an unsaturate route[18] in which H_2 interacts with a Ru(II) olefin intermediate, the olefin stabilizing the Ru(II) against reduction to metal.

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Registry No. *cis*-$RuCl_2(Me_2SO)_4$, 59091-96-2; $[Ru(Me_2SO)_6][BF_4]_2$, 66373-94-2.

Supplementary Material Available: Listings of the measured and calculated structure factors and the calculated hydrogen atom fractional coordinates (31 pages). Ordering information is given on any current masthead page.

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Unusual Coordination Behavior of Iminoalkyl Ligands. Crystal and Molecular Structure of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

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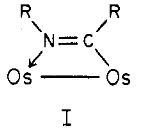
The crystal and molecular structure of the compound $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ has been obtained by single-crystal X-ray diffraction analysis using data collected by counter methods. The compound crystallized in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.098\ (2)$ Å, $b = 16.285\ (2)$ Å, $c = 15.577\ (4)$ Å, $\beta = 98.01\ (2)°$, $V = 2285.7$ Å^3, $Z = 4$, and $\rho_{\text{calcd}} = 2.818$ g cm^{-3}. The structure was solved by a combination of direct methods and difference Fourier analyses. Least-squares refinement employing 3805 reflections ($F^2 > 3.0\sigma(F^2)$) converged to the final discrepancy indices $R = 0.044$ and $R_w = 0.057$. The molecule contains a triangular arrangement of osmium atoms. Atoms Os(1) and Os(3) each contain three linear carbonyl groups while Os(2) contains four. The most interesting feature is a $\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3$ ligand which is bonded to atoms Os(1) and Os(3). The carbon–nitrogen multiple bond, C(17)–N, is 1.278 (10) Å. The bridging hydride ligand was not located but its position is strongly indicated by geometric considerations and comparisons with related molecules.

Introduction

Recent studies have revealed remarkable abilities of triosmium cluster compounds to produce chemical transformations upon small molecules.[1-10] One of the more fascinating of these is the ability to activate aliphatic C–H bonds positioned α to donor nuclei.[8-10] A recent report on the reaction of $Os_3(CO)_{12}$ with imines and trialkylamines describes the preparation of complexes believed to contain bridging η^2-iminoalkyl ligands, I.[10] The ability of the nitrogen atom of iminoalkyl ligands to engage in supplementary coordination was recently demonstrated through our characterizations of the first examples of η^2-iminoalkyl ligands bonded to single metal atoms, II.[11]



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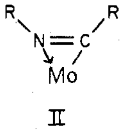


II

Muetterties has recently pointed out and emphasized the importance of polynuclear interactions in producing partial bond reductions in unsaturated ligands.[12] It thus seemed likely that comparisons of the type I and type II structures would yet provide another opportunity for testing this important hypothesis. Because of this and our continuing interest in the unusual coordination behavior of iminoalkyl ligands, we have performed a crystal structure analysis of the complex $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ which is reported here.

Experimental Section

A. Data Collection. The compound $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ was prepared by the method of Deeming from $Os_3(CO)_{12}$ and *N*-methylbenzaldimine.[10] Crystals were grown over a period of several days from pentane solutions cooled to −20 °C. A thick crystalline plate of dimensions 0.146 × 0.380 × 0.280 mm was cleaved from a large crystalline cluster. Crystal faces were subsequently identified as $(1\bar{2}5)$, $(\bar{1}2\bar{5})$, $(21\bar{1})$, $(\bar{2}\bar{1}1)$, (141), and $(1\bar{8}1)$ with the last being assigned to the cleavage face. The crystal was mounted and sealed in a thin-walled glass capillary. A preliminary orientation matrix and unit cell parameters were obtained through the search, centering, and indexing of 25 randomly collected reflections obtained using an Enraf-Nonius CAD-4 four-circle automatic diffractometer. ω-Scan peak widths at half-height were generally on the order of 0.1°. Final cell parameters were obtained by the centering and least-squares refinement of 25 high-angle reflections, $2\theta > 40°$. Inspection subsequently revealed the systematic absences $0k0 = 2n + 1$ and $h + l = 2n + 1$ and, thus, identified the space group as $P2_1/n$.[13] Pertinent crystal parameters are listed in Table I.

