−0.9990 (where −1 would characterize a perfect correlation) can be drawn. Clearly, the bond length is a linear function of cos (2χ), which means[4] that the bond lengthens in linear proportion to decreasing δ-bond strength. The line can be extrapolated to $\chi = 45°$ to predict a value of 2.193 ± 0.001 Å. The overall change, then, from a full δ bond to no δ bond is 0.055 (2) Å. This may well be the most unambiguous quantitative, experimental evaluation of how bond length depends on δ-bond order alone that it is possible to get. It has been obtained under circumstances where essentially no other factor such as ligand type, oxidation states, or atomic number of the metal atoms has been changed.

The Disorder. As is very common in compounds of this and related types, there is some disorder of the sort that leads to the observation of a second Mo–Mo unit perpendicular to the main one. Since the positional parameters for the secondary metal atoms (which are on the crystallographic 2 axis and thus crystallographically independent of each other) are not highly accurate and no ligand atoms belonging to this second orientation could be distinguished and refined, nothing can be said about the dimensions of this secondary molecule. The secondary Mo–Mo distance appears to be smaller, 2.13 (3) Å, but statistically the difference from the distance in the primary molecule is not significant.

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Registry No. β-$Mo_2Cl_4(dmpe)_2$, 85115-86-2; $Mo_2Cl_4(PEt_3)_4$, 59780-36-8; Mo, 7439-98-7.

Supplementary Material Available: Complete tables of anisotropic thermal parameters, torsional angles for the central portion of the molecule, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 24.[1,2] Crystal Structures of the 60-Electron Cluster $(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ and the 59-Electron Radical Cluster $(\mu\text{-}H)_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$

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The heteronuclear hydrido–metal-cluster complexes $(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (**1**) and $(\mu\text{-}H)_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (**2**), previously synthesized by Shore and co-workers,[3] have been characterized via single-crystal X-ray diffraction studies. Crystal data are as follows: **1**, space group *Pcam* (No. 57), $a = 14.554$ (3) Å, $b = 17.845$ (3) Å, $c = 15.008$ (3) Å, $V = 3898$ (1) Å^3, $Z = 8$, $R_F = 5.3\%$, $R_{wF} = 4.9\%$ for all 2683 independent data with $2\theta = 3.5\text{–}45.0°$ (Mo Kα); **2**, space group *Pcam* (No. 57), $a = 14.632$ (3) Å, $b = 17.872$ (5) Å, $c = 14.991$ (3) Å, $V = 3920$ (2) Å^3, $Z = 8$, $R_F = 5.2\%$, $R_{wF} = 5.0\%$ for all 1937 data with $2\theta = 4.0\text{–}40.0°$ (Mo Kα). **1** and **2** are isomorphous; each contains two independent sites of C_s symmetry for the constituent molecules. The molecular configurations in the two sites are identical, but there is a conformational charge in the $(\eta^5\text{-}C_5H_5)$ ligand that is rotated by π radians from one site to the other. Each molecule contains an apical $(\eta^5\text{-}C_5H_5)M$ (M = Ni, Co) fragment of approximate C_{5v} symmetry bonded in an apparently symmetrical fashion to a basal $(\mu\text{-}H)_3Os_3(CO)_9$ moiety of approximate C_{3v} symmetry. Osmium–nickel bond lengths in **1** range from 2.562 (2) through 2.578 (3) Å (average 2.567 Å), while osmium–cobalt bond lengths in **2** range from 2.578 (3) through 2.597 (4) Å (average 2.585 Å). The hydrido-bridged osmium–osmium distances are 2.859 (1)–2.874 (1) Å (average 2.871 Å) in **1** and 2.864 (1)–2.891 (1) Å (average 2.879 Å) in **2**.

Introduction

We have become interested in the structural chemistry of tetrahedral hydrido cluster species based on the Os_3M core (M = first-row transition metal) and have recently published reports on the structures of $(\mu\text{-}H)_2Os_3Fe(CO)_{13}$[2] and $(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$.[4] Entry into this chemical area has been greatly facilitated by the discovery by Shore and co-workers that $(\mu\text{-}H)_2Os_3(CO)_{10}$ provides a good starting material for the triosmium fragment.[5] More recently, it has been found that hydride-rich products can be obtained in excellent yield by including molecular dihydrogen in the synthesis.[3]

Thus, $(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ can be synthesized in 93% yield as shown in eq 1. In similar fashion, the reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with $(\mu\text{-}H)_2Os_3(CO)_{10}$ under H_2 yields a mixture of $(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$ (4%), *paramagnetic* $(\mu\text{-}H)_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (33%), and $(\mu\text{-}H)_4Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (32%).

$$[(\eta^5\text{-}C_5H_5)Ni(CO)]_2 + 2(\mu\text{-}H)_2Os_3(CO)_{10} + H_2 \xrightarrow[90\ °C,\ 10\ h]{toluene} 2(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5) + 4CO \quad (1)$$

We now report the results of single-crystal X-ray diffraction studies on two new trihydrido clusters—the diamagnetic 60-electron species $(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ and the paramagnetic 59-electron species $(\mu\text{-}H)_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$. A preliminary report of this work has appeared previously.[3]

Experimental Section

Samples of the two complexes were kindly provided by Professor S. G. Shore of The Ohio State University. They had previously been characterized fully via infrared and exact mass spectroscopy, ^1H NMR (Os_3Ni complex), and ESR (Os_3Co complex)—cf. ref 3.

$(\mu\text{-}H)_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (1). An irregular opaque dark crystal of average diameter 0.2 mm was mounted and aligned on our Syntex P2$_1$ automated four-circle diffractometer; diffraction data were collected as described previously,[6] details being given in Table I. All

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(1) Part 23 ($(\mu\text{-}H)(\mu\text{-}O_2CH)Os_3(CO)_{10}$): Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.*, **1982**, *21*, 3295–3303.

