X-Ray structural determination of the tetrahedral ruthenium–osmium carbonyl hydrides [H$_2$RuOs$_3$(CO)$_{13}$] and [Ph$_4$As][H$_3$RuOs$_3$(CO)$_{12}$]: an examination of bent semi-bridging metal–carbonyl bonding

A.L. Rheingold*,

Department of Chemistry, University of Delaware, Newark, Delaware 19716 (U.S.A.)

B.C. Gates, J.P. Scott and J.R. Budge

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716 (U.S.A.)

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Abstract

Two group-8, mixed-metal tetrahedral clusters have been crystallographically characterized. For [H$_2$RuOs$_3$(CO)$_{13}$] (I): triclinic, $P\bar{1}$, a 9.046(4), b 9.140(4), c 26.560(9) Å, α 81.88(3), β 91.81(3), γ 112.07(3)°, V 2014(6) Å^3, $Z = 4$, R_F 4.91%. For [Ph$_4$As][H$_3$RuO$_3$(CO)$_{12}$] (II): monoclinic, $P2_1/n$, a 21.580(5), b 8.165(1), c 21.815(6) Å, β 91.16(2)°, V 3843.2(9) Å^3, $Z = 4$, R_F 4.40%. The two crystallographically independent molecules of I exhibit a wide range of bent semi-bridging metal carbonyl bond parameters, and all conform to the Crabtree–Lavin empirical equation. The structure of II contains a μ-H edge-bridged basal plane of two Os atoms and one Ru atom positionally disordered. This plane is capped by an Os(CO)$_3$ group. In both I and II, structural heterogeneity created by mixed-metal atom identities was seen and quantitatively measured by occupancy refinement.

Introduction

Organometallic clusters are suitable precursors for the preparation of supported catalysts with molecular structures [1]. Our recently communicated results characterizing RuOs$_3$ clusters on γ-Al$_2$O$_3$ supports showed that the cluster anion [H$_3$RuOs$_3$(CO)$_{12}$]$^-$ was relatively stable on the support and an apparent precursor of a surface-bound molecular catalyst for alkene isomerization [2]. To provide a fuller understanding of the processes involved in the formation of molecular cluster anions on basic supports, we undertook the single-crystal structural characteriza-

tions of a precursor molecule, $[H_2RuOs_3(CO)_{13}]$ (I), and a discrete ionic derivative. $[Ph_4As][H_3RuOs(CO)_{12}]$ (II), which contains the supported anionic unit.

Experimentation with crystal growth techniques for I led to the discovery of two crystalline polymorphs: from pentane we obtained a monoclinic form and from CH_2Cl_2, a triclinic form. Full data collection and refinement of both forms was carried out; we found that the triclinic form produced more satisfactory results. Since the initiation of our structural studies, Shore et al. have obtained the structure of the monoclinic form [3]. They also encountered both forms, but in their hands the monoclinic form produced the superior results. A comparison of the two forms is of much interest; each of the forms contains two crystallographically independent molecules with different bridging carbonyl geometries.

Experimental

Synthesis

A full disclosure of the synthesis and spectroscopic characterization of I and II will appear elsewhere [2b]. I was obtained from the combination of $Ru(CO)_5$ and $[H_2Os_3(CO)_{10}]$ in hexane at room temperature, 10–12 h, and purified by column chromatography. I was converted into $[H_4RuOs_3(CO)_{12}]$ by heating an octane solution of I with H_2 bubbling. II was obtained by treatment of $[H_4RuOs_3(CO)_{12}]$ with EtOH/KOH followed by addition of $[Ph_4As]Cl$. II was purified by recrystallization from CH_2Cl_2.

X-ray structure determinations for $[H_2RuOs_3(CO)_{13}]$ (I) and $[Ph_4As][H_3RuOs_3(CO)_{12}]$ (II)

Specimens of $[H_2RuOs_3(CO)_{13}]$ (I) and $[Ph_4As][H_3RuOs_3(CO)_{12}]$ (II) suitable for single-crystal, X-ray diffraction were obtained as follows: I, slow evaporation of a pentane solution, and II, slow diffusion of hexane into a CH_2Cl_2 solution at room temperature [3]. Both were affixed to fine glass fibers with epoxy cement which was also used to coat the crystals to provide a barrier to the atmosphere. The unit-cell parameters, provided in Table 1, were determined from the angular settings of 25 reflections, $25° \leqslant 2\theta \leqslant 30°$, which included Friedel related reflections to check both diffractometer and crystal alignment.

Systematic absences in the diffraction data uniquely defined the space group for II as $P2_1/n$, and the choice of the centrosymmetric space group, $P\bar{1}$, for I was confirmed by the successful and chemically reasonable solution and refinement. Corrections for absorption were made by the empirical ψ-scan method; max./min. transmission: I, 0.055/0.020; II, 0.148/0.124.

Both structures were solved by the direct methods routine SOLV (all software, SHELXTL-ver. 4.1, Nicolet XRD Corp., Madison, WI) which was successful in locating the Os and Ru atoms in I, and the Os, Ru and As atoms in II. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. In both I and II, the locations of the bridging hydrido ligands were deduced from the metal–metal distances: those 2.95 ± 0.02 Å were considered bridged, whereas those 2.82 ± 0.02 Å were deemed unbridged. Hydrido H atoms for II were calculated at Os–H distances of 1.80 Å and allowed to refine isotropically with fixed thermal factors (U' 0.08 Å^2). In I, no attempt was made to include hydrido contributions in the refinement process. The phenyl hydrogen atoms in II

Table 1

Crystal data and data collection, reduction and refinement parameters for $H_2RuOs_3(CO)_{13}$ (I) and $[Ph_4As][H_3RuOs_3(CO)_{12}]$ (II)

	I	II
(a) Crystal data		
Formula	$C_{13}H_2O_{13}Os_3Ru$	$C_{36}H_{23}AsO_{12}Os_3Ru$
Space group	$P\bar{1}$	$P2_1/n$
$a, b, c,$ Å	9.046(4), 9.140 (4),	21.580(5), 8.165(1),
	26.560(9)	21.815(6)
$\alpha, \beta, \gamma,$ deg	81.88(3), 91.81(3), 112.07(3)	90, 91.16(2), 90
$V,$ Å^3	2014.1 (10)	3843.2 (15)
Z	4	4
d (calcd), g cm^{-3}	3.42	2.41
Crystal size, mm,	$0.06 \times 0.20 \times 0.38$,	$0.20 \times 0.20 \times 0.41$,
Color	orange	orange
(b) Data collection		
Diffractometer	Nicolet R3	
Radiation	Mo-K_α (λ 0.71073 Å)	
Temperature, °C	22	23
$\mu,$ cm^{-1}	196.8	111.9
Scan method	ω (full profile)	ω (full profile)
Scan limits, deg.	$4 \leqslant 2\theta \leqslant 46$	$4 \leqslant 2\theta \leqslant 47$
Data collected	$\pm h, \pm k, +l$	$\pm h, +k, +l$
Unique data	5397 (5532 collected)	5059 (5475 collected)
Unique data $F_o \geqslant 3\sigma(F_o)$	4576	4312
(c) Data reduction and refinement		
Standard reflections	3 std/197 rflns	3 stds/97 rflns
	(<1% decay)	(<1% decay)
R (int)	0.019	0.007
R_F, R_{wF} (%), GOF	4.91, 4.85, 1.379	4.40, 4.57, 1.181
g	0.008	0.001
Δ/σ(max), final cycle	0.176	0.166

were treated as idealized contributions, C–H = 0.95 Å, $U' = 1.2$ U attached carbon atom.