0020-1669/78/1317-1969$01.00/0

Table I. Experimental Data for X-ray Diffraction Study of $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

(A) Crystal Parameters at 20 ± 2 °C

Space group: $P2_1/n$
$a = 9.098$ (2) Å
$b = 16.285$ (2) Å
$c = 15.577$ (4) Å
$\beta = 98.01$ (2)°
$V = 2285.7$ Å^3
$Z = 4$
Mol wt 969.87
$\rho_{\text{calcd}} = 2.818$ g cm^{-3}

(B) Measurement of Intensity Data

Radiation: Mo Kα; λ 0.710 69 Å
Monochromator: graphite
Takeoff angle: 2.5°
Detector aperture: horizontal, $A + B \tan\theta$, $A = 3.0$ mm, $B = 1.0$ mm; vertical, 4.0 mm
Crystal–detector dist: 330 mm
Crystal orientation: +23.4° from [010]
Reflecns measd: $+h, +k, \pm l$
Max 2θ: 56°
Scan type: coupled θ(crystal)–2θ(counter)
Scan speed: variable, max $\theta = 10°$/min, min $\theta = 1.2°$/min
θ scan width $= 0.70 + 0.347 \tan\theta$
Bgd: moving crystal–moving counter, $^1/_4$ additional scan at each end of scan
Std reflecns: 4 measd after approx each 100 data reflections showed only random fluctuation of ±3%
No. of reflecns measd: 5580 including absences
Data used ($F^2 > 3.0\sigma(F^2)$): 3805 reflections

(C) Treatment of Data

Absorp coeff: $\mu = 177.46$ cm^{-1}
Transmission factors: max 0.123; min 0.034
Ignorance factor: $p = 0.03$

Table II. Final Atomic Coordinates with Esd's for $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

Atom	*x/a*	*y/b*	*z/c*
Os(1)	0.45951 (5)	0.22062 (3)	0.28262 (3)
Os(2)	0.21945 (5)	0.10728 (3)	0.24168 (4)
Os(3)	0.49948 (5)	0.07403 (3)	0.18065 (3)
C(1)	0.3451 (14)	0.2947 (8)	0.2057 (8)
O(1)	0.2794 (12)	0.3424 (6)	0.1618 (8)
C(2)	0.6300 (14)	0.2939 (8)	0.3028 (9)
O(2)	0.7235 (11)	0.3401 (7)	0.3131 (7)
C(3)	0.3652 (16)	0.2584 (8)	0.3765 (10)
O(3)	0.3146 (13)	0.2808 (7)	0.4355 (8)
C(4)	0.2940 (16)	0.0578 (8)	0.3519 (9)
O(4)	0.3313 (13)	0.0300 (7)	0.4178 (7)
C(5)	0.0643 (18)	0.1631 (10)	0.2945 (14)
O(5)	−0.0298 (13)	0.1937 (9)	0.3189 (11)
C(6)	0.1233 (17)	0.0080 (10)	0.1969 (13)
O(6)	0.0681 (14)	−0.0502 (7)	0.1694 (12)
C(7)	0.6908 (16)	0.0664 (9)	0.1463 (10)
O(7)	0.8043 (14)	0.0572 (10)	0.1235 (10)
C(8)	0.4506 (16)	−0.0411 (9)	0.1699 (9)
O(8)	0.4204 (14)	−0.1072 (7)	0.1660 (10)
C(9)	0.1602 (16)	0.1613 (10)	0.1311 (13)
O(9)	0.1149 (14)	0.1925 (8)	0.0666 (9)
C(10)	0.4110 (19)	0.0986 (12)	0.0625 (11)
O(10)	0.3730 (20)	0.1116 (13)	−0.0092 (9)
N	0.5822 (12)	0.1279 (6)	0.3552 (7)
C(17)	0.5968 (13)	0.0637 (7)	0.3099 (8)
C(18)	0.6496 (18)	0.1396 (10)	0.4470 (9)
C(11)	0.6857 (13)	−0.0106 (7)	0.3505 (8)
C(12)	0.8380 (15)	−0.0032 (9)	0.3746 (11)
C(13)	0.9160 (16)	−0.0718 (10)	0.4091 (12)
C(14)	0.8508 (21)	−0.1438 (11)	0.4214 (13)
C(15)	0.6934 (18)	−0.1506 (8)	0.3952 (11)
C(16)	0.6181 (15)	−0.0864 (8)	0.3608 (10)
H(12)	0.889	0.049	0.366
H(13)	1.022	−0.069	0.426
H(14)	0.907	−0.190	0.450
H(15)	0.647	−0.203	0.398
H(16)	0.511	−0.094	0.341
H(1)	0.672	0.065	0.344
H(2)	0.660	0.740	0.182
H(3)	0.631	0.645	0.344

In the final crystal orientation the crystal [010] direction was approximately 23.4° from the diffractometer ϕ axis. Data collection parameters are also listed in Table I.

