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Reactivity of Hydrogen Halide Adducts of Triosmium Clusters. 2. Synthesis of μ-η^1- and μ-η^1:η^6-Phenyl Clusters

Shariff E. Kabir, Edward Rosenberg,* Jeffrey Stetson, and Mingzhi Yin

Department of Chemistry, The University of Montana, Missoula, Montana 59812

Joana Ciurash, Karina Mnatsakanova, Kenneth I. Hardcastle, Hosai Noorani, and Naira Movsesian

Department of Chemistry, California State University, Northridge, California 91330

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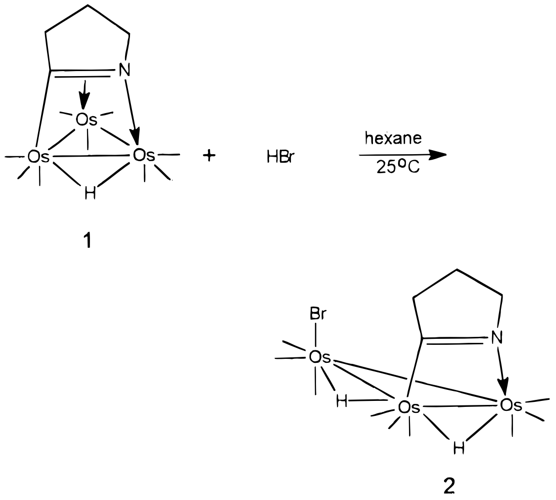
The reaction of $Os_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)Br$ (**2**) with diphenyl mercury yields the μ-η^1-phenyl derivative $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)(\mu\text{-}\eta^1\text{-}C_6H_5)$ (**3**). Compound **3** converts to the novel μ-η^1:η^6-phenyl derivative $Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)(\mu\text{-}\eta^1{:}\eta^6\text{-}C_6H_5)$ (**4**) on thermolysis in octane. The solid-state structure of **4** is reported. In order to clear up ambiguities in the location of the hydrides for the previously reported **2**, we report the solid-state structure and solution dynamics of $Os_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}C{=}NCH(CH_3)CH_2CH_2)Br$ (**6**), where carbon−nitrogen disordering is obviated by the presence of the 2-methyl group. The further reaction of **2** with excess HBr results in degradation of the cluster and the isolation of $Os_2(CO)_6(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CHNH(CH)_3)Br_2$ (**7**). This compound represents an unusual example of acid-promoted hydrogenation of a carbon−nitrogen double bond and is an essential reversal of the dehydrogenation associated with the formation of the μ-imidoyl ligands in the title complexes.

Introduction

The isolation of polymetallic complexes containing organic ligands in unusual bonding modes has shed considerable light on how a given organic ligand can interact with a polymetallic site on a metal surface.[1,2] Often stepwise reactions can be observed where progressive involvement of the metals with an increasing number of ligand atoms can be observed.[3] Taken together, these “snapshots” elucidate the sequence of changes which may occur after chemisorption of a ligand to a metal surface.[1−3] This is particularly true of benzene where μ-η^1-,[4] and μ-η^1:η^2-C_6H_5,[5] μ_3-η^1:η^2:η^1-C_6H_4,[6] μ_3-η^2:η^2-:η^2-C_6H_6,[7] and η^6-C_6H_6[8] bonding modes have been observed in metal cluster complexes (Figure 1). In the case of the face bridging μ_3-η^2:η^2:η^2, conversion to the μ_3-η^1:η^2:η^1 bonding mode has been induced photochemically.[9] We report here a related thermal interconversion from μ-η^1 to μ-η^1:η^6 but involving only two of the three metal atoms of the cluster. The μ-η^1 complex is synthesized by a transmetalation reaction from the hydrogen bromide adduct of $Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}C{=}N(CH_2)_3)$ (**1**), $Os_3(CO)_9(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)Br$ (**2**, eq 1).



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In addition, we also report the structure of hydrogen bromide adduct related to **2**, in which substitution of a

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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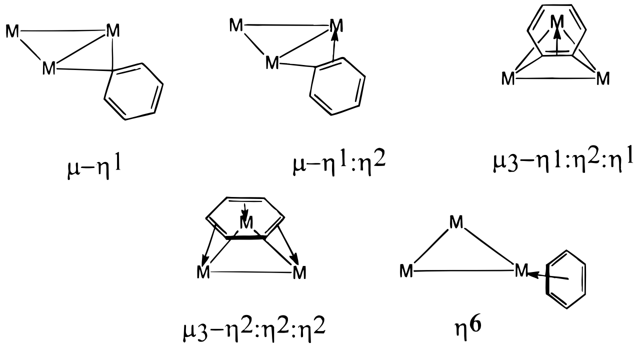
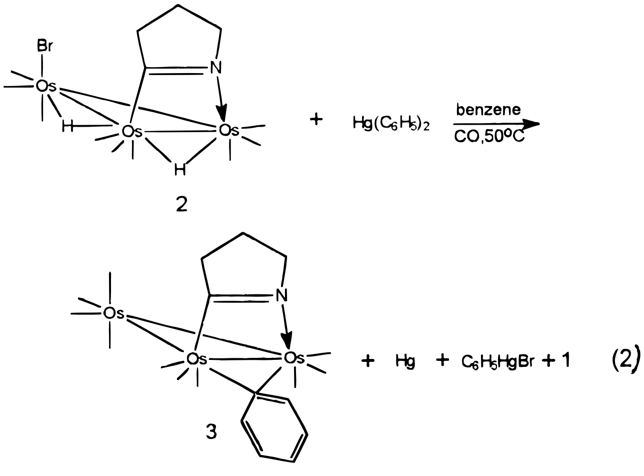


Figure 1. Previously reported bonding modes for benzene rings to polymetallic clusters.

methyl group on the pyrrolidine has resolved prior uncertainties in the hydride ligand location. The further reaction of **2** with excess HBr is also reported.

