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Contribution from the University Chemical Laboratory, Cambridge CB2 1EW, England,
and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Decacarbonylnitrosyltriosmate(3 *Os*-*Os*)(1-): Structural Analysis and Fluxional Properties

BRIAN F. G. JOHNSON,[*,†] JACK LEWIS,[†] JULIAN M. MACE,[†] PAUL R. RAITHBY,[†] ROBERT E. STEVENS,[‡] and WAYNE L. GLADFELTER[*,‡]

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The crystal and molecular structure of $\mathrm{PPN[Os_3(CO)_{10}(NO)]}$ ($\mathrm{PPN = [P(C_6H_5)_3]_2N^+}$) has been determined by a single-crystal X-ray analysis. The compound crystallizes in the monoclinic crystal system in space group $P2_1/c$ with $a = 16.848$ (2) Å, $b = 17.015$ (2) Å, $c = 17.740$ (2) Å, $\beta = 107.25$ (1)°, and ρ(calcd) = 1.94 g cm^{-3} for $Z = 4$ with molecular weight 1419.26. Diffraction data were recorded on a Stoe-Siemens diffractometer, and the structure was refined to $R = 0.045$ for 6261 observed diffractometer data. The three osmium atoms lie at the vertices of an isoceles triangle with the nitrosyl ligand bridging the shorter Os-Os edge. The arrangement of the three terminal carbonyl groups bound to each of the metal atoms bridged by the nitrosyl ligand is different from that in the saturated $\mathrm{HOs_3(CO)_{10}(X)}$ clusters, and the bridged Os-Os bond length of 2.751 (1) Å is shorter than that found in any of these related neutral species. This difference between the two types of systems may be attributed to the absence of a bridging hydride in the anion. The lack of this hydride is also proposed to be responsible for the lower activation barrier for CO scrambling observed in $\mathrm{[Os_3(CO)_{10}(NO)]^-}$.

Introduction

Although the solid-state[1,2] and solution structures[3] of many $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-X})]$ (X = three-electron donor) complexes have been closely examined, the corresponding $[\mathrm{Os_3(CO)_{10}}(\mu\text{-X})]^-$ anions are almost completely unknown. We have recently reported the synthesis[4] and spectroscopic characterization[5] of the cluster complex $\mathrm{PPN[Os_3(CO)_{10}}(\mu\text{-NO})]$ (PPN = bis(triphenylphosphine)nitrogen(1+)) from the reaction of $\mathrm{Os_3(CO)_{12}}$ with $\mathrm{PPN(NO_2)}$ (eq 1). Due to the lack of

$$\mathrm{Os_3(CO)_{12} + PPN(NO_2) \xrightarrow[30\ min]{THF} PPN[Os_3(CO)_{10}(\mu\text{-}NO)] + CO + CO_2} \quad (1)$$

structural information on this type of cluster complex and the need for verification of the presence of the bridging nitrosyl ligand, we undertook an investigation of the solid-state crystal structure and solution dynamics of this species and report the results herein.

Experimental Section

$\mathrm{Os_3(CO)_{12}}$[6] and $\mathrm{PPN[Os_3(CO)_{10}(NO)]}$[5] were prepared according to the published procedures. $\mathrm{Os_3(CO)_{12}}$ was enriched to ca. 30% ^{13}C by heating under ^{13}CO (<1 atm) to 120 °C in decalin for 70 h. The ^{13}CO-enriched anions were prepared from the enriched $\mathrm{Os_3(CO)_{12}}$ and either $\mathrm{PPN(NO_2)}$ or $\mathrm{PPN(^{15}NO_2)}$.

Variable-Temperature ^{13}C NMR Spectroscopy. The NMR data were obtained on a Nicolet NTCFT-1180 300-MHz spectrophotometer. The ^{13}C NMR spectra were obtained with use of $\mathrm{CD_2Cl_2}$ (temperature range -90 to 0 °C) or $\mathrm{CD_3CN}$ (temperature range 28-75 °C) as the solvent (~3.0 mL) in a 12-mm tube with a sample concentration of approximately 0.03 M and $\mathrm{Cr(acac)_3}$ (53 mg) added.

