

Table V. Intermolecular Contacts <3.25 Å for $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$

contact	symmetry operation ^a	distance, Å
O(11)··O(31)	3-1-1-1	3.19 (4)
O(13)··O(32)	1 1 0 0	3.04 (5)
O(14)··O(33)	4-1 0 0	3.21 (5)
O(14)··C(2)	2 0-1 0	3.24 (6)
O(22)··O(42)	2 0 0 0	3.25 (6)
O(23)··O(31)	1 1 0 0	3.23 (5)
O(23)··C(12)	3 0 0-1	3.19 (7)
O(31)··O(11)	3-1 0-1	3.19 (4)
O(31)··O(23)	1-1 0 0	3.23 (5)
O(32)··O(13)	1-1 0 0	3.04 (5)
O(33)··O(14)	4-1 0-1	3.21 (5)
O(33)··O(41)	3-1-1-1	2.94 (5)
O(41)··O(33)	3-1 0-1	2.94 (5)
O(41)··O(42)	2-1 0 0	2.90 (6)
O(41)··C(33)	3-1 0-1	3.21 (6)
O(42)··O(41)	2 0 0 0	2.90 (6)
C(2)··O(14)	2-1-1 0	3.24 (6)
C(12)··O(23)	3 0-1-1	3.19 (7)
C(33)··O(41)	3-1-1-1	3.21 (6)

^a The transformation of the second atom is given by a four-digit code. The first represents the equipoint (see below), while the second through fourth represent the addition (+) or subtraction (-) of unit cell vectors *a*, *b*, and *c*. The transformation code is as follows: 1, *x*, *y*, *z*; 2, $1/2 + x$, $1/2 - y$, $-z$; 3, $-x$, $1/2 + y$, $1/2 - z$; 4, $1/2 - x$, $-y$, $1/2 + z$.

hydride ligand lies in, or close to, the Os(1)-Os(2)-Os(3) plane (i.e., case I is indicated).

Finally, we note that a peak corresponding to the predicted position of the bridging hydride ligand was found in the final difference-Fourier map at $x = -0.370$, $y = 0.126$, $z = -0.188$. Attempts to include this atom in the least-squares refinement process were unsuccessful—the positional parameters failed

to converge and the isotropic thermal parameter became negative. The hydride ligand is, nevertheless, shown in all of the figures in its predicted position, to add clarity.

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Registry No. $(\mu\text{-H})\text{Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$, 68796-10-1.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Part 9: M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **18**, 161 (1979).
- (2) M. R. Churchill, F. J. Hollander, J. R. Shapley, and D. S. Foose, *J. Chem. Soc., Chem. Commun.*, 534 (1978).
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- (4) "Syntex XTL Operations Manual", 2nd ed., Syntex Analytical Instruments, Cupertino, Calif., 1976.
- (5) M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **17**, 1957 (1978).
- (6) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974: (a) pp 99-101; (b) pp 149-150.
- (7) The small percentage difference in scattering between W(0) and Os(0) [$Z(\text{W}) = 74$, $Z(\text{Os}) = 76$, $\Delta Z = 2$ electrons or 2.7% of $Z(\text{mean})$] makes differentiation between W and Os infeasible solely on the basis of crystallographic techniques.
- (8) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **16**, 878 (1977).
- (9) M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, **15**, 1843 (1976); see, particularly, the discussion on pages 1848-1852.
- (10) The term "electronically symmetrical" is coined in order to describe the situation in an $\text{M}(\mu\text{-CO})\text{M}'$ bridge where the M-CO and M'-CO distances are inequivalent but the M-CO and M'-CO bond orders are equivalent.
- (11) Assuming that a cyclopentadienyl group provides five electrons, a terminal carbonyl group provides two electrons, a bridging carbonyl group provides one electron to each metal atom, a bonded metal atom provides one electron, and a bridging hydride ligand shares one electron between the two bridged metal atoms.
- (12) M. R. Churchill, *Adv. Chem. Ser.*, No. 167, 36-60 (1978).

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 11. Crystal Structure and Molecular Geometry of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{N}^+\text{Et}_2)$, a Species Containing a μ_2 -Hydride Ligand and a μ_2 -1,3-Dipolar $>\text{C}^-\text{HCH}=\text{N}^+\text{Et}_2$ Ligand

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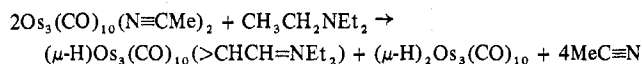
The species $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{N}^+\text{Et}_2)$, previously synthesized by Shapley and co-workers from $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and triethylamine, has been unambiguously identified and characterized via a full three-dimensional single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 7.676$ (2) Å, $b = 18.392$ (5) Å, $c = 16.026$ (4) Å, $\beta = 97.57$ (2)°, $V = 2243$ (1) Å³, and $\rho(\text{calcd}) = 2.813$ g cm⁻³ for mol wt 949.883 and $Z = 4$. Diffraction data [$3.5^\circ \leq 2\theta \leq 35^\circ$; Mo K α radiation] were collected with a Syntex $P2_1$ automated diffractometer, using graphite-monochromatized radiation. The structure was solved via direct methods (i.e., MULTAN), difference-Fourier techniques, and least-squares refinement techniques, the resulting discrepancy indices being $R_F = 5.03\%$ and $R_{wF} = 4.59\%$ for 1434 independent reflections. The molecule contains a triangular arrangement of osmium atoms. Os(1) and Os(2) are each associated with three carbonyl ligands, while Os(3) is linked to four such ligands. In addition, Os(1) and Os(2) are mutually bridged by a hydride ligand (which was located and refined in the course of the structural analysis) and by a 1,3-dipolar $>\text{C}^-\text{HCHN}^+\text{Et}_2$ ligand. Osmium-osmium bond lengths are Os(1)-Os(2) = 2.785 (2) Å, Os(1)-Os(3) = 2.870 (2) Å, and Os(2)-Os(3) = 2.866 (2) Å. Whereas a single unsupported μ_2 -hydride ligand normally causes a lengthening of its bridged metal-metal vector, this effect is counterbalanced by the (M-M) bond-shortening influence of the $>\text{C}^-\text{HCHN}^+\text{Et}_2$ ligand in the present molecule. Osmium-(μ_2 -hydride) distances are Os(1)-H(br) = 1.76 (15) Å and Os(2)-H(br) = 1.82 (17) Å, the angle Os(1)-H(br)-Os(2) being 102 (8)°.