Results and Discussion

A. Synthesis and Characterization of the μ-Phenyl Derivatives of 2. Compound **2** represents an unusual example of a trimetallic cluster containing a terminal halide.[10] Since direct arylation of metal atoms in carbonyl cluster halides is not a common reaction pathway, we thought it would be useful to explore the reactivity of **2** with common arylating reagents. Unfortunately, reaction with halide-free phenyllithium or thermolysis with tetraphenyltin did not succeed. Reaction with diphenylmercury at 50 °C under carbon monoxide did lead to the formation of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)(\mu\text{-}\eta^1\text{-}C_6H_5)$ in poor to moderate yield (eq 2).



Competitive elimination of HBr to form **1** along with some nonspecific decomposition accounts for the poor yield obtained. Metallic mercury and phenylmercuric bromide are the main mercury-containing byproducts. In the absence of CO, yields were even lower. Attempts to improve the yield by using large excesses of diphenylmercury or the use of other sources of phenylmercury bonds such as phenylmercuric bromide or (trifluoromethyl)phenylmercury failed to improve the yield. Treatment of **1** with these reagents did not yield any **3**. Compound **3** was characterized by ^1H- and ^{13}C-NMR. The ^{13}C-NMR in the carbonyl region of a 30% ^{13}CO-labeled sample of **3** shows 10 carbonyl resonances of equal relative intensity. Most importantly, two resonances show satellites due to $^{13}C-^{13}C$ coupling ($^2J(^{13}C-^{13}C) = 35$ Hz). The magnitude of this coupling indicates a *trans*-orientation of two carbonyl groups and is diagnostic for the presence of an $Os(CO)_4$ moiety in a triosmium cluster.[11] The ^1H-NMR shows the expected set of three methylene multiplet resonances and five distinct phenyl proton resonances at 9.04 (d, 1H), 7.87 (d, 1H), 7.68 (dd, 1H), 7.01 (dd, 1H), and 6.84 (dd, 1H) ppm. The large separation between the two downfield doublets and the essentially first-order nature of the phenyl region in the ^1H-NMR is most consistent with the suggested structure for **3**, where the μ-η^1-phenyl bridges the same two osmium atoms as the μ-imidoyl and where the plane of the benzene ring is perpendicular to that metal−metal vector and tucked toward the opposite face of the triosmium core as the μ-imidoyl ligand. A structure where the μ-η^1-phenyl bridges one of the unbridged edges of the cluster can be ruled out since one would expect two isomers to be populated for such a structure (*vide infra*). The closely related cluster $Ru_3(CO)_6(\mu\text{-}\eta^1\text{-}Ph)(\mu_3\text{-}\eta^2\text{-ampy})(\mu\text{-}PPh_2)_4$ (Hampy = 2-amino-6-methylpyridine) which has been crystallographically characterized shows phenyl resonances in exactly the same region (9.0−6.5 ppm).[4] Several other examples of trimetallic clusters containing μ_1-η^1-phenyl groups or μ_1-η^1-benzene interactions where the benzene ring is part of a more complex ligand system have been reported.[12,13] The pathway to formation of **3** remains unclear, but the isolation of phenylmercuric bromide and the known tendency for mercury aryls to undergo homolytic bond cleavage reactions with transition metal clusters[14] suggests a radical halide abstraction followed by cluster radical collapse with phenyl radical or reaction with a second molecule of diphenylmercury. In most cases transition metal cluster hydrides react with diphenylmercury to give benzene and a μ-Hg cluster derivative.[14] The presence of a halide on the cluster apparently completely alters this common reaction pathway. Attempts to grow X-ray-quality crystals of **3** in a variety of solvents failed. We were also unable to obtain accurate elemental analysis due to the tendency for **3** to undergo thermal reactions in solution (*vide infra*).

Thermolysis of **3** in hydrocarbon solvents at 100 °C leads to rapid decarbonylation and formation of one major cluster product $Os_3(CO)_8(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)(\mu\text{-}\eta^1\text{:}\eta^6\text{-}C_6H_5)$ (**4**, eq 3). The ^{13}C-NMR of a 30% ^{13}CO-enriched

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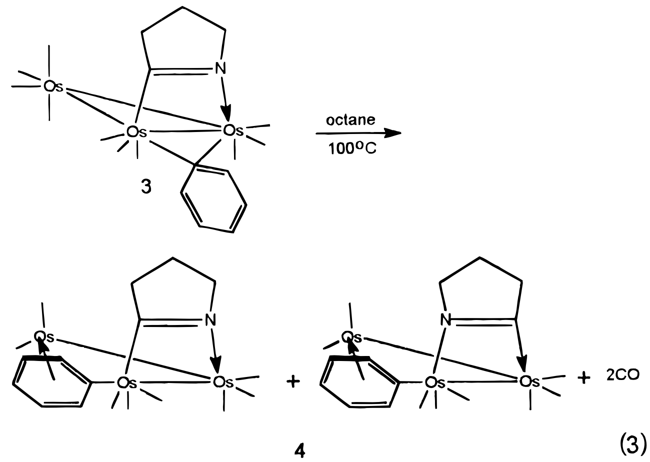

(3)

sample of **4** showed 16 carbonyl resonances of approximately equal intensity. The ^{1}H-NMR of **4** shows 10 aromatic resonances over a broad range of chemical shifts from 6.3 to 4.6 ppm and a series of complex multiplets attributable to the pyrrolidine methylenes from 1.6 to 4.7 ppm. The ten aromatic resonances appear as two sets of five multiplets with each pair of similar chemical shift in an approximate 5:4 ratio. These data clearly indicate the presence of two isomers of **4** in solution. There was no evidence of interconversion of these isomers up to 80 °C in benzene-d_6 by ^{1}H-NMR. The upfield shift of the aromatic resonances in **4** relative to **3** is a clear indication of π-complexation of the aromatic ring.[15] However, the exact bonding mode of the phenyl group could not be determined and so a solid-state structure of **4** was undertaken.