Crystallographic Studies. Crystals were obtained as dark red, elongated rectangular blocks by crystallization from THF/hexane. Several crystals were mounted in 0.5-mm Lindemann capillaries under a nitrogen atmosphere, and one, with dimensions 0.52 × 0.34 × 0.17 mm, was transferred to a Stoe-Siemens four-circle diffractometer.

The unit cell parameters and the orientation matrix were determined as described previously;[7] intensities were measured by profile analysis[8] (for details, see Table I). Data were corrected for Lorentz and polarization factors. Empirical absorption corrections, based on the measurement of sets of equivalent reflections at a series of azimuthal (ψ) angles, were also applied; the discrepency index for the azimuthal scan data was reduced from 0.0799 to 0.0343 by the derived corrections. Transmission factors for the complete data set ranged from 0.049 to 0.092. All data were reduced to $|F_0|$ values; any reflection with $I < 0.5\sigma(I)$ had its I value set to $0.25\sigma(I)$.

Table I. Data for the X-ray Diffraction Study of $\mathrm{[(Ph_3P)_2N][Os_3(CO)_{10}(NO)]}$

(A) Crystal Parameters

cryst syst: monoclinic	$V = 4857$ (3) Å^3
space group: $P2_1/c$	$Z = 4$
$a = 16.848$ (2) Å	mol wt = 1419.26
$b = 17.015$ (2) Å	formula: $\mathrm{C_{45}H_{30}N_2O_{11}Os_3P_2}$
$c = 17.740$ (2) Å	ρ(calcd) = 1.94 g cm^{-3}
$\beta = 107.25$ (1)°	$T = 18$ °C
$\mu = 79.27$ cm^{-1}	$F(000) = 2664$

(B) Measurement of Data

diffractometer: Stoe-Siemens automated four-circle
radiation: Mo Kα ($\bar{\lambda} = 0.71069$ Å)
monochromator: graphite
reflcns measd: $\pm h,+k,-l$ for $5.0° < 2\theta < 50.0°$
scan type: ω/θ
step width: 0.04°
step time: 1.50-4.00 s
no. of steps: 24
reflcns collected: 6387
unique reflcns with $F > 4\sigma(F)$: 6261
check reflcns: 3 stds measd every 97 data, showed no significant variation
$R = 0.045$
$R_W = 0.045$

Solution and Refinement of the Structure. All calculations were performed on the University of Cambridge IBM 3081 computer using a modified version of SHELX.[9] Scattering factors, including contributions for anomalous dispersion, were taken from ref 10.

[†] University Chemical Laboratory.
[‡] University of Minnesota.

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Table II. Atom Coordinates ($\times 10^4$)

