts, A, can also lose H_2 if conditions for other reactions are not obtained.

Finally, we would like to point out that we have not yet achieved complete hydrogenation of the original isocyanide ligands. These studies are now in progress. However, Muetterties has accomplished complete hydrogenations utilizing a different cluster system.[25] Here, we have delineated the important first steps of the reduction. It is important to recognize that, even at this very early stage, *the reduction process has assumed two very different pathways*, that is, transfer of a hydrogen to the nitrogen atom, A → E, and transfer to the carbon A → C. It is possible that the two pathways diverge. The ultimate outcomes could be fundamentally different products.

Experimental Section

General. Although the compounds generally appeared to be air stable, reactions were routinely performed under a nitrogen atmosphere. Except for *n*-butyl ether and THF, which were dried over sodium—benzophenone, no special effort was made to dry the reagent grade solvents, octane, hexanes, or pentane before use. $Os_3(CO)_{12}$ was purchased from Strem Chemicals, Newburyport, Mass. $H_2Os_3(CO)_{10}$ was made by the procedure of Kaesz.[6] The isocyanides $t\text{-}C_4H_9NC$,[26] CH_3NC,[26] and C_6H_5NC[27] were prepared by established procedures and stored at −20 °C. C_6H_5NC, which slowly decomposes at −20 °C, was usually vacuum distilled before use.

IR spectra were obtained on a Perkin-Elmer 237 infrared spectrophotometer and were calibrated with polystyrene, 1601.4 cm⁻¹

Table VI. Unit Weighted Least-Squares Planes

A. $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC=NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$			B. $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC=NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$		
plane no.	atoms	distance from plane, Å	plane no.	atoms	distance from plane, Å
1	Os(1)	0.000	1	Os(1)	0.000
	Os(2)	0.000		Os(2)	0.000
	Os(3)	0.000		Os(3)	0.000
	C(10)[a]	1.62 (2)		P[a]	−0.036 (4)
	N[a]	1.68 (1)		C(17)[a]	1.852 (13)
2	Os(1)	−0.005 (1)		N[a]	1.925 (11)
	Os(2)	0.005 (1)	2	Os(1)	−0.004 (1)
	C(10)	0.010 (15)		Os(3)	0.004 (1)
	N	−0.010 (13)		C(17)	−0.008 (15)
	C(11)[a]	0.157 (16)		N	0.008 (11)
3	Os(3)	0.000		C(11)[a]	−0.227 (15)
	C(10)	0.000	3	C(11)	0.001 (15)
	N	0.000		C(12)	−0.005 (17)
	C(11)[a]	−1.118 (16)		C(13)	0.011 (20)
4	C(11)	0.008 (15)		C(14)	−0.012 (18)
	C(12)	−0.007 (17)		C(15)	0.007 (18)
	C(13)	0.001 (18)		C(16)	−0.001 (16)
	C(14)	0.003 (19)		N[a]	0.003 (11)
	C(15)	−0.002 (19)		C(17)[a]	−0.912 (15)
	C(16)	−0.004 (17)			
	N[a]	−0.004 (14)			
	C(10)[a]	−0.935 (14)			

Dihedral Angles between the Planes

planes	angle, deg	planes	angle, deg	planes	angle, deg
1–2	58.8	2–3	70.2	1–2	76
1–3	−51.0	2–4	−45.3	1–3	−53.2
1–4	−54.0	3–4	87.6	2–3	−61.9

Equations of the Planes of the Form $Ax + By + Cz - D = 0$

plane	A	B	C	D	plane	A	B	C	D
1	−0.2806	0.9598	−0.0022	−1.1990	1	−0.3358	0.9213	−0.1961	2.0835
2	0.6529	0.7300	−0.2021	5.2449	2	−0.8226	−0.1537	−0.5475	−5.3489
3	0.8883	−0.3960	−0.2328	3.9506	3	0.8588	−0.4036	−0.3155	−0.5399
4	−0.4204	−0.7350	−0.5321	−6.3857					

[a] These atoms were not used in defining the plane.