The solid-state structure of **4** is shown in Figure 2, crystal data are given in Table 1, and selected distances and bond angles are given in Table 2. The structure of **4** is disordered with respect to the location of C(4) and N(1). The molecule pictured comprises 32% of the molecules with the alternate structure comprising 68%. This ratio is remarkably close to the ratio of isomers observed in solution (eq 3). The three metal atom core has two metal−metal bonds (Os(1)−Os(3) = 2.844(1) Å), Os(2)−Os(3) = 2.912(1) Å). The phenyl group is η^1-σ-bonded to Os(1) (Os(1)−C(41) = 2.12(1) Å) and η^6-π-bonded to Os(2) (Os(2)−C(41) to C(46) = 2.26−2.35(1) Å). The narrow range of the osmium−arene carbon bond lengths clearly indicates an η^6-π-interaction with Os(2), and the values are comparable to the same bond lengths in other (η^6-benzene)osmium clusters.[8,15] The imidoyl intraligand and ligand−metal bond lengths are very similar to previously reported complexes.[10,11] To the best of our knowledge, this represents a new μ-bonding mode for the phenyl ligand. The Os(1)−Os(2) distance of 3.999(2) Å clearly shows that cleavage of this bond has taken place to accommodate the η^6 bonding mode. The formation of **4** from **3** could well involve passage through a μ-η^1:η^2 complex following dissociation of one carbonyl group (Figure 1). Such a bonding mode has been observed in $Ru_3(CO)_7PPh_3(\mu$-η^1:η^2-Ph)(μ-PPh_2)(μ_3-S).[5] In that case, the presence of the face-capping sulfur may have prevented metal−metal bond rupture and the formation μ-η^1:η^6 bonding mode. We were unable to observe a μ-η^1:η^2 nonacarbonyl intermediate in the conversion of **3** to **4** by ^{1}H and ^{13}C-NMR.

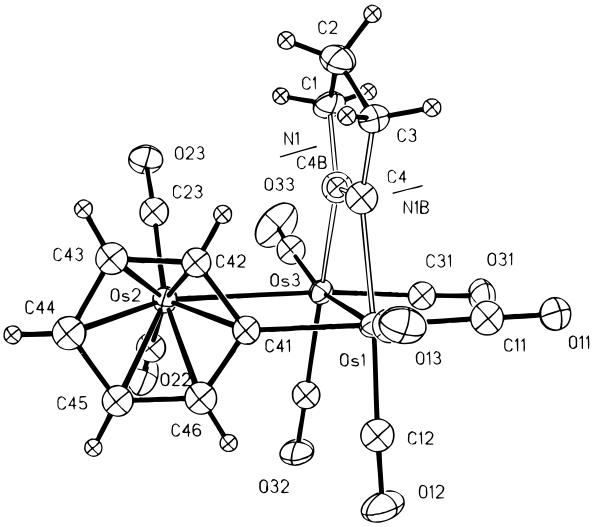

Figure 2. Solid-state structure of **4**.

B. Solid-State Structure of $Os_3(CO)_9(\mu$-η^2-C=NCH(CH_3)(CH_2)$_2$)(μ-H)$_2$Br (6). As for many of the μ- and μ_3-imidoyl cluster derivatives, disordering between the metal-bound carbon and nitrogen made definitive location of the hydride ligands using potential energy minimum calculations with the program Hydex difficult.[16] The location of the hydrides in turn had significance for our interpretation of the dynamical behavior of the hydride ligands.[10] We previously synthesized the 2-methylpyrrolidine analog of **1**, **5**,[17] which reacts quantitatively with HBr to give $Os_3(CO)_9(\mu$-η^2-C=NCH(CH_3)(CH_2)$_2$)(μ-H)$_2$Br (**6**, eq 4). The solid-state structure of **6** is shown in Figure 3, crystal data are found in Table 1, and selected distances and bond angles are given in Table 3. The overall structure of **6** is very similar to **2**, containing a triangular metal core with two elongated osmium−osmium bonds (Os(1)−Os(3) = 3.006(1) Å, Os(1)−Os(2) = 3.061(1) Å) and one shorter osmium−osmium bond (Os(2)−Os(3) = 2.847(1) Å). The hydride ligands are located unambigously along the elongated edges of the metal triangle. As for **2**, H(21)

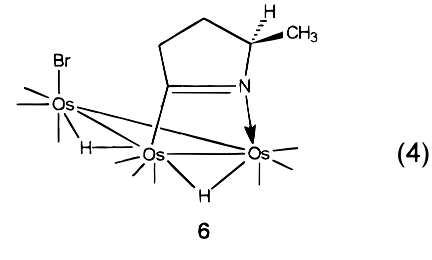

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Table 1. Crystal Data and Structure Refinement for 4, 6, and 7