	x/a	*y/b*	*z/c*
Os(1)	2423 (1)	2743 (1)	−936 (1)
Os(2)	3041 (1)	2218 (1)	594 (1)
Os(3)	3811 (1)	1643 (1)	−564 (1)
N(1)	3158 (5)	3233 (4)	62 (4)
O(1)	3385 (5)	3905 (4)	283 (4)
C(11)	2722 (8)	3249 (8)	−1775 (6)
O(11)	2886 (7)	3549 (7)	−2281 (5)
C(12)	1707 (7)	1934 (6)	−1548 (6)
O(12)	1280 (5)	1445 (3)	−1919 (5)
C(13)	1527 (7)	3423 (7)	−910 (7)
O(13)	1006 (5)	3851 (5)	−872 (7)
C(21)	2496 (9)	1232 (7)	628 (8)
O(21)	2139 (8)	673 (6)	665 (7)
C(22)	4062 (8)	2035 (7)	1455 (7)
O(22)	4689 (6)	1949 (7)	1937 (5)
C(23)	2440 (7)	2723 (7)	1214 (7)
O(23)	2084 (6)	3071 (5)	1577 (5)
C(31)	4450 (6)	2624 (6)	−422 (6)
O(31)	4835 (5)	3193 (5)	−357 (5)
C(32)	4703 (6)	1074 (6)	173 (6)
O(32)	5232 (5)	742 (5)	619 (5)
C(33)	3962 (7)	1500 (7)	−1585 (6)
O(33)	4064 (6)	1424 (6)	−2184 (5)
C(34)	3017 (7)	774 (7)	−737 (7)
O(34)	2559 (6)	249 (5)	−850 (6)
N(10)	7567 (4)	2341 (4)	1686 (4)
P(1)	7420 (1)	2949 (2)	981 (1)
P(2)	8295 (2)	2002 (1)	2395 (1)
C(101)	6643 (4)	3672 (4)	1080 (4)
C(102)	6609 (4)	4432 (4)	779 (4)
C(103)	5983 (4)	4946 (4)	835 (4)
C(104)	5392 (4)	4699 (4)	1192 (4)
C(105)	5426 (4)	3938 (4)	1494 (4)
C(106)	6052 (4)	3425 (4)	1438 (4)
C(111)	8391 (4)	3440 (3)	925 (3)
C(112)	8840 (4)	3143 (3)	443 (3)
C(113)	9622 (4)	3450 (3)	492 (3)
C(114)	9954 (4)	4054 (3)	1023 (3)
C(115)	9504 (4)	4351 (3)	1506 (3)
C(116)	8723 (4)	4045 (3)	1457 (3)
C(121)	6971 (5)	2437 (3)	67 (4)
C(122)	6655 (5)	2850 (3)	−638 (4)
C(123)	6271 (5)	2446 (3)	−1335 (4)
C(124)	6203 (5)	1629 (3)	−1327 (4)
C(125)	6519 (5)	1216 (3)	−623 (4)
C(126)	6902 (5)	1620 (3)	75 (4)
C(201)	7815 (4)	1239 (4)	2819 (3)
C(202)	6992 (4)	1026 (4)	2445 (3)
C(203)	6613 (4)	443 (4)	2771 (3)
C(204)	7055 (4)	74 (4)	3471 (3)
C(205)	7878 (4)	286 (4)	3845 (3)
C(206)	8258 (4)	869 (4)	3519 (3)
C(211)	9184 (3)	1573 (3)	2119 (4)
C(212)	9141 (3)	777 (3)	1923 (4)
C(213)	9766 (3)	433 (3)	1664 (4)
C(214)	10433 (3)	886 (3)	1600 (4)
C(215)	10476 (3)	1682 (3)	1796 (4)
C(216)	9851 (3)	2026 (3)	2055 (4)
C(221)	8732 (4)	2728 (4)	3155 (4)
C(222)	9542 (4)	2683 (4)	3659 (4)
C(223)	9824 (4)	3238 (4)	4258 (4)
C(224)	9296 (4)	3837 (4)	4352 (4)
C(225)	8486 (4)	3881 (4)	3848 (4)
C(226)	8204 (4)	3327 (4)	3249 (4)

The three Os atoms were located by automatic direct methods and the remaining non-hydrogen atoms by subsequent difference syntheses. Refinement, with anisotropic thermal parameters for the Os, N, P, and carbonyl C and O atoms and isotropic thermal parameters for the phenyl C atoms (phenyl rings refined as rigid bodies with C–C = 1.395 Å and C–C–C = 120°), was by a blocked-cascade least-squares method, the quantity $\sum w\Delta^2$ being minimized ($\Delta = |F_o| - |F_c|$; $w^{-1} = (\sigma(F_o))^2 + 0.0003F_o^2$, which produced a satisfactory analysis of variance). Phenyl H atoms were included in the refinement with constraints on the geometry (C–H = 1.08 Å, C–C–H = 120°) and with a common isotropic temperature factor.

