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Registry No. $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4] \cdot 2H_2O$, 70004-02-3; $[(C_6H_5)_4As]_2[Mo_2(O_2CCH_3)_2Cl_4] \cdot 2CH_3OH$, 69109-39-3; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

References and Notes

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Triosmium Cluster Compounds Containing Isocyanide and Hydride Ligands. Crystal and Molecular Structure of $(\mu-H)(\mu-\eta^1-C=N(H)(t-C_4H_9))Os_3(CO)_{10}$

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The crystal and molecular structure of the compound $(\mu-H)(\mu-\eta^1-C=N(H)(t-C_4H_9))Os_3(CO)_{10}$ has been determined by X-ray crystallographic methods. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ [C_{2h}^5]: $a = 13.651(4) \text{ \AA}$, $b = 9.156(4) \text{ \AA}$, $c = 18.275(5) \text{ \AA}$, $\beta = 111.42(2)^\circ$, $V = 2126.3(25) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.92 \text{ g cm}^{-3}$. A uniform triangular cluster of three osmium atoms contains ten linear carbonyl groups and a $\mu-\eta^1-C=N(H)(t-C_4H_9)$ iminyl ligand. The carbon atom of the iminyl ligand symmetrically bridges one osmium-osmium bond, as is shown by the internuclear separations $Os(2)-C(11) = 2.066(8) \text{ \AA}$ and $Os(3)-C(11) = 2.043(8) \text{ \AA}$. The iminyl bond, $C(11)-N$, is double with the C-N distance being $1.298(10) \text{ \AA}$.

Introduction

We have recently presented a detailed report of the way in which the cluster hydride complex $H_2Os_3(CO)_{10}$ reacts with isocyanide molecules and subsequently transfers hydrogen atoms to the isocyanide ligand.¹ One process involving a proton dissociation and readdition formally moves a hydrogen atom from the cluster to the nitrogen atom of the isocyanide ligand. This has been confirmed by an X-ray crystallographic analysis of the compound $(\mu-H)(\mu-\eta^1-C=N(H)(C_4H_9))Os_3(CO)_{10}$ which is reported here.

Experimental Section

The compound $(\mu-H)(\mu-\eta^1-C=N(H)(t-C_4H_9))Os_3(CO)_{10}$ was prepared from $(\mu-H)(H)Os_3(CO)_{10}(CN-t-C_4H_9)$ by treatment with triethylamine in chloroform solution as previously reported.¹ Crystals

were grown from concentrated hexanes solutions cooled to -20°C .

All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer by using graphite-monochromatized $Mo K\alpha$ radiation. Unit cells were determined and refined by using 25 randomly selected reflections obtained with the CAD-4 automatic search center, index, and least-squares routines. The space group $P2_1/n$ was determined from the systematic absences observed during data collection.

All calculations were performed on a Digital PDP 11/45 computer by using the Enraf-Nonius SDP program library. Anomalous dispersion corrections^{2a} were made for scattering^{2b} by all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$.

Crystal data and data collection parameters are listed in Table I. A cuboidal crystal with dimensions $0.114 \text{ mm} \times 0.174 \text{ mm} \times 0.138 \text{ mm}$ was mounted in a thin-walled glass capillary. The crystal faces

Table I. Experimental Data for X-ray Diffraction Study of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}\equiv\text{N}(\text{H})(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$

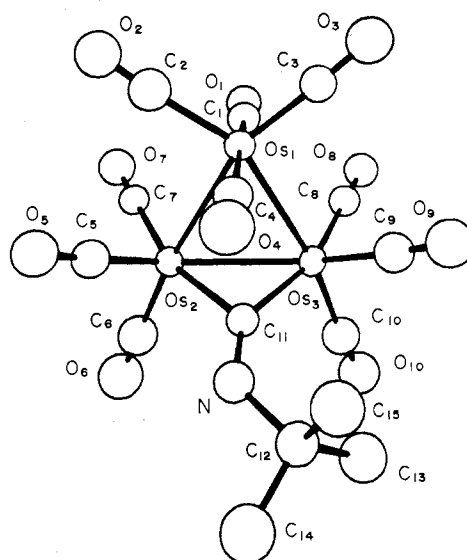
(A) Crystal Parameters at 20 °C
 space group: $P2_1/n$ $V = 2126 (3) \text{ \AA}^3$
 $a = 13.651 (4) \text{ \AA}$ $Z = 4$
 $b = 9.156 (4) \text{ \AA}$ mol wt 935.86
 $c = 18.275 (5) \text{ \AA}$ $\rho_{\text{calcd}} = 2.92 \text{ g cm}^{-3}$
 $\beta = 111.4 (2)^\circ$