Table VII. Final Fractional Atomic Coordinates for $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC=NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Os(1)	0.349 50 (6)	0.303 68 (5)	0.196 35 (4)	C(2)	−0.001 (2)	0.380 (1)	0.159 (1)
Os(2)	0.077 00 (7)	0.223 73 (5)	0.190 77 (5)	C(3)	0.171 (2)	0.074 (1)	0.236 (1)
Os(3)	0.142 00 (6)	0.250 31 (5)	0.399 63 (4)	C(4)	0.448 (2)	0.165 (1)	0.176 (1)
P	0.2330 (5)	0.2790 (3)	0.5475 (3)	C(5)	0.522 (2)	0.355 (1)	0.218 (1)
O(1)	0.124 (2)	0.218 (1)	−0.0532 (14)	C(6)	0.362 (2)	0.364 (1)	0.041 (1)
O(2)	−0.052 (1)	0.471 (1)	0.1368 (9)	C(7)	−0.055 (2)	0.272 (1)	0.456 (1)
O(3)	0.226 (1)	−0.017 (1)	0.2629 (11)	C(8)	0.162 (2)	0.093 (1)	0.458 (1)
O(4)	0.509 (1)	0.082 (1)	0.1590 (10)	C(9)	−0.110 (2)	0.175 (1)	0.236 (1)
O(5)	0.631 (1)	0.380 (1)	0.2323 (10)	C(11)	0.267 (2)	0.566 (1)	0.199 (1)
O(6)	0.362 (1)	0.397 (1)	−0.0535 (10)	C(12)	0.318 (2)	0.621 (1)	0.263 (1)
O(7)	−0.179 (1)	0.286 (1)	0.4886 (9)	C(13)	0.351 (2)	0.731 (2)	0.220 (1)
O(8)	0.174,(1)	−0.004 (1)	0.5001 (10)	C(14)	0.328 (2)	0.785 (1)	0.115 (1)
O(9)	−0.224 (2)	0.140 (1)	0.2671 (11)	C(15)	0.278 (2)	0.731 (1)	0.047 (1)
O(21)	0.408 (2)	0.253 (1)	0.5488 (13)	C(16)	0.245 (2)	0.620 (1)	0.090 (1)
O(22)	0.200 (2)	0.201 (2)	0.6646 (15)	C(17)	0.146 (2)	0.422 (1)	0.334 (1)
O(23)	0.219 (2)	0.400 (1)	0.5571 (11)	C(21)	0.492 (2)	0.152 (2)	0.541 (2)
N	0.235 (1)	0.4513 (9)	0.2426 (8)	C(22)	0.050 (3)	0.183 (2)	0.714 (2)
C(1)	0.101 (2)	0.215 (2)	0.044 (2)	C(23)	0.274 (3)	0.441 (2)	0.644 (2)

^{1}H NMR spectra were recorded on either the Southern New England High Field NMR Facility operating at 270 MHz or a Perkin-Elmer R-32 and were calibrated with Me₄Si. Mass spectra were run on a Perkin-Elmer RMU-6D mass spectrometer. Elemental analyses were performed by Midwest Microlab, Indianapolis, Ind. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Syntheses. $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CNR})$, R = C_6H_5, CH_3, $t\text{-C}_4\text{H}_9$. All compounds were prepared similarly. A typical preparation is listed here. $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (0.265 g) was dissolved in ~10 mL of pentane. At room temperature $t\text{-C}_4\text{H}_9\text{NC}$ was added dropwise via syringe until the purple color of the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was completely gone. The reagents react upon mixing. Rapid stirring induced precipitation of a yellow powder of $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CN}\text{-}t\text{-C}_4\text{H}_9)$. The flask was cooled

Table VIII. Bond Distances for $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$

atoms	distance, Å	atoms	distance, Å
Os(1)-Os(2)	2.863 (1)	O(22)-C(22)	1.463 (16)
Os(1)-Os(3)	2.961 (1)	O(23)-C(23)	1.488 (14)
Os(2)-Os(3)	2.893 (1)	C(17)-N	1.320 (10)
Os(1)-C(4)	1.894 (10)	N-C(11)	1.434 (10)
Os(1)-C(5)	1.881 (9)	C(11)-C(12)	1.345 (11)
Os(1)-C(6)	1.907 (10)	C(12)-C(13)	1.399 (14)
Os(1)-N	2.150 (6)	C(13)-C(14)	1.361 (13)
Os(2)-C(1)	1.856 (13)	C(14)-C(15)	1.361 (12)
Os(2)-C(2)	1.931 (10)	C(15)-C(16)	1.400 (13)
Os(2)-C(3)	1.928 (11)	C(16)-C(11)	1.409 (12)
Os(2)-C(9)	1.882 (11)	C(1)-O(1)	1.207 (13)
Os(3)-P	2.281 (2)	C(2)-O(2)	1.149 (10)
Os(3)-C(7)	1.881 (9)	C(3)-O(3)	1.165 (11)
Os(3)-C(8)	1.897 (10)	C(4)-O(4)	1.152 (11)
Os(3)-C(17)	2.075 (9)	C(5)-O(5)	1.156 (11)
P-O(21)	1.625 (10)	C(6)-O(6)	1.165 (10)
P-O(22)	1.566 (12)	C(7)-O(7)	1.175 (10)
P-O(23)	1.515 (9)	C(8)-O(8)	1.178 (11)
O(21)-C(21)	1.398 (14)	C(9)-O(9)	1.180 (12)