Table III. Bond Lengths (Å)

Os(1)–Os(2)	2.751 (1)	Os(1)–Os(3)	2.915 (1)
Os(1)–N(1)	2.014 (6)	Os(1)–C(11)	1.912 (13)
Os(1)–C(12)	1.937 (10)	Os(1)–C(13)	1.912 (12)
Os(2)–Os(3)	2.906 (1)	Os(2)–N(1)	2.005 (7)
Os(2)–C(21)	1.922 (13)	Os(2)–C(22)	1.957 (10)
Os(2)–C(23)	1.906 (14)	Os(3)–C(31)	1.963 (10)
Os(3)–C(32)	1.934 (9)	Os(3)–C(33)	1.918 (12)
Os(3)–C(34)	1.956 (12)	N(1)–O(1)	1.232 (10)
C(11)–O(11)	1.136 (17)	C(12)–O(12)	1.167 (13)
C(13)–O(13)	1.158 (15)	C(21)–O(21)	1.138 (18)
C(22)–O(22)	1.156 (13)	C(23)–O(23)	1.164 (17)
C(31)–O(31)	1.152 (13)	C(32)–O(32)	1.149 (12)
C(33)–O(33)	1.133 (16)	C(34)–O(34)	1.159 (15)
N(10)–P(1)	1.583 (8)	N(10)–P(2)	1.583 (7)
P(1)–C(101)	1.842 (7)	P(1)–C(111)	1.866 (7)
P(1)–C(121)	1.798 (7)	P(2)–C(201)	1.808 (7)
P(2)–C(211)	1.858 (7)	P(2)–C(221)	1.815 (7)

Table IV. Bond Angles (deg)

Os(2)–Os(1)–Os(3)	61.6 (1)	Os(2)–Os(1)–N(1)	46.7 (2)
Os(3)–Os(1)–N(1)	79.9 (2)	Os(2)–Os(1)–C(11)	143.5 (3)
Os(3)–Os(1)–C(11)	94.9 (4)	N(1)–Os(1)–C(11)	105.2 (4)
Os(2)–Os(1)–C(12)	108.2 (3)	Os(3)–Os(1)–C(12)	89.7 (3)
N(1)–Os(1)–C(12)	154.8 (4)	C(11)–Os(1)–C(12)	98.5 (5)
Os(2)–Os(1)–C(13)	104.1 (4)	Os(3)–Os(1)–C(13)	165.7 (4)
N(1)–Os(1)–C(13)	90.8 (4)	C(11)–Os(1)–C(13)	98.0 (6)
C(12)–Os(1)–C(13)	94.5 (5)	Os(1)–Os(2)–Os(3)	62.0 (1)
Os(1)–Os(2)–N(1)	46.9 (2)	Os(3)–Os(2)–N(1)	80.3 (2)
Os(1)–Os(2)–C(21)	105.7 (4)	Os(3)–Os(2)–C(21)	92.6 (5)
N(1)–Os(2)–C(21)	151.7 (4)	Os(1)–Os(2)–C(22)	144.1 (4)
Os(3)–Os(2)–C(22)	91.5 (4)	N(1)–Os(2)–C(22)	108.6 (4)
C(21)–Os(2)–C(22)	98.8 (5)	Os(1)–Os(2)–C(23)	108.2 (3)
Os(3)–Os(2)–C(23)	170.0 (3)	N(1)–Os(2)–C(23)	91.5 (4)
C(21)–Os(2)–C(23)	92.0 (6)	C(22)–Os(2)–C(23)	96.6 (5)
Os(1)–Os(3)–Os(2)	56.4 (1)	Os(1)–Os(3)–C(31)	81.7 (3)
Os(2)–Os(3)–C(31)	88.0 (4)	Os(1)–Os(3)–C(32)	152.2 (3)
Os(2)–Os(3)–C(32)	96.3 (4)	C(31)–Os(3)–C(32)	93.0 (4)
Os(1)–Os(3)–C(33)	101.0 (3)	Os(2)–Os(3)–C(33)	157.3 (3)
C(31)–Os(3)–C(33)	90.4 (5)	C(32)–Os(3)–C(33)	106.3 (5)
Os(1)–Os(3)–C(34)	89.2 (3)	Os(2)–Os(3)–C(34)	86.4 (4)
C(31)–Os(3)–C(34)	170.8 (5)	C(32)–Os(3)–C(34)	94.9 (4)
C(33)–Os(3)–C(34)	91.9 (5)	Os(1)–N(1)–Os(2)	86.4 (3)
Os(1)–N(1)–O(1)	135.6 (6)	Os(2)–N(1)–O(1)	135.6 (6)
Os(1)–C(11)–O(11)	178.9 (10)	Os(1)–C(12)–O(12)	179.6 (10)
Os(1)–C(13)–O(13)	177.3 (10)	Os(2)–C(21)–O(21)	175.8 (15)
Os(2)–C(22)–O(22)	176.0 (12)	Os(2)–C(23)–O(23)	176.2 (11)
Os(3)–C(31)–O(31)	177.8 (10)	Os(3)–C(32)–O(32)	179.2 (10)
Os(3)–C(33)–O(33)	178.8 (11)	Os(3)–C(34)–O(34)	178.3 (11)
P(1)–N(10)–P(2)	140.2 (5)	N(10)–P(1)–C(101)	108.1 (4)
N(10)–P(1)–C(111)	113.6 (3)	C(101)–P(1)–C(111)	111.4 (3)
N(10)–P(1)–C(121)	108.8 (3)	C(101)–P(1)–C(121)	106.8 (3)
C(111)–P(1)–C(121)	108.0 (3)	N(10)–P(2)–C(201)	104.8 (4)
N(10)–P(2)–C(211)	115.4 (4)	C(201)–P(2)–C(211)	108.8 (3)
N(10)–P(2)–C(221)	113.0 (4)	C(201)–P(2)–C(221)	108.2 (3)
C(211)–P(2)–C(221)	106.4 (3)	P(1)–C(101)–C(102)	122.2 (2)
P(1)–C(101)–C(106)	117.7 (2)	P(1)–C(111)–C(112)	120.9 (2)
P(1)–C(111)–C(116)	118.5 (2)	P(1)–C(121)–C(122)	120.8 (2)
P(1)–C(121)–C(126)	119.2 (2)	P(2)–C(201)–C(202)	119.5 (2)
P(2)–C(201)–C(206)	120.5 (2)	P(2)–C(211)–C(212)	117.4 (2)
P(2)–C(211)–C(216)	122.4 (2)	P(2)–C(221)–C(222)	122.9 (2)
P(2)–C(221)–C(226)	117.0 (2)		