Introduction

We have been interested in polynuclear osmium carbonyl hydride complexes for some time and have previously reported detailed X-ray crystallographic studies of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$,¹ $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}_2\text{PMe}_2\text{Ph})$,² $(\mu\text{-H})(\text{H})$ -

$\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)$,³ $\text{HOs}_3\text{Re}(\text{CO})_{15}$,⁴ $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$,⁵ $(\mu\text{-H})\text{Os}_3(\text{CO})_8[\text{C}(\text{O}-)\text{C}(\text{CHMe})\text{CHCHC}(\text{Et})_2]$,⁶ $(\mu\text{-H})_2\text{-Os}_3\text{Re}_2(\text{CO})_{20}$,⁷ $(\mu\text{-H})\text{Os}_3(\text{CO})_9[\text{-CHC}(\text{=O})\text{CH}=\text{C}(\text{Et})\text{C}(\text{=CHMe})]$,⁸ $(\mu\text{-H})_3\text{Os}_3\text{W}(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$,⁹ and $(\mu\text{-H})\text{-Os}_3\text{W}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$.¹⁰

Scheme I



Recently Shapley and co-workers¹¹ have shown that $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ reacts with triethylamine yielding equimolar quantities of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCHNEt}_2)$. (See Scheme I.) The latter of these species has now been studied via a three-dimensional X-ray structural analysis; our results, which indicate that the molecule contains a 1,3-dipolar bridging $>\text{C}^-\text{HCH}=\text{N}^+\text{Et}_2$ ligand, are given below.

Experimental Section

A. Data Collection. Yellow crystals of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCHNEt}_2)$ were provided by Professor J. R. Shapley of the University of Illinois at Urbana-Champaign. The crystal selected for data collection was 0.2 mm in length and had an approximately rectangular cross section (0.1 mm \times 0.08 mm). It was mounted on a glass fiber which was then inserted into a brass pin with beeswax and placed on a eucentric goniometer.

Preliminary precession photographs indicated $2/m$ Laue symmetry. The systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$ uniquely define the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 ; No. 14].

The crystal was then transferred to a Syntex $P2_1$ automated diffractometer under the control of a Data General Nova 1200 computer. The crystal was accurately centered and the unit cell parameters and orientation matrix were determined by a method previously described in detail.¹²

A series of θ - 2θ and ω scans was recorded graphically to determine the crystal quality. The customary θ - 2θ scan method of data collection was found to be acceptable. The data were collected for a hemisphere of reciprocal space using Mo $K\alpha$ radiation (50 kV and 20 mA) with a highly oriented graphite monochromator in a parallel geometry (assumed to be 50% perfect). Details of the data collection are listed in Table I.

The stability of the system was monitored by measuring the intensity of three strong reflections after every 47 data. No significant fluctuations were found.

All data were corrected for the effects of absorption [$\mu(\text{Mo } K\alpha) = 180.1 \text{ cm}^{-1}$] by an empirical method. Several high-intensity reflections ($I/\sigma(I) > 50$), in close-to-axial locations ($\chi_0 = 60$ - 85°) and distributed over the 2θ range used in data collection, were measured at 10° intervals of ψ from 0 to 350° . Each reflection was used to define a normalized absorption curve vs. ϕ , corrected for ω and χ . The two curves bracketing the 2θ value of the reflection considered were interpolated both in 2θ and ϕ to obtain the absorption correction. Reflections used are listed in Table I. All curves were mutually consistent, with similar profiles and with maxima and minima at common values.

Symmetry-absent reflections were examined and deleted, as were the check reflections (yielding 3108 data). Next, the data were averaged according to $2/m$ symmetry, resulting in 1434 independent reflections.

A correction was applied for Lorentz and polarization factors, and the intensities were reduced to unscaled, observed structure factor amplitudes.

B. Solution and Refinement of Structure. Initial portions of the structure determination were performed using the Syntex XTL System.¹³ Refinement of the structure was performed on a CDC 6600-Cyber 173 computer using the following programs: LSHF (full-matrix least-squares refinement and structure factor calculations, by B. G. DeBoer), JMDAP (Fourier synthesis, derived from the program FORDAP by A. Zalkin), HAICH (calculation of idealized atom positions, by B. G. DeBoer), STAN 1 (distances and angles, with esd's, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal ellipsoid plotting program, by C. K. Johnson).

The atomic scattering factors for neutral osmium, carbon, nitrogen, oxygen, and hydrogen were taken from the compilation of Cromer and Waber.^{14a} Both real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for nonhydrogen atoms, using the values of Cromer and Liberman.^{14b}

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights used were obtained from counting

Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$

(A) Crystal Data	
crystal system: monoclinic	$V = 2243 (1) \text{ \AA}^3$
space group: $P2_1/c$ [C_{2h}^2 ; No. 14]	$T = 22^\circ \text{C}$
$a = 7.676 (2) \text{ \AA}^a$	$Z = 4$
$b = 18.392 (5) \text{ \AA}^a$	mol wt 949.883
$c = 16.026 (4) \text{ \AA}^a$	$\rho(\text{calcd}) = 2.813 \text{ g cm}^{-3}$
$\beta = 97.57 (2)^\circ$	
(B) Intensity Data	
radiation: Mo $K\alpha$ (λ 0.710 730 \AA)	
monochromator: highly oriented graphite	
reflections measd: $+h, \pm k, \pm l$	
max 2θ : 35.0°	
min 2θ : 3.5°	
scan type: θ - 2θ	
scan speed: $4.0^\circ/\text{min}$	
scan range: symmetrical, $[2.2 + \Delta(\alpha_2 - \alpha_1)]^\circ$	
reflections collected: 3405 total, 1434 independent	
standard reflections: 3 measd every 47 reflections; max deviations from the mean were 4.77% for 008, 3.88% for 0,10,0, 4.97% for 400; there was no significant decay	
absorption coefficient: $\mu = 180.1 \text{ cm}^{-1}$	
reflections used for empirical absorption correction ^b (hkl , 2θ , $I_{\text{max}}/I_{\text{min}}$): $1\bar{1}0$, 5.78, 1.32; $2\bar{1}1$, 11.54, 1.23; 213, 14.16, 1.34; 311, 16.76, 1.21; 400, 21.49, 1.17; 424, 25.47, 1.28; 542, 29.53, 1.25; 600, 32.48, 1.20	
data averaging: $R(I) = 7.27\%$ for 1371 reflections with two or more contributors	

^a Based upon a least-squares fit to the setting angles of the unresolved Mo $K\alpha$ components of 24 reflections of the forms {008}, {019}, {0,10,0}, {137}, {257}, {391}, {402}, and {400}, all with $2\theta = 20$ - 26° . ^b For details of the experimental absorption correction, see M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 16, 2655 (1977).

statistics, modified by incorporating a term involving p , the "ignorance factor" (see eq 1). The final value for p was 0.040.

$$w = \{[\sigma_c(F_o)]^2 + [p|F_o|]^2\}^{-1} \quad (1)$$

The positions of the three osmium atoms were determined by direct methods (i.e., using MULTAN). Full-matrix least-squares refinement of the scale factor along with positional and isotropic thermal parameters of the osmium atoms led to convergence with $R_F = 14.9\%$; the use of anisotropic thermal parameters for the osmium atoms lowered the discrepancy indices to $R_F = 13.0\%$, $R_{wF} = 16.4\%$, and GOF = 4.20. A Fourier synthesis then led to the location of all remaining nonhydrogen atoms. Continued full-matrix least-squares refinement of all nonhydrogen atom positional parameters as well as anisotropic thermal parameters for all osmium and oxygen atoms and isotropic thermal parameters for the nitrogen and carbon atoms gave $R_F = 5.14\%$, $R_{wF} = 4.73\%$, and GOF = 0.946 (no data were omitted).

A difference-Fourier synthesis based on all data and upon the phasing of all nonhydrogen atoms yielded the position of the μ_2 -bridging hydride. (This was the strongest feature, a peak of height 0.94 e \AA^{-3} .) The position of H(1), the hydrogen atom bound to the μ_2 -bridging carbon atom of the $\text{CHCH}=\text{NEt}_2$ ligand, was also clearly revealed. There were also some indications of the locations of other hydrogen atoms on the $\text{CHCH}=\text{NEt}_2$ ligand. However, due to the relatively large thermal parameters of the carbon atoms to which they are bound, the positions of the hydrogens were not all unequivocally established. The positions of these hydrogen atoms were calculated ($d(\text{C-H}) = 0.95 \text{ \AA}$)¹⁵ and included in our model in fixed positions. Their isotropic thermal parameters (as well as the thermal parameter for H(1)) were also fixed at $B(\text{H}) = [B(\text{C}) + 1.0] \text{ \AA}^2$.

Full-matrix least-squares refinement was continued on the positional parameters of all nonhydrogen atoms, H(br) and H(1), the anisotropic thermal parameters of the osmium and oxygen atoms, and the isotropic thermal parameters of the nitrogen and carbon atoms. The final discrepancy indices at convergence (i.e., all shifts were $<0.2\sigma$ and maximum positional shifts were $<0.0004 \text{ \AA}$) were $R_F = 5.03\%$, $R_{wF} = 4.59\%$, and GOF = 0.920.

The best model seemed to be attained using H^- scattering factors for H(br) and fixing $B(\text{H}(\text{br})) = 4.0 \text{ \AA}^2$.

The final positional correlation matrix was used in STAN 1 for calculating esd's on interatomic distances and angles.

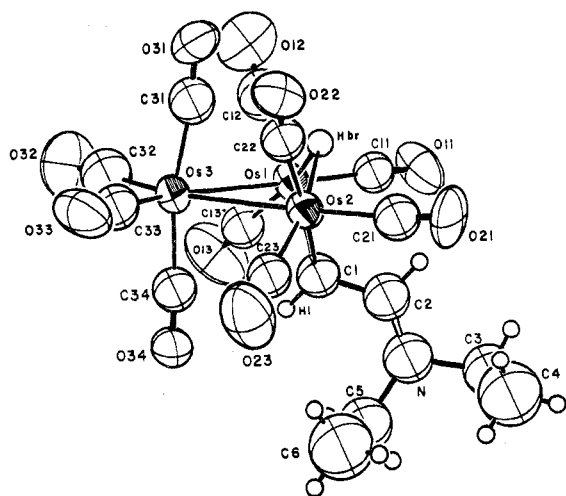


Figure 1. Labeling of atoms in the $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$ molecule. [ORTEP-II diagram; 50% ellipsoids for all atoms other than hydrogens.]

The function $\sum w(|F_o| - |F_c|)^2$ showed no appreciable dependence either upon $(\sin \theta)/\lambda$ or upon $|F_o|$; the weighting scheme is thus acceptable. There was no evidence for secondary extinction.

The final difference-Fourier synthesis showed no structurally significant features ($\rho(\text{max}) = 0.88 \text{ e } \text{\AA}^{-3}$) and the analysis was declared complete. Final positional and thermal parameters for the atoms are given in Tables II and III.

Results and Discussion

The crystal consists of discrete molecular units of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$ which are mutually separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. The atomic numbering scheme is shown in Figure 1 and a stereoscopic view of the molecular structure is presented as Figure 2. Interatomic distances and angles (and their esd's) are collected in Tables IV and V. Important least-squares planes and atomic deviations therefrom are listed in Table VI.