B. Solution and Refinement of the Structure. All programs used in this work were those of the Enraf-Nonius SDP program library, and all calculations were performed on a PDP-11/45 computer.

A total of 3805 reflections conforming to the relation $F^2 \geq 3.0\sigma(F^2)$ were used in the structure solution and refinement. The absorption coefficient μ is 177.46 cm^{-1} and an absorption correction was applied to the data using the Gaussian integration method and a grid of 10 × 8 × 10. Maximum and minimum transmission coefficients were 0.123 and 0.034, respectively.

Neutral atom scattering factors were calculated from the tables of Cromer and Waber.[14a] Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were made for all nonhydrogen atoms.[14b] The structure was solved by a combination of direct methods and difference Fourier analyses. The positions of the osmium atoms were obtained from a three-dimensional E map calculated on the basis of the phasing (MULTAN) of 261 reflections having E values greater than 1.60. Full-matrix least-squares refinement on these atoms with isotropic temperature factors produced the residuals $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.136$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.182$. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. A difference Fourier synthesis revealed the positions of all remaining nonhydrogen atoms. Refinement with anisotropic temperature factors for the metal atoms and isotropic temperature factors for all other atoms produced the residuals $R = 0.061$ and $R_w = 0.077$. Hydrogen atom positions for the phenyl ring were calculated assuming idealized geometry and C–H bond distances of 0.95 Å.[15] The hydrogen atoms on the methyl group were located in a difference Fourier synthesis. Hydrogen atoms were included in structure factor calculations but were not refined. One reflection, the (002), was obviously suffering from extinction effects and was deleted from the data set. Full-matrix refinement with anisotropic temperature factors for all nonhydrogen atoms converged to the residuals $R = 0.044$ and $R_w = 0.057$. A difference Fourier analysis showed several peaks 2.0–2.5 e/Å (approximately 3 times the size of the methyl hydrogens) clustered about the metal atoms. The size of these peaks seemed to depend on the quality of the absorption correction. In preliminary refinements using data corrected via coarser grids, these same peaks were considerably larger. They are presently believed to be structurally insignificant. No attempt was made to try to identify the location of the bridging hydride ligand believed to be interspersed among these residual metal peaks. The largest shift/error value on the final cycle of refinement was 0.17. The value of the standard deviation of an observation of unit weight was 2.69. Final atomic coordinates and thermal parameters are listed in Tables II and III, respectively. Bond distances and angles with errors obtained from the inverse matrix from the final cycle of refinement are listed in Tables IV and V. A table of observed and calculated structure factor amplitudes, a table of intermolecular contacts, and a crystal packing diagram are available.[16]

Results and Discussion

The crystal of $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ consists of discrete well-separated molecules. The shortest intermolecular contacts between nonhydrogen atoms are O(6)···O(7) = 2.975 Å, O(2)···O(10) = 3.013 Å, and O(3)···O(8) = 3.075 Å.

The molecular structure is shown in Figure 1. Intramolecular bond distances and angles are listed in Tables IV and V. A uniform triangular cluster of osmium atoms, Os(1)–Os(2) = 2.863 (1) Å, O(1)–Os(3) = 2.918 (1) Å, and Os(2)–Os(3) = 2.892 (1) Å, is similar to that observed in numerous related complexes.[17–25] The bridging hydride ligand was not located, but a conspicuous large cavity along the Os(1)–Os(3) bond circumscribed by the four carbonyl groups C(1)–O(1), C(2)–O(2), C(7)–O(7), and C(10)–O(10) seems to suggest its most probable location. A bridging hydride ligand was located in this same region in the structurally similar complex $HOs_3(CO)_{10}(\mu\text{-}CHCH_2P(CH_3)_2C_6H_5)$.[19] Unsupported bridging hydride ligands generally produce increases on the order of 0.10–0.15 Å on the associated metal–metal bonds.[17,20] However, this effect can be counterbalanced and completely nullified by supplementary bridging ligands.[19] In the present case, while the Os(1)–Os(3) bond is the longest in the molecule, its extension is not as large

Table III. Final Anisotropic Thermal Parameters (B_{ij}'s) for $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$[a, b]

