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Effect of Isocyanide Ligand on the Interaction of Triosmium Isocyanide Complexes with Amines

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The interaction of the osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (**1**) with primary amines leads initially to the formation of the carboxamido complexes $Os_3(CO)_{10}(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**2**) with a bridging aminocarbyne. The latter react with excess corresponding amines to yield $Os_3(CO)_9(NH_2R')(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**3**). Bubbling CO through the solution of **3** regenerates **2**. Treatment of complex **2** with PPh_3 affords $Os_3(CO)_9(PPh_3)(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**5**). Complex **3**, when passed through silica gel, results in structure transformation to the hydrido complexes $(\mu\text{-}H)Os_3(CO)_9(\mu_2\text{-}CONHR')(CNR)$ (**4**) with the regeneration of the isocyanide ligand. Treatment of **3** with CH_3CO_2H or CF_3CO_2H also results in the formation of **4**. In contrast, complex **2** or complex **5** remains unchanged when passed through silica gel. The transformation of the isocyanide ligand with the cleavage and formation of an Os–Os bond may play an important role in mediating the reactivity of the osmium cluster. The structures of $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHCH_2Ph)$ (**2c**), $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPh)$ (**3a**), and $(\mu\text{-}H)Os_3(CO)_9(\mu_2\text{-}CONHPr^i)(CNCH_2Ph)$ (**4c**) have been determined by X-ray crystallography. Crystal data are as follows. **2c**: $Pbca$; $a = 11.9975(14)$ Å, $b = 17.797(4)$ Å, $c = 25.819(3)$ Å; $V = 5512.9(14)$ Å^3, $Z = 8$; $R = 5.6\%$, $R_w = 5.9\%$. **3a**: $P\bar{1}$; $a = 8.7042(13)$ Å, $b = 13.1002(20)$ Å, $c = 13.546(4)$ Å, $\alpha = 93.456(17)°$; $\beta = 89.905(16)°$, $\gamma = 106.393(13)°$; $V = 1478.9(5)$ Å^3, $Z = 2$; $R = 3.8\%$, $R_w = 4.5\%$. **4c**: $P2_1/n$; $a = 9.3811(15)$ Å, $b = 10.0523(14)$ Å, c 28.265(17) Å; $\beta = 91.81(3)°$; $V = 2664.1(17)$ Å^3, $Z = 4$; $R = 3.6\%$, $R_w = 4.2\%$.

Introduction

Isocyanides are isoelectronic with CO. In composition and structure, metal isonitriles closely resemble the corresponding metal carbonyls, and the replacement of carbonyl ligands with isocyanides often leads to essentially no change in structural parameters.[1] Recently, we have reported[2] a facile synthesis of the osmium isocyanide clusters $Os_3(CO)_{11}(CNR)$ in very high yield by the reaction of $Os_3(CO)_{12}$ with phosphine imides by the ylide type reaction of metal carbonyl.[3-6] With the objective of evaluating the influence of isocyanide-carbonyl replacement on the reactivity of transition metal clusters, we thought it worthwhile to examine the behavior of $Os_3(CO)_{11}(CNR)$ toward Lewis bases.

Soluble transition-metal cluster compounds have attracted a great deal of interest as homogeneous catalysts and as models for catalysis at metal surfaces.[7] Addition of a substrate molecule with cleavage of a metal–metal bond and elimination of a substrate molecule with formation of a metal–metal bond could be the first and last steps, respectively, of a catalytic cycle with cluster participation.[8] Owing to the versatility of isocyanide ligand, we were interested in learning the effect of the coordinated isocyanide ligand on the transformation of substrate molecule in the coordination sphere of the cluster and the rupture or formation of the metal–metal bond.

In this report, we compare the subtle differences in the reactivity between $Os_3(CO)_{11}(CNR)$ and $Os_3(CO)_{12}$ toward amines. In these reactions, a series of derivatives involving the transformation of the coordinated isocyanide ligand in the cluster framework were observed. Owing to the modest stability of the products, we were able to isolate each of them and thus have the opportunity of gaining insight into these rearrangement processes. The transformation of isocyanide to bridging aminocarbyne, the cleavage and reformation of an Os–Os bond, the activation of a carboxamido ligand, and the deprotonation–protonation process catalyzed by silica gel are the features of these reactions.

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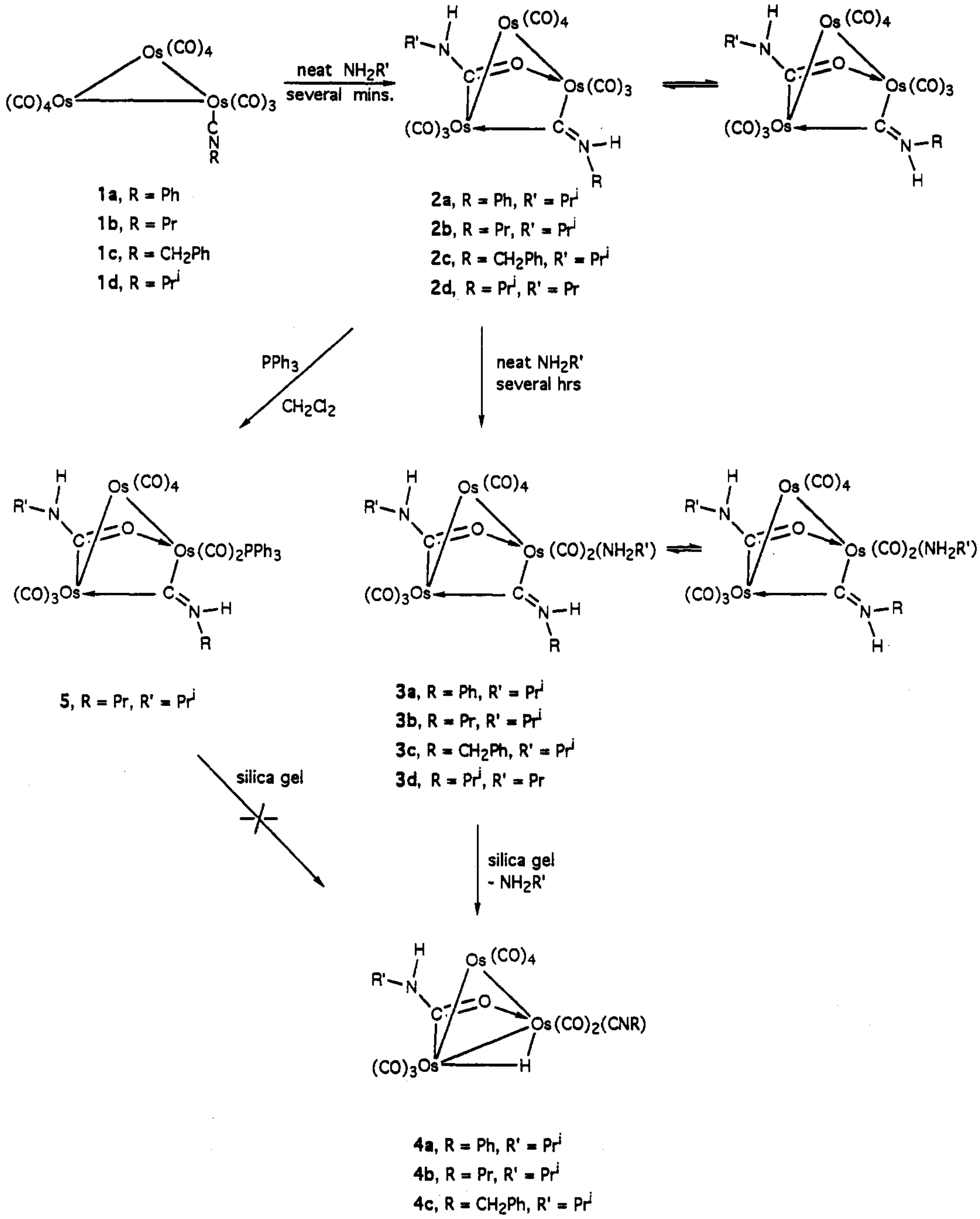
Scheme I



Results and Discussion

Reaction of $Os_3(CO)_{11}(CNR)$ with Primary Amine. The osmium isocyanide complexes $Os_3(CO)_{11}(CNR)$ (1) react with neat primary amines[2] at room temperature within a few minutes to form the carboxamido complexes $Os_3(CO)_{10}(\mu_2\text{-CONHR}')(\mu_2\text{-C=NHR})$ (**2a**, R = Ph, R′ = Pr^i; **2b**, R = Pr, R′ = Pr^i; **2c**, R = CH_2Ph, R′ = Pr^i; **2d**, R = Pr^i, R′ = Pr), which were isolated as yellow-orange microcrystalline powder (Scheme I).