As shown in Figure 3, the $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}$ portion of the molecule has approximate C_3 symmetry which is broken by slight rotations of the carbonyl ligands C(31)–O(31) and C(34)–O(34) from truly vertical positions above and below the triosmium plane. The bridging $\text{>CHCH}=\text{NEt}_2$ ligand causes a further major violation of the potential molecular C_3 symmetry.

The $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$ molecule is based upon a triangular cluster of osmium atoms, in which Os(3) is linked to four terminal carbonyl ligands and Os(1) and Os(2) are each associated with three such ligands and are, in addition, mutually bridged both by a hydride ligand and by a $\text{CHCH}=\text{NEt}_2$ ligand (which is derived by triple deprotonation of triethylamine).

The triosmium cluster defines an isosceles triangle in which the two nonbridged osmium–osmium vectors [Os(1)–Os(3) = 2.8701 (15) \AA and Os(2)–Os(3) = 2.8664 (15) \AA] are equivalent ($\Delta/\sigma = 1.7$) and are comparable to the osmium–osmium bond distance found in the parent molecule, $\text{Os}_3(\text{CO})_{12}$ (Os–Os(average) = 2.877 (3) \AA).¹

While a single, unsupported, μ_2 -hydride ligand is known to cause a lengthening of the bridged metal–metal vector from its normal (i.e., nonbridged) bond length,^{16,17} the doubly bridged Os(1)–Os(2) vector is 2.7849 (16) \AA in length and is decreased by 0.0834 (26) \AA from the average nonbridged osmium–osmium distance of 2.8683 (21) \AA in the parent molecule. This net shortening of the M–M distance in a $\text{M}(\mu\text{-H})(\mu\text{-C})\text{M}$ system appears to be general. Similar situations have previously been encountered in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}_2\text{PMe}_2\text{Ph})_2$ [Os–Os(bridged) = 2.8002 (6) \AA ,

Table II. Final Positional Parameters with Esd's^a for $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$

atom	x	y	z	B, \AA^2
Os(1)	0.26907 (12)	0.48404 (7)	0.31886 (6)	4.57 ^b
Os(2)	0.22862 (12)	0.60190 (7)	0.20953 (7)	4.50
Os(3)	-0.05714 (12)	0.50229 (7)	0.21159 (6)	4.59
C(11)	0.4899 (34)	0.4767 (16)	0.3805 (16)	4.9 (6)
O(11)	0.6163 (20)	0.4690 (14)	0.4235 (10)	8.1
C(12)	0.2853 (44)	0.3894 (24)	0.2747 (22)	7.8 (10)
O(12)	0.2964 (29)	0.3370 (15)	0.2418 (13)	8.9
C(13)	0.1348 (35)	0.4483 (18)	0.4061 (18)	5.8 (7)
O(13)	0.0601 (27)	0.4311 (17)	0.4559 (14)	11.2
C(21)	0.4339 (37)	0.6628 (19)	0.2137 (16)	6.3 (7)
O(21)	0.5515 (25)	0.6978 (14)	0.2063 (13)	9.7
C(22)	0.2186 (32)	0.5823 (17)	0.0944 (18)	5.7 (7)
O(22)	0.2352 (21)	0.5730 (11)	0.0264 (12)	6.6
C(23)	0.0634 (36)	0.6782 (19)	0.1865 (17)	5.8 (7)
O(23)	-0.0361 (27)	0.7230 (15)	0.1744 (16)	11.1
C(31)	0.0660 (36)	0.4530 (19)	0.1336 (18)	6.5 (8)
O(31)	0.1219 (23)	0.4199 (12)	0.0814 (12)	7.3
C(32)	-0.1777 (41)	0.4157 (22)	0.2435 (20)	8.0 (8)
O(32)	-0.2458 (31)	0.3661 (16)	0.2672 (17)	12.2
C(33)	-0.2306 (36)	0.5391 (18)	0.1330 (17)	6.1 (7)
O(33)	-0.3331 (25)	0.5644 (15)	0.0798 (13)	9.3
C(34)	-0.1331 (33)	0.5618 (19)	0.2959 (18)	5.9 (7)
O(34)	-0.1881 (19)	0.5975 (12)	0.3449 (11)	7.0
C(1)	0.2314 (33)	0.5972 (16)	0.3436 (16)	5.7 (6)
C(2)	0.3794 (34)	0.6332 (18)	0.3879 (17)	6.7 (7)
N	0.3803 (28)	0.6787 (17)	0.4484 (14)	7.6 (6)
C(3)	0.5691 (36)	0.7068 (20)	0.4982 (19)	8.4 (8)
C(4)	0.5770 (45)	0.7748 (25)	0.4607 (22)	12.5 (12)
C(5)	0.2194 (37)	0.7069 (21)	0.4893 (19)	8.8 (9)
C(6)	0.1195 (44)	0.7579 (25)	0.4348 (22)	12.6 (12)
H(br) ^c	0.346 (19)	0.516 (10)	0.228 (9)	2.0 ^d
H(1) ^e	0.132 (23)	0.593 (11)	0.381 (10)	6.7
H(2)	0.490	0.621	0.371	7.7
H(3a)	0.568	0.711	0.557	9.4
H(3b)	0.664	0.677	0.487	9.4
H(4a)	0.682	0.800	0.482	13.5
H(4b)	0.478	0.803	0.472	13.5
H(4c)	0.574	0.768	0.402	13.5
H(5a)	0.258	0.731	0.541	9.8
H(5b)	0.145	0.668	0.500	9.8
H(6a)	0.020	0.776	0.457	13.6
H(6b)	0.195	0.797	0.425	13.6
H(6c)	0.082	0.733	0.384	13.6

^a Esd's, shown in parentheses, are right-adjusted to the last digit of the preceding number. They are derived from the inverse of the least-squares matrix from the last cycle of refinement.