(B) Measurement of Intensity Data
 radiation: Mo $K\alpha$ (λ 0.710 73 Å)
 monochromator: graphite
 takeoff angle: 2.5°
 detector aperture: horizontal, $A + B \tan \theta$, $A = 2.6 \text{ mm}$, $B = 1.2 \text{ mm}$; vertical, 4.0 mm
 cryst-detector dist: 330 mm
 cryst orientn: [010] direction 4.3° from φ axis
 rflctns measd: $+h, +k, \pm l$
 max 2θ : 50°
 scan type: moving cryst-stationary counter
 scan speed: variable, max $\theta = 10^\circ/\text{min}$ and min $\theta = 1.4^\circ/\text{min}$
 θ scan width: $(0.90 + 0.347 \tan \theta)^\circ$ on each side of calcd position
 bkgd: moving cryst-stationary counter, $1/4$ additional scan at each end of scan
 std rflctns: 3 measd after approx each 60 data rflctns showed only random fluctuation of $\pm 2\%$
 rflctns measd: 4064 including absences
 data used ($F^2 > 3.0\sigma(F^2)$): 2606 rflctns

(C) Treatment of Data
 abs coeff: $\mu = 190.7 \text{ cm}^{-1}$
 grid: $10 \times 10 \times 10$
 transmission factors: max 0.179, min 0.075
 ignorance factor: $p = 0.03$

were identified as $10\bar{4}$, $\bar{1}04$, 100, $\bar{1}00$, 122, and 120. ω -Scan peak widths at half-height were in the range $0.15\text{--}0.25^\circ$. Of the 4064 reflections which were measured, 2606 conformed to the relation $F^2 \geq 3.0\sigma(F^2)$ and were used in the subsequent structure solution and refinement. The linear absorption coefficient is 190.7 cm^{-1} . The data were corrected for absorption by using the Gaussian integration method.

The structure was solved by a combination of Patterson and difference Fourier techniques. Full-matrix least-squares refinement with anisotropic thermal parameters for the osmium atoms and isotropic thermal parameters for the remaining nonhydrogen atoms converged to the final residuals $R_1 = 0.049$ and $R_2 = 0.058$. Hydrogen atom positions for the iminyl ($\text{C}\equiv\text{N}(\text{H})(t\text{-C}_4\text{H}_9)$) ligand were

**Figure 1.** ORTEP diagram of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}\equiv\text{N}(\text{H})(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$ showing 50% probability ellipsoids. Hydrogen atoms have been omitted.

calculated by using idealized geometry and three peaks from a different Fourier synthesis that could most reasonably be assigned as hydrogen atoms on each methyl group. These hydrogen atoms were included in structure factor calculations but were not refined. Comparison of F_o and F_c for intense low-angle data did not indicate the presence of any serious extinction effects. Thus, no correction was made, and no reflections were deleted from the data set. The largest peaks in a final difference Fourier synthesis were $1.6\text{--}1.7 \text{ e/\AA}^3$ and were clustered about the metal atoms. The largest value of the shift/error parameter on the final cycle of refinement was 0.03. The error in an observation of unit weight was 6.07. Final fractional atomic coordinates are listed in Table II. Bond distances and angles with estimated standard deviations determined from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV. A table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

The molecular structure of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}\equiv\text{N}(\text{H})(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$ is shown in Figure 1. The hydrogen atoms have been omitted. The compound consists of a triangular