The final discrepancy factors were $R = 0.045$ and $R_w = [\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|] = 0.045$. In the final cycle the maximum shift/estimated standard deviation was 0.011. The final difference synthesis showed ripples of ca. 1 e Å^{-3} in the region of the Os atoms but no other significant features.

Final positional parameters for the non-hydrogen atoms appear in Table II. Observed and calculated structure factors, thermal parameters, and hydrogen atom parameters are available as supplementary data.

Results

X-ray Crystallographic Analysis of PPN[$Os_3(CO)_{10}(NO)$]. The crystal structure consists of discrete bis(triphenylphosphine)nitrogen(1+) cations and decacarbonylnitrosyltriosmate anions. No significant interionic interactions are

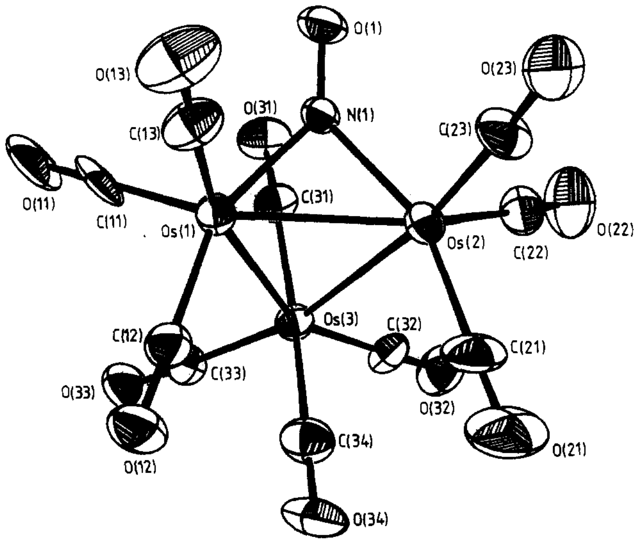


Figure 1. ORTEP plot of $[Os_3(CO)_{10}(\mu\text{-}NO)]^-$ with the atomic labeling schemes.