	compd		
	4	**6**	**7**
empirical formula	$C_{18}H_{11}NO_8Os_3$	$C_{14}H_{10}BrNO_9Os_3$	$C_{10}H_9Br_2NO_6Os_2$
fw	939.88	986.74	779.40
temp	293(2) K	293(2) K	293(2) K
wavelength	0.710 73 Å	0.710 73 Å	0.710 73 Å
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
unit cell dimens	$a = 8.117(2)$ Å, $\alpha = 81.37(1)°$ $b = 8.934(2)$ Å, $\beta = 85.38(2)°$ $c = 14.886(3)$ Å, $\gamma = 70.85(2)°$	$a = 7.634(2)$ Å, $\alpha = 93.69(2)°$ $b = 8.977(2)$ Å, $\beta = 94.46(2)°$ $c = 15.662(3)$ Å, $\gamma = 99.80(2)°$	$a = 16.741(5)$ Å, $\alpha = 90.00(2)°$ $b = 8.663(3)$ Å, $\beta = 110.34(2)°$ $c = 12.374(3)$ Å, $\gamma = 90.00(2)°$
V, Z	1007.6(3) $Å^3$, 2	1051.2(4) $Å^3$, 2	1682.7(9) $Å^3$, 4
D(calcd)	3.098 g/cm^3	3.118 g/cm^3	3.077 g/cm^3
abs coeff	189.14 cm^{-1}	200.31 cm^{-1}	198.58 cm^{-1}
F(000)	836	872	1384
cryst size	0.20 × 0.15 × 0.075 mm	0.26 × 0.15 × 0.04 mm	0.38 × 0.38 × 0.20 mm
θ range for data collcn	1.38−24.97°	1.31−27.49°	2.60−30.99°
limiting indices	$-9 \le h \le 9, -10 \le k \le 10, -17 \le l \le 17$	$-9 \le h \le 9, -11 \le k \le 11, -20 \le l \le 20$	$-24 \le h \le 24, 0 \le k \le 12, -17 \le l \le 17$
reflcns collcd	7100	9928	11314
indepdt reflcns	3550 ($R_{int} = 0.0657$)	4803 ($R_{int} = 0.056$)	5663 ($R_{int} = 0.062$)
abs corr	ψ	ψ	ψ
max and min transm	0.9988 and 0.5478	0.9994 and 0.4625	0.9997 and 0.5087
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least-squares on F^2
data/restraints/params	3550/0/186	4800/0/254	2670/0/89
goodness-of-fit on F^2	1.861	0.931	1.890
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0455$, w$R2 = 0.0833$	$R1 = 0.0571$, w$R2 = 0.1434$	$R1 = 0.0634$, w$R2 = 0.0952$
R indices (all data)	$R1 = 0.0502$, w$R2 = 0.0848$	$R1 = 0.0700$, w$R2 = 0.1611$	$R1 = 0.0873$, w$R2 = 0.0973$
extinction coeff	$1.46(7) \times 10^{-6}$	$8(3) \times 10^{-7}$	$3.1(3) \times 10^{-7}$
largest diff peak and hole	2.095 and −2.131 e $Å^{-3}$	4.107 and −4.803 e $Å^{-3}$	3.647 and −4.278 e $Å^{-3}$

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4[a]

Distances			
Os(1)−Os(3)	2.844(1)	Os(1)−N(1B)	2.135(1)
Os(2)−Os(3)	2.912(1)	Os(3)−N(1)	2.147(1)
Os(1)−C(41)	2.12(1)	C(4)−N(1)	1.280(1)
Os(2)−C(41)	2.35(1)	C(4B)−N(1B)	1.280(1)
Os(2)−C(42)	2.26(1)	C(4)−C(3)	1.46(1)
Os(2)−C(43)	2.26(1)	C(4B)−C(1)	1.49(2)
Os(2)−C(44)	2.32(2)	C(3)−N(1B)	1.46(1)
Os(2)−C(45)	2.30(2)	C(2)−C(3)	1.49(2)
Os(2)−C(46)	2.26(2)	Os−CO[b]	1.89(2)
Os(1)−C(4)	2.135(1)	C−O[b]	1.14(2)
Os(3)−C(4B)	2.147(1)		
Angles			
Os(1)−Os(3)−Os(2)	88.01(4)	C(41)−Os(1)−C(4)	87.1(4)
C(41)−Os(1)−Os(3)	74.4(4)	C(4B)−Os(3)−Os(2)	88.81(3)
C(41)−Os(1)−N(1B)	87.1(4)	C(45)−Os(2)−Os(3)	87.0(4)
C(42)−Os(2)−Os(3)	90.6(3)	C(45)−Os(2)−Os(3)	121.3(3)
C(43)−Os(2)−Os(3)	125.7(3)	Os−C−O[b]	177.8(2)
C(41)−Os(2)−Os(3)	70.1(3)		

[a] Numbers in parentheses are estimated standard deviations. [b] Average values.

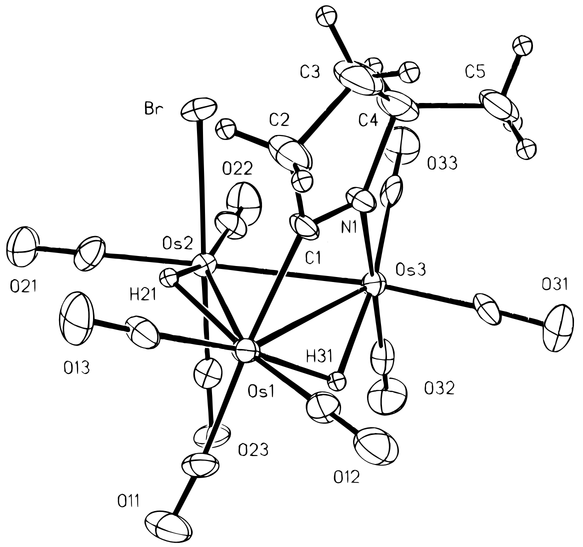


Figure 3. Solid-state structure of **6** showing the calculated positions of the hydride ligands.

is tilted distinctly toward the opposite face of the metal triangle as H(31). The H(21)−Br distance is 2.828(3) Å which is suggestive of some residual bromine hydrogen interaction as was observed for **2** and related compounds.[10] However, the displacement of H(21) toward the bromine atom in these complexes could also be due to the steric repulsions between bromine and the pyrrolidine ring. This causes a tilting of the local metal octehedra such that CO(12) and CO(31) are tilted below the face of the Os_3 triangle and causes an upward tilt of the Os(1)−H(21) and Os(2)−H(21) vectors which want to be directly *trans* to CO(12). Thus, H(21) is displaced 0.577(1) Å above the least-squares Os_3 plane.