^b For the osmium and oxygen atoms, so-called "equivalent" isotropic thermal parameters are listed. The corresponding anisotropic thermal parameters are given in Table III. ^c The positions of H(br) and H(1) are taken from a difference-Fourier synthesis and subsequently refined. All other hydrogen atoms are in idealized positions. ^d The isotropic thermal parameter for H(br) was fixed at a value of 2.0 \AA^2 . For the other hydrogen atoms the isotropic thermal parameters were set as $B(\text{H}) = [B_{\text{equiv}}(\text{C}) + 1.0] \text{\AA}^2$. ^e The position for H(1) given here is that from the penultimate cycle of refinement. During the final cycle it was fixed.

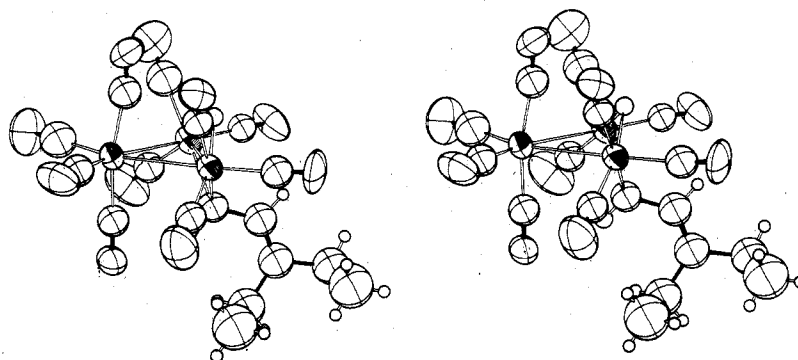
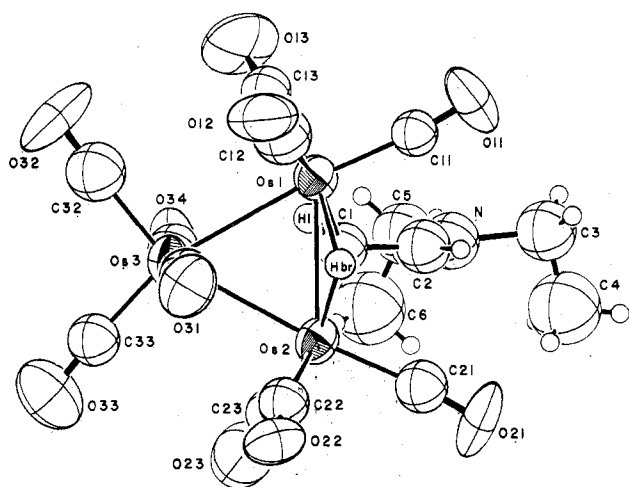
Os–Os(nonbridged) = 2.8688 (6) and 2.8729 (6) \AA] and in $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\text{C}=\text{NMe}_2)$ ¹⁶ [Ru–Ru(bridged) = 2.8007 (10) \AA (average) and Ru–Ru(nonbridged) = 2.8280 (25) \AA (average)]. We should also note that, in general, M–M bond lengths for carbonyl-bridged bonds are shorter than the corresponding nonbridged M–M distances (e.g., Fe–Fe(bridged) = 2.558 (1) \AA and Fe–Fe(nonbridged) = 2.677 (2) and 2.683 (1) \AA in the $\text{Fe}_3(\text{CO})_{12}$ molecule).¹⁸ A ligand with a single carbon atom as its bridging atom appears, therefore, to exert a net bond-shortening influence on the bridged M–M vector and to counterbalance the bond-lengthening effect of a single μ_2 -hydride ligand.

The μ_2 -hydride ligand has been located directly. The Os(1)–H(br)–Os(2) angle is 102 (8) $^\circ$ and the individual osmium–hydrogen distances are Os(1)–H(br) = 1.76 (15) \AA and Os(2)–H(br) = 1.82 (17) \AA . The Os(1)–H(br)–Os(2)

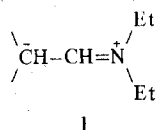
Table III. Final Anisotropic Thermal Parameters,^a with Esd's,^b for the Osmium and Oxygen Atoms in (μ -H)Os₃(CO)₁₀(CHCH=NEt₂)

atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Os(1)	3.85 (6)	5.62 (8)	4.38 (6)	0.19 (5)	1.07 (4)	0.24 (5)
Os(2)	4.00 (6)	4.47 (8)	5.24 (6)	-0.13 (5)	1.32 (4)	-0.21 (5)
Os(3)	3.51 (5)	5.29 (8)	5.07 (6)	-0.33 (5)	0.91 (4)	-0.64 (5)
O(11)	4.8 (9)	15.1 (20)	4.1 (9)	2.4 (10)	-0.3 (8)	-0.2 (10)
O(12)	12.2 (16)	6.8 (17)	7.7 (13)	-0.6 (13)	0.9 (10)	2.2 (12)
O(13)	10.9 (14)	14.6 (24)	9.4 (14)	0.3 (15)	6.7 (12)	3.3 (15)
O(21)	7.1 (11)	9.7 (18)	12.6 (16)	-5.5 (12)	2.3 (10)	-1.8 (13)
O(22)	7.8 (10)	6.0 (13)	6.4 (11)	0.5 (9)	2.7 (8)	1.1 (9)
O(23)	8.2 (12)	8.6 (19)	16.6 (20)	0.8 (13)	2.0 (12)	2.3 (15)
O(31)	8.2 (11)	5.9 (13)	7.8 (11)	-1.0 (10)	1.5 (9)	-2.2 (10)
O(32)	12.4 (16)	8.8 (19)	16.7 (21)	-5.3 (15)	6.5 (15)	1.6 (16)
O(33)	7.7 (11)	11.3 (19)	8.8 (13)	3.8 (12)	0.7 (10)	-0.8 (12)
O(34)	4.9 (8)	10.1 (17)	6.1 (10)	-0.2 (9)	1.0 (8)	-3.5 (10)

^a The anisotropic thermal parameters enter the equation for F_o in the form $\exp[-1/4[B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*]]$. ^b See footnote a to Table II.