The ^1H NMR spectrum of **2b** showed a broad doublet at δ 5.75 assigned to the proton of the μ_2–η^2-carboxamido ligand. Two broad singlets at δ 9.16 and 9.00 in a 4:6 ratio were also observed, which can be attributed to the *H*N of the bridging aminocarbyne of each isomer, respectively. This was corroborated by the ^{13}C NMR spectrum of **2b**, which showed the presence of *C*=NHR resonances at δ 272.2 and 271.6, consistent with the formation of an aminocarbyne ligand in each isomer. The equilibrium may likely occur due to the restricted rotation about the C–N bond in the bridging carbyne in solution.[9] A high rotational barrier about a C=N bond was also observed by Yin and Deeming[10] in the related complex $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-C=NMeCH}_2\text{Ph})$. The IR spectrum confirmed that there is no signal which can be attributed to a coordinated isocyanide ligand. The FAB MS spectrum exhibited the molecular ion at 1009. All the compounds synthesized were characterized by IR and NMR spectroscopy and mass spectrometry. Single crystals of **2c** were grown from hexane/CH_2Cl_2 solution, and an X-ray diffraction analysis was performed. An ORTEP drawing of complex **2c** is shown in Figure 1, and pertinent crystallographic data are given in Tables I–III. The three Os atoms define an isosceles triangle, with Os(2) and Os(3) bridged by both

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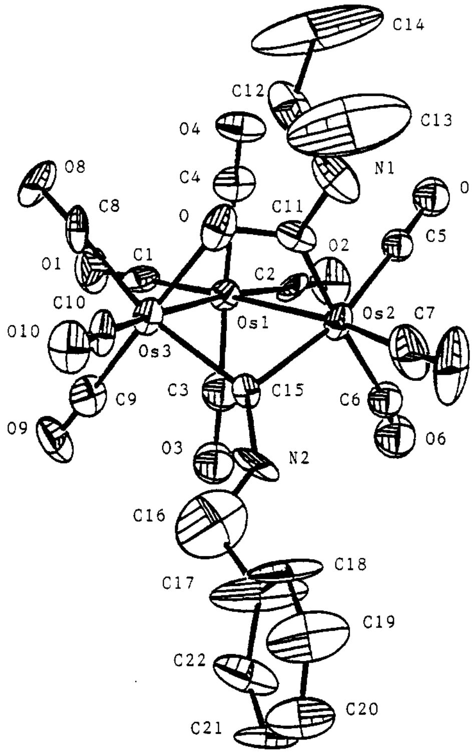

Figure 1. ORTEP diagram of $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHCH_2Ph)$ (**2c**) with 30% probability thermal ellipsoids.

Table I. Crystal and Intensity Collection Data for 2c, 3a, and 4c

compd	**2c**	**3a**	**4c**
formula	$C_{22}H_{16}N_2O_{11}Os_3$	$C_{22}H_{21}N_3O_{10}Os_3$	$C_{21}H_{16}N_2O_{10}Os_3$
fw	1054.98	1058.02	1026.96
space grp	*Pbca*	$P\bar{1}$	$P2_1/n$
a, Å	11.9975(14)	8.7042(13)	9.3811(15)
b, Å	17.797(4)	13.1002(20)	10.0523(14)
c, Å	25.819(3)	13.546(4)	28.265(17)
α, deg		93.456(17)	
β, deg		89.905(16)	91.81(3)
γ, deg		106.393(13)	
V, Å^3	5512.9(14)	1478.9(5)	2664.1(17)
ρ(calcd), g cm^{-3}	2.542	2.376	2.560
Z	8	2	4
cryst dimens, mm	0.20 × 0.20 × 0.20	0.43 × 0.39 × 0.20	0.56 × 0.32 × 0.44
abs coeff μ(Mo Kα),mm^{-1}	13.87	12.92	14.34
temp	room temp	room temp	room temp
radiatn	Mo Kα	Mo Kα	Mo Kα
2θ(max), deg	44.8	44.9	44.9
scan type	θ/2θ	θ/2θ	θ/2θ
total no. of reflns	3582	4165	3884
no. of obsd reflns $I_o > 2\sigma(I_o)$	1887	3279	2570
no. of params	313	343	329
R	0.056	0.038	0.036
R_w	0.059	0.045	0.042
Δ(ρ), e Å^{-3}	3.13	1.350	1.21
Δ/σ_{max}	0.285	0.385	0.293
GOF	2.22	2.35	1.88

an aminocarbyne group and a carboxamido ligand. Each of the two metal centers, possessing three carbonyl ligands, bears a pseudooctahedral geometry. The doubly bridged Os(2)–Os(3) vector (3.4074(20) Å) is much longer than the nonbridged bonds (Os(1)–Os(2) = 2.8924(19) Å and Os(1)–Os(3) = 2.8869(18) Å), indicating that the metal–metal bond has been cleaved. The aminocarbyne ligand is structurally similar to those found in the clusters $Os_3(CO)_{10}(\mu_2\text{-}O\text{-}COC{\equiv}CH)(\mu_2\text{-}C{=}NHPr)$,[11] $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}CNMe_2)$,[12] and $(\mu\text{-}H)Os_3(CO)_7(\mu\text{-}CNMe_2)(\mu\text{-}H_2CNMe_2)(\mu\text{-}SPh)$.[13] The restricted rotation about the C–N bond of the aminocarbyne ligand is supported by the short C(15)–N(2) distance of 1.26(4) Å that is indicative of C–N multiple-bond character.

Table II. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHCH_2Ph)$ (2c)

atom	*x*	*y*	*z*	B_{iso}[a]
Os1	0.70055(9)	0.09951(8)	0.16127(5)	3.90(6)
Os2	0.83175(11)	0.19715(8)	0.09566(6)	4.48(7)
Os3	0.82177(11)	0.00603(8)	0.08931(5)	4.27(7)
N1	1.0756(21)	0.1624(18)	0.1194(12)	7.6(18)
N2	0.7467(24)	0.1183(17)	0.0025(9)	6.9(17)
O	0.9715(18)	0.0599(12)	0.1104(9)	5.8(12)
O1	0.5869(22)	−0.0302(14)	0.2184(12)	8.7(18)
O2	0.5997(20)	0.2324(14)	0.2230(11)	8.2(15)
O3	0.5276(17)	0.1045(14)	0.0768(10)	7.4(6)
O4	0.9162(14)	0.0933(15)	0.2266(9)	6.6(14)
O5	0.8882(16)	0.2946(13)	0.1914(9)	6.2(6)
O6	0.6267(17)	0.2845(13)	0.0775(11)	7.6(6)
O7	0.9721(27)	0.2800(15)	0.0131(12)	12.2(22)
O8	0.8593(20)	−0.1102(13)	0.1804(9)	7.5(15)
O9	0.6068(19)	−0.0688(13)	0.0580(11)	7.7(15)
O10	0.9502(18)	−0.0829(13)	0.0096(9)	6.8(14)
C1	0.6302(24)	0.0195(19)	0.1969(12)	4.7(17)
C2	0.6352(24)	0.1832(18)	0.2002(12)	4.8(17)
C3	0.6227(26)	0.1022(20)	0.1052(14)	6.5(8)
C4	0.8415(21)	0.0950(21)	0.2059(12)	5.3(18)
C5	0.8619(21)	0.2591(16)	0.1555(13)	4.3(6)
C6	0.6934(23)	0.2650(18)	0.0840(14)	5.3(8)
C7	0.9177(33)	0.2505(23)	0.0420(18)	8.6(26)
C8	0.8493(25)	−0.0683(16)	0.1475(14)	4.9(16)
C9	0.6833(24)	−0.0416(19)	0.0696(15)	5.6(18)
C10	0.9067(26)	−0.0477(16)	0.0396(12)	4.6(17)
C11	0.9715(21)	0.1364(18)	0.1092(11)	4.5(16)
C12	1.1803(23)	0.1045(22)	0.1279(20)	9.4(30)
C13	1.2570(42)	0.1451(50)	0.0842(28)	27.7(78)
C14	1.2392(63)	0.1243(57)	0.1717(19)	31.0(88)
C15	0.7878(24)	0.1057(17)	0.0466(10)	4.4(16)
C16	0.7026(40)	0.0782(35)	−0.0325(27)	17.1(50)
C17	0.7209(31)	0.1197(38)	−0.0890(13)	15.7(49)
C18	0.8280(26)	0.1299(30)	−0.1043(16)	11.0(33)
C19	0.8524(28)	0.1442(32)	−0.1584(18)	12.1(36)
C20	0.7679(32)	0.1460(28)	−0.1907(13)	9.5(29)
C21	0.6576(28)	0.1290(27)	−0.1753(14)	8.5(27)
C22	0.6325(30)	0.1157(28)	−0.1234(16)	10.1(30)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

The electronic properties of the coordinated isocyanide effect the amount of charge on the metal atom in complexes. Therefore, the isocyanide with different R groups plays an important role in determining the rates of reaction of complexes 1 with amines. The osmium isocyanide complex 1 with electron-withdrawing phenyl isocyanide shows the fastest rate. The rate of reaction of complex 1 with amines decreases in the order Ph > Pr > Pr^i, with the completion time ranging between 3 and 30 min to afford 2. The more electron-withdrawing isocyanide group introduces a more positive charge on the carbonyl carbon, consequently making it more susceptible to nucleophilic attack.

Complex 2 reacts readily with excess amine for several hours to yield $Os_3(CO)_9(NH_2R')(\mu_2\text{-}CONHR')(\mu_2\text{-}C{=}NHR)$ (**3a**, R = Ph, R′ = Pr^i; **3b**, R = Pr, R′ = Pr^i; **3c**, R = CH$_2$Ph, R′ = Pr^i; **3d**, R = Pr^i, R′ = Pr) in which one of the carbonyl ligands is replaced by an amine.