(2) Part 22 ($(\mu\text{-}H)_2Os_3Fe(CO)_{13}$): Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958–1963.

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(4) Part 20 ($(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$): Churchill, M. R.; Bueno, C.; Kennedy, S.; Bricker, J. C.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 627–633.

(5) Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 6156–6157.

(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265–271.

Table I. X-ray Data for $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (1) and $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (2)

	Os_3Ni (1)	Os_3Co (2)
(A) Crystal Parameters at 23 °C[a]		
cryst system	orthorhombic	[b]
space group	*Pcam* (No. 57)	[b]
a, Å	14.554 (3)	14.632 (3)
b, Å	17.845 (3)	17.872 (5)
c, Å	15.008 (3)	14.991 (3)
V, Å^3	3897.9 (12)	3920.3 (15)
Z	8	8
mol wt	949.5	949.8
ρ(calcd), g cm^{-3}	3.24	3.23
μ, cm^{-1}	216.5	214.4
(B) Data Collection		
diffractometer	Syntex $P2_1$	[b]
radiation	Mo Kα	[b]
$\bar{\lambda}$, Å	0.710 730	[b]
monochromator	graphite	[b]
2θ range, deg	3.5–45.0	4.0–40.0
octants	$+h, +k, \pm l$	$+h, +k, \pm l$
2θ scan, deg	$2.0 + \Delta(\alpha_2 - \alpha_1)$	[b]
scan speed, deg min^{-1}	2.0	[b]
bkgd	stationary cryst and counter, at each end of 2θ scan	[b]
total reflcns	5753	4451
independent reflcns	2683	1944
std reflcns	3	3
cryst decay	5%, cord	2.5%, cord

[a] Unit cell measurements are derived by a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 25 reflections with 2θ = 20–30°. [b] Same entry as for the Os_3Ni complex, 1.

data were converted to $|F_o|$ values following correction for absorption and for Lorentz and polarization factors. All calculations were performed on our SUNY-modified Syntex XTL system. The structure was solved with use of MULTAN,[7] difference-Fourier syntheses, and full-matrix least-squares refinement.

The completed structural analysis showed the true space group to be the centrosymmetric *Pcam*, rather than the possible noncentrosymmetric space group $Pca2_1$, which exhibits the same systematic absences: $0kl$ for $l = 2n + 1$ and $h0l$ for $h = 2n + 1$ ($00l$ for $l = 2n + 1$). All atoms, including all of the hydride ligands, were located and refined by using anisotropic thermal parameters for all non-hydrogen atoms. Final discrepancy indices[8] are R_F = 5.3% and R_{wF} = 4.9% for all 2683 independent reflections (273 variable parameters) and R_F = 3.4% and R_{wF} = 4.2% for those 2129 reflections with $|F_o| > 3\sigma(|F_o|)$.

$(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$ (2). A small dark crystal of average diameter ~0.1 mm was used in the diffraction study. The crystal quality was inferior to that of the Os_3Ni complex, 1, with no observable data beyond 2θ = 40°. Details of data collection appear in Table I. This complex is isomorphous with the Os_3Ni complex, 1. The structure was solved by starting with the heavy-atom coordinates of 1. Difference-Fourier syntheses and least-squares refinement led to R_F = 5.2% and R_{wF} = 5.0% for all 1937 reflections (146 parameters) or R_F = 4.2% and R_{wF} = 4.8% for those 1628 reflections with $|F_o| > 3\sigma(|F_o|)$. It should be noted that only those hydride ligands associated with "molecule B" were located and refined. Anisotropic thermal parameters were used for the metal atoms and isotropic thermal parameters for all other atoms.

During all calculations the analytical scattering factors for *neutral* atoms were corrected for both $\Delta f'$ and $i\Delta f''$ terms.[9] Final positional parameters are collected in Table II; thermal parameters appear in the supplementary material.

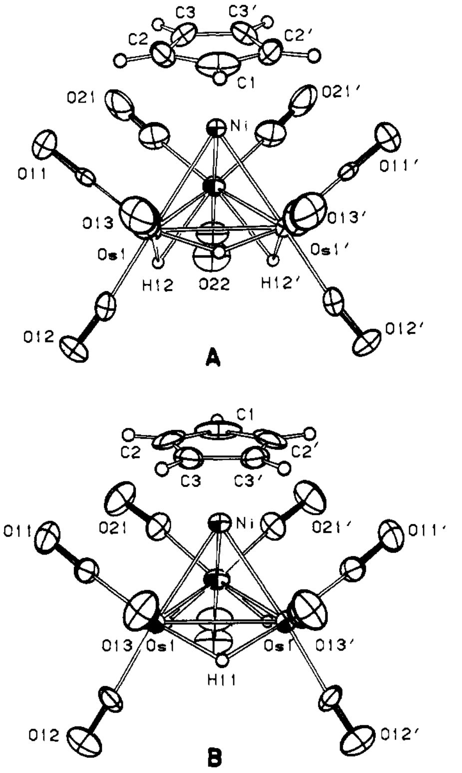

Figure 2. General views of the two distinct molecules of $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$.

Discussion

Structure of $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$ (1). Crystals of the Os_3Ni complex (1) contain ordered molecular units, which are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The molecules occupy two unrelated sites, each of which has crystallographically imposed C_s symmetry. (Crystal packing is illustrated in Figure 1 (supplementary data).) The crystallographic "asymmetry unit" thus consists of two distinct "half-molecules" of $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$. Molecules at the two sites are chemically equivalent but differ in the conformation of the $\eta^5\text{-}C_5H_5$ ligand relative to the Os_3 triangle (compare parts A and B in Figure 2.)