							Rms amplitudes, Å		
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Min	Intermed	Max
Os(1)	2.923	2.180	3.023	0.059	0.114	0.353	0.160	0.188	0.207
Os(2)	2.505	2.507	5.186	0.002	0.332	0.865	0.169	0.178	0.264
Os(3)	2.850	3.276	2.729	0.234	−0.152	−0.205	0.171	0.195	0.216
C(1)	3.774	3.746	3.027	−0.909	0.209	1.678	0.139	0.207	0.269
O(1)	4.927	4.286	6.664	1.275	−0.628	2.070	0.163	0.273	0.322
C(2)	3.485	3.237	3.497	0.327	−0.165	0.202	0.185	0.209	0.232
O(2)	3.554	5.833	5.302	−1.445	−0.056	0.133	0.188	0.259	0.293
C(3)	5.276	2.374	5.280	0.744	1.989	0.399	0.167	0.221	0.287
O(3)	6.030	6.165	4.601	1.692	1.227	0.447	0.232	0.240	0.315
C(4)	4.711	3.387	4.145	0.013	1.747	1.825	0.141	0.234	0.276
O(4)	6.738	5.501	5.124	0.897	1.631	1.942	0.206	0.270	0.319
C(5)	4.170	3.813	10.059	−0.009	2.305	1.539	0.199	0.225	0.365
O(5)	5.875	6.809	15.129	1.298	5.597	−0.597	0.196	0.306	0.453
C(6)	3.415	3.837	8.690	−0.470	−1.045	0.542	0.192	0.221	0.305
O(6)	5.699	2.797	14.411	−0.938	−1.758	0.373	0.178	0.259	0.450
C(7)	4.445	3.440	4.487	0.029	0.460	0.471	0.203	0.236	0.246
O(7)	5.732	9.798	9.962	0.986	3.992	1.073	0.218	0.337	0.388
C(8)	4.607	4.644	2.802	0.878	−0.732	−1.447	0.156	0.218	0.292
O(8)	5.984	4.207	10.502	−0.801	−0.954	−2.277	0.194	0.280	0.392
C(9)	3.052	4.908	7.806	−1.011	−0.097	0.150	0.181	0.258	0.321
O(9)	6.879	5.602	8.309	−0.112	−3.201	3.508	0.167	0.277	0.417
C(10)	4.753	8.142	4.014	1.153	−0.605	−0.366	0.202	0.260	0.332
O(10)	10.838	17.576	4.083	3.060	−2.673	2.031	0.172	0.397	0.487
N	3.100	2.289	3.138	0.534	−0.148	−0.257	0.160	0.184	0.225
C(17)	2.975	3.817	5.612	0.651	0.561	0.270	0.182	0.229	0.268
C(18)	3.722	4.983	6.306	1.460	0.022	0.506	0.184	0.274	0.289
C(11)	8.667	6.947	5.817	5.015	1.954	2.104	0.181	0.261	0.409
C(12)	5.943	2.237	5.751	0.111	0.576	0.842	0.161	0.270	0.280
C(13)	3.635	3.373	4.649	0.459	0.992	0.648	0.194	0.210	0.253
C(14)	2.591	2.587	3.293	−0.512	0.355	−0.684	0.156	0.190	0.217
C(15)	5.481	4.919	2.625	0.526	0.094	0.017	0.181	0.243	0.274
C(16)	3.792	2.817	2.417	−0.121	−0.108	0.878	0.147	0.202	0.232

[a] The form of the expression for the anisotropic temperature factors is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}\cdot hla^*c^* + 2B_{23}klb^*c^*)]$. [b] All hydrogen atoms were assigned isotropic temperature factors of 5.0 Å^2. This value was not refined.

Table IV. Intramolecular Distances (Å) with Esd's for $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