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Table III. Selected Bond Distances and Angles for $Os_3(CO)_{10}(\mu_2\text{-CONHPr}^i)(\mu_2\text{-C=NHCH}_2\text{Ph})$ (2c)

Bond Distances, Å			
Os(1)–Os(2)	2.8924(19)	Os(1)–Os(3)	2.8869(18)
Os(1)–C(1)	1.89(3)	O(9)–C(9)	1.08(4)
Os(1)–C(2)	1.96(3)	O(10)–C(10)	1.12(3)
Os(1)–C(3)	1.72(4)	C(12)–C(13)	1.63(9)
Os(1)–C(4)	2.05(3)	C(12)–C(14)	1.38(8)
Os(2)–C(5)	1.93(3)	Os(2)–C(6)	2.07(3)
Os(2)–C(7)	1.97(4)	Os(2)–C(11)	2.03(3)
Os(2)–C(15)	2.13(3)	Os(3)–O	2.108(23)
Os(3)–C(8)	2.03(3)	Os(3)–C(9)	1.93(3)
Os(3)–C(10)	1.90(3)	Os(3)–C(15)	2.13(3)
C(16)–C(17)	1.65(8)	N(1)–C(11)	1.36(4)
N(1)–C(12)	1.64(5)	N(2)–C(15)	1.26(4)
C(17)–C(18)	1.36(5)	N(2)–C(16)	1.27(7)
C(17)–C(22)	1.39(5)	C(18)–C(19)	1.45(6)
O–C(11)	1.36(4)	O(1)–C(1)	1.17(4)
C(19)–C(20)	1.31(6)	O(2)–C(2)	1.14(4)
O(3)–C(3)	1.36(4)	C(20)–C(21)	1.41(5)
O(4)–C(4)	1.04(3)	O(5)–C(5)	1.17(4)
C(21)–C(22)	1.39(6)	O(6)–C(6)	0.89(4)
O(7)–C(7)	1.12(5)	O(8)–C(8)	1.14(4)
Os(2)–Os(3)	3.4074(20)		
Bond Angles, deg			
C(1)–Os(1)–C(2)	98.3(13)	C(1)–Os(1)–C(3)	100.8(15)
C(1)–Os(1)–C(4)	93.8(12)	C(2)–Os(1)–C(3)	101.1(14)
C(2)–Os(1)–C(4)	94.1(13)	C(3)–Os(1)–C(4)	157.1(13)
C(5)–Os(2)–C(6)	86.2(12)	C(5)–Os(2)–C(7)	101.0(15)
C(5)–Os(2)–C(11)	90.7(12)	C(5)–Os(2)–C(15)	163.4(12)
C(6)–Os(2)–C(7)	92.1(16)	C(6)–Os(2)–C(11)	176.4(12)
C(6)–Os(2)–C(15)	99.3(12)	C(7)–Os(2)–C(11)	86.9(15)
C(7)–Os(2)–C(15)	94.5(14)	C(11)–Os(2)–C(15)	84.2(12)
O–Os(3)–C(8)	88.0(11)	O–Os(3)–C(9)	179.0(12)
O–Os(3)–C(10)	86.9(11)	Os(2)–C(15)–Os(3)	106.4(12)
O–Os(3)–C(15)	85.3(9)	Os(2)–C(15)–N(2)	119.8(23)
C(8)–Os(3)–C(9)	92.8(14)	Os(3)–C(15)–N(2)	133.8(23)
C(8)–Os(3)–C(10)	94.9(13)	N(2)–C(16)–C(17)	108(5)
C(8)–Os(3)–C(15)	163.4(11)	C(9)–Os(3)–C(10)	93.6(14)
C(9)–Os(3)–C(15)	93.7(13)	C(10)–Os(3)–C(15)	99.9(12)
C(11)–N(1)–C(12)	121(3)	C(15)–N(2)–C(16)	134(4)
C(16)–C(17)–C(18)	116(3)	Os(3)–O–C(11)	116.6(17)
C(16)–C(17)–C(22)	116(4)	Os(1)–C(1)–O(1)	179(3)
C(18)–C(17)–C(22)	123(3)	Os(1)–C(2)–O(2)	178(3)
C(17)–C(18)–C(19)	119(3)	Os(1)–C(3)–O(3)	155(3)
Os(1)–C(4)–O(4)	176(3)	Os(2)–C(5)–O(5)	174.9(22)
C(18)–C(19)–C(20)	117(3)	Os(2)–C(6)–O(6)	167(3)
Os(2)–C(7)–O(7)	175(4)	Os(3)–C(8)–O(8)	176(3)
C(19)–C(20)–C(21)	122(4)	Os(3)–C(9)–O(9)	178(3)
Os(3)–C(10)–O(10)	174(3)	Os(2)–C(11)–N(1)	127.8(25)
C(20)–C(21)–C(22)	120(3)	Os(2)–C(11)–O	122.6(18)
N(1)–C(11)–O	109(3)	N(1)–C(12)–C(13)	93(3)
C(17)–C(22)–C(21)	116(3)	N(1)–C(12)–C(14)	109(4)
C(13)–C(12)–C(14)	99(5)		

The ^1H NMR spectrum for **3a** exhibited the presence of the following three kinds of *H*N resonances with broad peaks: a μ_2–η^2-carboxamido ligand (δ 5.75, μ_2-CON*H*Pr^i), a coordinated amine (δ 3.08, N$H_2$$Pr^i$), and a bridging aminocarbyne group (δ 10.63, 10.43, μ_2-C=N*H*Ph, two isomers in a 1:9 ratio), showing that complex **3** also exists in two isomeric forms similar to complex **2** in equilibrium in solution at room temperature. An X-ray crystal analysis of complex **3a** was also undertaken in order to obtain unambiguous information on its molecular stereochemistry (Figure 2). Final atomic positional parameters are listed in Table IV. Selected bond distances and angles are listed in Table V. The cluster possesses two Os–Os bonds of length 2.9054(9) Å (Os(2)–Os(3)) and 2.9318(10) Å (Os(1)–Os(3)) and a nonbonded Os(1)···Os(2) separation of 3.356(1) Å. Atoms Os(1) and Os(2) are mutually bridged by both a carboxamido and an aminocarbyne ligand. Os(2) is coordinated to the oxygen end of the bridging carboxamido ligand, two CO ligands and an amine. The bridging aminocarbyne shows partial double-bond character for the C(17)–N(3) (1.339(18) Å), bond, similar to complex **2c**.

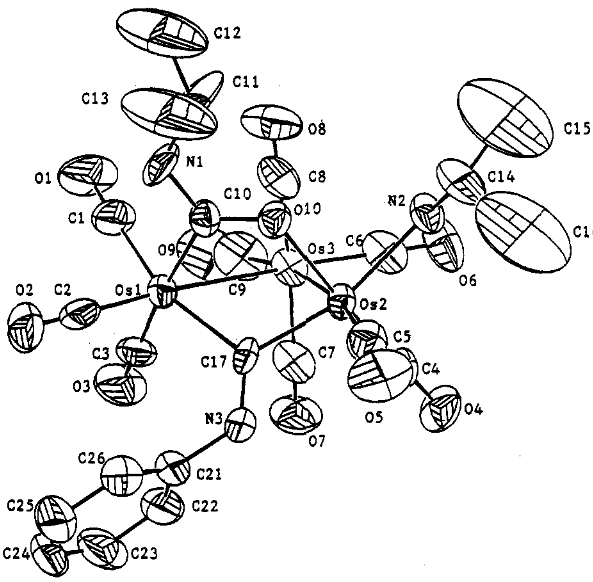


Figure 2. ORTEP diagram of $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-CONHPr}^i)(\mu_2\text{-C=NHPh})$ (3a).

Table IV. Atomic Coordinates and Isotropic Thermal Parameters ($Å^2$) for $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-CONHPr}^i)(\mu_2\text{-C=NHPh})$ (3a)

atom	*x*	*y*	*z*	B_{iso}[a]
Os1	0.28842(7)	0.12326(4)	0.17094(4)	3.34(3)
Os2	0.29483(6)	0.33966(4)	0.31851(4)	2.89(2)
Os3	0.57760(7)	0.28274(5)	0.24912(5)	3.87(3)
N1	0.1550(16)	0.2462(11)	0.0250(8)	4.9(7)
N2	0.3978(13)	0.5094(9)	0.2828(8)	3.9(6)
N3	0.1514(14)	0.1218(9)	0.3809(8)	3.7(6)
O1	0.4596(18)	0.1112(11)	−0.0266(9)	8.5(9)
O2	−0.0323(17)	−0.0345(11)	0.1079(9)	7.7(7)
O3	0.4363(17)	−0.0410(10)	0.2568(9)	7.4(8)
O4	0.4206(13)	0.3613(9)	0.5267(8)	5.9(6)
O5	−0.0202(14)	0.3482(11)	0.4080(9)	6.8(8)
O6	0.7743(15)	0.4921(10)	0.3486(11)	7.5(8)
O7	0.5380(15)	0.1581(11)	0.4376(9)	6.9(7)
O8	0.5406(15)	0.3900(11)	0.0576(10)	7.7(8)
O9	0.8147(19)	0.1650(13)	0.1746(13)	11.4(11)
O10	0.2136(10)	0.3327(7)	0.1721(6)	3.5(4)
C1	0.3999(20)	0.1137(13)	0.0461(11)	4.9(8)
C2	0.0911(25)	0.0264(13)	0.1336(10)	5.3(10)
C3	0.3795(21)	0.0210(12)	0.2263(11)	4.9(8)
C4	0.3733(16)	0.3535(11)	0.4465(11)	3.7(7)
C5	0.0977(19)	0.3517(12)	0.3696(11)	4.1(7)
C6	0.7006(19)	0.4123(15)	0.3113(13)	5.2(9)
C7	0.5524(18)	0.2039(13)	0.3692(14)	4.9(9)
C8	0.5530(18)	0.3495(13)	0.1297(14)	5.1(9)
C9	0.7307(21)	0.2125(17)	0.1994(15)	7.2(12)
C10	0.2089(15)	0.2488(11)	0.1182(9)	3.2(6)
C11	0.1110(34)	0.3399(22)	−0.0174(12)	9.5(17)
C12	0.1697(34)	0.3550(23)	−0.1162(25)	12.7(21)
C13	−0.0500(48)	0.3167(50)	−0.0176(34)	30.9(57)
C14	0.2744(41)	0.5768(16)	0.2659(17)	12.3(22)
C15	0.3875(36)	0.6744(26)	0.2292(27)	15.7(27)
C16	0.2522	0.6075	0.3635	10.7
C17	0.2207(15)	0.1810(10)	0.3071(9)	3.0(6)
C21	0.0825(20)	0.0071(12)	0.3784(11)	4.4(8)
C22	0.1660(21)	−0.0544(13)	0.4224(12)	5.3(9)
C23	0.0994(28)	−0.1616(15)	0.4262(15)	7.1(12)
C24	−0.0515(31)	−0.2064(14)	0.3846(15)	7.1(12)
C25	−0.1361(24)	−0.1465(17)	0.3417(14)	6.6(11)
C26	−0.0690(22)	−0.0380(14)	0.3421(11)	5.5(9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