In both structures, a refinement of occupancies of the metal atoms revealed disordering of the metal atom identities, more so in II than in I. In II, Os(1) has no Ru contribution and was refined normally (Os scattering factors, s.o.f. = 1.00 [15*]), but those metal atoms in the hydrido-bridged basal plane labeled OsRu(2), OsRu(3) and OsRu(4) are each 2/3 Os and 1/3 Ru in character. These hybrid atoms were treated as Os atoms of reduced occupancy, i.e., Os scattering factors with s.o.f. = 0.88(1). The s.o.f. obtained by refinement agrees well with the value of 0.86 for uniform disorder $(2/3 \; Z_{Os} + 1/3 \; Z_{Ru})/Z_{Os} = 0.86$. In I, The Ru atom positions were more clearly defined, although some Os atom character is found in Ru(2) in molecule B, refined s.o.f. = 1.15 reflecting only 79% Ru character; the s.o.f. for the

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* This and other references marked with asterisks indicate notes occurring in the list of references.

Table 2

Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$) for $H_2RuOs_3(CO)_{13}$

Atom	x	y	z	U
Os(1)	7197.1(8)	3194.0(8)	496.2(3)	35(1)
Os(2)	7072.1(1)	636.6(11)	1265.7(4)	38(1)
Os(3)	9028.7(10)	39.8.1(10)	1434.8(4)	34(1)
Ru(1)	5687.9(17)	2809.2(19)	1431.9(6)	25(1)
Os(4)	4094.3(9)	8992.6(9)	3805.6(3)	41(1)
Os(5)	1778.0(10)	5701.6(10)	3820.2(3)	42(1)
Os(6)	1370.2(9)	8160.3(9)	3116.3(3)	43(1)
Ru(2)	936.5(13)	8073.7(13)	4160.5(4)	34(1)
O(1)	9033(22)	2331(23)	−268(7)	70(9)
O(2)	7525(23)	6189(22)	−235(7)	74(9)
O(3)	4014(15)	1159(15)	102(5)	56(6)
O(4)	5861(17)	5931(17)	812(6)	68(7)
O(5)	2137(17)	1096(21)	1244(7)	86(9)
O(6)	5332(19)	4482(25)	2293(8)	111(11)
O(7)	3898(16)	−1682(15)	944(5)	62(6)
O(8)	7480(24)	−1723(21)	2146(6)	99(10)
O(9)	5418(19)	372(21)	2354(7)	83(9)
O(10)	9049(19)	−312(18)	563(5)	69(8)
O(11)	8919(18)	3350(20)	2593(5)	77(9)
O(12)	12618(15)	4754(16)	1376(6)	66(7)
O(13)	9381(20)	7369(19)	1434(7)	83(9)
O(14)	5205(19)	8493(20)	4895(6)	78(8)
O(15)	7298(16)	9567(20)	3299(7)	79(8)
O(16)	4720(19)	12528(19)	3786(8)	95(9)
O(17)	2341(20)	7232(19)	2151(6)	85(8)
O(18)	1197(23)	11138(20)	2480(7)	98(10)
O(19)	−2175(17)	6092(20)	3043(6)	87(8)
O(20)	813(17)	11247(16)	3645(5)	63(7)
O(21)	−2690(19)	6559(21)	4243(7)	81(8)
O(22)	1392(19)	9453(22)	5152(7)	90(9)
O(23)	1733(17)	5891(17)	5006(5)	58(7)
O(24)	−1662(17)	3286(17)	3815(7)	78(7)
O(25)	2799(23)	3334(20)	4562(7)	100(10)
O(26)	2664(20)	4535(19)	2893(6)	82(8)
C(1)	8408(20)	2654(23)	37(7)	46(8)
C(2)	7390(22)	5072(20)	49(7)	43(8)
C(3)	5180(21)	1894(22)	246(8)	49(8)
C(4)	5926(21)	4691(20)	959(8)	47(8)
C(5)	3458(22)	1722(27)	1322(8)	63(10)
C(6)	5469(23)	3841(26)	1970(8)	57(9)
C(7)	5103(19)	−877(17)	1064(7)	35(7)
C(8)	7358(26)	−809(24)	1821(8)	59(10)
C(9)	5707(24)	1105(20)	1938(7)	50(8)
C(10)	8352(23)	122(23)	809(3)	54(9)
C(11)	8995(21)	3594(21)	2164(7)	42(8)
C(12)	11282(19)	4411(18)	1386(8)	40(6)
C(13)	9252(19)	6097(21)	1416(7)	43(8)
C(14)	4835(26)	8773(28)	4474(10)	68(11)
C(15)	6097(23)	9340(22)	3491(8)	53(9)
C(16)	4494(22)	11181(23)	3794(9)	57(9)
C(17)	1963(25)	7514(25)	2513(8)	58(10)
C(18)	1259(26)	10027(22)	2744(8)	60(10)
C(19)	−865(25)	6853(27)	3069(7)	59(10)
C(20)	883(22)	9965(20)	3770(8)	49(8)

Table 2 (continued)

Atom	x	y	z	U^a
C(21)	−1328(22)	7102(27)	4217(9)	63(10)
C(22)	1209(24)	8995(27)	4777(8)	60(10)
C(23)	1510(19)	6383(19)	4597(8)	44(8)
C(24)	−385(27)	4171(23)	3814(7)	56(10)
C(25)	2404(26)	4176(26)	4288(9)	63(10)
C(26)	2340(25)	5022(24)	3228(8)	58(9)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Os atoms in molecule B averaged 0.97 reflecting 93% Os character. The s.o.f.'s for molecule A did not deviate significantly from unity on refinement.

All non-hydrogen atoms were refined with anisotropic temperature factors except for the $AsPh_4^+$ carbon atoms in II. In both structures, the final difference maps showed somewhat noisy backgrounds in the vicinity of the metal atoms (1.1 to 0.8 e $Å^{-3}$ at distances of 0.4 to 1.1 Å; a typical C atom was scaled at 3.6 e $Å^{-3}$).