Table IIFinal Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C}\equiv\text{N}(\text{H})(t\text{-C}_4\text{H}_9))\text{Os}_3(\text{CO})_{10}$

atom	x/a	y/b	z/c	$B, \text{ \AA}^2$	atom	x/a	y/b	z/c	$B, \text{ \AA}^2$
Os(1)	0.19425 (6)	0.07524 (9)	0.07267 (4)	a	C(1)	0.307 (2)	0.009 (2)	0.168 (1)	3.8 (4)
Os(2)	0.27822 (6)	0.36278 (9)	0.11332 (4)	a	C(2)	0.098 (2)	0.094 (3)	0.129 (1)	5.0 (5)
Os(3)	0.36338 (6)	0.17830 (9)	0.02870 (4)	a	C(3)	0.174 (2)	-0.112 (2)	0.030 (1)	3.7 (4)
O(1)	0.368 (1)	-0.033 (2)	0.2245 (8)	4.8 (3)	C(4)	0.094 (1)	0.167 (2)	-0.022 (1)	3.5 (4)
O(2)	0.038 (1)	0.098 (2)	0.1584 (9)	5.8 (4)	C(5)	0.144 (2)	0.434 (2)	0.098 (1)	3.9 (4)
O(3)	0.159 (1)	-0.232 (2)	0.0034 (9)	5.6 (4)	C(6)	0.344 (2)	0.547 (3)	0.133 (1)	5.2 (5)
O(4)	0.034 (1)	0.216 (2)	-0.0753 (9)	5.7 (4)	C(7)	0.310 (1)	0.312 (2)	0.224 (1)	3.3 (4)
O(5)	0.058 (1)	0.473 (2)	0.0863 (8)	5.2 (4)	C(8)	0.451 (2)	0.021 (2)	0.091 (1)	3.7 (4)
O(6)	0.388 (1)	0.655 (2)	0.1481 (10)	7.0 (5)	C(9)	0.310 (2)	0.067 (3)	-0.064 (1)	4.4 (5)
O(7)	0.327 (1)	0.276 (2)	0.2683 (9)	5.2 (4)	C(10)	0.478 (2)	0.277 (3)	0.011 (1)	4.9 (5)
O(8)	0.503 (1)	-0.073 (2)	0.1264 (8)	4.7 (3)	C(11)	0.266 (1)	0.355 (2)	-0.003 (1)	2.9 (4)
O(9)	0.273 (1)	-0.003 (2)	-0.1213 (9)	5.6 (4)	C(12)	0.209 (2)	0.450 (2)	-0.146 (1)	3.9 (4)
O(10)	0.549 (1)	0.325 (2)	0.0034 (10)	6.0 (4)	C(13)	0.317 (2)	0.417 (3)	-0.152 (1)	5.6 (6)
N	0.218 (1)	0.443 (2)	-0.0605 (9)	3.9 (4)	C(14)	0.173 (2)	0.604 (3)	-0.173 (1)	5.8 (6)
					C(15)	0.127 (2)	0.343 (3)	-0.194 (1)	5.2 (5)

Final Anisotropic Thermal Parameters for the Os Atoms

atom	B_{11}^b	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.939	2.656	2.999	-0.135	1.198	-0.025
Os(2)	3.811	2.549	2.582	-0.040	1.340	-0.349
Os(3)	3.230	2.971	2.894	-0.300	1.492	-0.505

^a The final anisotropic thermal parameters for the osmium atoms are given in the lower part of the table. ^b The form of the anisotropic thermal parameter is $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances (Å) with Esd's for $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)(}t\text{-C}_4\text{H}_9\text{))Os}_3(\text{CO})_{10}$