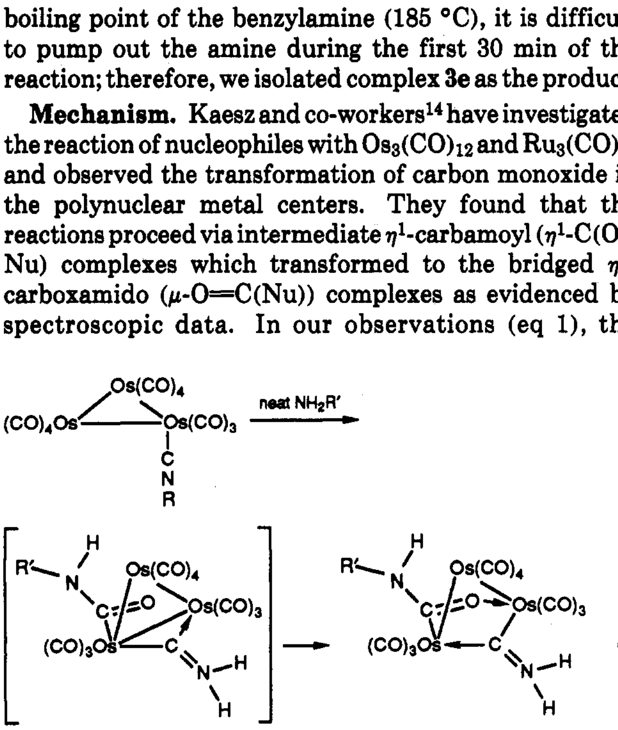
Reaction of complex $Os_3(CO)_{11}(CNPh)$ (**1a**) with excess benzylamine for 10 h affords $Os_3(CO)_9(NH_2CH_2Ph)(\mu_2\text{-CONHCH}_2\text{Ph})(\mu_2\text{-C=NHPh})$ (**3e**). Owing to the high

Table V. Selected Bond Distances and Angles for $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPh)$ (3a)

Bond Distances, Å			
Os(1)–Os(3)	2.9318(10)	Os(1)–C(1)	1.964(15)
O(10)–C(10)	1.273(15)	Os(1)–C(2)	1.874(21)
Os(1)–C(3)	1.926(17)	Os(1)–C(10)	2.117(13)
Os(1)–C(17)	2.098(11)	Os(2)–Os(3)	2.9054(9)
Os(2)–N(2)	2.233(12)	Os(2)–O(10)	2.095(8)
Os(2)–C(4)	1.844(14)	Os(2)–C(5)	1.893(16)
Os(2)–C(17)	1.991(13)	Os(3)–C(6)	1.882(19)
Os(3)–C(7)	1.958(19)	Os(3)–C(8)	1.925(20)
Os(3)–C(9)	1.921(17)	N(1)–C(10)	1.342(16)
N(1)–C(11)	1.528(25)	N(2)–C(14)	1.59(3)
N(3)–C(17)	1.339(18)	N(3)–C(21)	1.450(19)
O–C(av)	1.15(2)	Os(1)–Os(2)	3.356(1)
Bond Angles, deg			
Os(3)–Os(1)–C(1)	88.8(5)	Os(3)–Os(1)–C(2)	173.3(4)
Os(3)–Os(1)–C(3)	85.2(5)	Os(1)–C(10)–N(1)	122.0(9)
Os(3)–Os(1)–C(10)	88.6(3)	Os(1)–C(10)–O(10)	122.0(9)
Os(3)–Os(1)–C(17)	75.1(4)	N(1)–C(10)–O(10)	116.0(12)
C(1)–Os(1)–C(2)	97.7(6)	C(1)–Os(1)–C(3)	91.1(6)
C(1)–Os(1)–C(10)	89.7(6)	C(1)–Os(1)–C(17)	162.0(6)
C(2)–Os(1)–C(3)	96.3(7)	C(2)–Os(1)–C(10)	89.8(6)
C(2)–Os(1)–C(17)	98.3(5)	C(3)–Os(1)–C(10)	173.7(6)
C(3)–Os(1)–C(17)	95.3(5)	C(10)–Os(1)–C(17)	82.2(5)
Os(3)–Os(2)–N(2)	92.2(3)	Os(3)–Os(2)–O(10)	89.95(23)
Os(3)–Os(2)–C(4)	89.7(4)	Os(3)–Os(2)–C(5)	170.0(5)
Os(3)–Os(2)–C(17)	77.1(4)	N(2)–Os(2)–O(10)	79.5(4)
N(2)–Os(2)–C(4)	97.3(5)	N(2)–Os(2)–C(5)	97.8(5)
N(2)–Os(2)–C(17)	162.3(5)	O(10)–Os(2)–C(4)	176.8(5)
O(10)–Os(2)–C(5)	92.3(5)	O(10)–Os(2)–C(17)	86.2(4)
C(4)–Os(2)–C(5)	88.6(6)	C(4)–Os(2)–C(17)	96.8(5)
C(5)–Os(2)–C(17)	93.3(6)	Os(1)–Os(3)–Os(2)	70.190(23)
Os(1)–Os(3)–C(6)	157.2(4)	Os(1)–Os(3)–C(7)	87.4(5)
Os(1)–Os(3)–C(8)	82.1(5)	Os(1)–Os(3)–C(9)	97.4(6)
Os(2)–Os(3)–C(6)	87.5(4)	Os(2)–Os(3)–C(7)	83.9(4)
Os(2)–Os(3)–C(8)	86.5(4)	Os(2)–Os(3)–C(9)	166.7(6)
C(6)–Os(3)–C(7)	94.9(7)	C(6)–Os(3)–C(8)	92.4(7)
C(6)–Os(3)–C(9)	105.2(8)	Os(1)–C(17)–Os(2)	110.3(7)
C(7)–Os(3)–C(8)	167.7(6)	Os(1)–C(17)–N(3)	126.0(9)
C(7)–Os(3)–C(9)	90.8(7)	Os(2)–C(17)–N(3)	123.4(8)
C(8)–Os(3)–C(9)	96.9(8)	C(10)–N(1)–C(11)	122.9(11)
Os(2)–N(2)–C(14)	117.0(12)	C(17)–N(3)–C(21)	128.0(10)
Os(2)–O(10)–C(10)	117.3(8)		

boiling point of the benzylamine (185 °C), it is difficult to pump out the amine during the first 30 min of the reaction; therefore, we isolated complex **3e** as the product.

Mechanism. Kaesz and co-workers[14] have investigated the reaction of nucleophiles with $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ and observed the transformation of carbon monoxide in the polynuclear metal centers. They found that the reactions proceed via intermediate η^1-carbamoyl (η^1-C(O)-Nu) complexes which transformed to the bridged η^2-carboxamido (μ-O=C(Nu)) complexes as evidenced by spectroscopic data. In our observations (eq 1), the formation of complex **2** possesses two unique features compared to the previous observations by Kaesz. First, the amine is believed to attack the carbonyl carbon and produce the carbamoyl group (η^1-C(O)Nu) with the transfer of a hydrogen atom from amine to isocyanide to afford the bridging carbyne. Second, the oxygen atom of the carbamoyl ligand attacks the vicinal osmium atom, which leads to the formation of bridged μ-O=C(Nu) derivatives with the concomitant cleavage of the Os–Os bond. Thus, our experiments provide a unique model in which the unsaturation required for the generation of carboxamido ligand is not generated by a prior CO elimination, but by the scission of a metal–metal bond. It is likely that the complex **2** is stabilized by the bridging carbyne and is isolated as an intermediate which is stable in air. In contrast, the ionic intermediate $[H_2NMe_2][Os_3(\mu\text{-}CO{=}CNMe_2)(CO)_{10}]$ proposed in the Kaesz's mechanism[14] is too unstable to be isolated and could only be identified through spectroscopic studies.



(1)

Labilizing Ability of the Coordinated Oxygen End of the Carboxamido Ligand. The facile replacement of CO in the complex $Os_3(CO)_{10}(\mu_2\text{-}OCNHR')(\mu_2\text{-}C{=}NHR)$ (**2**) by amine at ambient temperature indicates some labilization of geminal CO groups cis to the oxygen end of the carboxamido ligand. The crystal structure of **3a** confirms that the coordinated amine ligand and the oxygen end of the carboxamido group are arranged in a cis form.

These observations are analogous to the cis-CO-labilizing ability of oxygen donor ligands reported in the literature involving metal carbonyls containing phosphine oxides, formate ligands, and an acyl group.[15,16] Kaesz also reported that geminal or vicinal CO groups are labile in the η^1-C(O)Nu complexes which transformed into the bridging η^2-carboxamido (μ-O=C(Nu)) derivatives at low temperature.[14] Recently, we reported a similar observation during the study of the addition of iodine to the metal–metal bond of a (carboxamido)triosmium cluster.[17]

The complex **2b** reacts slowly with PPh_3 at room temperature, leading to the new product $Os_3(CO)_9(PPh_3)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHPr)$ (**5**).