The variable-temperature ^{1}H-NMR of **6** is very similar to **2**. The low-temperature limiting spectrum is realized at −40 °C, and as for **2**, three sets of hydride resonances are observed at −14.33, −16.10; −15.00, −16.65; and −15.64, −15.97 ppm in a ratio of 19:11:70 (Figure 4). Interestingly, two additional very low intensity pairs of hydride resonances appearing at −15.18, −16.59 and −15.74, −15.89 ppm are also observed (Figure 4). The major set of three pairs of resonances can be attributed to the three possible hydride location isomers with the major isomer being the one found in the solid state (Scheme 1).[10] The two additional isomers are most likely due to the diastereomeric set where the methyl group on the pyrrolidine ring points toward the bromine atom (Scheme 1). This set of isomers should be on a separate exchange matrix from the major set. However, due to the low abundance of these isomers, this is not obvious from the 1D-VT-^{1}H-NMR. The 2D-^{1}H-EXSY spectra show no common off diagonal elements for these two apparently separate sets of isomers. That no third isomer is detected for isomer set 2 is probably due to

Table 3. Selected Distances (Å) and Bond Angles (deg) for 6[a]

Distances			
Os(1)−Os(2)	3.061(1)	C(1)−N(1)	1.27(2)
Os(1)−Os(3)	3.006(1)	C(1)−C(2)	1.51(2)
Os(2)−Os(3)	2.847(1)	C(2)−C(3)	1.49(2)
Os(2)−Br	2.588(2)	C(3)−C(4)	1.55(2)
Os(1)−C(1)	2.08(1)	C(4)−C(5)	1.5(2)
Os(3)−N(1)	2.13(1)	C(4)−N(1)	1.51(2)
Os−CO[b]	1.91(2)	C−O[b]	1.14(2)
Angles			
Os(1)−Os(2)−Os(3)	61.04(3)	N(1)−Os(3)−Os(2)	89.8(3)
Os(1)−Os(3)−Os(2)	63.00(3)	Os(3)−Os(1)−H(21)	85.3
Os(2)−Os(1)−Os(3)	55.96(3)	Os(3)−Os(2)−H(21)	90.3
Os(1)−Os(2)−Br	96.21(5)	Os(2)−Os(31)−H(31)	82.9
Os(3)−Os(2)−Br	92.44(5)	Os(2)−Os(1)−H(31)	76.9
C(1)−Os(1)−Os(2)	86.5(4)	Os−C−O[b]	177(2)

[a] Numbers in parentheses are estimated standard deviations. [b] Average values.

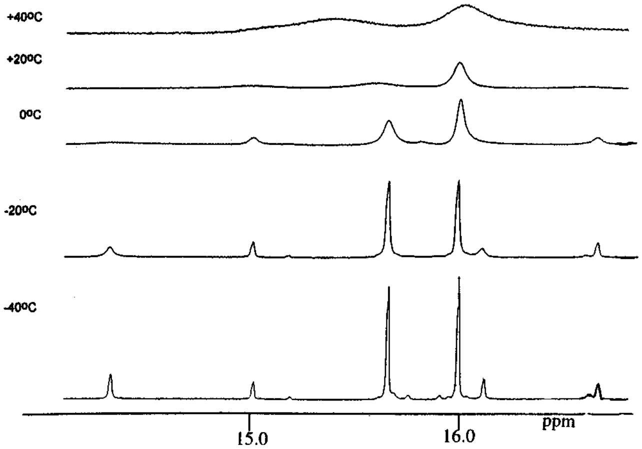
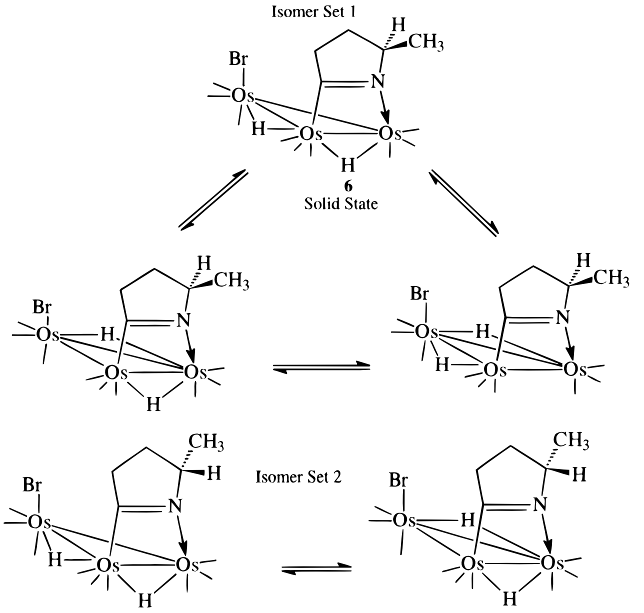


Figure 4. Variable-temperature ^{1}H-NMR of **6** at 400 MHz in $CDCl_3$ in the hydride region.

Scheme 1. Proposed Isomer Sets for 6



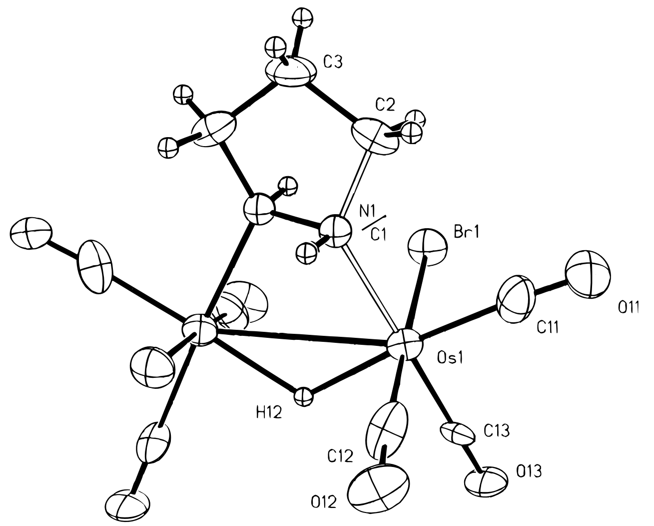
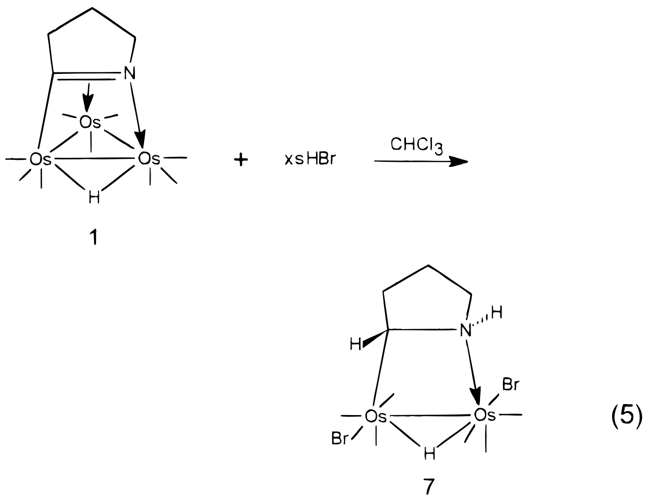