Each molecule consists of an apical $(\eta^5\text{-}C_5H_5)Ni$ unit of approximate C_{5v} symmetry bonded symmetrically to a basal $(\mu\text{-H})_3Os_3(CO)_9$ moiety of approximate C_{3v} symmetry. Figure 3 provides a general view of the molecular geometry. Interatomic distances and their estimated standard deviations (esd's) are collected in Table III, while interatomic angles appear in Table IV.

The complex is based upon a closed Os_3Ni cluster. There are the usual 60 valence electrons associated with such an array (three d^8 Os(0) atoms, one d^{10} Ni(0) atom, one electron from each hydride ligand, two electrons from each carbonyl ligand, and five electrons from the $\eta^5\text{-}C_5H_5$ ligand).[10]

The basal $(\mu\text{-H})_3Os_3(CO)_9$ groups each have approximate C_{3v} symmetry. The hydrido-bridged osmium-osmium bond lengths range from 2.859 (1) through 2.874 (1) Å, averaging 2.871 [6] Å.[11] If the osmium–osmium bonds are neglected, each osmium atom is in an approximately octahedral coor-

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(7) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(8) $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%).

(9) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

(10) For simplicity, we are treating all metals and ligands as neutral. It is equally acceptable to treat all metals as in a +1 oxidation state in conjunction with $\eta^5\text{-}C_5H_5^-$ and H^- anions.

(11) Values in square brackets are internal esd's of the mean value, calculated via the scatter formula

$$[\sigma] = [\sum_{i=1}^{i=N}(d_i - \bar{d})^2/(N-1)]^{1/2}$$

where d_i is the ith of N equivalent values and $\bar{d}$ is the mean value.

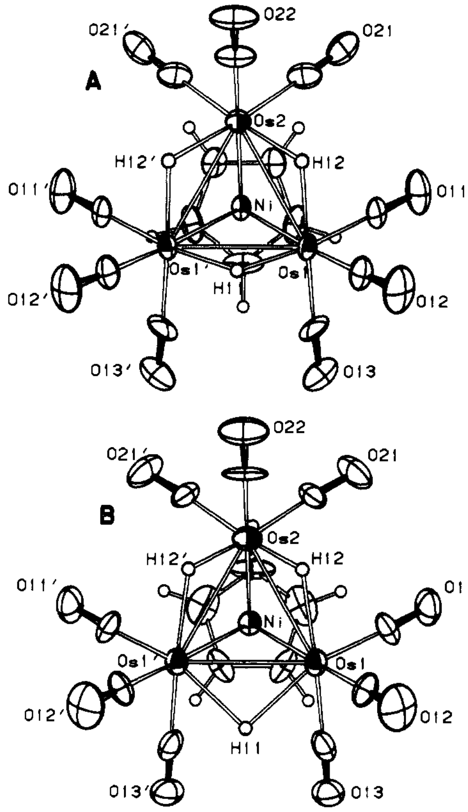

Figure 3. The two Os_3Ni molecules showing the different orientations of the η^5-C_5H_5 ring relative to the Os_3 triangle.

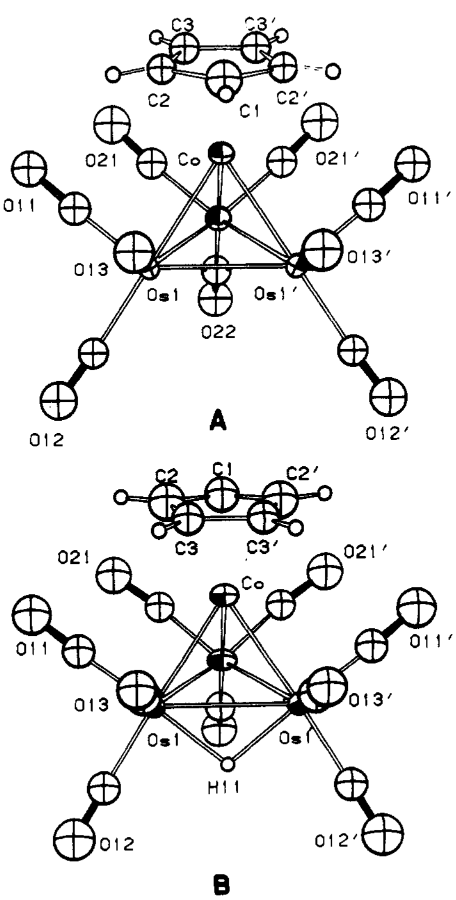

Figure 4. The $(\mu$-$H)_3Os_3Co(CO)_9(\eta^5$-$C_5H_5)$ molecules.

dination environment. The OC–Os–CO angles range from 91.3 (8) through 95.7 (8)° and Os–C–O angles from 175.1 (15) through 179.5 (14)°. Although the bridging hydride ligands are located with poor precision, it is clear that each is approximately trans to two carbonyl ligands (e.g., H(11)–Os(1)–C(11) = H(11)–Os(1')–C(11') = 159 (8)°, H(12)–Os(1)–C(13) = 166 (7)°, and H(12)–Os(2)–C(21') = 165 (7)° on molecule A).