**Figure 2.** Stereoscopic view of the (μ -H)Os₃(CO)₁₀(CHCH=NEt₂) molecule.**Figure 3.** The (μ -H)Os₃(CO)₁₀(CHCH=NEt₂) molecule, viewed 7° from the triosmium plane.

bridge makes an angle of 110.66° with the triosmium plane and an angle of 143.40° with the Os(1)-C(1)-Os(2) plane (see Figures 1 and 4). The CHCH=NEt₂ ligand is in a symmetrical bridging location (with Os(1)-C(1)-Os(2) = 80.6 (9)°) and is best described as a 1,3-dipolar species (see I). The



osmium-carbon bond lengths to this ligand are equivalent, individual values being Os(1)-C(1) = 2.15 (3) Å and Os(2)-C(1) = 2.16 (3) Å. The average value (2.16 (1) Å) is slightly shorter than the predicted Os-C(sp³) single-bond distance of 2.21 Å (based on $r(\text{Os}) = 1.439 \text{ \AA}$ and $r(\text{C}(\text{sp}^3)) = 0.77 \text{ \AA}$ ¹⁹) but is equivalent to the value of 2.161 (17) Å

Table IV. Intramolecular Distances with Esd's (Å) for (μ -H)Os₃(CO)₁₀(CHCH=NEt₂)

(A) Osmium-Osmium Distances			
Os(1)-Os(2)	2.7849 (16)	Os(2)-Os(3)	2.8664 (15)
Os(1)-Os(3)	2.8701 (15)		
(B) Osmium-(Bridging Ligand) Distances			
Os(1)-H(br)	1.76 (15)	Os(1)-C(1)	2.15 (3)
Os(2)-H(br)	1.82 (17)	Os(2)-C(1)	2.16 (3)
(C) Osmium-Carbonyl Distances			
Os(1)-C(11)	1.85 (3)	Os(2)-C(21)	1.93 (3)
Os(1)-C(12)	1.89 (4)	Os(2)-C(22)	1.88 (3)
Os(1)-C(13)	1.96 (3)	Os(2)-C(23)	1.90 (3)
Os(3)-C(31)	1.90 (3)	Os(3)-C(33)	1.84 (3)
Os(3)-C(32)	1.95 (4)	Os(3)-C(34)	1.89 (3)
(D) Carbon-Oxygen Distances			
C(11)-O(11)	1.12 (2)	C(21)-O(21)	1.13 (3)
C(12)-O(12)	1.11 (4)	C(22)-O(22)	1.13 (3)
C(13)-O(13)	1.09 (3)	C(23)-O(23)	1.12 (3)
C(31)-O(31)	1.17 (3)	C(33)-O(33)	1.18 (3)
C(32)-O(32)	1.14 (4)	C(34)-O(34)	1.15 (3)
(E) Distances in the CHCH=NEt ₂ Ligand			
C(1)-C(2)	1.42 (3)	N-C(5)	1.57 (3)
C(1)-H(1) ^a	1.04	C(3)-C(4)	1.40 (5)
C(2)-N	1.28 (3)	C(5)-C(6)	1.44 (5)
N-C(3)	1.65 (3)		

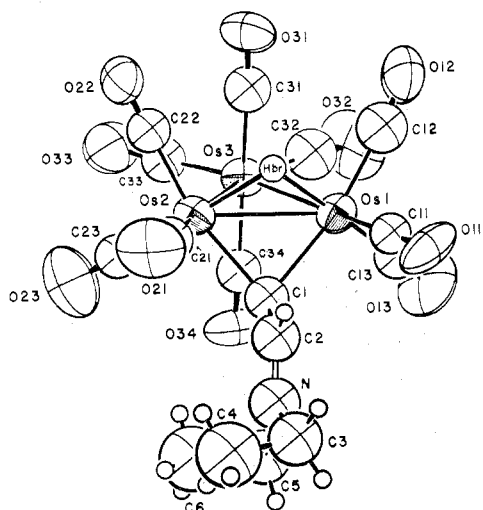
^a In the final cycle of least-squares refinement the position of H(1) was fixed; thus no esd is given.

found in (μ -H)Os₃(CO)₁₀(CHCH₂PMe₂Ph).²

The nitrogen atom in the CHCH=NEt₂ ligand has a planar geometry with individual C-N-C angles as follows: C(2)-N-C(3) = 119 (2)°, C(2)-N-C(5) = 128 (3)°, C(3)-N-C(5) = 113 (2)°. Nitrogen-carbon distances fall into two categories. The N-C(2) bond length of 1.28 (3) Å is consistent with a C=N linkage (comparable to 1.280 (1) Å (average) in (μ -H)Ru₃(CO)₁₀(C=NMe₂)¹⁶ and 1.258 (9) Å (average) in [(CF₃)₂C=N]₂Mn₂(CO)₇²⁰). The other nitro-

Table V. Interatomic Angles with Esd's (deg) for $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$