The ^1H NMR spectrum of **5** showed that the molecule also contains both a carboxamido ligand and a bridging aminocarbyne group. This reaction was carried out at mild conditions suggesting that a CO ligand on complex **2b** is labile due to the labilizing ability of the carboxamido group. Bubbling CO gas through a solution of the amine-substituted complex $Os_3(CO)_9(NH_2Pr^i)(\mu_2\text{-}CONHPr^i)(\mu_2\text{-}C{=}NHCH_2Ph)$ (**3c**) in CH_2Cl_2 leads to the regeneration of **2c** in almost quantitative yield when monitored with IR spectroscopy, pointing out that the coordinated amine is labile and the amine–carbonyl replacement reactions are facile and reversible.

Transformation of Complex 3 to 4. It is interesting that complex **3** converts into the hydrido complexes $(\mu\text{-}H)Os_3(CO)_9(\mu_2\text{-}CONHR')(CNR)$ (**4**) with the elimination of amine when passed through silica gel. This reaction also yields trace amount of complex **2**.

The IR spectrum of **4a** showed that an absorption is observed at 2158 cm^{-1}, which is the characteristic ν_{CN}

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[14] Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704.

[15] (a) Darensbourg, D. J.; Walker, N.; Darensburg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kuddararoski, R. *Inorg. Chem.* **1982**, *21*, 1656. (c) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

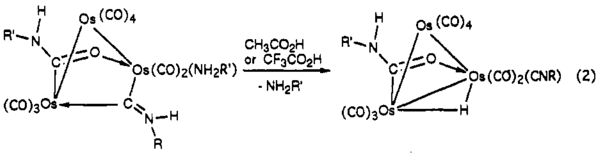
[16] Brown, T. L.; Bellus, P. A. *Inorg. Chem.* **1978**, *17*, 3726.

[17] Lu, K. L.; Lin, Y. C.; Wang, Y. *Organometallics* **1990**, *9*, 1320.

stretching vibration of a coordinated isocyanide.[18a] The ^1H NMR spectrum confirmed that there are no signals which can be attributed to a coordinated amine ligand. The MS spectrum showed the molecular ion at 1017 as well as the CO-loss fragmentation.

The Role of Silica Gel. In contrast to complex **3**, complexes **2** and **5** with a carbonyl or a phosphine group occupying the same coordinated site as the amine does in complex **3** gave no change in their structure when passed through a silica gel column, indicating that the coordinated amine in complex **3** plays an important role in controlling the reactivity in the first step of the transformation. The effect of silica gel may be due to the slight acidity of the silanol group (SiOH) in the surface of silica gel.[19] It is most likely that the protonation of **3** by the acidic sites on silica gel, with a consequent elimination of amine, and protonation of the metal–metal bond followed by deprotonation of aminocarbyne lead to the formation of the bridging hydrido complex **4**.

Treatment of **3a** and **3b** with dilute acetic acid or trifluoroacetic acid in CH_2Cl_2 at room temperature also yielded **4a** and **4b** in 30–60% yield (eq 2).

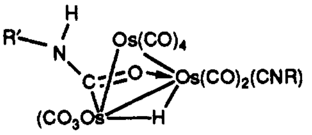


3a, R = Ph, R' = Pr^i
3b, R = Pr, R' = Pr^i

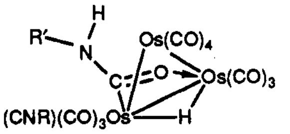
4a, R = Ph, R' = Pr^i
4b, R = Pr, R' = Pr^i

These results are in agreement with the suggestion that the acidic sites on silica gel may be responsible for the transformation observed. The process of protonation/elimination of amine ultimately creates a vacant site on the Os atom which accommodates the isocyanide ligand and induces the transformation of the bridging aminocarbyne group. The interesting feature of this transformation is that it led to the re-formation of an Os–Os bond which was initially broken.

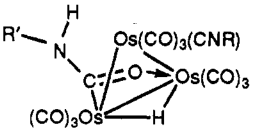
The ^1H NMR spectrum of **4a** shows three peaks at δ −13.62, −14.24, and −15.06 in the hydride region, which may be attributed to the three positional isomers with different environment of the bridging hydride. The structures of three isomers are listed as follows:



I



II



III

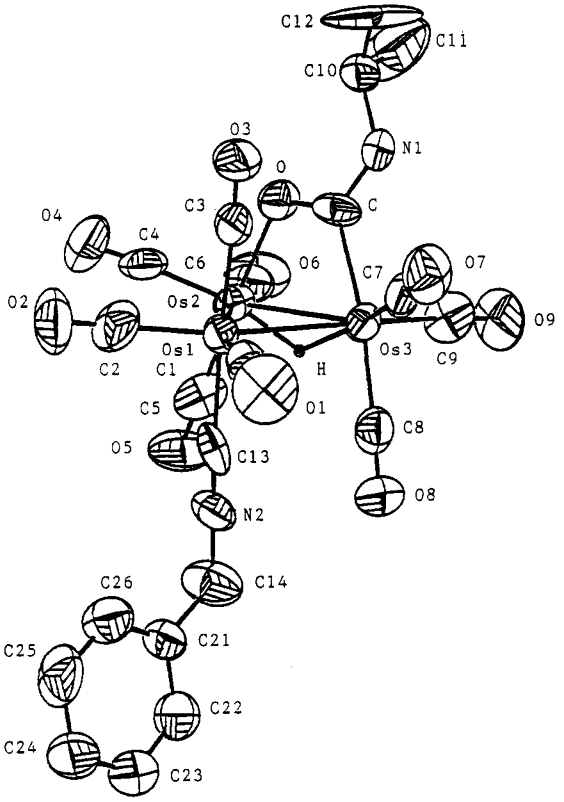


Figure 3. ORTEP diagram of $(\mu\text{-H})Os_3(CO)_9(\mu_2\text{-}CONHPr^i)(CNCH_2Ph)$ (**4c**).

The major isomer is likely the isomer **I**; this is plausible because the protonation of **3** by silica gel followed by the elimination of amine introduces a vacant site which tends to accommodate the isocyanide ligand to afford **I**. However, in silica gel, the isocyanide ligand in isomer **I** may have the opportunity to be protonated again to transform to a bridging aminocarbyne along with the transformation of one terminal carbonyl to form a bridging one, then the deprotonation of the bridging aminocarbyne takes place to induce the formation of isomers **II** and **III**. Attempts to separate these isomers by chromatography were unsuccessful. However, we were able to characterize the single crystal of **4c** as the type of isomer **III**, which was mounted from the crystals of the three isomers. This structure was obtained for a different isomer than the one depicted in Scheme I. The X-ray structure analysis of **4c** suggests the existence of the positional isomers **I** to **III**. However, we cannot rule out the possibility that different substitution positions at the same metal center are occupied. An ORTEP drawing of **4c** is shown in Figure 3. Final atomic positional parameters are listed in Table VI. Selected bond distances and angles are listed in Table VII. This molecule consists of a triosmium cluster with three Os–Os bonds. A hydride ligand (located and refined) and a carboxamido group mutually bridge the Os(2)–Os(3) bond and cause it to lengthen (Os(2)–Os(3) = 2.8986(15) Å). It is well-known that bridging hydride ligands produce a lengthening effect on metal–metal bonds. Os(1) is unique since it contains three carbonyl and an isocyanide ligand. Both the carboxamido group and the isocyanide ligand occupy the axial sites of different Os atoms and are trans to each other with respect to the triosmium plane. The carboxamido ligand shows partial double-bond character for both C–O (1.259(21) Å) and C–N(1) (1.331(20) Å) bonds, similar to that found for other osmium carboxamido cluster complexes.

Concluding Remarks. In summary, we compared the different reactivity between $Os_3(CO)_{11}(CNR)$ and Os_3-

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[18] (a) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579. (b) Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67. (c) Rosenberg, E. *Polyhedron* **1989**, *8*, 383.

[19] Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980; p 92.

Table VI. Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for (μ-H)$Os_3(CO)_9(\mu_2\text{-CONHPr}^i)(CNCH_2Ph)$ (4c)