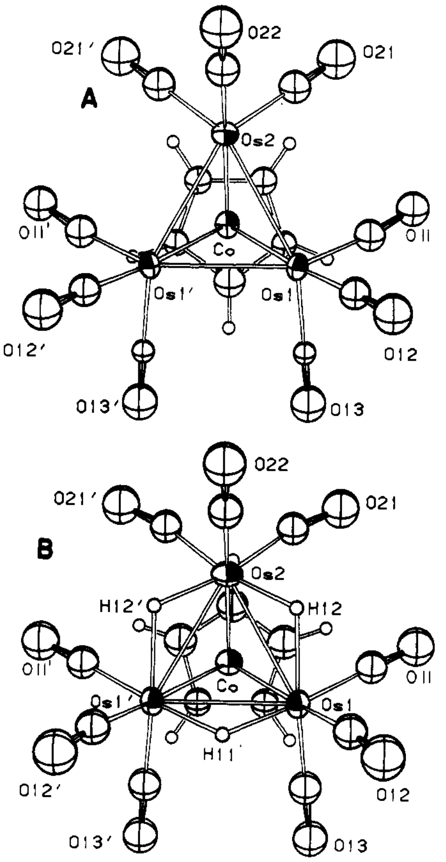

Figure 5. The $(\mu$-$H)_3Os_3(CO)_9(\eta^5$-$C_5H_5)$ molecules, showing relative orientations of η^5-C_5H_5 and Os_3 systems. (Note that the hydride ligands were not directly located in molecule A.)

The $(\mu$-$H)_3Os_3(CO)_9$ base is linked symmetrically to the apical $(\eta^5$-$C_5H_5)Ni$ group, with osmium–nickel bond lengths ranging from 2.562 (2) though 2.578 (3) Å and averaging 2.567 [6] Å. Individual nickel–carbon (η^5-C_5H_5) distances range from 2.089 (22) though 2.136 (23) Å (averaging 2.116 [14] Å) while the Ni···Cp distances are 1.763 and 1.749 Å (average 1.756 Å).

The average osmium–nickel bond length of 2.567 [6] Å in this complex may be compared to values of 2.605 (1), 2.668 (1) (both carbonyl bridged), and 2.733 (1) Å (hydrido bridged) in $(\mu$-$H)_2Os_3Ni(CO)_{10}(PPh_3)_2$[12] and values of 2.58 (1)–2.66 (1) Å in the capped trigonal-bipyramidal species $(\eta^5$-$C_5H_5)_3Ni_3Os_3(CO)_9$.[13]

Taken overall, $(\mu$-$H)_3Os_3Ni(CO)_9(\eta^5$-$C_5H_5)$ is a symmetrical molecule of expected quasi-cylindrical symmetry, closely related to such species as $(\mu$-$H)_3Fe_3(CO)_9(\mu_3$-$CCH_3)$,[14] $(\mu$-$H)_3Ru_3(CO)_9(\mu_3$-$CCH_3)$,[15] $(\mu$-$H)_3Ru(CO)_9(\mu_3$-$CCl)$,[16] $Co_3(CO)_9(\mu_3$-$CCH_3)$,[17] and $Co_3(CO)_9(\mu_3$-$CH)$.[18]

Structure of Paramagnetic $(\mu$-$H)_3Os_3Co(CO)_9(\eta^5$-$C_5H_5)$ (2).

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Table II. Positional Parameters