Os(1)-Os(2)	2.859 (1)	C(1)-O(1)	1.125 (1)
Os(1)-Os(3)	2.867 (1)	C(2)-O(2)	1.131 (11)
Os(2)-Os(3)	2.812 (1)	C(3)-O(3)	1.192 (10)
Os(1)-C(1)	1.956 (9)	C(4)-O(4)	1.116 (10)
Os(1)-C(2)	1.948 (11)	C(5)-O(5)	1.179 (10)
Os(1)-C(3)	1.861 (9)	C(6)-O(6)	1.140 (12)
Os(1)-C(4)	1.957 (9)	C(7)-O(7)	1.130 (9)
Os(2)-C(5)	1.860 (9)	C(8)-O(8)	1.153 (10)
Os(2)-C(6)	1.884 (12)	C(9)-O(9)	1.167 (10)
Os(2)-C(7)	1.956 (8)	C(10)-O(10)	1.126 (10)
Os(2)-C(11)	2.066 (8)	C(11)-N	1.298 (10)
Os(3)-C(8)	1.948 (9)	N-C(12)	1.514 (11)
Os(3)-C(9)	1.889 (10)	C(12)-C(13)	1.549 (13)
Os(3)-C(10)	1.927 (11)	C(12)-C(14)	1.516 (14)
Os(3)-C(11)	2.043 (8)	C(12)-C(15)	1.508 (13)

Table IV. Bond Angles (deg) with Esd's for $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)(}t\text{-C}_4\text{H}_9\text{))Os}_3(\text{CO})_{10}$

Os(1)-Os(2)-Os(3)	60.73 (1)	Os(1)-Os(3)-C(10)	169.8 (3)
Os(2)-Os(1)-Os(3)	58.83 (1)	Os(1)-Os(3)-C(11)	80.2 (2)
Os(1)-Os(3)-Os(2)	60.44 (1)	Os(2)-Os(3)-C(8)	114.5 (3)
Os(2)-Os(1)-C(1)	86.8 (3)	Os(2)-Os(3)-C(9)	136.1 (3)
Os(2)-Os(1)-C(2)	93.7 (3)	Os(2)-Os(3)-C(10)	109.5 (3)
Os(2)-Os(1)-C(3)	160.2 (3)	Os(2)-Os(3)-C(11)	47.2 (2)
Os(2)-Os(1)-C(4)	85.3 (2)	C(8)-Os(3)-C(9)	94.3 (4)
Os(3)-Os(1)-C(1)	84.1 (2)	C(8)-Os(3)-C(10)	94.4 (4)
Os(3)-Os(1)-C(2)	152.3 (3)	C(8)-Os(3)-C(11)	161.7 (3)
Os(3)-Os(1)-C(3)	101.3 (3)	C(9)-Os(3)-C(10)	99.9 (4)
Os(3)-Os(1)-C(4)	89.1 (2)	C(9)-Os(3)-C(11)	100.3 (4)
C(1)-Os(1)-C(2)	91.2 (4)	C(10)-Os(3)-C(11)	93.9 (4)
C(1)-Os(1)-C(3)	91.9 (4)	Os(1)-C(1)-O(1)	175.5 (8)
C(1)-Os(1)-C(4)	171.4 (4)	Os(1)-C(2)-O(2)	175.5 (9)
C(2)-Os(1)-C(3)	106.1 (4)	Os(1)-C(3)-O(3)	178.1 (8)
C(2)-Os(1)-C(4)	92.5 (4)	Os(1)-C(4)-O(4)	176.8 (8)
C(3)-Os(1)-C(4)	94.6 (4)	Os(2)-C(5)-O(5)	176.9 (8)
Os(1)-Os(2)-C(5)	90.3 (3)	Os(2)-C(6)-O(6)	176.9 (9)
Os(1)-Os(2)-C(6)	173.0 (3)	Os(2)-C(7)-O(7)	177.1 (8)
Os(1)-Os(2)-C(7)	87.9 (2)	Os(3)-C(8)-O(8)	179.3 (9)
Os(1)-Os(2)-C(11)	80.1 (2)	Os(3)-C(9)-O(9)	177.0 (8)
Os(3)-Os(2)-C(5)	134.8 (2)	Os(3)-C(10)-O(10)	174.7 (9)
Os(3)-Os(2)-C(6)	112.3 (3)	Os(2)-C(11)-N	130.1 (6)
Os(3)-Os(2)-C(7)	116.2 (2)	Os(3)-C(11)-N	143.3 (6)
Os(3)-Os(2)-C(11)	46.5 (2)	Os(3)-C(11)-Os(2)	86.4 (3)
C(5)-Os(2)-C(6)	95.1 (4)	C(11)-N-C(12)	133.5 (7)
C(5)-Os(2)-C(7)	94.5 (4)	N-C(12)-C(13)	110.6 (7)
C(5)-Os(2)-C(11)	98.3 (3)	N-C(12)-C(14)	105.4 (8)
C(6)-Os(2)-C(7)	96.0 (4)	N-C(12)-C(15)	109.7 (7)
C(6)-Os(2)-C(11)	94.8 (4)	C(13)-C(12)-C(14)	111.4 (8)
C(7)-Os(2)-C(11)	162.5 (3)	C(13)-C(12)-C(15)	110.8 (8)
Os(1)-Os(3)-C(8)	89.0 (2)	C(14)-C(12)-C(15)	108.8 (8)
Os(1)-Os(3)-C(9)	89.5 (3)		