(A) Osmium–Osmium Distances			
Os(1)–Os(2)	2.863 (1)	Os(2)–Os(3)	2.892 (1)
Os(1)–Os(3)	2.918 (1)		
(B) Osmium–Carbonyl Distances			
Os(1)–C(1)	1.904 (8)	Os(2)–C(6)	1.923 (10)
Os(1)–C(2)	1.948 (9)	Os(2)–C(9)	1.943 (13)
Os(1)–C(3)	1.898 (10)	Os(3)–C(7)	1.895 (10)
Os(2)–C(4)	1.932 (10)	Os(3)–C(8)	1.928 (10)
Os(2)–C(5)	1.954 (11)	Os(3)–C(10)	1.945 (11)
(C) Carbon–Oxygen Distances			
C(1)–O(1)	1.147 (8)	C(6)–O(6)	1.128 (12)
C(2)–O(2)	1.130 (10)	C(7)–O(7)	1.148 (11)
C(3)–O(3)	1.143 (11)	C(8)–O(8)	1.111 (12)
C(4)–O(4)	1.130 (11)	C(9)–O(9)	1.150 (14)
C(5)–O(5)	1.102 (12)	C(10)–O(10)	1.141 (14)
(D) Distances in Iminoalkyl Ligand			
Os(1)–N	2.111 (6)	C(11)–C(12)	1.390 (11)
Os(3)–C(17)	2.090 (8)	C(12)–C(13)	1.391 (13)
C(17)–N	1.278 (10)	C(13)–C(14)	1.339 (17)
N–C(18)	1.486 (11)	C(14)–C(15)	1.438 (17)
C(17)–C(11)	1.542 (10)	C(15)–C(16)	1.322 (12)
		C(16)–C(11)	1.399 (11)

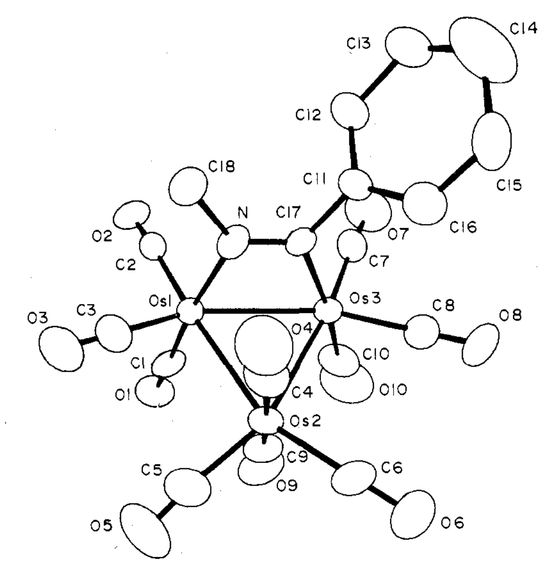


Figure 1. ORTEP diagram of the molecule $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ showing 50% probability ellipsoids.

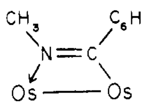
as would be expected due to the presence of a bridging hydride ligand. It does seem probable, though, that the hydride-lengthening effect might be inhibited by the presence of the iminoalkyl ligand which also bridges the Os(1)–Os(3) bond.

The $\mu\text{-}\eta^2$-iminoalkyl ligand defined by the atoms C(11)–C(17)–N–C(18) serves as a symmetrical bridge across the Os(1)–Os(3) bond. The nitrogen atom is bonded solely to osmium atom Os(1) with the distance Os(1)–N = 2.111 (6) Å while the carbon atom C(17) is bonded solely to Os(3); Os(3)–C(17) = 2.090 (8) Å. The carbon–nitrogen distance C(17)–N = 1.278 (10) Å is similar to the distances 1.266 (12) and 1.287 (13) Å observed for this bond in η^1-iminoalkyl ligands in the mononuclear metal complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(OCH_3)_3)(\eta^1\text{-}CH_3CNC_6H_5)$[11] and $Pt^{I}(P(C_6H_5)_3)_2(\eta^1\text{-}CH_3CNC_6H_4Cl)$,[26] respectively. It is, however, significantly longer than the corresponding distance of 1.233 (6) Å observed for the η^2-iminoalkyl ligand in the mononuclear metal complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^2\text{-}CH_3CNC_6H_5)$.[11] The angles C(17)–N–C(18) = 125.1 (7)° and N–C(17)–C(11) = 120.2 (7)°, I, are also similar to the corresponding angles, 124.9 (9)

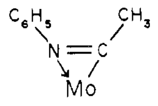
Table V. Interatomic Angles (deg) with Esd's for $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$