The atomic coordinates for I and II are given in Tables 2 and 4, respectively. Selected bond distances and angles are given in Table 3 for I, and Table 5 for II. Additionally, observed and calculated structure factors, anisotropic temperature factors, complete lists of bond distances and angles, and hydrogen atom coordinates are available from the authors.

Results and discussion

The structure of $H_2RuOs_3(CO)_{13}$ (I). The triclinic form of I crystallizes as discrete molecules with two independent molecules forming the crystallographic asymmetric unit [4*]. Both molecules (A and B) are shown in Fig. 1. The major features of the structure resemble closely the structures of the monoclinic form of I [3], and also those of $H_2FeRu_3(CO)_{13}$ [5], $H_2FeOs_3(CO)_{13}$ [6], and $H_2Ru_4(CO)_{13}$ [7]. A tetrahedral metal atom frame is bridged on adjacent edges by bent semi-bridging carbonyl groups. In all of the heterometallic cases, the angle formed by the carbonyl-bridged edges is centered at the single lighter metal atom. The two μ-H ligands form edge bridges to the metal atom not involved in the μ-CO bridges. The charge distribution factors involved in the locations of the bridges have been thoroughly discussed previously [6].

A rare, if not unique, opportunity exists in the four independent molecules of the two polymorphs of I (combining our data with that of Shore et al. for the monoclinic form [3]) to examine some of the very recent thoughts about the structural forms of bent semibridging carbonyl bonding [8]. The two polymorphs contain eight semibridging CO groups in identical chemical environments. Table 6 provides the Crabtree–Lavin parameters for all eight. While the eight independent μ-CO structures show a wide range of distances and angles (e.g., θ varies from 146(1) to 163(1)° and b varies from 2.28(2) to 2.74(2) Å), all eight are, within experimental error, linearly related by the empirical expression, $\theta = n\psi + m$. These data give $n = 1.52$ and $m = 64.6$, in remarkable agreement with 35 data from iron carbonyl bent semi-bridging structures, $n = 1.51$ and $m = 64.5$ [8]. Because the differences among the individual bond distances and angles must arise from lattice energy factors alone, the wide range seen provides a clear warning against drawing

Table 3

Selected bond distances and angles for $[H_2RuOs_3(CO)_{13}]$ (I)

mol. A		mol. B	
(a) Bond distances (Å)			
Os(1)–Os(2)	2.850(1)	Os(5)–Os(6)	2.842(1)
Os(1)–Os(3)	2.963(1)	Os(4)–Os(6)	2.950(1)
Os(2)–Os(3)	2.945(1)	Os(4)–Os(5)	2.945(1)
Os(1)–Ru(1)	2.787(2)	Os(6)–Ru(2)	2.799(1)
Os(2)–Ru(1)	2.803(2)	Os(5)–Ru(2)	2.817(2)
Os(3)–Ru(1)	2.803(2)	Os(4)–Ru(2)	2.810(1)
Os(1)–C(1)	1.89(2)	Os(6)–C(17)	1.94(2)
Os(1)–C(2)	1.90(2)	Os(6)–C(18)	1.88(2)
Os(1)–C(3)	1.92(2)	Os(6)–C(19)	1.94(2)
Os(1)–C(4)	2.54(2)	Os(6)–C(20)	2.71(2)
Os(2)–C(7)	1.92(2)	Os(5)–C(24)	1.93(2)
Os(2)–C(8)	1.92(2)	Os(5)–C(25)	1.97(2)
Os(2)–C(9)	2.38(2)	Os(5)–C(23)	2.28(2)
Os(2)–C(10)	1.92(2)	Os(5)–C(26)	1.92(2)
Os(3)–C(11)	1.92(2)	Os(4)–C(14)	1.89(2)
Os(3)–C(12)	1.92(2)	Os(4)–C(15)	1.92(2)
Os(3)–C(13)	1.92(2)	Os(4)–C(16)	1.89(2)
Ru(1)–C(4)	1.93(2)	Ru(2)–C(20)	1.90(2)
Ru(1)–C(5)	1.92(2)	Ru(2)–C(21)	1.90(2)
Ru(1)–C(6)	1.87(3)	Ru(2)–C(22)	1.91(2)
Ru(1)–C(9)	1.91(2)	Ru(2)–C(23)	2.02(2)
C(1)–O(1)	1.13(3)	C(17)–O(17)	1.13(3)
C(2)–O(2)	1.15(3)	C(18)–O(18)	1.17(3)
C(3)–O(3)	1.11(2)	C(19)–O(19)	1.13(2)
C(4)–O(4)	1.17(3)	C(20)–O(20)	1.20(2)
C(5)–O(5)	1.14(2)	C(21)–O(21)	1.14(2)
C(6)–O(6)	1.14(3)	C(22)–O(22)	1.12(3)
C(7)–O(7)	1.13(2)	C(24)–O(24)	1.13(2)
C(8)–O(8)	1.15(3)	C(25)–O(25)	1.13(2)
C(9)–O(9)	1.19(2)	C(23)–O(23)	1.16(2)
C(10)–O(10)	1.13(3)	C(26)–O(26)	1.14(3)
C(11)–O(11)	1.13(2)	C(14)–O(14)	1.18(3)
C(12)–O(12)	1.13(2)	C(15)–O(15)	1.15(3)
C(13)–O(13)	1.13(3)	C(16)–O(16)	1.17(3)
(b) Bond angles (deg)			
Os(2)–Os(1)–Os(3)	60.8(0)	Os(5)–Os(6)–Os(4)	61.1(0)
Os(2)–Os(1)–Ru(1)	59.6(0)	Os(5)–Os(6)–Ru(2)	59.9(0)
Os(3)–Os(1)–Ru(1)	58.3(0)	Os(4)–Os(6)–Ru(2)	58.5(0)
Os(1)–Os(2)–Os(3)	61.5(0)	Os(4)–Os(5)–Os(6)	61.3(0)
Os(1)–Os(2)–Ru(1)	59.1(0)	Os(6)–Os(5)–Ru(2)	59.3(0)
Os(3)–Os(2)–Ru(1)	58.3(0)	Os(4)–Os(5)–Ru(2)	58.3(0)
Os(1)–Os(3)–Os(2)	57.7(0)	Os(5)–Os(4)–Os(6)	57.6(0)
Os(1)–Os(3)–Ru(1)	57.7(0)	Os(6)–Os(4)–Ru(2)	58.1(0)
Os(2)–Os(3)–Ru(1)	58.3(0)	Os(5)–Os(4)–Ru(2)	58.5(0)
Os(1)–Ru(1)–Os(2)	61.3(0)	Os(5)–Ru(2)–Os(6)	60.8(0)
Os(1)–Ru(1)–Os(3)	64.0(0)	Os(4)–Ru(2)–Os(6)	63.5(0)
Os(2)–Ru(1)–Os(3)	63.4(0)	Os(4)–Ru(2)–Os(5)	61.1(0)
Os(2)–Os(1)–C(1)	93.5(6)	Os(5)–Os(6)–C(17)	96.2(7)
Os(3)–Os(1)–C(1)	109.0(5)	Os(4)–Os(6)–C(17)	109.4(7)
Ru(1)–Os(1)–C(1)	153.1(6)	Ru(2)–Os(6)–C(17)	156.0(7)
Os(2)–Os(1)–C(2)	172.6(6)	Os(5)–Os(6)–C(18)	169.5(7)
Os(3)–Os(1)–C(2)	112.0(5)	Os(4)–Os(6)–C(18)	109.9(6)