molecule A					molecule B				
atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
(A) $(\mu\text{-H})_3Os_3Ni(CO)_9(\eta^5\text{-}C_5H_5)$[a]									
Os(1)	0.48838 (4)	0.10142 (3)	0.15476 (4)		Os(1)	−0.12369 (4)	0.43414 (3)	0.34573 (4)	
Os(2)	0.41164 (6)	0.22636 (5)	0.25000 (0)		Os(2)	0.01512 (6)	0.35277 (5)	0.25000 (0)	
Ni	0.34205 (16)	0.09352 (15)	0.25000 (0)		Ni	−0.15569 (18)	0.31809 (14)	0.25000 (0)	
O(11)	0.3571 (9)	0.1193 (9)	−0.0004 (9)		O(11)	−0.1184 (10)	0.3275 (7)	0.5062 (9)	
O(12)	0.6579 (9)	0.1200 (8)	0.0377 (8)		O(12)	−0.0738 (11)	0.5733 (8)	0.4524 (11)	
O(13)	0.4813 (9)	−0.0655 (8)	0.1361 (10)		O(13)	−0.3326 (9)	0.4593 (8)	0.3653 (9)	
O(21)	0.2761 (9)	0.2708 (8)	0.1067 (9)		O(21)	0.0412 (10)	0.2397 (8)	0.3999 (11)	
O(22)	0.5105 (14)	0.3783 (10)	0.25000 (0)		O(22)	0.2154 (12)	0.3986 (10)	0.25000 (0)	
C(11)	0.4072 (9)	0.1122 (9)	0.0594 (10)		C(11)	−0.1215 (13)	0.3690 (9)	0.4468 (12)	
C(12)	0.5965 (12)	0.1139 (9)	0.0848 (11)		C(12)	−0.0904 (11)	0.5228 (9)	0.4118 (11)	
C(13)	0.4844 (13)	−0.0043 (10)	0.1450 (12)		C(13)	−0.2565 (15)	0.4485 (9)	0.3577 (12)	
C(21)	0.3289 (12)	0.2538 (10)	0.1600 (14)		C(21)	0.0308 (11)	0.2806 (10)	0.3402 (12)	
C(22)	0.4772 (16)	0.3243 (14)	0.25000 (0)		C(22)	0.1391 (16)	0.3823 (13)	0.25000 (0)	
C(1)	0.2684 (16)	−0.0100 (13)	0.25000 (0)		C(1)	−0.1558 (19)	0.2010 (13)	0.25000 (0)	
C(2)	0.2440 (12)	0.0336 (12)	0.1741 (12)		C(2)	−0.2021 (16)	0.2246 (10)	0.3234 (15)	
C(3)	0.2032 (11)	0.0996 (9)	0.2057 (11)		C(3)	−0.2770 (13)	0.2668 (9)	0.2975 (12)	
H(11)	0.523 (17)	0.086 (14)	0.25000 (0)		H(11)	−0.185 (10)	0.491 (8)	0.25000 (0)	
H(12)	0.528 (17)	0.220 (16)	0.163 (16)		H(12)	0.009 (8)	0.409 (7)	0.327 (9)	
H(1)	0.2958	−0.0583	0.2500		H(1)	−0.1004	0.1728	0.2500	
H(2)	0.2538	0.0202	0.1135		H(2)	−0.1852	0.2136	0.3832	
H(3)	0.1792	0.1385	0.1694		H(3)	−0.3199	0.2908	0.3353	
(B) $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$									
Os(1)	0.48817 (5)	0.10201 (4)	0.15447 (5)		Os(1B)	−0.12336 (5)	0.43466 (4)	0.34644 (5)	
Os(2)	0.41253 (7)	0.22744 (6)	0.25000 (0)		Os(2B)	0.01440 (7)	0.35294 (7)	0.25000 (0)	
Co	0.34198 (22)	0.09452 (21)	0.25000 (0)		Co(B)	−0.15798 (24)	0.31831 (21)	0.25000 (0)	
O(11)	0.3559 (10)	0.1225 (9)	0.0010 (10)	5.6 (4)	O(11B)	−0.1191 (11)	0.3272 (11)	0.5062 (12)	7.4 (4)
O(12)	0.6590 (11)	0.1197 (9)	0.0375 (11)	6.2 (4)	O(12B)	−0.0752 (13)	0.5768 (12)	0.4529 (13)	8.4 (5)
O(13)	0.4816 (10)	−0.0659 (10)	0.1378 (11)	6.2 (4)	O(13B)	−0.3299 (11)	0.4589 (10)	0.3655 (11)	6.3 (4)
O(21)	0.2760 (12)	0.2707 (10)	0.1061 (12)	7.5 (4)	O(21B)	0.0374 (11)	0.2436 (10)	0.3986 (13)	7.2 (4)
O(22)	0.5148 (16)	0.3764 (16)	0.25000 (0)	7.0 (6)	O(22B)	0.2123 (18)	0.3989 (16)	0.25000 (0)	7.7 (7)
C(11)	0.4100 (14)	0.1102 (13)	0.0600 (15)	4.7 (5)	C(11B)	−0.1179 (15)	0.3685 (13)	0.4439 (16)	5.1 (5)
C(12)	0.5977 (13)	0.1166 (12)	0.0832 (14)	4.0 (4)	C(12B)	−0.0871 (14)	0.5215 (14)	0.4133 (15)	5.1 (5)
C(13)	0.4852 (11)	−0.0022 (11)	0.1442 (11)	2.44 (35)	C(13B)	−0.2490 (17)	0.4514 (12)	0.3584 (16)	5.3 (5)
C(21)	0.3325 (15)	0.2563 (13)	0.1608 (15)	4.9 (5)	C(21B)	0.0336 (15)	0.2835 (13)	0.3350 (15)	4.8 (5)
C(22)	0.4780 (21)	0.3199 (21)	0.25000 (0)	4.8 (7)	C(22B)	0.1346 (23)	0.3859 (20)	0.25000 (0)	5.1 (7)
C(1)	0.2631 (22)	−0.0069 (20)	0.25000 (0)	5.6 (8)	C(1B)	−0.1576 (23)	0.2031 (21)	0.25000 (0)	5.7 (8)
C(2)	0.2416 (13)	0.0325 (11)	0.1736 (13)	3.5 (4)	C(2B)	−0.2032 (17)	0.2232 (15)	0.3242 (17)	6.3 (6)
C(3)	0.2031 (13)	0.0981 (12)	0.2043 (13)	4.1 (4)	C(3B)	−0.2772 (14)	0.2631 (12)	0.2977 (13)	4.4 (5)
H(1)	0.2895	−0.0555	0.2500	6.0	H(11B)	−0.115 (15)	0.501 (14)	0.25000 (0)	4.0
H(2)	0.2512	0.0177	0.1134	6.0	H(12B)	0.005 (11)	0.405 (10)	0.342 (11)	4.0
H(3)	0.1801	0.1372	0.1677	6.0	H(1B)	−0.1004	0.1778	0.2500	6.0
					H(2B)	−0.1866	0.2116	0.3836	6.0
					H(3B)	−0.3208	0.2865	0.3354	6.0

[a] H(11) and H(12) in each molecule were assigned $B = 4.0$ Å^2; atoms H(1), H(2), and H(3) were assigned $B = 6.0$ Å^2.

This species has 59 outer valence electrons—one less than the electron-precise Os_3Ni complex, **1**. The overall images of molecules A and B are shown in Figures 4 and 5. Although of lower precision, the resulting molecular structure appears (at first sight) to be very similar to that of the Os_3Ni complex, **1**. Indeed, a careful comparison of geometric parameters in Tables III and IV shows only the following minor differences.

(1) The hydrido-bridged Os–Os distances in **2** range from 2.864 (1) through 2.891 (1) Å, averaging 2.879 [9] Å (cf. 2.871 [6] Å in **1**).

(2) The osmium–cobalt bond lengths in **2** range from 2.578 (3) through 2.597 (4) Å, averaging 2.585 [7] Å[19,20]—a value only 0.018 ± 0.009 Å greater than the average Os–Ni distance of 2.567 [6] Å in **1**.

(3) Cobalt–carbon (η^5-C_5H_5) distances in **2** range from 2.060 (38) through 2.167 (19) Å, averaging 2.136 [30] Å—cf. Ni–C = 2.116 [14] Å in **1**.

(4) Co···Cp distances are 1.808 and 1.771 Å (average 1.790 Å) in **2**—cf. Ni···Cp = 1.756 Å (average) in **1**.

All the above observed differences are rather small and are close to the borderline of statistical significance.