cluster of three osmium atoms. The osmium-osmium distances are Os(1)-Os(2) = 2.859 (1) Å, Os(1)-Os(3) = 2.867 (1) Å, and Os(2)-Os(3) = 2.812 (1) Å and are typical of the distances found in numerous triosmium carbonyl clusters.³⁻¹⁰ The shortest distance occurs for the bond which contains the μ -iminyl ligand (C=N(H)(*t*-C₄H₉)). A very similar bond shortening was observed in the compounds $(\mu\text{-H})(\mu\text{-}\eta^1\text{-CHCH}_2\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5))\text{Os}_3(\text{CO})_{10}$ ⁷ and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}\text{(CHCH=NEt}_2\text{)}$ ⁸ which also contain a single carbon atom bridging an osmium-osmium bond. Ten linear carbonyl groups with Os-C-O angles ranging from 174.7 to 179.3° are distributed such that Os(1) contains four while Os(2) and Os(3) have three each.

The most interesting feature is the presence of a $\mu\text{-}\eta^1\text{-C=N(H)(}t\text{-C}_4\text{H}_9\text{)}$ ligand which symmetrically bridges the Os(2)-Os(3) bond through the single atom C(11). The osmium-carbon distances are Os(2)-C(11) = 2.066 (8) Å and Os(3)-C(11) = 2.043 (8) Å. The presence of a hydrogen atom on the nitrogen atom was confirmed through infrared spectroscopy which showed a prominent absorption at 3295 cm⁻¹. The iminyl bond C(11)-N is formally double, and this for-

Table V. Unit-Weighted Least-Squares Planes for $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)(}t\text{-C}_4\text{H}_9\text{))Os}_3(\text{CO})_{10}$

plane	atoms	dist, Å	atoms	dist, Å	
1	Os(1)	0.00	C(3) ^a	0.02 (2)	
	Os(2)	0.00	C(4) ^a	1.95 (2)	
	Os(3)	0.00	C(5) ^a	1.10 (2)	
	C(11) ^a	1.45 (2)	C(6) ^a	0.01 (2)	
	N ^a	2.67 (2)	C(7) ^a	-1.66 (2)	
	C(12) ^a	3.77 (2)	C(8) ^a	-1.70 (2)	
	C(1) ^a	-1.95 (2)	C(9) ^a	1.04 (2)	
	C(2) ^a	-0.13 (2)	C(10) ^a	-0.06 (2)	
	2	Os(2)	-0.006 (1)	C(12) ^a	-0.06 (2)
		Os(3)	-0.008 (1)	Os(1) ^a	-2.385 (1)
C(11)		0.03 (2)	C(13) ^a	-1.02 (3)	
N		-0.02 (2)	C(14) ^a	-0.53 (3)	
			C(15) ^a	1.33 (3)	

Equations of the Planes: $Ax + By + Cz - D = 0$

plane	A	B	C	D
1	-0.3738	0.3499	-0.8590	-1.6307
2	-0.7728	-0.5900	-0.2339	-4.7549

Dihedral Angle between Planes 1 and 2: 73.5°

^a These atoms were not used in defining the plane.