Table 3 (continued)

mol. A		mol. B	
Ru(1)–Os(1)–C(2)	115.7(7)	Ru(2)–Os(6)–C(18)	111.3(7)
Os(2)–Os(1)–C(3)	90.3(6)	Os(5)–Os(6)–C(19)	89.9(7)
Os(3)–Os(1)–C(3)	143.4(6)	Os(4)–Os(6)–C(19)	144.3(6)
Ru(1)–Os(1)–C(3)	88.5(6)	Ru(2)–Os(6)–C(19)	89.9(6)
Os(2)–Os(1)–C(4)	101.5(4)	Os(5)–Os(6)–C(20)	100.0(6)
Os(3)–Os(1)–C(4)	73.6(5)	Os(4)–Os(6)–C(20)	72.1(7)
Ru(1)–Os(1)–C(4)	42.1(4)	Ru(2)–Os(6)–C(20)	40.4(7)
Os(1)–Os(2)–C(7)	96.4(5)	Os(6)–Os(5)–C(24)	97.2(7)
Os(3)–Os(2)–C(7)	149.9(6)	Os(4)–Os(5)–C(24)	151.4(8)
Ru(1)–Os(2)–C(7)	93.3(6)	Ru(2)–Os(5)–C(24)	95.2(8)
Os(1)–Os(2)–C(8)	169.3(5)	Os(6)–Os(5)–C(25)	171.5(6)
Os(3)–Os(2)–C(8)	108.6(6)	Os(4)–Os(5)–C(25)	111.7(6)
Ru(1)–Os(2)–C(8)	120.5(8)	Ru(2)–Os(5)–C(25)	122.5(8)
Os(1)–Os(2)–C(9)	101.4(5)	Os(6)–Os(5)–C(23)	104.1(5)
Os(3)–Os(2)–C(9)	75.9(4)	Os(4)–Os(5)–C(23)	74.4(4)
Ru(1)–Os(2)–C(9)	42.4(5)	Ru(2)–Os(5)–C(23)	45.0(5)
Os(1)–Os(2)–C(10)	86.5(6)	Os(6)–Os(5)–C(26)	84.5(7)
Os(3)–Os(2)–C(10)	104.2(5)	Os(4)–Os(5)–C(26)	104.2(5)
Ru(1)–Os(2)–C(10)	145.5(6)	Ru(2)–Os(5)–C(26)	143.8(7)
Os(1)–Os(3)–C(11)	146.8(5)	Os(6)–Os(4)–C(14)	147.6(6)
Os(2)–Os(3)–C(11)	98.7(5)	Os(5)–Os(4)–C(14)	98.0(6)
Ru(1)–Os(3)–C(11)	90.7(5)	Ru(2)–Os(4)–C(14)	91.9(7)
Os(1)–Os(3)–C(12)	116.8(6)	Os(6)–Os(4)–C(15)	114.2(6)
Os(2)–Os(3)–C(12)	113.5(5)	Os(5)–Os(4)–C(15)	112.8(6)
Ru(1)–Os(3)–C(12)	171.5(6)	Ru(2)–Os(4)–C(15)	170.2(6)
Os(1)–Os(3)–C(13)	99.4(6)	Os(6)–Os(4)–C(16)	99.2(7)
Os(2)–Os(3)–C(13)	149.4(5)	Os(5)–Os(4)–C(16)	149.0(6)
Ru(1)–Os(3)–C(13)	93.1(5)	Ru(2)–Os(4)–C(16)	92.4(6)
Os(1)–Ru(1)–C(4)	62.0(7)	Os(6)–Ru(2)–C(20)	67.2(7)
Os(2)–Ru(1)–C(4)	123.0(7)	Os(5)–Ru(2)–C(20)	127.4(7)
Os(3)–Ru(1)–C(4)	86.9(5)	Os(4)–Ru(2)–C(20)	87.9(6)
Os(1)–Ru(1)–C(5)	105.3(7)	Os(6)–Ru(2)–C(21)	100.0(7)
Os(2)–Ru(1)–C(5)	104.4(8)	Os(5)–Ru(2)–C(21)	102.7(8)
Os(3)–Ru(1)–C(5)	166.2(8)	Os(4)–Ru(2)–C(21)	161.7(8)
Os(1)–Ru(1)–C(6)	145.1(6)	Os(6)–Ru(2)–C(22)	154.2(6)
Os(2)–Ru(1)–C(6)	137.4(7)	Os(5)–Ru(2)–C(22)	134.8(8)
Os(3)–Ru(1)–C(6)	96.1(6)	Os(4)–Ru(2)–C(22)	102.6(6)
Os(1)–Ru(1)–C(9)	118.1(7)	Os(6)–Ru(2)–C(23)	113.8(6)
Os(2)–Ru(1)–C(9)	56.8(7)	Os(5)–Ru(2)–C(23)	53.3(6)
Os(3)–Ru(1)–C(9)	86.7(6)	Os(4)–Ru(2)–C(23)	81.5(5)
C(1)–Os(1)–C(2)	90.8(9)	C(17)–Os(6)–C(18)	92.1(10)
C(1)–Os(1)–C(3)	93.9(8)	C(17)–Os(6)–C(19)	93.1(9)
C(2)–Os(1)–C(3)	95.4(8)	C(18)–Os(6)–C(19)	96.1(9)
C(1)–Os(1)–C(4)	163.6(7)	C(17)–Os(6)–C(20)	161.8(9)
C(2)–Os(1)–C(4)	73.6(8)	C(18)–Os(6)–C(20)	70.9(8)
C(3)–Os(1)–C(4)	92.4(8)	C(19)–Os(6)–C(20)	95.0(8)
C(7)–Os(2)–C(8)	94.2(7)	C(24)–Os(5)–C(25)	91.9(9)
C(7)–Os(2)–C(9)	90.1(7)	C(24)–Os(5)–C(23)	95.0(7)
C(8)–Os(2)–C(9)	78.7(9)	C(25)–Os(5)–C(23)	77.4(9)
C(7)–Os(2)–C(10)	93.9(8)	C(24)–Os(5)–C(26)	91.2(9)
C(8)–Os(2)–C(10)	92.6(10)	C(25)–Os(5)–C(26)	93.0(10)
C(9)–Os(2)–C(10)	170.6(8)	C(23)–Os(5)–C(26)	168.7(9)
C(11)–Os(3)–C(12)	93.2(8)	C(14)–Os(4)–C(15)	94.1(10)
C(11)–Os(3)–C(13)	91.7(8)	C(14)–Os(4)–C(16)	93.4(11)
C(12)–Os(3)–C(13)	94.4(7)	C(15)–Os(4)–C(16)	95.0(9)
C(4)–Ru(1)–C(5)	95.4(9)	C(20)–Ru(2)–C(21)	92.8(9)
C(4)–Ru(1)–C(6)	90.0(10)	C(20)–Ru(2)–C(22)	91.8(10)