atom	*x*	*y*	*z*	B_{iso}[a]
Os1	0.81805(7)	0.95454(6)	0.397985(23)	3.98(3)
Os2	0.73265(8)	1.00217(6)	0.302034(24)	4.60(3)
Os3	0.52712(7)	1.02699(6)	0.375975(23)	4.10(3)
N1	0.4117(13)	0.7555(12)	0.3406(5)	5.0(7)
N2	0.9059(15)	1.2607(14)	0.4050(5)	5.2(7)
O	0.6021(12)	0.8319(10)	0.3043(4)	4.9(5)
O1	0.8104(17)	0.9551(15)	0.5054(5)	8.3(8)
O2	1.1240(14)	0.8622(14)	0.3871(6)	9.5(10)
O3	0.7171(13)	0.6658(11)	0.3898(5)	6.9(8)
O4	0.9909(16)	0.8457(14)	0.2724(6)	10.0(10)
O5	0.9060(17)	1.2550(12)	0.3003(5)	8.0(8)
O6	0.6206(20)	1.0619(15)	0.2014(5)	9.5(10)
O7	0.4522(14)	0.8782(14)	0.4658(4)	6.9(8)
O8	0.5902(14)	1.2979(13)	0.4229(5)	8.1(8)
O9	0.2315(14)	1.1230(14)	0.3466(6)	9.1(9)
C	0.5099(18)	0.8495(15)	0.3351(6)	4.5(8)
C1	0.8123(18)	0.9535(17)	0.4650(7)	5.4(9)
C2	1.0117(22)	0.8976(17)	0.3900(7)	6.5(11)
C3	0.7479(17)	0.7737(16)	0.3923(6)	5.0(9)
C4	0.8930(22)	0.8997(16)	0.2851(7)	6.2(10)
C5	0.8406(23)	1.1608(19)	0.3026(6)	6.2(11)
C6	0.6583(21)	1.0366(18)	0.2389(7)	6.4(10)
C7	0.4809(18)	0.9365(18)	0.4331(7)	5.3(9)
C8	0.5659(17)	1.1939(18)	0.4070(6)	5.0(9)
C9	0.3394(22)	1.0841(18)	0.3548(6)	6.0(9)
C10	0.3999(18)	0.6336(17)	0.3131(6)	5.4(9)
C11	0.296(3)	0.636(3)	0.2773(10)	14.1(20)
C12	0.380(4)	0.5192(19)	0.3448(9)	14.6(23)
C13	0.8792(15)	1.1519(19)	0.4016(5)	4.6(8)
C14	0.9388(23)	1.3942(18)	0.4052(7)	7.7(11)
C21	1.0656(18)	1.4343(17)	0.4339(6)	4.9(8)
C22	1.0779(20)	1.5665(18)	0.4452(7)	6.3(10)
C23	1.1924(25)	1.6082(20)	0.4720(9)	8.2(13)
C24	1.2971(24)	1.522(3)	0.4866(8)	8.5(14)
C25	1.2834(22)	1.3864(23)	0.4763(8)	7.8(12)
C26	1.1683(21)	1.3461(18)	0.4504(6)	6.1(10)
H	0.626(12)	1.113(11)	0.315(4)	3.7(27)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table VII. Selected Bond Distances and Angles for (μ-H)$Os_3(CO)_9(\mu_2\text{-CONHPr}^i)(CNCH_2Ph)$ (4c)

Bond Distances, Å

Os(1)–Os(2)	2.8441(19)	O(5)–C(5)	1.131(24)
Os(1)–Os(3)	2.8738(10)	O(6)–C(6)	1.13(3)
Os(1)–C(1)	1.897(19)	O(7)–C(7)	1.133(24)
Os(1)–C(2)	1.925(20)	O(8)–C(8)	1.158(22)
Os(1)–C(3)	1.938(17)	O(9)–C(9)	1.104(23)
Os(1)–C(13)	2.067(19)	C(10)–C(11)	1.39(3)
Os(2)–Os(3)	2.8986(15)	C(10)–C(12)	1.47(3)
Os(2)–O	2.107(10)	Os(2)–C	2.779(17)
Os(2)–C(4)	1.897(20)	Os(2)–C(5)	1.889(21)
Os(2)–C(6)	1.928(21)	Os(3)–C	2.129(15)
Os(3)–C(7)	1.915(20)	C(14)–C(21)	1.48(3)
Os(3)–C(8)	1.923(18)	Os(3)–C(9)	1.929(19)
C(21)–C(22)	1.371(25)	N(1)–C	1.331(20)
C(21)–C(26)	1.38(3)	N(1)–C(10)	1.454(20)
C(22)–C(23)	1.36(3)	N(2)–C(13)	1.126(23)
C(23)–C(24)	1.36(4)	N(2)–C(14)	1.377(22)
O–C	1.259(21)	C(24)–C(25)	1.40(3)
O(1)–C(1)	1.144(23)	O(2)–C(2)	1.117(24)
C(25)–C(26)	1.35(3)	O(3)–C(3)	1.125(20)
O(4)–C(4)	1.135(24)		

Bond Angles, deg

Os(2)–Os(1)–Os(3)	60.92(3)	C–N(1)–C(10)	125.3(13)
Os(2)–Os(1)–C(1)	159.6(5)	Os(2)–Os(1)–C(2)	100.2(6)
Os(2)–Os(1)–C(3)	89.6(5)	C(13)–N(2)–C(14)	175.2(18)
Os(2)–Os(1)–C(13)	87.4(4)	Os(2)–O–C	108.7(9)
Os(3)–Os(1)–C(1)	99.3(5)	Os(2)–C–Os(3)	71.0(4)
Os(3)–Os(1)–C(2)	160.6(6)	Os(2)–C–N(1)	164.0(12)
Os(3)–Os(1)–C(3)	84.4(4)	Os(2)–C–O	45.9(7)
Os(3)–Os(1)–C(13)	91.6(4)	Os(3)–C–N(1)	124.9(13)
C(1)–Os(1)–C(2)	99.9(8)	Os(3)–C–O	116.8(11)
C(1)–Os(1)–C(3)	93.3(7)	N(1)–C–O	118.2(13)
C(1)–Os(1)–C(13)	88.4(7)	C(2)–Os(1)–C(3)	91.7(7)
C(2)–Os(1)–C(13)	91.7(7)	C(3)–Os(1)–C(13)	175.8(6)
Os(1)–Os(2)–Os(3)	60.05(4)	Os(1)–Os(2)–O	88.9(3)
Os(1)–Os(2)–C	77.2(3)	Os(1)–Os(2)–C(4)	87.0(6)
Os(1)–Os(2)–C(5)	89.9(5)	Os(1)–Os(2)–C(6)	175.1(6)
N(1)–C(10)–C(11)	114.7(17)	N(1)–C(10)–C(12)	110.0(15)
Os(3)–Os(2)–O	69.3(3)	Os(3)–Os(2)–C	44.0(3)
C(11)–C(10)–C(12)	110.9(21)	Os(3)–Os(2)–C(4)	141.2(6)
Os(3)–Os(2)–C(5)	106.8(5)	Os(3)–Os(2)–C(6)	115.0(6)
O–Os(2)–C	25.4(4)	O–Os(2)–C(4)	91.9(6)
O–Os(2)–C(5)	176.1(6)	C–Os(2)–C(4)	113.3(6)
C–Os(2)–C(5)	150.7(6)	C–Os(2)–C(6)	99.0(6)
C(4)–Os(2)–C(5)	91.8(8)	C(4)–Os(2)–C(6)	97.5(9)
Os(1)–C(13)–N(2)	176.1(14)	N(2)–C(14)–C(21)	116.4(15)
C(5)–Os(2)–C(6)	92.0(8)	Os(1)–Os(3)–Os(2)	59.04(4)
Os(1)–Os(3)–C	87.7(4)	Os(1)–Os(3)–C(7)	86.3(5)
Os(1)–Os(3)–C(8)	87.6(5)	Os(1)–Os(3)–C(9)	173.7(5)
Os(2)–Os(3)–C	65.0(5)	Os(2)–Os(3)–C(7)	137.8(5)
Os(2)–Os(3)–C(8)	106.5(5)	Os(2)–Os(3)–C(9)	115.1(5)
C–Os(3)–C(7)	92.5(7)	C–Os(3)–C(8)	171.5(7)
C–Os(3)–C(9)	91.6(7)	C(7)–Os(3)–C(8)	94.3(7)
C(7)–Os(3)–C(9)	100.0(7)	C(8)–Os(3)–C(9)	92.2(7)

$(CO)_{12}$ toward amines. This paper explains the significant effect of the isocyanide–carbonyl replacement on the reactivity of the osmium cluster. In these reactions the transformations of the coordinated isocyanide,[18] first into the bridging carbyne and then back into the isocyanide with the cleavage and re-formation of the Os–Os bond, most likely play an important role in the reactivity of these osmium clusters.

Experimental Section

General Data. The complexes $Os_3(CO)_{11}(CNPr)$, $Os_3(CO)_{11}(CNPr^i)$, $Os_3(CO)_{11}(CNPh)$, and $Os_3(CO)_{11}(CNCH_2Ph)$ were prepared previously.[2,20] Other reagents were purchased from commercial sources and were used as received. All manipulations, except for thin-layer chromatography (TLC), were preformed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (tetrahydrofuran, ether) or CaH_2 (hexane, CH_2Cl_2) and were freshly distilled prior to use. IR spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Brucker MSL-200, an AC-200, or an AMX-500 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer.

Reaction of $Os_3(CO)_{11}(CNR)$ (1) with Primary Amines for Several Minutes. $Os_3(CO)_{10}(\mu_2\text{-CONHPr}^i)(\mu_2\text{-C=NHPh})$ (2a). A solution of $Os_3(CO)_{11}(CNPh)$ (150 mg, 0.15 mmol) in NH_2Pr^i (10 mL) was stirred at room temperature for 3 min. The amine was removed under vacuum, and the residue was chromatographed by silica gel TLC plate with hexane as eluent to give **2a** (141 mg, 0.14 mmol, 89%). IR (CH_2Cl_2): ν_{CO} = 2091 (w), 2055 (s), 2039 (m), 2004 (s), 1975 (sh), 1960 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.00, 10.85 (br, μ_2-C=N*H*Ph, two isomers in a 5:5 ratio), 7.34–7.43 (m, 5 H, Ph), 5.73 (d, br, 1 H, μ_2-CON*H*Pr^i), 3.96 (m, 1 H, C*H*Me$_2$), 1.04 (d, 6 H, C*H*$_3$). Anal. Calcd for $C_{21}H_{14}N_2O_{11}Os_3$: C, 24.23; H, 1.36. Found: C, 24.29; H, 1.42.