(A) Os-Os-Os Angles			
Os(3)-Os(1)-Os(2)	60.89 (4)	Os(2)-Os(3)-Os(1)	58.09 (4)
Os(1)-Os(2)-Os(3)	61.02 (4)		
(B) Angles Involving the Bridging Ligands			
Os(1)-H(br)-Os(2)	102 (8)	Os(1)-C(1)-Os(2)	80.6 (9)
H(br)-Os(1)-Os(2)	40 (6)	C(1)-Os(1)-Os(2)	49.8 (7)
H(br)-Os(2)-Os(1)	38 (5)	C(1)-Os(2)-Os(1)	49.6 (8)
H(br)-Os(1)-C(1)	84 (6)	C(1)-Os(2)-H(br)	82 (5)
H(br)-Os(1)-Os(3)	80 (5)	C(1)-Os(1)-Os(3)	82.5 (6)
H(br)-Os(2)-Os(3)	79 (5)	C(1)-Os(2)-Os(3)	82.4 (7)
H(br)-Os(1)-C(11)	95 (5)	C(1)-Os(1)-C(11)	96.2 (11)
H(br)-Os(1)-C(12)	87 (6)	C(1)-Os(1)-C(12)	186.6 (14)
H(br)-Os(1)-C(13)	168 (6)	C(1)-Os(1)-C(13)	95.5 (12)
H(br)-Os(2)-C(21)	96 (5)	C(1)-Os(2)-C(21)	95.1 (10)
H(br)-Os(2)-C(22)	87 (5)	C(1)-Os(2)-C(22)	166.5 (13)
H(br)-Os(2)-C(23)	168 (6)	C(1)-Os(2)-C(23)	98.2 (10)
(C) Osmium-Osmium-Carbonyl Angles			
Os(2)-Os(1)-C(11)	114.3 (8)	Os(1)-Os(2)-C(21)	114.1 (9)
Os(2)-Os(1)-C(12)	119.2 (11)	Os(1)-Os(2)-C(22)	117.4 (10)
Os(2)-Os(1)-C(13)	133.4 (9)	Os(1)-Os(2)-C(23)	135.8 (8)
Os(3)-Os(1)-C(11)	174.6 (8)	Os(3)-Os(2)-C(21)	175.0 (10)
Os(3)-Os(1)-C(12)	88.8 (10)	Os(3)-Os(2)-C(22)	87.5 (8)
Os(3)-Os(1)-C(13)	88.2 (7)	Os(3)-Os(2)-C(23)	88.9 (9)
Os(1)-Os(3)-C(31)	82.4 (8)	Os(2)-Os(3)-C(31)	81.2 (9)
Os(1)-Os(3)-C(32)	98.9 (9)	Os(2)-Os(3)-C(32)	156.9 (9)
Os(1)-Os(3)-C(33)	162.2 (10)	Os(2)-Os(3)-C(33)	104.1 (9)
Os(1)-Os(3)-C(34)	88.0 (8)	Os(2)-Os(3)-C(34)	87.0 (8)
(D) Carbonyl-Osmium-Carbonyl Angles			
C(11)-Os(1)-C(12)	91.9 (13)	C(21)-Os(2)-C(22)	94.1 (11)
C(11)-Os(1)-C(13)	97.2 (10)	C(21)-Os(2)-C(23)	95.7 (13)
C(12)-Os(1)-C(13)	91.5 (14)	C(22)-Os(2)-C(23)	90.6 (12)
C(31)-Os(3)-C(32)	94.6 (14)	C(32)-Os(3)-C(33)	98.9 (13)
C(31)-Os(3)-C(33)	95.8 (12)	C(32)-Os(3)-C(34)	94.7 (13)
C(31)-Os(3)-C(34)	167.6 (12)	C(33)-Os(3)-C(34)	90.8 (12)
(E) Osmium-Carbon-Oxygen Angles			
Os(1)-C(11)-O(11)	173 (3)	Os(2)-C(21)-O(21)	172 (3)
Os(1)-C(12)-O(12)	173 (3)	Os(2)-C(22)-O(22)	171 (3)
Os(1)-C(13)-O(13)	177 (2)	Os(2)-C(23)-O(23)	178 (2)
Os(3)-C(31)-O(31)	172 (3)	Os(3)-C(33)-O(33)	176 (2)
Os(3)-C(32)-O(32)	176 (2)	Os(3)-C(34)-O(34)	176 (2)
(F) Angles in the CHCH=NEt ₂ Ligand			
Os(1)-C(1)-C(2)	115.2 (20)	C(2)-N-C(3)	119 (2)
Os(2)-C(1)-C(2)	112.5 (20)	C(2)-N-C(5)	128 (3)
Os(1)-C(1)-H(1) ^a	99.6	C(3)-N-C(5)	113 (2)
Os(2)-C(1)-H(1)	132.3	N-C(3)-C(4)	99 (3)
H(1)-C(1)-C(2)	110.2	N-C(5)-C(6)	110 (3)
C(1)-C(2)-N	127.4 (3)		

^a See footnote a in Table IV.**Figure 4.** The $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$ molecule, showing the conformation of the bridging $\text{CHCH}=\text{NEt}_2$ ligand.**Table VI**Selected Least-Squares Planes and Deviations (Å) of Atoms Therefrom^a

atom	dev, Å	atom	dev, Å
Plane I: $-0.447626X + 0.549963Y + 0.705104Z = 7.8646$			
Os(1)*	0.000	C(11)	-0.08 (3)
Os(2)*	0.000	O(11)	-0.07 (2)
Os(3)*	0.000	C(21)	-0.04 (3)
H(br)	-1.05 (16)	O(21)	-0.18 (2)
C(1)	1.58 (3)	C(32)	-0.07 (4)
H(1)	2.34 (3)	O(32)	-0.05 (3)
C(2)	1.97 (3)	C(33)	0.01 (3)
N	3.17 (3)	O(33)	-0.03 (2)
C(13)	1.16 (3)	C(12)	-1.55 (4)
O(13)	1.85 (3)	O(12)	-2.52 (2)
C(23)	1.06 (3)	C(22)	-1.57 (3)
O(23)	1.71 (3)	O(22)	-2.55 (2)
C(34)	1.89 (3)	C(31)	-1.87 (3)
O(34)	3.04 (2)	O(31)	-3.04 (2)
Plane II: $0.678350X + 0.474695Y + 0.560808Z = 8.0254$			
Os(1)*	0.000	C(13)	-0.36 (3)
Os(2)*	0.000	O(13)	-0.53 (3)
H(br)*	0.000	C(23)	-0.37 (3)
C(1)	0.98 (3)	O(23)	-0.59 (3)
Plane III: $0.982349X + 0.137353Y + 0.126983Z = 3.2356$			
Os(1)*	0.000	C(12)	-0.11 (4)
Os(2)*	0.000	O(12)	-0.16 (2)
C(1)*	0.000	C(22)	-0.12 (3)
H(br)	0.67 (16)	O(22)	-0.01 (2)
Dihedral Angles, Deg			
plane I-plane II			110.66
plane I-plane III			105.94
plane II-plane III			143.40

^a Atoms marked with asterisks were used in calculating the planes.

gen-carbon distances, $\text{N}-\text{C}(3) = 1.65 (3) \text{ \AA}$ and $\text{N}-\text{C}(5) = 1.57 (3) \text{ \AA}$, are consistent with being $\text{N}-\text{C}$ single bonds on a substituted iminium cation.