Table 3 (continued)

mol. A		mol. B	
C(5)–Ru(1)–C(6)	97.4(10)	C(21)–Ru(2)–C(22)	95.7(10)
C(4)–Ru(1)–C(9)	172.5(7)	C(20)–Ru(2)–C(23)	167.0(7)
C(5)–Ru(1)–C(9)	91.4(9)	C(21)–Ru(2)–C(23)	99.6(8)
C(6)–Ru(1)–C(9)	86.8(9)	C(22)–Ru(2)–C(23)	83.3(10)
Os(1)–C(1)–O(1)	174(2)	Os(6)–C(17)–O(17)	176(2)
Os(1)–C(2)–O(2)	178(2)	Os(6)–C(18)–O(8)	175(2)
Os(1)–C(3)–O(3)	179(2)	Os(6)–C(19)–O(19)	180(2)
Os(1)–C(4)–O(4)	127(2)	Os(6)–C(20)–O(20)	124(2)
Ru(1)–C(4)–O(4)	157(2)	Ru(2)–C(20)–O(20)	163(2)
Ru(1)–C(5)–O(5)	178(2)	Ru(2)–C(21)–O(21)	178(2)
Ru(1)–C(6)–O(6)	179(2)	Ru(2)–C(22)–O(22)	176(2)
Os(2)–C(7)–O(7)	175(2)	Os(5)–C(24)–O(24)	179(2)
Os(2)–C(8)–O(8)	177(1)	Os(5)–C(25)–O(25)	178(2)
Os(2)–C(9)–O(9)	127(2)	Os(5)–C(23)–O(23)	132(2)
Ru(1)–C(9)–O(9)	152(2)	Ru(2)–C(23)–O(23)	146(2)
Os(2)–C(10)–O(10)	174(2)	Os(5)–C(26)–O(26)	176(2)
Os(3)–C(11)–O(11)	177(1)	Os(4)–C(14)–O(14)	174(2)
Os(3)–C(12)–O(12)	176(2)	Os(4)–C(15)–O(15)	179(2)
Os(3)–C(13)–O(13)	176(2)	Os(4)–C(16)–O(16)	179(2)

detailed conclusions about intramolecular steric and electronic effects from solid-state μ-CO bond parameters.

Refinement of the crystallographic site occupancies for the metal atoms in I revealed that the sites designated for Ru differed in their site purity; in mol. A, Ru(1) is 100% Ru within experimental error, but in mol. B, Ru(2) is only 79% with the residual 21% Ru evenly distributed among the three Os sites.

The structure of [Ph$_4$As][H$_3$RuOs$_3$(CO)$_{12}$] (II). The ionic compound II contains no noteworthy interionic contact distances. The structure and labeling scheme for the tetrahedral anion are shown in Fig. 2. The four metal atoms form a tetrahedron with an Os(CO)$_3$ group capping a (μ-H)$_3$RuOs$_2$(CO)$_9$ basal plane. All carbonyl groups are terminal. The structures of the related single-metal salts [PPN][H$_3$Ru$_4$(CO)$_{12}$] (two isomers) [9] and [Me$_4$N][H$_3$Os$_4$(CO)$_{12}$] [10] have been determined. The two isomers of the Ru$_4$ structure represent different edge μ-H bonding patterns; one isomer has μ-H bridging on the three sides of an Ru$_3$ basal plane (C_{3v}), the other has C_2 symmetry. The former isomer is the only one found for the Os$_4$ structure. The mixed-metal [H$_3$RuOs$_3$(CO)$_{12}$]$^-$ structure has C_{3v} symmetry; the three μ-H ligands were found and refined. As previously noted [9,10], the carbonyl groups are somewhat bent away from the hydrido bridges; the hydride bridges are below the basal plane.

As in I, disordering of metal identity is seen in II. While the apical Os atom, Os(1), was found to be pure Os, the three basal plane metal atoms are each 1/3 Ru and 2/3 Os in character and are labeled as "OsRu" atoms. The average Os(1)–OsRu distance, 2.803(1) Å, and the average bridged OsRu–OsRu distance, 2.941(1) Å, are both very similar to those found in I, and not significantly different from those found in the all-Os analogue (2.798 and 2.948 Å) [10] and the all-Ru analogue (2.787 and 2.937 Å). The similarity of all three structures suggests that the Os/Ru disorder in II creates no structural artifacts. In II, the hydrido bridges favor attachment to

Table 4

Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$) and [Ph$_4$As][H$_3$RuOs$_3$(CO)$_{12}$]