to −20 °C to complete precipitation. The solvent was decanted and the powder washed with pentane and dried in vacuo, yield 0.29 g (essentially 100%). In Table 1 is presented further information about these compounds and reactions.

Thermolyses in Poor Donor Solvents: Preparation of the Complexes $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NR})\text{Os}_3(\text{CO})_{10}$, R = C_6H_5, CH_3. $\text{H}_2\text{Os}_3(\text{CO})_{10}$-$(\text{CNC}_6\text{H}_5)$ (0.209 g) was dissolved in 50 mL of n-butyl ether. A hot heating mantle was placed around the flask. Within 5 min the yellow solution began to turn red. After 15 min it began to turn back to yellow. When fully returned to yellow, heating was stopped and the solvent removed in vacuo. The residue was chromatographed over $\text{Al}_2\text{O}_3\cdot6\%\text{H}_2\text{O}$ with hexanes solvent. A single yellow band eluted and was collected. IR showed it to be the expected product with a small amount of $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$. Final purification was obtained by crystallization from hexanes solvent, yield 0.134 g, 64%. Note: equivalent and perhaps better yields are obtained using octane solvent.

Preparation of the Complexes $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{NR})\text{Os}_3(\text{CO})_9$, R = C_6H_5, CH_3. $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CNC}_6\text{H}_5)$ (0.157 g) was dissolved in 25 mL of n-butyl ether. After the solution was refluxed for 2.5 h the

solvent was removed in vacuo. The residue was chromatographed over $\text{Al}_2\text{O}_3\cdot6\%\text{H}_2\text{O}$ with hexanes solvent. A single yellow band of product was eluted and collected. The product was recrystallized from pentane solvent, yield: 0.0974 g, 64%.

Interconversion of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$ and $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$. $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3$-$(\text{CO})_{10}$ (0.061 g) was refluxed in n-butyl ether. After 2 h the solution was quantitatively transformed into $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{N-}\text{C}_6\text{H}_5)\text{Os}_3(\text{CO})_9$.

$(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$ (0.03 g) was dissolved in 15 mL of octane and placed under an atmosphere of CO. After the solution was refluxed for 1 h, IR showed essentially complete conversion into $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$.

Preparation of $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$. $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9$ (0.065 g) was dissolved in 5 mL of $\text{P(OCH}_3)_3$ at room temperature. After 10 min stirring the $\text{P(OCH}_3)_3$ was removed in vacuo. The residue was chromatographed over $\text{Al}_2\text{O}_3\cdot0\%\text{H}_2\text{O}$. With 2/1 hexanes/benzene solvent a yellow band eluted. A second yellow band was eluted with pure benzene solvent. The first band was recrystallized from hexanes solvent at −20 °C, and gave 0.012 g (16%) of product, $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3$-$(\text{CO})_9(\text{P(OCH}_3)_3)$. The second band resisted crystallization and was not fully characterized. Spectra suggest it was an isomer of the first product.

Preparation of the Complexes $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CNR})$, R = C_6H_5, CH_3, $t\text{-C}_4\text{H}_9$. These compounds can be obtained by stopping the synthesis reactions of the formimidoyl ligand complexes (vide supra) in the higher boiling solvents (octane, n-butyl ether) by discontinuing heating of the reactions when they attain a maximum red coloration. Alternatively, higher yields are obtained by using lower boiling nondonor solvents as shown by the following example.

$\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CNC}_6\text{H}_5)$ (0.141 g) was refluxed in CHCl_3 for 45 min. During this time the yellow reaction solution turned red. Reaction solvent was removed in vacuo. The residue was taken up in hexanes and chromatographed quickly over a short (3 in.) column of Florisil. A red band was collected. The solution was concentrated and placed at −20 °C. Overnight red crystals of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CNC}_6\text{H}_5)$ formed. Impurity $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_{10}$, sometimes present in small amounts, can be removed by washing with cold pentane, yield 0.035 g, 26%.