(A) Os-Os-Os Angles			
Os(3)-Os(1)-Os(2)	60.02 (1)	Os(2)-Os(3)-Os(1)	59.04 (1)
Os(1)-Os(2)-Os(3)	60.94 (1)		
(B) Os-Os-Carbonyl Angles			
Os(3)-Os(1)-C(1)	105.9 (3)	Os(3)-Os(2)-C(4)	89.9 (3)
Os(3)-Os(1)-C(2)	115.6 (2)	Os(3)-Os(2)-C(5)	161.2 (3)
Os(3)-Os(1)-C(3)	142.1 (3)	Os(3)-Os(2)-C(6)	95.8 (3)
Os(2)-Os(1)-C(1)	86.3 (2)	Os(3)-Os(2)-C(9)	86.7 (3)
Os(2)-Os(1)-C(2)	175.3 (3)	Os(2)-Os(3)-C(7)	172.4 (3)
Os(2)-Os(1)-C(3)	88.2 (3)	Os(2)-Os(3)-C(8)	90.4 (3)
Os(1)-Os(2)-C(4)	84.8 (3)	Os(2)-Os(3)-C(10)	90.3 (3)
Os(1)-Os(2)-C(5)	100.4 (3)	Os(1)-Os(3)-C(7)	113.4 (3)
Os(1)-Os(2)-C(6)	156.6 (3)	Os(1)-Os(3)-C(8)	142.9 (3)
Os(1)-Os(2)-C(9)	90.8 (3)	Os(1)-Os(3)-C(10)	106.3 (4)
(C) Carbonyl-Os-Carbonyl Angles			
C(1)-Os(1)-C(2)	93.8 (3)	C(4)-Os(2)-C(5)	90.3 (5)
C(1)-Os(1)-C(3)	90.8 (4)	C(4)-Os(2)-C(6)	93.3 (5)
C(2)-Os(1)-C(3)	96.5 (4)	C(4)-Os(2)-C(9)	175.3 (4)
C(7)-Os(3)-C(8)	96.9 (4)	C(5)-Os(2)-C(6)	103.0 (5)
C(7)-Os(3)-C(10)	91.2 (4)	C(5)-Os(2)-C(9)	92.0 (5)
C(8)-Os(3)-C(10)	93.3 (5)	C(6)-Os(2)-C(9)	90.2 (5)
(D) Osmium-Carbonyl-Oxygen Angles			
Os(1)-C(1)-O(1)	176.7 (8)	Os(2)-C(6)-O(6)	178.8 (12)
Os(1)-C(2)-O(2)	175.9 (8)	Os(2)-C(9)-O(9)	175.2 (9)
Os(1)-C(3)-O(3)	176.8 (10)	Os(3)-C(7)-O(7)	175.9 (10)
Os(2)-C(4)-O(4)	176.6 (8)	Os(3)-C(8)-O(8)	177.7 (10)
Os(2)-C(5)-O(5)	175.0 (14)	Os(3)-C(10)-O(10)	173.1 (11)
(E) Angles Involving Iminoalkyl Ligand			
Os(2)-Os(1)-N	89.3 (2)	Os(3)-Os(1)-N	67.0 (2)
Os(2)-Os(3)-C(17)	88.5 (2)	Os(1)-Os(3)-C(17)	67.0 (2)
C(1)-Os(1)-N	172.9 (3)	C(17)-N-C(18)	125.1 (7)
C(2)-Os(1)-N	91.5 (2)	N-C(17)-C(11)	120.2 (7)
C(3)-Os(1)-N	94.6 (3)	C(17)-C(11)-C(12)	119.3 (7)
C(7)-Os(3)-C(17)	89.1 (4)	C(17)-C(11)-C(16)	121.8 (7)
C(8)-Os(3)-C(17)	93.9 (3)	C(16)-C(11)-C(12)	118.9 (7)
C(10)-Os(3)-C(17)	172.7 (4)	C(11)-C(12)-C(13)	118.0 (9)
Os(1)-N-C(17)	112.1 (5)	C(12)-C(13)-C(14)	123.1 (10)
Os(3)-C(17)-N	113.9 (6)	C(13)-C(14)-C(15)	118.1 (9)
Os(1)-N-C(18)	122.7 (6)	C(14)-C(15)-C(16)	119.6 (9)
Os(3)-C(17)-C(11)	125.9 (5)	C(15)-C(16)-C(11)	122.2 (9)

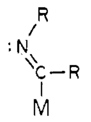
and 119.4 (9)°[11] and 125.4 (10) and 115.4 (10)°,[26] found for the more commonly occurring η^1 ligand, III, but are considerably more acute than the angles, 138.9 (4) and 134.7 (5)°, found for the η^2 ligand, II.[11]



I



II



III

In Table VI are listed various least-squares planes. The iminoalkyl ligand, plane B, and the phenyl group, plane C, are both planar but are inclined 65.3° to one another. This is unlike the η_2 ligand, II.[11] In that case the two groups were coplanar which suggested the possibility of conjugation between the π-bonding systems on the two functions. In the present case, these conjugation effects may be nullified by more important steric interactions introduced by the smaller bond angles at the imino carbon and nitrogen atoms. To relieve these effects the ring, then, twists out of the plane of the ligand. All ten carbonyl groups are essentially linear and similar to those found in related complexes.[17-25]