$Os_3(CO)_{10}(\mu_2\text{-CONHPr}^i)(\mu_2\text{-C=NHPr})$ (2b). A solution of $Os_3(CO)_{11}(CNPr)$ (103 mg, 0.11 mmol) in NH_2Pr^i (10 mL) was stirred at room temperature for 10 min. The amine was removed under vacuum, and the residue was chromatographed by silica gel TLC plate with hexane as solvent to give **2b** (99 mg, 0.10 mmol, 91%). IR (CH_2Cl_2): ν_{CO} = 2090(w), 2053 (s), 2037 (m), 2003 (s), 1975 (sh), 1958 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.16, 9.00 (br, μ_2-C=N*H*Pr, two isomers in a 4:6 ratio), 5.75 (d, br, 1 H, μ_2-CON*H*Pr^i), 3.96 (m, 1 H, C*H*Me$_2$), 3.59 (m, 2 H, C*H*$_2$CH$_2$CH$_3$), 1.87 (m, 2 H, C*H*$_2$CH$_3$), 1.08 (t, 3 H, CH$_2$C*H*$_3$), 1.06 (d, 6 H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$): δ 272.2, 271.6 (μ_2-*C*NHPr, two

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[20] Lu, K. L.; Chen, C. C.; Lin, Y. W.; Hong, F. E.; Gau, H. M.; Gan, L. L.; Luoh, H. D. *J. Organomet. Chem.*, in press.

isomers), 213.1, 212.9 (μ_2-CONHPr^i, two isomers), 186.5, 184.9, 183.0, 182.2, 181.5, 180.4, 180.1, 178.7, 177.4, 177.1, 176.6, 172.9, 172.3, 172.2, 171.5 (CO, 2 isomers), 62.8, 62.6 (NHCH$_2$ and NHCH), 42.8 (CH$_2$CH$_3$), 22.9, 22.5, 22.3, 21.8 (CH(CH$_3$)), 11.3 (CH$_2$$CH_3$). MS (FAB): m/z 1009 (M$^+$), 981 (M$^+$ − CO), 953, (M$^+$ − 2CO) 925 (M$^+$ − 3CO), 897 (M$^+$ − 4CO), 869 (M$^+$ − 5CO), 841 (M$^+$ − 6CO). Anal. Calcd for $C_{18}H_{16}N_2O_{11}Os_3$: C, 21.47; H, 1.60. Found: C, 21.54; H, 1.55.

$Os_3(CO)_{10}$(μ_2-CONHPr^i)(μ_2-C=NHCH$_2$Ph) (2c). A solution of $Os_3(CO)_{11}$(CNCH$_2$Ph) (150 mg, 0.15 mmol) in NH$_2$Pr^i (10 mL) was stirred at room temperature for 3 min. The amine was removed under vacuum, and the residue was chromatographed by silica gel TLC plate with hexane as eluent to give **2c** (137 mg, 0.13 mmol, 85%). IR (CH$_2$Cl$_2$): ν_{CO} = 2090 (w), 2053 (s), 2037 (m), 2004 (s), 1973 (m), 1954 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.26, 9.11 (br, μ_2-C=NHCH$_2$Ph, two isomers in a 7:3 ratio), 7.49–7.36 (m, 5 H, Ph), 5.77 (d, br, 1 H, μ_2-CONHPr^i), 4.79, 4.72 (d, 2 H, CH_2Ph, two isomers in a 3:7 ratio), 4.00 (m, 1 H, CHMe$_2$), 1.10 (d, 3 H, CH_3), 1.06 (d, 3 H, CH_3).

$Os_3(CO)_{10}$(μ_2-CONHPr)(μ_2-C=NHPr^i) (2d). A solution of $Os_3(CO)_{11}$(CNPr^i) (120 mg, 0.13 mmol) in NH$_2$Pr (10 mL) was stirred at room temperature for 30 min. The amine was removed under vacuum, and the residue was chromatographed by silica gel TLC plate with hexane as solvent to give **2d** (111 mg, 0.11 mmol, 85%). IR (CH$_2$Cl$_2$): ν_{CO} = 2090 (w), 2053 (s), 2036 (m), 2002 (s), 1978 (sh), 1957 (br) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.09, 8.95 (d, br, μ_2-C=NH, two isomers in 6:4 ratio), 5.93 (br, 1 H, μ_2-CONH), 4.20–3.93 (m, 1 H, CHMe$_2$), 3.09 (m, 2 H, CH_2CH$_2$CH$_3$), 1.44 (m, 2 H, CH_2CH$_3$), 1.41 (d, 6 H, CH(CH_3)$_2$), 0.87 (t, 3 H, CH$_2$CH_3). ^{13}C NMR (CDCl$_3$): δ 265.6, 264.8 (μ_2-CNHPr^i), 213.5 (μ_2-CONHPr), 186.3, 184.9, 184.1, 183.1, 182.3, 181.6, 180.4, 180.0, 178.9, 177.5, 177.3, 176.8, 172.7, 172.2, 171.3 (CO, two isomers), 64.2, 64.1 (NCCH and NHCH$_2$), 43.0 (CH$_2$$CH_2CH_3$), 22.4, 21.4 (CH($CH_3$)$_2$), 11.3 (CH$_2$$CH_3$).

Reaction of Complex 2b with PPh$_3$. The complex **2b** (117 mg, 0.12 mmol) and excess PPh$_3$ (337 mg, 1.28 mmol) were stirred in CH$_2$Cl$_2$ (50 mL) at room temperature for 7 d. The solvent was removed under vacuum, and the residue was chromatographed by silica gel TLC plate. Elution with hexane afforded a yellow fraction, from which microcrystalline $Os_3(CO)_9$(PPh$_3$)(μ_2-CONHPr^i)(μ_2-C=NHPr) (5) was obtained (31 mg, 0.03 mmol, 21%) after evaporation of the solvent. IR (CH$_2$Cl$_2$): ν_{CO} = 2071 (m), 2032 (s), 1991 (vs), 1947 (m), 1908 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.87 (br, 1 H, μ_2-C=NHPr), 7.61–7.26 (m, Ph), 5.65 (d, br, 1 H, μ_2-CONHPr^i), 3.84–3.57 (m, 3 H, CHMe$_2$ and CH_2CH$_2$CH$_3$), 1.87 (m, 2 H, CH_2CH$_3$), 1.12 (d, 6 H, CH(CH_3)$_2$), 0.82 (t, 3 H, CH$_2$CH_3).

Reaction of $Os_3(CO)_{11}$(CNR) (1) with Primary Amines for Several Hours. $Os_3(CO)_9$(NH$_2$Pr^i)(μ_2-CONHPr^i)(μ_2-C=NHPh) (**3a**). A solution of $Os_3(CO)_{11}$(CNPh) (**1a**) (126 mg, 0.13 mmol) in NH$_2$Pr^i (10 mL) was stirred at room temperature. Complex **1a** reacts with amine to give complex **2a** at first and then continues to react with amine to produce complexes **3a**. The reaction was finished in 10 h by monitoring with IR spectroscopy. The amine was removed under vacuum, and the residue was recrystallized form CH$_2$Cl$_2$/hexane to give **3a** (114 mg, 0.11 mmol, 83%). IR (CH$_2$Cl$_2$): ν_{CO} = 2071 (m), 2029 (s), 1992 (s, br), 1982 (s, br), 1958 (sh), 1943 (sh), 1902 (w) cm^{-1} [μ_2-CO = 1436 cm^{-1} (KBr)]. ^{1}H NMR (CDCl$_3$): δ 10.63, 10.43 (br, μ_2-C=NHPh, two isomers in a 1:9 ratio), 7.35–7.43 (m, 5 H, Ph), 5.75 (d, br, 1 H, μ_2-CONHPr^i), 4.02 (m, 1 H, μ_2-CONHCHMe$_2$), 3.23 (m, 1 H, NH$_2$CH), 3.08 (br, 2 H, NH_2CH), 1.27 (dd, 6 H, NH$_2$CH(CH_3)$_2$), 1.11 (dd, 6 H, μ_2-CONHCH(CH_3)$_2$). Anal. Calcd for $C_{23}H_{23}N_3O_{10}Os_3$: C, 25.76; H, 2.15. Found: C, 25.72; H, 1.90.

$Os_3(CO)_9$(NH$_2$Pr^i)(μ_2-CONHPr^i)(μ_2-C=NHPr) (3b). A solution of $Os_3(CO)_{11}$(CNPr) (120 mg, 0.13 mmol) in NH$_2$Pr^i (10 mL) was stirred at room temperature for 18 h. The amine was removed under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/hexane to give **3b** (110 mg, 0.11 mmol, 82%). IR (CH$_2$Cl$_2$): ν_{CO} = 2069 (m), 2027 (s), 1992 (s, br), 1983 (s, br), 1957 (sh), 1945 (sh), 1902 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.77, 8.58 (br, μ_2-C=NHPh, two isomers in a 4:6 ratio), 5.76 (br, 1 H, μ_2-CONHPr^i), 3.97 (m, 1 H, μ_2-CONHCHMe$_2$), 3.60 (m, 2 H, CH_2CH$_2$CH$_3$), 3.16 (m, 1 H, NH$_2$CHMe$_2$), 3.02 (br, 2 H, NH_2CHMe$_2$), 1.81 (m, 2 H, CHCH_2CH$_3$), 1.25 (dd, 6 H, NH$_2$CH(CH_3)$_2$, 1.09 (dd, 6 H, μ_2-CONHCH(CH_3)$_2$), 1.01 (t, 3 H, CH$_2$CH_3). Anal. Calcd for $C_{20}H_{25}N_3O_{10}Os_3$: C, 23.14; H, 2.43. Found: C, 23.17; H, 2.54.