Dahl and co-workers have previously shown that oxidation of the 60-electron, electron-precise tetrahedral complex $Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4$ to the 59-electron species $[Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4^+]$ causes a reduction in symmetry from T_d to D_{2d}, coupled with a small *decrease* in iron–iron distance from a mean value of 2.520 Å to a new value of 2.484 Å.[21,22] Here it was concluded that oxidation of a "completely bonding tetrahedral metal cluster" *which has no electrons in strongly antibonding metal orbitals* will cause little change in metal–metal distances.

Our observations in going from the 60-electron Os_3Ni species (**1**) to the 59-electron Os_3Co species (**2**) parallel those of Dahl and co-workers—i.e., small decreases in some metal–metal and metal–ligand distances are observed. Our case is, however, more complicated insofar as (i) we have a system of much lower symmetry than the T_d symmetry of the Fe_4-

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(19) Osmium–cobalt bond distances in other molecules include the following: 2.645 (2) Å (carbonyl bridged) and 2.672 (2) and 2.680 (2) Å in $(\mu\text{-H})_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$;[4] 2.690 (1), 2.695 (2), and 2.698 (1) Å in $(\mu\text{-H})_3Os_3Co(CO)_{12}$.[20]

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(21) $Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4$: Neuman, M. A.; Trinh-Toan; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3383–3388.

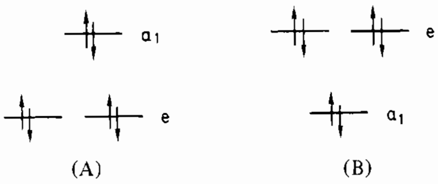
(22) $[Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4^+][PF_6^-]$: Trinh-Toan; Fehlhammer, W. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 3389–3397.

Table III. Selected Interatomic Distances (Å)

bond	Os_3Ni complex molecule A	Os_3Ni complex molecule B	Os_3Co complex molecule A	Os_3Co complex molecule B
	(A) Metal–Metal Distances			
Os(1)–Os(1′)[a]	2.859 (1)	2.873 (1)	2.864 (1)	2.891 (1)
Os(1)–Os(2)	2.874 (1)	2.873 (1)	2.881 (1)	2.879 (1)
Os(1′)–Os(2)	2.874 (1)	2.873 (1)	2.881 (1)	2.879 (1)
Os(1)–M[b]	2.569 (2)	2.563 (2)	2.578 (3)	2.583 (3)
Os(1′)–M	2.569 (2)	2.563 (2)	2.578 (3)	2.583 (3)
Os(2)–M	2.578 (3)	2.562 (2)	2.590 (4)	2.597 (4)
	(B) Metal–Carbonyl Distances			
Os(1)–C(11)	1.866 (15)	1.911 (17)	1.826 (22)	1.881 (24)
Os(1)–C(12)	1.904 (17)	1.929 (16)	1.943 (20)	1.921 (24)
Os(1)–C(13)	1.892 (18)	1.958 (22)	1.870 (20)	1.872 (25)
Os(2)–C(21)	1.875 (19)	1.882 (18)	1.852 (20)	1.801 (23)
Os(2)–C(22)	1.991 (24)	1.880 (23)	1.910 (35)	1.854 (34)
C(11)–O(11)	1.164 (20)	1.160 (21)	1.206 (26)	1.192 (30)
C(12)–O(12)	1.145 (21)	1.115 (22)	1.131 (25)	1.166 (32)
C(13)–O(13)	1.103 (23)	1.130 (26)	1.143 (27)	1.195 (29)
C(21)–O(21)	1.150 (24)	1.166 (24)	1.192 (29)	1.192 (30)
C(22)–O(22)	1.080 (30)	1.149 (29)	1.145 (45)	1.160 (44)
	(C) Metal–Hydride Distances			
Os(1)–H(11)	1.54 (9)	1.98 (9)	*d*	1.87 (16)
Os(1)–H(12)	2.19 (28)	2.01 (11)	*d*	1.96 (16)
Os(2)–H(12)	2.15 (25)	1.53 (12)	*d*	1.66 (16)
	(D) Distances Involving η^5-C_5H_5 Ligand			
M–C(1)	2.136 (23)	2.089 (22)	2.150 (35)	2.060 (38)
M–C(2)	2.116 (19)	2.110 (20)	2.167 (19)	2.136 (26)
M–C(3)	2.130 (16)	2.112 (18)	2.145 (20)	2.129 (21)
M···Cp[c]	1.763	1.749	1.808	1.771
C(1)–C(2)	1.424 (23)	1.358 (27)	1.381 (27)	1.346 (32)
C(2)–C(3)	1.402 (26)	1.381 (28)	1.380 (28)	1.356 (32)
C(3)–C(3′)	1.329 (23)	1.424 (25)	1.369 (27)	1.431 (28)

[a] Atoms labeled with a prime are related to the basic asymmetric unit via the transformation $[x, y, {}^1/_2 - z]$. [b] M = Ni or Co. [c] Cp is the centroid of the η^5-C_5H_5 ring defined by C(1)–C(2)–C(3)–C(3′)–C(2′). [d] Hydride ligands of molecule A of the Os_3Co complex were not located.

Scheme I



(η^5-C_5H_5)$_4$(CO)$_4$ system and (ii) we have changed the identity (and therefore the covalent radius) of the principal atom of interest (i.e., Ni → Co).