Table VI

Intermolecular Contacts for $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N(H)(}t\text{-C}_4\text{H}_9\text{))Os}_3(\text{CO})_{10}$ under 3.3 Å

atoms	dist, Å	atoms	dist, Å
C(1)-O(7) ^I	3.12 (1)	O(4)-O(7) ^V	3.02 (1)
O(1)-O(5) ^I	3.23 (1)	O(5)-O(5) ^{IV}	3.01 (1)
O(1)-O(6) ^{II}	3.24 (1)	O(6)-O(8) ^{VI}	3.04 (1)
O(1)-C(7) ^I	3.24 (1)	O(6)-C(10) ^{VII}	3.19 (1)
O(1)-O(7) ^I	3.13 (1)	O(8)-C(9) ^{VIII}	3.15 (1)
C(2)-O(7) ^I	3.28 (1)	O(8)-O(9) ^{VIII}	3.17 (1)
O(2)-O(4) ^{III}	3.23 (1)	O(8)-C(10) ^{VIII}	3.22 (1)
O(4)-O(5) ^{IV}	3.09 (1)	O(8)-O(10) ^{VIII}	3.20 (1)

Symmetry Transforms

I	$1/2 - x, y - 1/2, 1/2 - z$	V	$x - 1/2, 1/2 - y, z - 1/2$
II	$x, y - 1, z$	VII	$x, y + 1, z$
III	$-x, -y, -z$	VIII	$1 - x, 1 - y, -z$
IV	$-x, 1 - y, -z$		

mulation is supported by the short internuclear distance at 1.298 (10) Å. This distance is similar to those found in the related ruthenium complex $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C=N}(\text{CH}_3)_2\text{Ru}_3(\text{CO})_{10}$, C=N = 1.280 (6) Å,¹⁰ and the cation $(\text{C}_6\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-}\eta^1\text{-C=N(H)(CH}_3\text{)})$, C=N = 1.28 (1) Å, each of which contains a carbon-bonded η^1 -iminyl ligand bridging two metal atoms. The angle C(11)-N-C(12) of 133.5 (7)° is significantly larger than the corresponding angles of 122.2-123.7 (5)° and 124 (1)° found in the ruthenium¹⁰ and iron¹¹ complexes, respectively. However, in each of the latter cases, the alkyl substituents were methyl groups. In the present case, the increased angle could result from steric repulsion effects caused by the much larger *tert*-butyl group. The plane of the iminyl ligand is nearly perpendicular to the plane of the triosmium triangle. The dihedral angle is 73°. Least-squares planes are listed in Table V.

The compound contains a bridging hydride ligand as indicated by ¹H NMR spectroscopy.¹ Although this ligand was not observed crystallographically, its position along the Os(2)-Os(3) bond on the opposite side of the metal triangle from the iminyl ligand is strongly indicated by the presence of a large cavity circumscribed by the four carbonyl groups C(6)-O(6), C(7)-O(7), C(8)-O(8), and C(10)-O(10). The bridging hydride ligand in the ruthenium complex was observed in the analogous position.¹¹

The possibility that $\mu\text{-}\eta^1$ -iminyl ligands may be very strongly trans directing was suggested by the observation that the

metal-carbon bond distances to the carbonyl ligands trans to the iminyl ligand in the ruthenium complex were unusually long.¹⁰ We find that the analogous distances in this osmium complex Os(2)-C(7) and Os(3)-C(8) are also the longest for those carbonyl ligands that are attached to osmium atoms Os(2) and Os(3) (cf. Table III).

There are no unusually short intermolecular contacts. The shortest contacts are between oxygen atoms of the carbonyl ligands, O(5)...O(5) = 3.007 (13) Å and O(4)...O(7) = 3.022 (10) Å. (cf. Table VI).

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Registry No. (μ -H)(μ - η^1 -C=N(H)(*t*-C₄H₉))Os₃(CO)₁₀, 70377-88-7.