Table VI. Unit Weighted Least-Squares Planes for $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$ and Deviations (Å) of Atoms Therefrom

Atom	Dev	Atom	Dev
(A) Osmium Atoms			
$-0.1928x + 0.5065y - 0.8404z = 2.5321$			
Os(1)[a]	0.000	C(16)	−3.79 (1)
Os(2)[a]	0.000	C(1)	1.78 (1)
Os(3)[a]	0.000	C(2)	0.05 (1)
C(17)	−1.88 (1)	C(3)	−0.70 (1)
C(18)	−3.06 (1)	C(4)	−1.92 (1)
N	−1.89 (1)	C(5)	0.07 (2)
C(11)	−3.16 (1)	C(6)	−0.09 (2)
C(12)	−3.66 (2)	C(7)	0.03 (1)
C(13)	−4.80 (2)	C(8)	−0.73 (1)
C(14)	−5.43 (2)	C(9)	1.94 (2)
C(15)	−4.89 (2)	C(10)	1.84 (2)
(B) Iminoalkyl Ligand			
$0.8767x + 0.3774y - 0.2984z = 3.1278$			
C(17)[a]	0.009 (12)	Os(3)	0.136 (1)
C(18)[a]	0.004 (16)	C(12)	1.10 (1)
N[a]	−0.009 (11)	C(13)	1.08 (2)
C(11)[a]	−0.004 (12)	C(14)	0.03 (2)
Os(1)	0.055 (1)	C(15)	−1.09 (2)
Os(2)	−2.290 (1)	C(16)	−1.08 (1)
(C) Phenyl Ring			
$0.2871x - 0.2829y - 0.9152z = -3.3175$			
C(11)[a]	−0.010 (13)	N	−0.99 (1)
C(12)[a]	−0.001 (16)	C(17)	0.02 (1)
C(13)[a]	0.010 (18)	Os(1)	−0.665 (1)
C(14)[a]	−0.009 (19)	Os(2)	−0.166 (1)
C(15)[a]	−0.003 (17)	Os(3)	1.618 (1)
C(16)[a]	0.011 (15)		
Dihedral Angles (deg)			
A-B	74.2	B-C	65.3
A-C	55.2		

[a] These atoms were used to define the plane.

Muetterties has recently pointed out the importance of polynuclear coordination in causing partial bond reductions in unsaturated ligands.[12] He summarized that the $\mu_x\text{-}\eta^2$ structural arrangement should be the most effective of all common coordination forms. Bond distance data were cited as a useful way of measuring reduction effects such that longer bonds implied greater reduction effects and vice versa. The present study provides another opportunity to test this hypothesis. Basically, structures I and II differ only in the number of metal atoms bonded to the unsaturated carbon-nitrogen function and structure I has a $\mu\text{-}\eta^2$ form. Comparison of the carbon-nitrogen distances 1.278 (10) Å, I, and 1.233 (6) Å, II, suggests that the dinuclear coordination, I, does, indeed, cause a greater reduction in the carbon-nitrogen bond than the mononuclear form. However, we feel these results are still only tentative, and a greater number of studies on this ligand in related systems should be performed to truly confirm the effect.

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Registry No. $HO_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)$, 63363-66-6.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes, a table of intermolecular contact distances, and a stereoscopic view of the entire unit cell (30 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of (Acetylene)bis(trimethylphosphine)(tetracarbonyl)dicobalt(0)

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The structure of (acetylene)bis(trimethylphosphine)(tetracarbonyl)dicobalt(0), $(C_2H_2)Co_2(P(CH_3)_3)_2(CO)_4$, has been determined crystallographically at −50 °C. The dinuclear complex possesses a C_{2v} perfect symmetry. Each cobalt atom is bonded to two carbon atoms of the carbonyl groups to two carbon atoms of the acetylene group and to a phosphorus atom of the phosphine ligand in a square-pyramidal type arrangement. Furthermore the two cobalt atoms are linked by a metal–metal bond of 2.464 (1) Å. The compound crystallizes in space group $C_{2v}{}^{19}$-*Fdd*2 of the orthorhombic system with 16 half-formulas in a cell of dimensions a = 20.846 (8) Å, b = 26.656 (8) Å, and c = 6.668 (1) Å. The 93 structural data were refined by full-matrix least-squares methods to a conventional R index of 0.024 based on those 1085 reflections having $F_o{}^2 > 3\sigma(F_o{}^2)$.