observed. Figure 1 is a view of a single anion showing the system used for numbering the atoms. Interatomic distances with their estimated standard deviations are listed in Table III, and the interbond angles are shown in Table IV. Important least-squares planes are collected in Supplementary Table III.

The anion has approximate C_s symmetry with a triangular arrangement of osmium atoms. One of the metals (Os3) has four terminal carbonyl ligands while the other two osmiums (Os1 and Os2) each have three terminal carbonyl ligands and are bridged by the nitrosyl ligand. The two nonbridged metal–metal vectors, Os1–Os3 and Os2–Os3, of length 2.915 (1) and 2.906 (1) Å, respectively, are significantly longer than the bridged Os1–Os2 distance of 2.751 (1) Å.

The bridging nitrosyl ligand is bound to the triosmium core via the bonds Os1–N1 = 2.014 (7) Å and Os2–N1 = 2.005 (7) Å; the Os1–N1–Os2 angle is 86.4 (3)°. The N1–O1 bond distance is 1.23 (1) Å, and the Os1–N1–O1 and Os2–N1–O1 angles are both 135.6 (6)°. The Os1–Os2–N1 plane forms a dihedral angle of 103.6° with the triosmium plane. The nitrosyl oxygen O1 is situated significantly out (0.24 Å) of the Os1–Os2–N1 plane, on the distal side with respect to Os3.

Osmium–carbon and carbon–oxygen bond lengths are all within their expected range, and all Os–C–O systems are nearly linear. The $[(PPh_3)_2N]^+$ cation is in a bent configuration with a P1–N10–P2 angle of 140.2 (5) Å. The remaining distances and angles of the cation are also normal.

Variable-Temperature ^{13}C NMR. The spectra taken at various temperatures are shown in Figure 2. At −90 °C the observation of six singlets at 192.8, 186.6, 181.0, 179.7, 179.0, and 178.3 ppm in a 2:1:1:2:2:2 ratio is consistent with the solid-state structure of the anion. The resonances located at 186.6 and 181.0 ppm exhibit a ^{13}C–^{13}C coupling of 17.4 Hz. As the temperature is raised, two distinct processes average the carbonyl into two resonances at 185.8 and 183.4 ppm (75 °C).

Discussion

Solid-State Structure. The overall molecular geometry of the $[Os_3(CO)_{10}(NO)]^-$ anion is similar to that found in many protonated analogues having the general formula $HOs_3(CO)_{10}(\mu\text{-}X)$.[1] Churchill and co-workers have extensively investigated[1] the structures of many of these triosmium clusters, and a comparison of this deprotonated derivative is valuable. The bridged osmium–osmium bond in $[Os_3(CO)_{10}(NO)]^-$ is the shortest (2.751 (1) Å) such single bond within this series. The analogous bond distances in $HOs_3(CO)_{10}(\mu\text{-}X)$ range from 2.786 (1) Å when X = $NHN{=}CPh_2$[1a] to 2.876 (1) Å[1e] when X = Br. There is a general trend within this series of increasing the bridged Os–Os bond distance with increasing covalent radius of the bridging atom. The dihedral angle between the Os_3 and the Os_2X planes shows a reduction (103.6 (1)°) compared to the range of values 105.7 (1)–110.3 (1)° for the $HOs_3(CO)_{10}(\mu\text{-}X)$ complexes.[1] The nitrosyl ligand is tending to occupy a more nearly axial position as in the case of the formato cluster $HOs_3(CO)(\mu\text{-}O_2CH)$,[11] where the dihedral angle between the Os_3 and the Os_2O_2C plane is 98.6 (1)°. The N1–Os–C(carbonyl) angles for Os(1) and Os(2) in $[Os_3(CO)_{10}(NO)]^-$ also show marked differences from those in the related $HOs_3(CO)_{10}(\mu\text{-}X)$ systems.[1] In particular, the X–Os–C(carbonyl) angle for the carbonyl group that is pseudotrans to the bridging X group in the protonated species[1] is reduced by ca. 15° (N(1)–Os(1)–C(12) = 154.8 (4)°; N(1)–Os(2)–C(21) = 151.7 (4)°) in $[Os_3(CO)_{10}(NO)]^-$. This is consistent with the narrowing of the cis Os–Os–C(carbonyl) angles for the same carbonyl groups in the anion (Os(2)–Os(1)–C(12) = 108.2 (3)°; Os(1)–Os(2)–C(21) = 105.7 (4)°) because of the absence of a bridging hydride, whose steric influence has been shown to bend carbonyls back in related protonated complexes.[12]