Thermolyses of $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CN-}t\text{-C}_4\text{H}_9)$ did not produce formimidoyl-containing compounds, even after a 6-h reflux in octane. Instead the principal products were $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CN-}t\text{-C}_4\text{H}_9)$ (22%) and $\text{Os}_3(\text{CO})_{11}(\text{CN-}t\text{-C}_4\text{H}_9)$ (12%). The latter was isolated by chromatography over $\text{Al}_2\text{O}_3\cdot6\%\text{H}_2\text{O}$ using benzene solvent. It is

Table IX. Bond Angles for $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC}=\text{NC}_6\text{H}_5)\text{Os}_3(\text{CO})_9(\text{P(OCH}_3)_3)$

atoms	angle, deg	atoms	angle, deg	atoms	angle, deg
Os(1)-Os(2)-Os(3)	61.93 (1)	C(1)-Os(2)-C(3)	92.2 (5)	O(21)-P-O(23)	97.9 (5)
Os(2)-Os(1)-Os(3)	59.53 (1)	C(1)-Os(2)-C(9)	100.2 (5)	P-O(21)-C(21)	126.8 (9)
Os(1)-Os(3)-Os(2)	58.54 (1)	C(2)-Os(2)-C(3)	171.8 (4)	P-O(22)-C(22)	120.9 (10)
Os(3)-Os(1)-C(4)	106.2 (3)	C(2)-Os(2)-C(9)	91.9 (4)	P-O(23)-C(23)	125.3 (8)
Os(3)-Os(1)-C(5)	113.6 (2)	C(3)-Os(2)-C(9)	92.5 (4)	Os(3)-C(17)-N	116.0 (6)
Os(3)-Os(1)-C(6)	143.3 (3)	Os(1)-Os(3)-P	111.20 (6)	Os(1)-N-C(17)	109.8 (6)
Os(3)-Os(1)-N	67.2 (2)	Os(1)-Os(3)-C(7)	142.8 (3)	Os(1)-N-C(11)	127.2 (5)
Os(2)-Os(1)-C(4)	90.2 (3)	Os(1)-Os(3)-C(8)	108.6 (3)	N-C(11)-C(12)	119.5 (8)
Os(2)-Os(1)-C(5)	172.2 (3)	Os(1)-Os(3)-C(17)	67.1 (2)	N-C(11)-C(16)	120.2 (7)
Os(2)-Os(1)-C(6)	89.3 (3)	Os(2)-Os(3)-P	169.71 (6)	C(11)-C(12)-C(13)	119.1 (9)
Os(2)-Os(1)-N	89.5 (2)	Os(2)-Os(3)-C(7)	93.5 (3)	C(12)-C(13)-C(14)	121.0 (10)
C(4)-Os(1)-C(5)	92.0 (4)	Os(2)-Os(3)-C(8)	92.3 (3)	C(13)-C(14)-C(15)	121.0 (10)
C(4)-Os(1)-C(6)	91.6 (4)	Os(2)-Os(3)-C(17)	89.5 (2)	C(14)-C(15)-C(16)	118.6 (9)
C(4)-Os(1)-N	172.3 (3)	P-Os(3)-C(7)	96.1 (3)	C(15)-C(16)-C(11)	119.9 (8)
C(5)-Os(1)-C(6)	97.1 (4)	P-Os(3)-C(8)	90.5 (3)	C(16)-C(11)-C(12)	120.3 (9)
C(5)-Os(1)-N	87.4 (3)	P-Os(3)-C(17)	86.7 (2)	Os(1)-C(4)-O(4)	177.1 (9)
C(6)-Os(1)-N	96.1 (3)	C(7)-Os(3)-C(8)	95.5 (4)	Os(1)-C(5)-O(5)	176.3 (8)
Os(1)-Os(2)-C(1)	98.9 (4)	C(7)-Os(3)-C(17)	90.7 (4)	Os(1)-C(6)-O(6)	175.8 (9)
Os(1)-Os(2)-C(2)	86.7 (3)	C(8)-Os(3)-C(17)	173.4 (4)	Os(2)-C(1)-O(1)	173.9 (11)
Os(1)-Os(2)-C(3)	86.9 (3)	Os(3)-P-O(21)	116.7 (4)	Os(2)-C(2)-O(2)	176.3 (8)
Os(1)-Os(2)-C(9)	160.9 (3)	Os(3)-P-O(22)	120.6 (5)	Os(2)-C(3)-O(3)	178.8 (9)
Os(3)-Os(2)-C(1)	160.6 (4)	Os(3)-P-O(23)	115.2 (4)	Os(2)-C(9)-O(9)	177.2 (9)
Os(3)-Os(2)-C(2)	88.6 (3)	O(21)-P-O(22)	92.8 (6)	Os(3)-C(7)-O(7)	176.8 (7)
Os(3)-Os(2)-C(3)	84.0 (3)	O(22)-P-O(23)	109.5 (5)	Os(3)-C(8)-O(8)	176.1 (8)
Os(3)-Os(2)-C(9)	99.0 (3)				
C(1)-Os(2)-C(2)	93.7 (5)				