Figure 5. Solid-state structure of **7** showing the calculated positions of the hydride ligand and the hydrogens on the imidoyl ligand.

the low overall population of this isomer set making the third least abundant isomer undetectable by NMR techniques.

C. Reaction of 2 with Excess Hydrogen Bromide. Although the synthesis of compounds **2** and **6** proceeds virtually quantitatively from **1** and **5**, respectively, we noted that the addition of excess HBr to the reaction mixture of **2** and HBr in $CHCl_3$ leads to bleaching of the initially yellow-orange solution and the isolation after chromatography of $Os_2(CO)_6Br_2$-(μ-H)(μ-η^2-$\overline{\mathrm{CHNH(CH_2)_3}}$) (**7**) as the only product (eq 5).



Compound **7** was characterized by ^{1}H- and ^{13}C-NMR and a solid-state structure determination. The ^{1}H-NMR of **7** shows a hydride resonance at −16.53 ppm and a broad NH resonance at 4.38 ppm which correlates (2D ^{1}H COSY) with a CH doublet of triplets at 4.23 ppm and one of the pyrrolidine methylene multiplets. The ^{13}C-NMR of **7** shows six carbonyl resonances and one CH and three CH_2 resonances (attached proton test) as expected from the solid-state structure (see below).

The solid-state structure of **7** is shown in Figure 5, crystal data are given in Table 1, and selected distances and bond angles are in Table 4. Owing to the disordering of C(1) and N(1), the molecule sits on a psuedo-C_2 symmetry axis in the lattice and consists of a diosmium metal core bridged by a μ-η^2-pyrrolidinyl ligand and a hydride. Two terminal bromine atoms and six carbonyls complete the coordination of this 34e$^-$ cluster. Although the metal−metal bond is markedly elongated (Os−Os = 3.197(1) Å), it is required if **7** is to be considered a valence-saturated bimetallic cluster. This elongation

Table 4. Bond Distances (Å) and Angles (deg) for 7[a]

	Distances		
Os(1)−C(1)	2.127(1)	Os(1)−N(1)	2.127(1)
Os(1)−H(12)	1.89(1)	Os(1)−Br(1)	2.565(2)
C(1)−C(2)	1.44(2)	C(1)−C(1)^1	1.509(1)
C(1)−H(1)	0.98	N(1)−C(2)	1.44(2)
N(1)−N(1)^1	1.509(1)	N(1)−N(1)	0.91
C(2)−C(3)	1.52(2)	C(2)−H(2A)	0.97
C(2)−H(2B)	0.97	C(3)−C(2)^1	1.52(2)
C(3)−H(3A)	0.97	C(3)−H(3B)	0.97
Os−CO[b]	1.88(2)	C−O[b]	1.12(B)
	Angles		
C(11)−Os(1)−Br(1)	88.4(4)	C(13)−Os(1)−Br(1)	86.7(4)
N(1)−Os(1)−Br(1)	87.58(5)	C(1)−Os(1)−Br(1)	87.58(5)
C(1)−Os(1)−H(12)	96.2(7)	Br(1)−Os(1)−H(12)	95.1(1)
C(2)−C(1)−Os(1)	126.8(5)	C(2)−C(1)−C(1)^1	102.8(4)
C(2)−C(1)−H(1)	106.0(5)	C(1)^1−C(1)−Os(1)	107.9(1)
C(2)−N(1)−Os(1)	126.8(5)	C(1)^1−C(1)−H(1)	106.0
C(2)−N(1)−H(1)	106.0(5)	N(1)^1−N(1)−Os(1)	107.9(1)
Os(1)−N(1)−H(1)	106.0(1)	N(1)^1−N(1)−H(1)	106.0
C(1)−C(2)−C(3)	106.0(1)	N(1)−C(2)−C(3)	106.0(1)
C(3)−C(2)−H(2A)	110.6(5)	C(1)−C(2)−H(2A)	110.6(5)
C(3)−C(2)−H(2B)	110.6(8)	C(1)−C(2)−H(2B)	110.6(4)
C(2)−C(3)−C(2)^1	104.0(2)	H(2A)−C(2)−H(2B)	108.8
Os−C−O[b]		C(2)−C(3)−H(3A)	110.9(6)

[a] A superscript 1 indicates the following symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 1/2$. Numbers in parentheses are estimated standard deviations. [b] Average values.

may be ascribed to the electron-withdrawing effect of the two bromine atoms. The osmium−bromine bonds are very similar to those in **2** and **6** (2.560(2) Å). The Os−C(1) and Os−N(1) bonds are identical due to the above mentioned disordering but on average are very similar to the carbon−metal and carbon−nitrogen bonds in related μ-η^2-amino ligands.[18]

This binuclear complex could be the result of the addition of 2 mol of HBr to the imidoyl bridged edge of **2** with the expected coproduct being $Os(CO)_3HBr$. It is not possible to determine whether one of the bromine atoms in **7** results from internal transfer from the bromine bearing the Os atom in **2**. It is difficult to imagine that hydrogenation of the C−N occurs via a protonated nitrogen intermediate. Although we have previously observed protonation of an osmium-bound imino nitrogen,[19] in the case of the formation of **7**, this would lead to a carbocation from which it is hard to imagine a reasonable pathway to **7**. The most reasonable pathway seems to be formation of a trihydrido intermediate resulting from the addition of 1 mol of HBr to an intact trinuclear fragment followed by reductive elimination of C−H and N−H bonds and then fragmentation by further reaction with bromide ion and a second 1 mol of HBr.