Introduction

It is well-known that the reaction of alkynes with dicobalt octacarbonyl gives $(RC{\equiv}CR)Co_2(CO)_6$ complexes at room temperature.[1] The molecular structures of such compounds are well established for R = C_6H_5[2] and R = $(CH_3)_3C$.[3] These structures are deduced from that of dicobalt octacarbonyl replacing the two bridging carbonyl groups by the alkyne. Although the action of group 5 ligands is quite well studied and is known to give rise to $(RC{\equiv}CR)Co_2(CO)_{6-n}L_n$ compounds,[1,4] with n ranging from 1 to 4, the only structural information for these compounds was deduced from IR and NMR data. We present here the synthesis and crystal structure of $HC{\equiv}CHCo_2(CO)_4(P(CH_3)_3)_2$ which we have undertaken in order to check structural hypothesis given elsewhere[1,4] and to assess the influence of the phosphine ligand on the molecular structure, in particular on the metal–metal bond.

Experimental Section

Infrared spectra were recorded in a solution of hexadecane on a Perkin-Elmer 225 spectrometer and proton NMR data were recorded on a Varian A60A.

All reactions were carried out under nitrogen atmosphere. Dicobalt octacarbonyl was purchased from Pressure Chemical Co.; $HC{\equiv}CHCo_2(CO)_6$ and $P(CH_3)_3$ were prepared following literature methods.[5,6]

Synthesis of $HC{\equiv}CHCo_2(CO)_4(P(CH_3)_3)_2$. A mixture of 1 g of $HC{\equiv}CHCo_2(CO)_6$ (3.2 mol) and 0.8 cm³ (8.4 mol) of phosphine $P(CH_3)_3$ in 40 cm³ of benzene was refluxed for 2 h at room temperature. The reaction solution was then cooled and filtered; the benzene was evaporated under vacuum. Recrystallization of the crude product from methanol gives 0.8 g (yield 60%) of long red needles of $HC{\equiv}CHCo_2(CO)_4(P(CH_3)_3)_2$.

Preliminary X-ray Study. Examination of crystals of the title compound by precession methods using Mo Kα radiation showed that the compound belongs to the orthorhombic system. Systematic absences hkl ($h + k$ odd), hkl ($k + l$ odd), $0kl$ ($k + l \neq 4n$), and $h0l$ ($h + l \neq 4n$) lead to the *Fdd*2 ($C_{2v}{}^{19}$, No. 43) space group. Cell constants at −50 °C and corresponding standard deviations, listed in Table I, were derived from a least-squares refinement of the settings

Table I

Physical and Crystallographic Data

Formula: $(C_2H_2)Co_2(CO)_4$-$(P(CH_3)_3)_2$
Crystal system: orthorhombic
a = 20.846 (8) Å
b = 26.656 (8) Å
c = 6.668 (1) Å
ρ_{exptl} = 1.42 g cm^{-3}
ρ_X = 1.463 g cm^{-3}
Mol wt: 408.1
Space group: *Fdd2*($C_{2v}{}^{19}$, No. 43)
V = 3 705 Å³
Z = 16 (half of the formula)
Abs factor: μ(Mo Kα) 20.38 cm^{-1}

Data Collection

Temperature: −50 °C
Radiation: molybdenum $\lambda(K\alpha_1)$ 0.709 26 Å
Monochromatization: graphite
Crystal-detector distance: 273 mm
Detector window: height = 4 mm, width = (3.2 + 0.75 tan θ) mm
Takeoff angle: 4°
Scan mode: $\omega/2\theta$
Maximum Bragg angle: 27°
Scan angle: (0.7 + 0.35 tan θ)°
Reflections for intensity controls: $\bar{4}80$, $\bar{8}20$, and $\bar{2}22$
Periodicity: every 2 h

Conditions for Refinement

Reflections for the refinement of the cell dimensions: 25
Recorded independent reflections: 2274 ($-h,+k,+l$)
Utilized reflections: 1085 with $F^2 > 3\sigma(F_o{}^2)$
Refined parameters: 93
Reliability factors: $R = \Sigma|k|F_o| - |F_c||/\Sigma k|F_o|$
$R_w = [\Sigma w(k|F_o| - |F_c|)^2/\Sigma w k^2 F_o{}^2]^{1/2}$

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