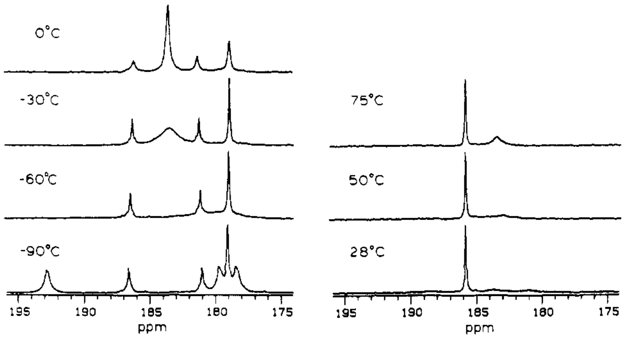
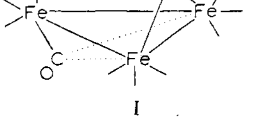


Figure 2. Variable-temperature ^{13}C NMR spectra of $PPN[Os_3(CO)_{10}(NO)]$. Only the CO region of the spectrum is shown. The spectra on the left (−90 → 0 °C) were recorded in a 5:1 CH_2Cl_2/CD_2Cl_2 solvent mixture. The spectra on the right (28 → 75 °C) were recorded in CD_3CN.

The effect of bridging ligands on the structure and bonding in clusters is not well-understood. Formation of a bridging hydrogen usually results in a 0.1-Å lengthening of the metal–metal bond.[12] Yet in cases where a second ligand bridges the same M–M bond as the hydrogen, a *shortening* of the M–M bond commonly occurs. This has been attributed to the bonding characteristics of the second ligand,[13] but actual data supporting this idea was lacking. The structure of $[Os_3(CO)_{10}(NO)]^-$ contains a μ-X group without the bridging hydrogen and does indeed add support to this argument. If we were to add the usual 0.1 Å to the Os(1)–Os(2) bond distance, the value of 2.851 Å falls in the middle of the range of Os–Os distances for the $HOs_3(CO)_{10}X$ clusters.

This anionic osmium cluster is also isoelectronic with $[Fe_3(CO)_{11}]^{2-}$ (I), which has an additional semitriply bridging carbonyl to help distribute the negative charge.[14] There is



I

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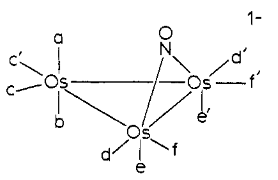
no evidence to suggest any such semitriply bridging interaction exists in $[Os_3(CO)_{10}(NO)]^-$.