$Os_3(CO)_9$(NH$_2$Pr^i)(μ_2-CONHPr^i)(μ_2-C=NHCH$_2$Ph) (3c) was obtained under reaction conditions similar to **3a**. The isolation of pure product **3c** was difficult, as it was easily contaminated with **2c**; therefore, the control of reaction time (about 6 h) is important. Yield: 70–80%. IR (CH$_2$Cl$_2$): ν_{CO} = 2069 (m), 2026 (s), 1992 (s, br), 1981 (s, br), 1956 (sh), 1940 (sh), 1900 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.86, 8.74 (br, μ_2-C=NHCH$_2$Ph, two isomers in a 6:4 ratio), 7.41–7.31 (m, 5 H, Ph), 5.79 (d, br, 1 H, μ_2-CONHPr^i), 4.77 (d, 2 H, CH_2Ph), 4.01 (m, 1 H, μ_2-CONHCHMe$_2$), 3.26 (m, 1 H, NH$_2$CH), 3.11 (br, 2 H, NH_2CH), 1.24 (dd, 6 H, NH$_2$CH(CH_3)$_2$), 1.11 (dd, 6 H, μ_2-CONHCH(CH_3)$_2$).

$Os_3(CO)_9$(NH$_2$Pr)(μ_2-CONHPr)(μ_2-C=NHPr^i) (3d). A solution of $Os_3(CO)_{11}$(CNPr^i) (120 mg, 0.13 mmol) in NH$_2$Pr (10 mL) was stirred at room temperature for 18 h. The amine was removed under vacuum, and the residue was recrystallized from CH$_2$Cl$_2$/hexane to give **3d** (110 mg, 0.10 mmol, 80%). IR (CH$_2$Cl$_2$): ν_{CO} = 2069 (m), 2027 (s), 1988 (s, br), 1961 (sh), 1955 (sh), 1942 (br), 1902 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.65, 8.47 (br, μ_2-C=NH, two isomers in a 6:4 ratio), 5.94 (br, 1 H, μ_2-CONH), 4.12 (m, 1 H, CHMe$_2$), 3.07 (m, 4 H, NHCH_2CH$_2$ and NH$_2$CH_2), 2.28 (br, 2 H, NH_2CH$_2$), 1.66 (m, 2 H, NHCH$_2$CH_2), 1.52 (m, 2 H, NH$_2$CH$_2$CH_2), 1.37 (d, 6 H, CH(CH_3)$_2$), 0.94 (t, 3 H, NH(CH$_2$)$_2$CH_3), 0.86 (t, 3 H, NH$_2$(CH$_2$)$_2$CH_3). Anal. Calcd for $C_{20}H_{25}N_3O_{10}Os_3$: C, 23.14; H, 2.43. Found: C, 23.27; H, 2.40.

$Os_3(CO)_9$(NH$_2$CH$_2$Ph)(μ_2-CONHCH$_2$Ph)(μ_2-C=NHPh) (3e). A solution of $Os_3(CO)_{11}$(CNPh) (100 mg, 0.1 mmol) in NH$_2$CH$_2$Ph (10 mL) was stirred at room temperature. The reaction was finished in 10 h by monitoring with IR spectroscopy. The amine was removed under vacuum, and the residue was recrystallized form CH$_2$Cl$_2$/hexane to give **3e** (89 mg, 0.08 mmol, 75%). IR (CH$_2$Cl$_2$): ν_{CO} = 2072 (m), 2030 (s), 1993 (s, br), 1958 (sh), 1954 (sh), 1906 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.67, 10.46 (br, μ_2-C=NHPh, two isomers in a 3:7 ratio), 7.47–7.28 (m, 15 H, 3 Ph), 6.17 (br, 1 H, μ_2-CONHPh), 4.37 (d, 2 H, NHCH_2Ph), 4.15 (m, 2 H, NH$_2$CH_2Ph), 3.45 (br, 2 H, NH_2CH$_2$Ph). MS (EI): m/z 1167 (M$^+$), 1139 (M$^+$ − CO), 1090 (M$^+$ − Ph), 1062 (M$^+$ − CO − Ph). Anal. Calcd for $C_{31}H_{23}N_3O_{10}Os_3$: C, 31.86; H, 1.97. Found: C, 31.73; H, 1.94.

The Transformation of 3 to 4 through Silica Gel. (μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNPh) (**4a**). The complex **3a** (100 mg, 0.10 mmol) was chromatographed on a silica gel column with CH$_2$Cl$_2$/hexane (10:90) as eluent to afford **4a** (73 mg, 0.07 mmol, 75%) and trace amounts of **2a** along with other unidentified minor species. (μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNPh) (**4a**). IR (n-hex): ν_{CN} = 2158 (w), ν_{CO} = 2053 (s), 2033 (s), 1994 (br), 1961 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.14–7.39 (Ph), 5.56 (d, 1 H, μ_2-CONH), 3.90 (m, 1 H, CHMe$_2$), 0.98 (d, 6 H, CH_3), −15.06, −14.24, −13.62 (s, OsHOs, three isomers). MS (EI): m/z 1017 (M$^+$), 988 (M$^+$ − CO), 960 (M$^+$ − 2CO), 931 (M$^+$ − 3CO), 911 (M$^+$ − CO − Ph), 886 (M$^+$ − 2CO − Ph). Anal. Calcd for $C_{20}H_{14}N_2O_{10}Os_3$: C, 23.72; H, 1.39. Found: C, 23.62; H, 1.35.

(μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNPr) (4b). The complex **3b** (100 mg, 0.10 mmol) was chromatographed on a silica gel column with CH$_2$Cl$_2$/hexane (10:90) as eluent to afford **4b** (69 mg, 0.07 mmol, 73%) and trace amounts of **2b** along with other unidentified minor species. (μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNPr) (**4b**). IR (CH$_2$Cl$_2$): ν_{CN} = 2194 (w). ν_{CO} = 2051 (s), 2032 (s), 1988 (br), 1965 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.60 (br, 1 H, μ_2-CONH), 3.98 (m, 1 H, CHMe$_2$), 3.78 (t, 2 H, CNCH_2), 1.86 (m, 2 H, CH$_2$CH_2CH$_3$), 0.98 (t, 3 H, CH$_2$CH_3), 0.83 (t, 6 H, CH(CH_3)$_2$), −15.39, −14.40, −13.45 (s, OsHOs, three isomers).

(μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNCH$_2$Ph) (4c). The complex **3c** (100 mg, 0.09 mmol) was chromatographed on silica gel column with CH$_2$Cl$_2$/hexane (10:90) as eluent to afford **4c** (57 mg, 0.06 mmol, 61%) and trace amounts of **2c** along with other unidentified minor species. (μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNCH$_2$Ph) (**4c**). IR (CH$_2$Cl$_2$): ν_{CN} = 2190 (w), ν_{CO} = 2047 (s), 2030 (s), 2000 (br), 1976 (sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.41–7.34 (m, 5 H, Ph), 5.56 (d, 1 H, μ_2-CON*H*), 5.02 (s, 2 H, CH$_2$Ph), 3.94 (m, 1 H, C*H*Me$_2$), 0.97 (d, 6 H, C*H*$_3$), −13.45, −14.38, −15.30 (s, OsHOs, three isomers). MS (FAB): *m/z* 1029 (M$^+$), 1001 (M$^+$ − CO), 973 (M$^+$ − 2CO), 945 (M$^+$ − 3CO), 917 (M$^+$ − 4CO), 889 (M$^+$ − 5CO).

Attempted Transformation of 2 to 4 by Treatment with Silica Gel. When passed through a silica gel column eluted with CH$_2$Cl$_2$/hexane (10:100) complex **2** did not show any change and was recovered almost quantitatively.

Attempted Transformation of 5 to 4 by Treatment with Silica Gel. When passed through a silica gel column eluted with CH$_2$Cl$_2$/hexane (10:100) complex **5** did not show any change and was recovered almost quantitatively.

Carbonylation of 3c. When CO gas was bubbled through a solution of complex **3c** (59 mg, 0.06 mmol) in CH$_2$Cl$_2$ (30 mL) at room temperature for 1 h, complex **2c** was generated almost quantitatively when monitored with IR spectroscopy.

Treatment of 3a and 3b with Organic Acid in CH$_2$Cl$_2$ Solution. Stirring complex **3a** and **3b** with small amount (0.1–0.5 mL) of acid (CH$_3$COOH or CF$_3$COOH) in CH$_2$Cl$_2$ solution at room temperature gives complex **4a** and **4b** as the major product in 30–60% yield.

Crystallographic Structure Determination. Crystallographic data for the three complexes are shown in Table I. Crystals of Os$_3$(CO)$_{10}$(μ_2-CONHPr)(μ_2-C=NHCH$_2$Ph) (**2c**), Os$_3$(CO)$_9$(NH$_2$Pr^i)(μ_2-CONHPr^i)(μ_2-C=NHPh) (**3a**), and (μ-H)-Os$_3$(CO)$_9$(μ_2-CONHPr^i)(CNCH$_2$Ph) (**4c**) were grown from CH$_2$Cl$_2$/hexane solutions at −5 °C. Specimens of suitable quality were mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. All diffraction measurements were made on an Enraf-Norius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.709 30 Å) with a θ–2θ scan mode. 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 group were determined from the systematic absences observed during data collection. An empirical absorption correction was applied to each of the data sets. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for **3a**. The systematic absences in the diffraction data of **2c** and **4c** unambiguously established the space group as *Pbca* and $P2_1/n$, respectively. The structures were each solved by a heavy-atom method, which located the Os atoms. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier syntheses. The huge thermal parameters for **2c** are not only related to thermal motion but also likely due to the slight ligand disorder. A satisfactory disorder model could not be devised. The hydride peak in **4c** was located and refined. All the data processing was carried out on a Microvax 3600 using the NRCC Package.[21]

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Supplementary Material Available: Tables of crystal and density collection data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2c**, **3a**, and **4c** (17 pages). Ordering information is given on any current masthead page.

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[21] Gabe, E. J.; Lee, F. L.; Le Page, Y. In *Crystallographic Computing 3; Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 167–174.