Despite the basic agreement of our results with those of Dahl and co-workers, we began to be concerned over the following problem: Was the observed structure of (μ-H)$_3$Os$_3$Co(CO)$_9$(η^5-C_5H_5) the true image of a molecule with "cylindrical" symmetry or was it a composite of several (probably three) images of a molecule with lower symmetry? A comprehensive molecular orbital study is beyond our current capability, but we may note that a study of Co$_3$(CO)$_9$(μ_3-CR) has recently appeared[23] as have comparative quantum-chemical calculations on Co$_3$(CO)$_9$(μ_3-CCH$_3$) and (μ-H)$_3$Fe$_3$(CO)$_9$(μ-CCH$_3$).[24]

Table IV. Selected Interatomic Angles (deg)

angle	Os_3Ni complex molecule A	Os_3Ni complex molecule B	Os_3Co complex molecule A	Os_3Co complex molecule B
	(A) Intermetallic Angles			
Os(1′)–Os(1)–Os(2)	60.18 (2)	60.00 (2)	60.20 (3)	59.85 (3)
Os(1′)–Os(1)–M	56.19 (5)	55.91 (5)	56.25 (7)	55.96 (7)
Os(2)–Os(1)–M	56.20 (5)	55.88 (5)	56.32 (7)	56.48 (7)
Os(1)–Os(2)–Os(1′)	59.64 (2)	60.01 (2)	59.61 (3)	60.29 (3)
Os(1)–Os(2)–M	55.90 (5)	55.93 (5)	55.91 (7)	56.00 (7)
Os(1)–M–Os(1′)	67.61 (5)	68.18 (6)	67.50 (7)	68.08 (8)
Os(1)–M–Os(2)	67.90 (5)	68.19 (6)	67.77 (8)	67.52 (8)
	(B) M–Os–CO and Os–M–Cp Angles			
Os(1′)–Os(1)–C(11)	140.1 (5)	142.5 (5)	140.9 (7)	141.0 (7)
Os(1′)–Os(1)–C(12)	123.4 (5)	120.9 (5)	123.3 (6)	121.4 (7)
Os(1′)–Os(1)–C(13)	94.4 (6)	95.2 (5)	94.7 (6)	95.5 (7)
Os(2)–Os(1)–C(11)	93.2 (5)	94.5 (5)	94.7 (7)	92.4 (7)
Os(2)–Os(1)–C(12)	120.3 (5)	119.7 (5)	119.1 (6)	118.6 (7)
Os(2)–Os(1)–C(13)	143.1 (6)	143.7 (6)	143.8 (5)	144.8 (7)
M–Os(1)–C(11)	84.7 (5)	87.5 (6)	85.2 (7)	86.4 (7)
M–Os(1)–C(12)	176.4 (5)	175.2 (5)	175.3 (6)	174.9 (7)
M–Os(1)–C(13)	87.9 (6)	88.7 (6)	88.6 (6)	89.4 (7)
Os(1)–Os(2)–C(21)	94.5 (6)	94.1 (5)	95.8 (7)	95.9 (7)
Os(1)–Os(2)–C(21′)	144.1 (6)	142.3 (5)	145.0 (7)	144.5 (7)
Os(1)–Os(2)–C(22)	119.6 (6)	122.2 (6)	118.7 (8)	120.2 (9)
M–Os(2)–C(21)	89.3 (6)	87.3 (5)	90.2 (7)	89.3 (7)
M–Os(2)–C(22)	174.5 (6)	177.7 (6)	173.4 (8)	175.3 (9)
Os(1)–M–Cp	140.6	140.5	140.4	141.5
Os(2)–M–Cp	138.5	137.9	139.1	136.7
	(C) OC–Os–CO Angles			
C(11)–Os(1)–C(12)	95.1 (7)	95.0 (7)	94.6 (9)	95.2 (10)
C(11)–Os(1)–C(13)	91.4 (7)	91.3 (8)	90.1 (9)	93.9 (10)
C(12)–Os(1)–C(13)	95.7 (8)	95.4 (7)	96.1 (8)	95.3 (10)
C(21)–Os(2)–C(21′)	92.2 (8)	91.9 (8)	92.5 (10)	90.1 (10)
C(21)–Os(2)–C(22)	94.5 (8)	94.3 (8)	94.4 (11)	94.1 (11)
	(D) Os–C–O Angles			
Os(1)–C(11)–O(11)	179.5 (14)	177.4 (15)	173.4 (19)	176.7 (20)
Os(1)–C(12)–O(12)	175.1 (15)	177.2 (16)	173.8 (18)	172.4 (21)
Os(1)–C(13)–O(13)	177.4 (17)	177.6 (17)	178.7 (17)	177.1 (20)
Os(2)–C(21)–O(21)	178.0 (17)	175.5 (16)	174.7 (20)	170.3 (20)
Os(2)–C(22)–O(22)	178.0 (18)	178.3 (17)	177.9 (25)	173.0 (25)
	(E) Os–Os–H and M–Os–H Angles			
Os(1′)–Os(1)–H(11)	21 (8)	43 (3)		39 (6)
Os(1′)–Os(1)–H(12)	87 (7)	82 (3)		88 (5)
Os(2)–Os(1)–H(11)	78 (8)	102 (3)		83 (6)
Os(2)–Os(1)–H(12)	48 (7)	30 (3)		34 (5)
M–Os(1)–H(11)	75 (8)	86 (3)		95 (6)
M–Os(1)–H(12)	104 (7)	85 (3)		87 (5)
Os(1)–Os(2)–H(12)	49 (7)	42 (5)		41 (6)
Os(1)–Os(2)–H(12′)	87 (7)	91 (5)		94 (6)
M–Os(2)–H(12)	105 (7)	96 (5)		93 (6)
	(F) H–Os–CO Angles			
H(11)–Os(1)–C(11)	159 (8)	154 (3)		174 (6)
H(11)–Os(1)–C(12)	105 (8)	94 (3)		83 (6)
H(11)–Os(1)–C(13)	85 (8)	63 (3)		92 (6)
H(12)–Os(1)–C(11)	96 (7)	88 (3)		79 (5)
H(12)–Os(1)–C(12)	72 (7)	91 (3)		89 (5)
H(12)–Os(1)–C(13)	166 (7)	174 (3)		173 (5)
H(12)–Os(2)–C(21)	95 (7)	85 (5)		79 (6)
H(12)–Os(2)–C(21′)	165 (7)	175 (5)		169 (6)
H(12)–Os(2)–C(22)	71 (7)	82 (5)		84 (6)
	(G) H–Os–H and Os–H–Os Angles			
H(11)–Os(1)–H(12)	91 (10)	116 (5)		95 (8)
H(12)–Os(2)–H(12′)	75 (10)	98 (6)		112 (8)
Os(1)–H(11)–Os(1′)	137 (14)	93 (5)		101 (9)
Os(1)–H(12)–Os(2)	83 (9)	108 (6)		105 (9)
	(H) C–C–C Angles			
C(2′)–C(1)–C(2)	106.2 (16)	108.4 (19)	112.0 (22)	111.4 (26)
C(1)–C(2)–C(3)	107.1 (16)	109.4 (18)	104.5 (19)	107.2 (23)
C(2)–C(3)–C(3′)	109.8 (15)	106.4 (16)	109.5 (18)	107.0 (19)