Experimental Section

All reactions were done under an atmosphere of prepurified nitrogen, but compound purifications were performed in air by thin-layer chromatography (E&M silica gel PF254). Benzene was purified by distillation from sodium benzophenone ketyl, hexane was stirred over sodium wire, and methylene chloride and chloroform were dried over molecular sieves (4A, Mallincrodt). Compounds **1**, **2**, and **5** were synthesized by known literature procedures.[10,11,17] ^1H- and ^{13}C-NMR were obtained on a Varian Unity Plus NMR at 400 and 100 MHz, respectively. Elemental analyses were performed by Schwarzkopf Microanalytical Labs, Woodside, NY.

Preparation of $Os_3(CO)_{10}(\mu$-η^2-$C{=}N(CH_2)_3)(\mu$-η^1-$C_6H_5)$ (3). In a 100 mL Schlenk tube were combined 70−100 mg (0.072−0.103 mmol) of **2** and 10 mL of benzene under a CO atmosphere. A solution of 38−59 mg (0.108−0.166 mmol) of diphenylmercury in 10 mL of benzene was added dropwise over the course of 1 h while the reaction solution was heated at 50−60 °C with stirring. The solution was heated at this temperature for an additional 18−24 h and then rotary evaporated, taken up in minimum methylene chloride, decanted from a small amount of metallic mercury, and eluted on preparative thin-layer chromatography plates (20 × 40 cm × 1 mm silica gel) using 8:2 hexane−methylene chloride by volume. The fastest moving orange band yielded 11−27 mg (13−26%) of $Os_3(CO)_{10}(\mu$-η^2-$C{=}N(CH_2)_3)(\mu$-η^1-$C_6H_5)$ (**3**). Several other minor bands including **1**, unreacted **2**, and C_6H_5HgBr were isolated in amounts ranging from 10−20 mg each.

Spectroscopic Data for 3. IR (ν(CO), hexane): 2089 (m), 2056 (vs), 2038 (s), 2008 (s), 1994 (s), 1976 (m), 1954 (w) cm^{-1}. ^1H-NMR ($CDCl_3$): 9.04 (d, 1H), 7.87 (d, 1H), 7.68 (dd, 1H), 7.01 (dd, 1H), 6.84 (dd, 1H), 3.91 (t, 2H), 2.79 (t, 2H), 2.04 ppm (m, 2H). ^{13}C-NMR ($CDCl_3$, carbonyl region): 183.86 (1C), 183.36 (1C), 182.24 (1C), 180.99 (1C), 179.71 (1C), 178.73 (1C), 178.30 (1C), 178.12 (1C), 170.53 (1C), 168.49 (1C).

Preparation of $Os_3(CO)_8(\mu$-η^2-$C{=}N(CH_2)_3)(\mu$-$\eta^1{:}\eta^6$-$C_6H_5)$ (4). Compound **3** (27 mg, 0.027 mmol) and 25 mL of octane were combined in a 50 mL round bottom flask and refluxed for 2 h under an atmosphere of nitrogen. The pale yellow solution was evaporated to dryness, taken up in methylene chloride, and purified by preparative thin-layer chromatography using 8:2 hexane−methylene chloride as eluent to yield 15 mg (60%) of a single major band identified as $Os_3(CO)_8(\mu$-η^2-$C{=}N(CH_2)_2)(\mu$-$\eta^1{:}\eta^6$-$C_6H_5)$ (**4**). Several other minor bands were noted but in amounts too small to characterize.

Spectroscopic and Analytical Data for 4. Anal. Calcd for $C_{18}H_{11}NO_8Os_3$: 23.00, C; 1.18, H, 1.40, N. Found: 23.43, C; 1.13, H; 1.48, N. IR(ν(CO), CH_2Cl_2): 2063 (m), 2026 (s), 1998 (m, br), 1977 (s, br), 1965 (m, br), 1941 (w, br) cm^{-1}. ^1H-NMR ($CDCl_3$, two isomers): Isomer A (45%), 6.69 (dd, 1H), 5.95 (d, 1H), 5.63 (dd, 1H), 5.38 (dd, 1H), 3.62 (d, 1H), 3.60 (m, 2), 3.30 (m, 1H), 2.72 (m, 1H), 1.87 (m, 2H); isomer B(55%), 6.63 (dd, 1H), 6.20 (d, 1H), 5.80 (dd, 1H), 5.54 (dd, 1H), 3.90 (d, 1H), 3.60 (m, 2H), 2.45 (m, 2H), 1.87 (2H). ^{13}C-NMR ($CDCl_3$, carbonyl region): 186.92 (1C), 186.74 (1C), 186.33 (1C), 186.07 (1C), 185.93 (1C), 184.12 (1C), 184.04 (1C), 183.98 (1C), 181.48 (1C), 180.98 (1C), 179.74 (1C), 178.50 (1C), 177.39 (1C), 174.54 (1C), 172.76 (1C), 167.75 (1C).

Synthesis of $Os_3(CO)_9(\mu$-$H)_2(\mu$-η^2-$CNCH(CH_3)CH_2CH_2)$(Br) (6). A 100 mg amount of **5** (0.10 mmol) was dissolved in 20 mL of chloroform and added dropwise to 100 mL of a solution of HBr in chloroform (HBr was bubbled through the chloroform for 2 min). The solution was stirred for 1 h at which time complete consumption of **5** was observed. The solvent was removed by rotary evaporation and dried under vacuum overnight. The yellow-orange residue was recrystallized from methylene chloride/hexane at −20 °C to yield 97 mg (90%) of $Os_3(CO)_9(\mu$-$H)_2(\mu$-η^2-$C{=}NCH(CH_3)CH_2)Br$ (**6**).