atom	x	y	z	U_{iso}
Os(1)	2913.0(3)	7691.7(7)	157.4(3)	51(1) [b]
OsRu(2) [a]	2395.1(3)	6036.8(7)	−855.9(3)	42(1) [b]
OsRu(3) [a]	1699.2(3)	8542.5(7)	−203.9(3)	48(1) [b]
OsRu(4) [a]	1985.0(3)	5404.1(8)	405.3(3)	47(1) [b]
As	36.3(6)	3757.8(7)	2632.9(3)	49(1) [b]
O(1)	2995(5)	2930(13)	686(5)	83(5) [b]
O(2)	1962(5)	6704(14)	1697(5)	76(4) [b]
O(3)	872(5)	3125(14)	552(6)	83(5) [b]
O(4)	3549(5)	3895(13)	−752(5)	80(4) [b]
O(5)	3038(5)	8360(13)	−1717(5)	72(4) [b]
O(6)	1721(5)	4115(13)	−1860(4)	78(4) [b]
O(7)	4062(5)	5686(13)	393(5)	82(5) [b]
O(8)	3005(6)	9437(14)	1380(5)	90(5) [b]
O(9)	3608(5)	10255(13)	−556(5)	80(4) [b]
O(10)	2235(5)	11334(11)	−920(5)	70(4) [b]
O(11)	1659(6)	10366(14)	982(5)	97(5) [b]
O(12)	364(4)	9153(14)	−600(5)	80(4) [b]
C(1)	2615(6)	3897(16)	595(6)	53(5) [b]
C(2)	1983(7)	6249(18)	1218(7)	55(5) [b]
C(3)	1308(7)	3994(18)	482(7)	62(6) [b]
C(4)	3110(7)	4675(15)	−788(6)	51(5) [b]
C(5)	2792(6)	7490(17)	−1384(6)	55(5) [b]
C(6)	1947(6)	4858(16)	−1476(6)	51(5) [b]
C(7)	3594(8)	6431(15)	290(7)	63(6) [b]
C(8)	2915(8)	8777(17)	908(6)	67(6) [b]
C(9)	3334(7)	9316(16)	−310(6)	58(5) [b]
C(10)	2043(7)	10288(15)	−656(6)	54(5) [b]
C(11)	1715(7)	9675(17)	540(6)	62(5) [b]
C(12)	861(7)	8891(16)	−465(6)	53(5) [b]
C(21)	−1213(7)	2839(18)	2848(6)	57(4)
C(22)	−1747(10)	1862(23)	2763(9)	80(6)
C(23)	−1714(9)	471(22)	2420(8)	72(5)
C(24)	−1185(8)	−25(22)	2187(7)	80(5)
C(25)	−627(7)	963(18)	2248(7)	67(4)
C(26)	−678(7)	2396(17)	2597(6)	45(3)
C(31)	728(8)	1011(19)	3055(7)	75(5)
C(32)	1249(9)	−62(25)	3049(8)	91(6)
C(33)	1719(9)	258(22)	2698(7)	81(5)
C(34)	1743(9)	1537(22)	2843(8)	92(6)
C(35)	1244(7)	2627(20)	2314(7)	71(4)
C(36)	746(7)	2350(18)	2673(7)	50(4)
C(41)	370(8)	4956(21)	3816(7)	74(5)
C(42)	357(10)	6117(25)	4297(10)	93(7)
C(43)	−51(8)	7489(23)	4228(9)	92(6)
C(44)	−399(8)	7704(21)	3740(8)	81(5)
C(45)	−376(7)	6578(17)	3266(7)	62(4)
C(46)	17(7)	5231(17)	3299(6)	55(4)
C(51)	−315(7)	4609(18)	1415(6)	53(4)
C(52)	−338(8)	5518(22)	896(8)	87(5)
C(53)	−2(8)	6896(22)	885(8)	84(5)
C(54)	352(8)	7446(22)	1359(8)	83(5)
C(55)	375(8)	6482(18)	1901(7)	71(4)
C(56)	37(7)	5026(17)	1907(6)	54(4)
Hb(1) [c]	2071	8046	−946	80
Hb(2)	2393	4552	−238	80
Hb(3)	1614	7369	492	80

[a] s.o.f. = 0.88, each 2/3 Os, 1/3 Ru. [b] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [c] The hydrido ligands were not refined in the final cycles.

Table 5

Selected bond distances and angles for [Ph$_4$As][H$_3$RuOs$_3$(CO)$_{12}$] (II)

(a) Bond distances (Å)

Os(1)–OsRu(2)	2.804(1)	O(1)–C(1)	1.15(2)
Os(1)–OsRu(3)	2.807(1)	O(2)–C(2)	1.11(2)
Os(1)–OsRu(4)	2.799(1)	O(3)–C(3)	1.19(2)
OsRu(2)–OsRu(3)	2.924(1)	O(4)–C(4)	1.14(2)
OsRu(2)–OsRu(4)	2.953(1)	O(5)–C(5)	1.15(2)
OsRu(3)–OsRu(4)	2.946(1)	O(6)–C(6)	1.13(2)
Os(1)–C(7)	1.81(1)	O(7)–C(7)	1.20(2)
Os(1)–C(8)	1.86(1)	O(8)–C(8)	1.17(2)
Os(1)–C(9)	1.91(1)	O(9)–C(9)	1.11(2)
OsRu(2)–C(4)	1.91(1)	O(10)–C(10)	1.11(2)
OsRu(2)–C(5)	1.87(1)	O(11)–C(11)	1.13(2)
OsRu(2)–C(6)	1.91(1)	O(12)–C(12)	1.13(2)
OsRu(3)–C(10)	1.89(1)	OsRu(2)–Hb(1)	1.79(5)
OsRu(3)–C(11)	1.87(1)	OsRu(2)–Hb(2)	1.81(5)
OsRu(3)–C(12)	1.91(1)	OsRu(3)–Hb(1)	1.87(6)
OsRu(4)–C(1)	1.87(1)	OsRu(3)–Hb(3)	1.81(5)
OsRu(4)–C(2)	1.90(1)	OsRu(4)–Hb(2)	1.81(5)
OsRu(4)–C(3)	1.87(1)	OsRu(4)–Hb(3)	1.81(6)

(b) Bond angles (deg.)