Now, the μ_3-CH, (μ-H)$_3$Os$_3$(CO)$_9$, and (η^5-C_5H_5)Ni fragments are isolobal. We can therefore ask the question as to what the symmetry of the HOMO in the (μ-H)$_3$Os$_3$Ni(CO)$_9$(η^5-C_5H_5) molecule is. Clearly, with use of the isolobal analogy, the (μ-H)$_3$Os$_3$(CO)$_9$ and (η^5-C_5H_5)Ni fragments combine to form mutually bonding molecular orbitals of a_1 symmetry (which is cylindrically symmetric) and a degenerate pair of orbitals of e symmetry (equivalent to the two π orbitals

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(23) Chesky, P. T.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 4419–4425.
(24) DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3203–3209.

Table V. Root-Mean-Square Amplitudes (Å) for the Principal Axes of the Atomic Vibration Ellipsoids of Metal Atoms in **1** and **2**[a]

atom	$(\overline{U^2})^{1/2}$	(Os_3Ni), **1**	(Os_3Co), **2**
	Molecule A		
Os(1)	maj[b]	0.209	0.200*[c]
	med	0.167	0.174
	min	0.145	0.156
Os(2)	maj	0.199	0.204
	med	0.194	0.196
	min	0.172	0.173
Ni or Co	maj	0.211	0.210*
	med	0.160	0.192
	min	0.145	0.157
	Molecule B		
Os(1)	maj	0.223	0.230
	med	0.182	0.186
	min	0.173	0.167*
Os(2)	maj	0.238	0.245
	med	0.199	0.204
	min	0.176	0.170*
Ni or Co	maj	0.206	0.219
	med	0.193	0.212
	min	0.162	0.167

[a] Calculated by using ORTEP-II. [b] These are the major, median and minor axes. [c] Entries marked with an asterisk are those for which the value for **2** is *smaller* than that for **1** (i.e., the exceptions to the general trend).

of the methylidyne fragment). Under the molecular point group C_{3v}, which is valid if we regard the cyclopentadienyl ligand as freely rotating, the group theoretical representations are A_1, A_2, and E. The probable scenarios for the highest energy occupied molecular orbitals are shown in Scheme I.[25] (Note that it is unimportant, from our present viewpoint, whether the orbitals are of a_1 and e or of a_2 and e symmetry. The most important feature is the dimensionality of the highest occupied molecular orbital (HOMO).)

If the HOMO is of a_1 symmetry (case A), then removal of one electron (i.e., replacement of Ni (in **1**) by Co (in **2**)) will leave a nondegenerate ground state and the molecule will remain "cylindrical symmetric." In this case our crystallographically observed image gives a true picture of the molecular geometry of $(\mu\text{-H})_3Os_3Co(CO)_9(\eta^5\text{-}C_5H_5)$.

However, if the HOMO is of e symmetry (case B), then removal of one electron (i.e., Ni → Co) leaves a degenerate state, which is predicted (by the Jahn–Teller theorem) to distort. In this case our observed crystallographic image is the composite of several (probably three) distorted molecules.

A tabulation of data concerning the anisotropic thermal vibration ellipsoids of the metal atoms in the two structures is given in Table V. Taken overall, 14 of the 18 axes of the six ellipsoids are larger for the Os_3Co structure than for the isomorphous Os_3Ni structure. The differences are, however, very small. Thus, on this evidence, we elect to favor (marginally) case B in Scheme I—suggesting that the structure is, in fact, disordered. Clearly, however, confirmation of this hypothesis depends on either (i) a detailed molecular orbital treatment or (ii) a crystallographic study of a related, less symmetrical, pair of molecules.

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Registry No. 1, 82678-96-4; **2**, 82678-94-2; Os, 7440-04-2; Ni, 7440-02-0; Co, 7440-48-4.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and anisotropic thermal parameters for **1** and **2** and Figure 1, showing the packing of molecules in the Os_3Ni structure (31 pages). Ordering information is given on any current masthead page.

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(25) Note that we have carefully refrained from speculating further on the nature of these highest energy occupied orbitals. Clearly, however, they are essentially nonbonding with respect to the Ni or Co to Os_3 linkages; they could also be very slightly bonding with respect to the Os–Os bonds, since the Os–Os distances increase very slightly upon removal of one electron from the system. If we assume that the molecular orbital treatment of $(\mu\text{-H})_3Fe_3(CO)_9(\mu_3\text{-}CCH_3)$ is applicable to our present case, then there appear to be two degenerate orbitals as the highest lying occupied molecular orbitals. (See Discussion and Figure 5B of ref 24.)