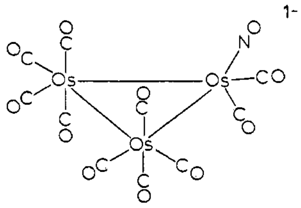
The Os–N distances of 2.014 (7) and 2.005 (7) Å are ca. 0.10 Å shorter than the Os–N distances in the only other structurally characterized osmium clusters with a μ-NO, $[Os_{10}C(CO)_{24}(\mu\text{-NO})]^-$ and $[H_3Os_4(CO)_{12}(\mu\text{-NO})]$, which are 2.10 (7) and 2.10 (2) Å, respectively.[15,16] However, in those clusters there is no metal–metal bond between the bridged osmiums. The N–O bond length of 1.232 (10) Å agrees well with the reported distances of 1.23 (11) Å in $[Os_{10}C(CO)_{24}(\mu\text{-NO})]^-$,[15] 1.230 (9) Å in $HRu_3(CO)_7[P(OMe)_3]_3(\mu\text{-NO})$,[17] and the mean value of 1.22 (2) Å in $Ru_3(CO)_{10}(\mu\text{-NO})_2$.[18] This distance is longer than the mean N–O bond length of 1.14 (2) Å in $Ru_6C(CO)_{14}(NO)_2$, in which the nitrosyls are terminal and linear,[19] and it is also shorter than the N–O single-bond distance of 1.433 (6) Å in $Ru_3(CO)_{10}NOCH_3$).[20] A comparison of this structure with that of $HOs_3(CO)_{10}(NO)$ would be valuable, but we have not obtained X-ray-quality crystals of the latter compound.

Fluxional Properties. The ^{13}C NMR spectrum of $[Os_3(CO)_{10}(NO)]^-$ at −90 °C has the appropriate number of resonances to be consistent with the solid-state structure II. The specific assignment of each of these is not possible, but sets of carbonyls can be labeled. The two resonances that exhibit ^{13}C–^{13}C coupling can be assigned to the carbonyls (a and b) that are mutually trans to one another on Os(3). We prepared the doubly labeled cluster $[Os_3(^{13}CO)_{10}(^{15}NO)]^-$ with the hope that observation of a ^{13}C–^{15}N coupling would allow us to assign one additional resonance. Unfortunately, we were not able to obtain the spectrum at low enough temperatures to allow such an observation. The three carbonyls that exchange positions rapidly at −30 °C are assigned to carbonyls d, d′, e, e′, f, and f′. The resonance at 179.0 ppm is assigned to the two equivalent carbonyls c and c′, which exchange with carbonyls a and b at 28 °C. The striking feature of this study is apparent when it is compared to $HOs_3(CO)_{10}(NO)$ and all other $HOs_3(CO)_{10}X$ clusters.[3] These retain their static structure up to +70 °C. At that point it is the carbonyls on the unique osmium that interconvert with each other, not those bound to the bridged osmium atoms. Once again, we see an important effect of the bridging hydrogen. It has been pointed out previously that the structures of many $HOs_3(CO)_{10}X$ clusters are based on three individual octahedral fragments joined to each other. Removal of the bridging hydrogen would reduce the coordination number of the metals to 5 and greatly reduce the activation barrier for the rearrangement.



II

At higher temperatures we were not able to see any evidence for scrambling of carbonyls among the metals. In the synthesis of $[Os_3(CO)_{10}(NO)]^-$ a short-lived intermediate is formed that has a terminal nitrosyl ligand and no bridging carbonyls.[5] The structure of this isomer (III) was proposed to be similar to the dinitrosyl cluster $Os_3(CO)_9(NO)_2$.[21] On the basis of an estimated half-life of 3–5 min a $\Delta G^{\ddagger} \approx 21$ kcal was derived. If this isomerization were to occur reversibly, the carbonyls would exchange metal sites. Using the above $\Delta G^{\ddagger}$ and the $\Delta\delta$ obtained from the two resonances at +75 °C, we estimate that a temperature of 170 °C would be required to observe coalescence of these two resonances. Unfortunately, this is higher than the decomposition temperature of the cluster.



III

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Registry No. PPN$[Os_3(CO)_{10}(NO)]$, 79061-77-1.

Supplementary Material Available: Listings of the temperature factors, H atom coordinates and temperature factors, least-squares planes, and observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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