OsRu(2)–Os(1)–OsRu(3)	62.8(0)	OsRu(3)–OsRu(2)–OsRu(4)	68.2(0)
OsRu(3)–Os(1)–OsRu(4)	63.4(0)	OsRu(3)–OsRu(2)–C(4)	142.5(4)
OsRu(3)–Os(1)–C(7)	159.1(4)	Os(1)–OsRu(2)–C(5)	90.0(4)
OsRu(2)–Os(1)–C(8)	156.4(5)	OsRu(4)–OsRu(2)–C(5)	146.5(4)
OsRu(4)–Os(1)–C(8)	97.8(5)	Os(1)–OsRu(2)–C(6)	172.1(4)
OsRu(2)–Os(1)–C(9)	95.7(4)	OsRu(4)–OsRu(2)–C(6)	114.5(4)
OsRu(4)–Os(1)–C(9)	156.2(4)	C(5)–OsRu(2)–C(6)	96.7(6)
C(8)–Os(1)–C(9)	98.4(6)	Os(1)–OsRu(3)–OsRu(2)	58.5
Os(1)–OsRu(2)–OsRu(4)	58.1(0)	OsRu(2)–OsRu(3)–OsRu(4)	60.4
Os(1)–OsRu(2)–C(4)	84.9(4)	OsRu(2)–OsRu(3)–C(10)	93.6(4)
OsRu(4)–OsRu(2)–C(4)	94.7(4)	Os(1)–OsRu(3)–C(11)	83.0(5)
OsRu(3)–OsRu(2)–C(5)	95.9(4)	OsRu(4)–OsRu(3)–C(11)	92.2(4)
C(4)–OsRu(2)–C(5)	92.2(6)	Os(1)–OsRu(3)–C(12)	174.2(4)
OsRu(3)–OsRu(2)–C(6)	116.2(4)	OsRu(4)–OsRu(3)–C(12)	117.0(4)
C(4)–OsRu(2)–C(6)	99.0(6)	C(11)–OsRu(3)–C(12)	100.7(6)
Os(1)–OsRu(3)–OsRu(4)	58.2	OsRu(2)–OsRu(4)–OsRu(3)	59.4
Os(1)–OsRu(3)–C(10)	87.7(4)	OsRu(2)–OsRu(4)–C(1)	95.2(4)
Os(4)–Os(3)–C(18)	144.0(4)	Os(1)–OsRu(4)–C(2)	87.3(4)
Os(2)–Os(3)–C(11)	140.2(5)	OsRu(3)–OsRu(4)–C(2)	95.8(4)
C(10)–OsRu(3)–C(11)	94.6(6)	Os(1)–OsRu(4)–C(3)	172.4(5)
OsRu(2)–OsRu(3)–C(12)	116.9(4)	OsRu(3)–OsRu(4)–C(3)	114.8(5)
C(10)–OsRu(3)–C(12)	96.4(6)	Os(1)–OsRu(4)–OsRu(2)	58.3
Os(1)–OsRu(4)–OsRu(3)	58.4	C(1)–OsRu(4)–C(3)	98.1(6)
Os(1)–OsRu(4)–C(1)	87.8(4)	OsRu(4)–C(2)–O(2)	177.1(12)
OsRu(3)–OsRu(4)–C(1)	144.6(4)	OsRu(2)–C(4)–O(4)	178.1(12)
OsRu(2)–OsRu(4)–C(2)	144.2(4)	OsRu(2)–C(6)–O(6)	175.1(12)
C(1)–OsRu(4)–C(2)	92.7(6)	Os(1)–C(8)–O(8)	170.6(15)
OsRu(2)–OsRu(4)–C(3)	116.1(5)	OsRu(3)–C(10)–O(10)	178.6(12)
OsRu(2)–Os(1)–OsRu(4)	63.6(0)	OsRu(3)O–C(12)–O(12)	176.8(13)
OsRu(2)–Os(1)–C(7)	99.3(4)	C(2)–OsRu(4)–C(3)	97.1(6)
OsRu(4)–Os(1)–C(7)	99.9(5)	OsRu(4)–C(1)–O(1)	176.6(12)
OsRu(3)–Os(1)–C(8)	96.6(5)	OsRu(4)–C(3)–O(3)	177.4(14)
C(7)–Os(1)–C(8)	98.2(7)	OsRu(2)–C(5)–O(5)	178.7(12)
OsRu(3)–Os(1)–C(9)	97.4(5)	Os(1)–C(7)–O(7)	178.5(13)
C(7)–Os(1)–C(9)	95.0(6)	Os(1)–C(9)–O(9)	175.7(13)
Os(1)–OsRu(2)–OsRu(3)	58.7(0)	OsRu(3)–C(11)–O(11)	172.7(15)

Fig. 1. The molecular structure and labeling scheme for the two crystallographically independent molecules of I.
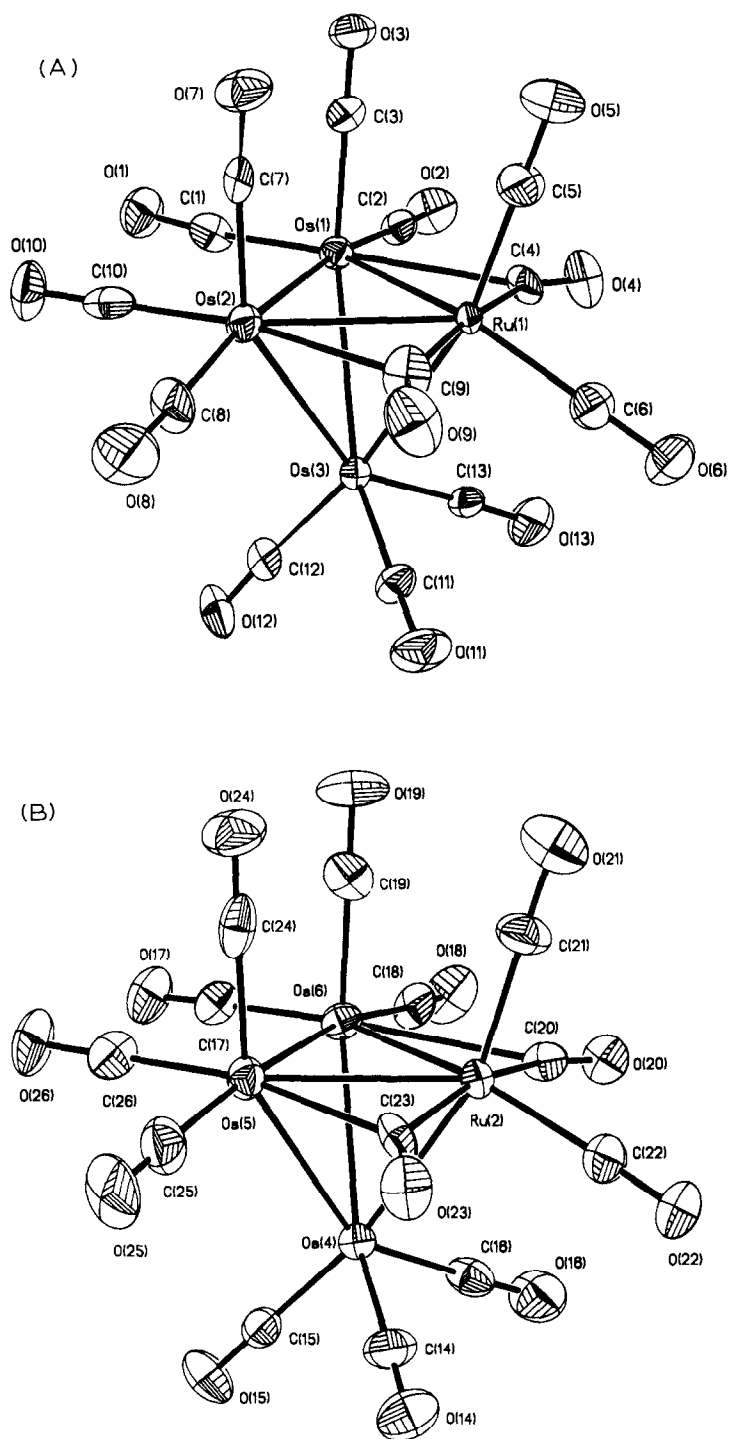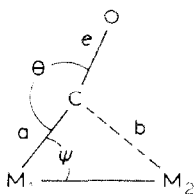
Table 6

A comparison of the Crabtree-Lavin [8] parameters for the eight chemically identical semibridging carbonyl bonds in both polymorphs of I

	M_1	θ	ψ	a	b	c
I (triclinic)	Ru(1)	157(1)	62(1)	1.93(2)	2.54(2)	1.17(3)
		152(1)	57(1)	1.91(2)	2.38(2)	1.19(2)
	Ru(2)	163(1)	67(1)	1.90(2)	2.74(2)	1.20(3)
		146(1)	53(1)	2.20(2)	2.28(2)	1.16(2)
I (monoclinic) [3]	Ru(14)	157(1)	61(1)	2.00(2)	2.53(2)	1.11(2)
		155(1)	60(1)	1.97(2)	2.49(2)	1.14(2)
	Ru(24)	160(1)	63(1)	1.95(2)	2.57(2)	1.14(2)
		151(1)	56(1)	2.01(2)	2.37(2)	1.13(2)

the Ru-rich basal edges in contrast to both I and $H_2FeOs_3(CO)_{13}$ [8] in which the hydrido bridges involve only Os–Os edges.