important to point out that the compounds $(\mu$-$H)_2Os_3(CO)_9(CNR)$ undergo considerable decomposition upon chromatographic treatment and this greatly contributes to the low yields observed.

Addition of CO to the Compounds $(\mu$-$H)_2Os_3(CO)_9(CNR)$, $R = C_6H_5$, CH_3, t-C_4H_9. At room temperature, red solutions of each of the compounds $(\mu$-$H)_2Os_3(CO)_9(CNR)$, $R = C_6H_5$, CH_3, t-C_4H_9, turn yellow within 30 min to 2 h when placed under 1 atm of CO. IR and ^1H NMR analyses indicate quantitative conversion into each of the respective compounds $H_2Os_3(CO)_{10}(CNR)$, $R = C_6H_5$, CH_3, t-C_4H_9, which are the identical compounds produced by the addition of isocyanide to $H_2Os_3(CO)_{10}$.

Thermolyses in Strong Donor Solvents (Base-Catalyzed Reaction). Preparation of the Compounds $(\mu$-$H)(\mu$-$C=N(H)R)Os_3(CO)_{10}$, $R = CH_3$, t-C_4H_9, and C_6H_5. This reaction proceeds similarly in refluxing THF or $CHCl_3$ containing a trace of $N(C_2H_5)_3$. Since the latter produces a cleaner reaction, an example of that procedure will be described. $H_2Os_3(CO)_{10}(CN$-t-$C_4H_9)$ (0.10 g) was dissolved in 10 mL of predistilled $CHCl_3$. At room temperature 2 drops of $N(C_2H_5)_3$ was added. IR showed that the reaction was complete in 15 min. The solution was concentrated to the point of incipient crystallization, 6 mL of pentane was added, and the solution was cooled to -78 °C. A light yellow powder precipitated. The mother liquor was decanted, and the powder was washed with pentane and dried in vacuo, yield 0.06 g, 60%. It is important to note that in the absence of $N(C_2H_5)_3$ the starting material does not show any significant conversion to product after 4 h of stirring.

Structure Analyses. Crystals of both $(\mu$-$H)(\mu_3$-η^2-$HC=N$-$C_6H_5)Os_3(CO)_9$ and $(\mu$-$H)(\mu$-η^2-$HC=NC_6H_5)Os_3(CO)_9(P$-$(OCH_3)_3)$ were grown from concentrated hexane solutions cooled to -20 °C. All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite monochromatized Mo Kα radiation. Unit cells were determined and refined using 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index, and least-squares routines. Space groups were determined from the systematic absences observed during data collection.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. Both structures were solved by the heavy-atom method. Anomalous dispersion corrections were made for scattering by all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$. Unweighted and weighted residuals were determined by the formulas

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2}$$

Crystal data, data collection parameters, structure solution, and refinement data for the individual structures are presented in Table II. Tables III and VII list final fractional atomic coordinates, Tables IV and VIII list bond distances, while Tables V and IX list bond angles. Table VI presents information about selected least-squares planes. Tables of final values of the thermal parameters and structure factors are available.[28] Final values of the structure factors for $(\mu$-$H)(\mu_3$-η^2-$HC=NC_6H_5)Os_3(CO)_9$ were reported previously.[8]

Supplementary Material Available: Structure factors, thermal parameters, and a crystal packing diagram of $(\mu$-$H)(\mu_3$-η^2-$HC=N$-$C_6H_5)Os_3(CO)_9$ (29 pages). Ordering information is given on any current masthead page.

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