Supplementary Material Available: Structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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Metal-Metal Interactions in One Dimension. 1. Synthesis and Structural and Spectroscopic Properties of Dithioacetic Acid Derivatives of Palladium(II)

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Three distinct dithioacetato complexes of Pd(II) have been prepared and characterized. They correspond to a common 2:1 ligand to metal ratio but display different structures and spectra. The structures of two derivatives have been solved by X-ray methods. They contain approximately square-planar chromophores, stacking in columns, with the Pd atoms directly over each other. In one structure mononuclear and binuclear units alternate along the *a* axis (monoclinic space group *C2/c*) with metal-repeat separations of 2.754 (1) (in the dimer) and 3.399 (1) Å. The other structure consists of dimers only, stacking along the fourfold axes (tetragonal space group *P4/ncc*) with CS₂ molecules incorporated between different columns. The intra- and interdimer Pd-Pd distances are 2.738 (1) and 3.257 (1) Å, respectively. Monomeric and dimeric molecules coexist not only in the solid state but also in solution, where they are found to be of approximately the same stability, and in the vapor. Vibrational, NMR, vis-UV, and mass spectral data are reported and discussed.

Introduction

One-dimensional inorganic complexes¹ and multinuclear d⁸-d¹⁰ metal ion complexes with sulfur-containing ligands² are receiving considerable attention. One reason these materials are so interesting is that they display a great variety of metal-metal interactions and structural types with consequent wide variations in the physical properties. There is no better example than the metal-chain compounds which span the entire range from localized to collective behavior.³ This outlines the perspective of a systematic chemical control of the unique electronic properties of such systems. Clearly, to understand the important chemical variables to be controlled in inorganic synthesis, in order to construct new molecular systems with specific amounts of a certain physical property associated with them, an adequate theoretical insight into the optical, magnetic, and electron-transport properties of known species is required. Our present understanding of the metal-metal interactions, mainly based on theoretical models of the solid state and MO theories, appears to have poor predictive value when applied to inorganic synthesis and in only few cases has resulted in the enunciation of coherent sets of chemical criteria.^{1,4} The development of experimental chemical trends, therefore, appears useful. In this regard, the dithioacetic acid derivatives of palladium(II), reported in the present paper, have several points of interest. Quite unusual in transition-metal chemistry with sulfur ligands,⁵ several forms

having the same ligand to metal ratio but different structures and physical properties can be isolated. Linear metal chains with short M-M contacts are present in the structures which are the result of a one-dimensional arrangement of either dimeric or dimeric and monomeric units. The coexistence of dimers and monomers is not confined to the solid state, and they are found to be of comparable stability when isolated in solution. A preliminary report of this work has appeared.⁶

Experimental Section

Reagents. Dithioacetic acid (hereafter dtaH) was prepared according to known procedures.^{7,8} K₂PdCl₄ was used as obtained from ICN Pharmaceutical, Inc. Plainview, N.Y.

Preparation of Complexes. Form A. Solid K₂PdCl₄ (2 g, 6 mmol) was added to a solution of dtaH (1.1 g, 12 mmol) in 50 mL of diethyl ether, in the air. After ~48 h of stirring at room temperature, the reaction mixture was filtered. The brick red solid was treated with two 100-mL portions of boiling benzene and the resulting red solution filtered. A small amount of dark, insoluble residue was discarded. Upon cooling of the benzene solution at room temperature, brick-red monoclinic crystals, of composition Pd(CH₃CS₂)₂, were obtained: 1.31 g, 75% yield, referred to original palladium. Anal. Calcd for Pd(CH₃CS₂)₂: C, 16.64; H, 2.10; S, 44.41; Pd, 36.85. Found: C, 16.98; H, 2.20; S, 44.30; Pd, 37.67.

Form B. Upon dissolution of A in carbon disulfide at room temperature, a red solution was obtained which almost instantly became turbid, and, in a few minutes, a green microcrystalline material separated. The residual solution was red. Tetragonal crystals of larger size, suitable for X-ray diffraction studies, were obtained either upon addition of carbon disulfide to a benzene solution (~1:1 volumes) of A or upon slowly cooling (~3 h) a saturated 1:3 carbon di-

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