Formal electron counts for the metal atoms of $H_3RuOs_3(CO)_{12}$ provide $18e^-$ for each basal plane atom, and $17e^-$ for the apical $Os(CO)_3$ group, suggesting significant localization of the anionic charge at this position. Three neutral 60-electron
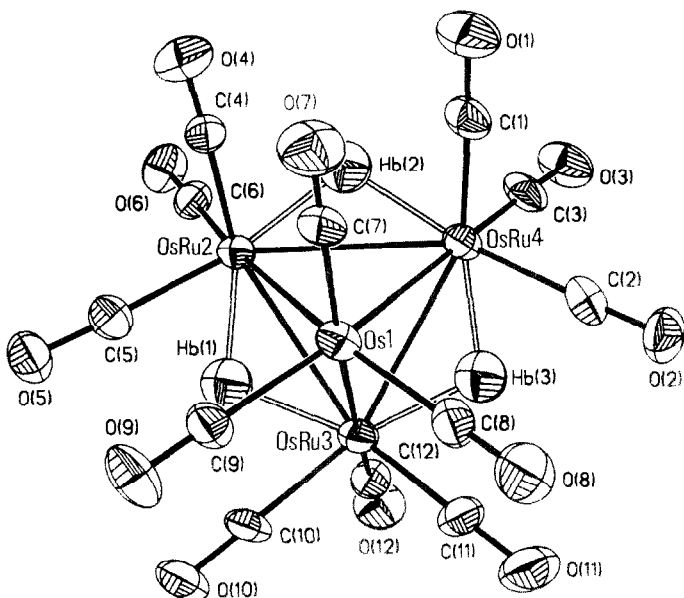

Fig. 2. The molecular structure and labeling scheme for II.

clusters that are isolobal analogues have been structurally characterized, (η^6-$C_6H_5CH_3$)Rh[$Os_3(CO)_9H_3$], [11] CpNi[$Os_3(CO)_9H_3$] [12*] and (CO)$_3$Co[Os_3-$(CO)_9H_3$] [13*]; all contain Os_3 basal plane μ-H bridging analogous to II. The av. Os–Os distances in the (arene)Rh complex, 2.888 Å, in the CpNi complex, 2.871 Å, and in the Co(CO)$_3$ complex, 2.901 Å, are all significantly shorter than in II and the all-Ru and all-Os anion complexes. It is difficult, however, to provide a detailed rationale for these differences except to suggest that the localization of charge on the Os(CO)$_3^-$ apex lengthens the Os–H–Os bridges. Electron "deficiency" at the apex as in the 59-electron complex CpCo[$Os_3(CO)_9H_3$] does not significantly affect the Os–Os distance, av. 2.897 Å [12*]. Calculations of charge distribution in a different, but clearly related analogue, CH_3C[$Fe_3(CO)_9H_3$], indicate a very substantial negative charge localization at the apical carbon atom [14*]. Apparently, further increase in the electron density at the apical position leads to redistribution to basal plane antibonding levels.

Acknowledgments

References

1 B.C. Gates, L. Guczi, and H. Knözinger, Eds., Metal Clusters in Catalysis, Elsevier, Amsterdam, 1986.
2 (a) J.R. Budge, J.P. Scott, and B.C. Gates, J. Chem. Soc., Chem. Commun., (1983) 342; (b) J.P. Scott, J.R. Budge, A.L. Rheingold, and B.C. Gates, J. Am. Chem. Soc., accepted for publication.
3 U. Siriwardane, L.-Y. Hsu, S.L. Mullen, A.G. Marshall and S.G. Shore. 188th National Meeting of the American Chemical Society, Philadelphia, PA. 1984, INOR 181 and private communications. Full disclosure to be submitted: S. Upali, L.-Y. Hsu, J. Krause, J. Wermer and S. Shore.
4 It is of some curious interest that I in both polymorphs and all of the $H_2M_4(CO)_{13}$ (M = Fe, Ru or Os) complexes characterized [5–7], except for $H_2FeOs_3(CO)_{13}$, crystallize with two independent molecules, although no two lattices are isomorphous.
5 C.J. Gilmore and P. Woodward, J. Chem. Soc. A, (1971) 3453.
6 (a) M.R. Churchill, C. Bueno, W.L. Hsu, J.S. Plotlein and S.G. Shore, Inorg. Chem., 21 (1982) 1958; (b) M.R. Churchill, Adv. Chem. Ser., 167 (1978) 36.
7 D.B.W. Yawney and R.J. Doedens, Inorg. Chem., 11 (1972) 838.
8 R.H. Crabtree and M. Lavin, Inorg. Chem., 25 (1986) 805.
9 P.F. Jackson, B.F.G. Johnson, J. Lewis, M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Chem. Commun., (1978) 920; M. McPartlin and W.J.H. Nelson, J. Chem. Soc., Dalton Trans., (1986) 1557.
10 B.F.G. Johnson, J. Lewis, P.R. Raithby, and C. Zuccaro, Acta Cryst. B, 34 (1978) 3765.
11 S.G. Shore, W.-L. Hsu, M.R. Churchill and C. Bueno, J. Am. Chem. Soc., 105 (1983) 655.
12 M.R. Churchill and C. Bueno, Inorg. Chem., 22 (1983) 1510. A low-temperature structure of the CpNi cluster is also available: G. Lavigne, F. Papageorgiou, C. Bergounhou and J.-J. Bonnet, Inorg. Chem., 22 (1983) 2485.
13 S. Bhaduri, B.F.G. Johnson, J. Lewis, P.R. Raithby and D.J. Watson, J. Chem. Soc., Chem. Commun., (1978) 343. (CO)$_3$Co[Ru(CO)$_9$H$_3$] has also been characterized: W.L. Gladfelter, G.L. Geoffroy and J.C. Calabrese, Inorg. Chem., 19 (1980) 2569.
14 R.L. DeKock, K.S. Wong and T.P. Fehlner, Inorg. Chem., 21 (1982) 3203.
15 s.o.f. = site occupancy factor.