Analytical and Spectroscopic Data for 6. Anal. Calcd for $C_{14}H_{10}BrNO_9Os_3$: 17.04, C; 1.01, H; 1.42, N. Found: 17.19, C; 1.08, H; 1.46, N. IR (ν(CO), CH_2Cl_2): 2117 (m), 2087 (s), 2059 (vs), 2034 (m), 2001 (m), 1985 (br), 1968 (w) cm^{-1}. ^1H-NMR ($CDCl_3$, −40 °C, major isomer): 4.04 (m, 1H), 2.59 (m, 1H), 2.42 (m, 1H), 2.09 (m, 1H), 1.21 (m, 1H), 1.07 (d, 3H), −15.64 (s, 1H), −15.97 (s, 1H).

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Synthesis of $\mathrm{Os_2(CO)_6(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}\overline{CHNH(C}H_2)_3)Br_2}$ (7). A 95 mg amount of **1** (0.10 mmol) dissolved in 10 mL of chloroform was added dropwise to a solution of HBr in chloroform (HBr was bubbled through the solution for 5 min). There was an immediate color change from yellow to orange and then a more gradual change from orange to pale yellow over the course of 1 h. The solution was then rotary evaporated and vacuum dried overnight. The reaction mixture was purified by thin-layer chromatography using hexane/methylene chloride as eluent. Two bands were isolated, a very minor yellow band and a major colorless band which was recrystallized from hexane/methylene chloride at −20 °C to yield 30 mg (38%) of $\mathrm{Os_2(CO)_6(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}\overline{CHNH(C}H_2)_3)Br_2}$ (**7**) as colorless crystals.

Analytical and Spectroscopic Data for 7. Anal. Calcd for $\mathrm{C_{10}H_9Br_2NO_6Os_2}$: 15.41, C; 1.17, H; 1.78, N. Found: 15.72, C; 1.34, H; 1.86, N. IR (ν(CO), $\mathrm{CH_2Cl_2}$): 2126 (m), 2107 (s), 2057 (m), 2036 (s, br), 2012 (m). ^{1}H-NMR ($\mathrm{CDCl_3}$): 4.37 (br, 1H), 4.13 (dt, 1H), 2.95 (m, 2H), 1.90 (m, 4H), −16.53 (s, 1H) ppm. ^{13}C-NMR ($\mathrm{CDCl_3}$): 170.33 (CO), 168.21 (CO), 167.80 (CO), 166.55 (CO), 163.70 (CO), 162.20 (CO), 55.27 ($\mathrm{CH_2}$), 34.34 ($\mathrm{CH_2}$), 28.33 (CH), 26.75 ($\mathrm{CH_2}$) ppm.

X-ray Structure Determination of 4, 6, and 7. Crystals of **4**, **6**, and **7** for X-ray examination were obtained from saturated solutions of each in hexane/dichloromethane solvent systems at −20 °C. Suitable crystals of each were mounted on glass fibers, placed in a goniometer head on the Enraf-Nonius CAD4 diffractometer, and centered optically. Unit cell parameters and an orientation matrix for data collection were obtained by using the centering program in the CAD4 system. Details of the crystal data are given in Table 1. For each crystal, the actual scan range was calculated by scan width = scan range + 0.35 tan θ and backgrounds were measured by using the moving-crystal, moving-counter technique at the beginning and end of each scan. Two representative reflections were monitored every 2 h as a check on instrument and crystal stability, and an additional two reflections were monitored periodically for crystal orientation control. Lorentz, polarization, and decay corrections were applied, as was an empirical absorption correction based on a series of ψ scans, for each crystal. The weighting schemes used during refinement were $1/\sigma^2$ for **4** and **7**, based on counting statistics, and $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ with $a = 0.100$ for **6**.[20]

Each of the structures was solved by the Patterson method using SHELXS-86,[21] which revealed the positions of the metal atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. The expected hydride positions in **6** and **7** were calculated by using the program HYDEX;[16] all hydrogen atoms were included in each structure and were placed in their expected chemical positions using the HFIX command in SHELXL-93.[20] The hydrides were given fixed positions and *U*'s in **6** and **7**, and other hydrogen atoms were included as riding atoms in the final least-squares refinements with *U*'s which were related to the atoms ridden upon. All non-hydrogen atoms were refined anisotropically in **6** and **7** except for the disordered N(1)/C(1) atoms in the ligand in **6**, while, in **4**, the osmium atoms and carbonyl oxygens as well as the nondisordered ligand atoms were refined anistropically.

The refinement of **7** presented several problems. Since the molecule possesses an approximate 2-fold rotation axis perpendicular to the Os−Os bond, except for the N and C atoms of the pyrrolidine ligand, and the osmium atoms dominate the least-squares refinement, it was necessary to carry out the final least-squares refinements in space group *C*2/*c*(No. 15) with molecules centered at special positions 4e. Early attempts to refine a structure with two unique molecules in $P\bar{1}$ (No. 2) or in *Cc* (No. 9) led to large disruptive correlations between related atoms and divergence in the refinements.[22]

Scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion corrections were those of Cromer.[24] All data processing was carried out on a DEC 3000 AXP computer using the Open MolEN system of programs.[25] Structure solution, refinement, and preparation of figures and tables for publication were carried out on PC's using SHELXS-86,[21] SHELXL-93,[20] and XP/PC[26] programs.

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Supporting Information Available: Tables listing complete distances and bond angles, atomic coordinates, anisotropic displacement parameters, and hydrogen coordinates for **4**, **6**, and **7**, respectively (16 pages). Ordering information is given on any current masthead page.

OM960378Z

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