There are five symmetry-independent types of carbonyl ligands within the structure but there are no discernible differences between the various Os-CO bond lengths. The osmium-carbonyl distances range from 1.84 (3) to 1.96 (3) Å, with an average value of 1.90 (4) Å. The carbon-oxygen distances within the carbonyl ligands lie in the range from 1.09 (3) to 1.18 (3) Å, the average value being 1.13 (3) Å.

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Registry No. $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\text{CHCH}=\text{NEt}_2)$, 69010-47-5.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Molecular Configuration of a Tetranuclear Copper(II) Complex Active as a Catalyst in the Oxidative Coupling of Phenols by Dioxygen: $\text{Cu}_4\text{OCl}_6(\text{nmp})_3(\text{OH}_2\cdots\text{nmp})$ (nmp = *N*-Methyl-2-pyrrolidinone)

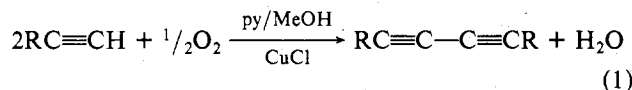
MELVYN ROWEN CHURCHILL* and FRANK J. ROTELLA

Received October 4, 1978

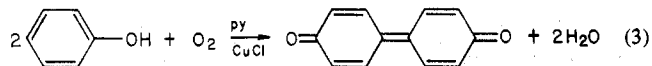
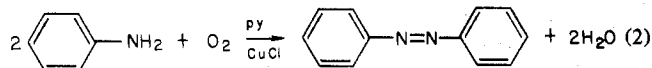
The species $\text{Cu}_4\text{OCl}_6(\text{nmp})_3(\text{OH}_2\cdots\text{nmp})$, an active catalyst for the oxidative coupling of phenols by dioxygen, has been studied by means of a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 9.062$ (2) Å, $b = 22.051$ (5) Å, $c = 17.278$ (3) Å, $\beta = 96.65$ (1)°, $V = 3429.4$ (11) Å³, $\rho(\text{obsd}) = 1.733$ (5) g cm⁻³, and $\rho(\text{calc}) = 1.738$ g cm⁻³ for formula weight 879.43 and $Z = 4$. Diffraction data were collected on a Syntex P2₁ diffractometer using graphite-monochromatized Mo K α radiation. The structure was solved via direct methods (using MULTAN) and refined via least-squares methods to $R_F = 5.65\%$ and $R_{wF} = 4.69\%$ for those 3203 independent reflections with $4.5 < 2\theta < 40.0^\circ$. The complex has a central μ_4 -oxide ion [O(50)] surrounded tetrahedrally by four copper atoms [Cu-O(50)(av) = 1.896 ± 0.005 Å; Cu...Cu(av) = 3.095 ± 0.025 Å]; the six chloride ligands are each in a μ_2 -bridging mode and bridge each of the Cu...Cu vectors. The Cu_4OCl_6 core of the molecule has approximate T_d symmetry. Three of the copper atoms are linked to nmp ligands [Cu(2)-O(20) = 1.913 (5) Å, Cu(3)-O(30) = 1.919 (5) Å, Cu(4)-O(40) = 1.923 (5) Å] while the fourth copper atom is linked to an aquo ligand [Cu(1)-OH₂ = 1.936 (6) Å]. The aquo ligand is additionally involved in hydrogen bonding to an otherwise free nmp molecule in the crystal lattice.

Introduction

The utility of copper(I) chloride as a catalyst in the oxidative coupling of terminal acetylenes by dioxygen (eq 1) in pyridine



(py) has been known for some time.¹⁻³ Copper(I) chloride is also an active catalyst for the coupling of aromatic amines⁴⁻⁶ (eq 2) and phenols⁷ (eq 3).

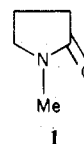


Davies and co-workers⁸⁻¹⁰ have examined the reaction of copper(I) chloride with oxygen in pyridine, with a view toward determining the stoichiometry for the formation of the initiator of the above catalytic processes. The important overall stoichiometry appears to be⁹ that shown in eq 4. (All pyridine



ligands are omitted in this equation.) The "CuCl₂" component has been identified specifically as py₂CuCl₂,^{8,9} but the precise nature of the "CuO" component is unknown, although a copper peroxide moiety is believed to be present.⁸ Attempts to crystallize "CuO" from the separated initiator solution yields insoluble, catalytically inactive, copper(II) oxide.

Recently, Davies and co-workers^{10,11} have studied the use of the amide *N*-methyl-2-pyrrolidinone (nmp), **1**, in place of



pyridine. The reaction of copper(I) chloride with dioxygen in **1** yields a brown, catalytically active solution, which resists all attempts at separation and is believed to contain a single copper-containing product (i.e., the "CuCl₂" and "CuO" moieties of eq 4 appear now to be combined into a single species).¹⁰ Spectroscopic, cryoscopic, and other physical measurements of this product strongly suggest the formula (nmp)₃Cu₄Cl₆O₂. Again, attempts to crystallize this material from nmp have been unsuccessful. However, addition of 1,2-dimethoxyethane (DME) to an nmp solution of this product yields an unstable, amorphous, yellow-green solid; if this solid is washed with DME and allowed to stand under DME in a loosely closed container, orange-brown crystals of a *catalytically active* (relative to eq 3) complex are obtained.^{10,11} The present paper describes the identification of this material, by X-ray diffraction, as the polynuclear species $\text{Cu}_4\text{OCl}_6(\text{nmp})_3(\text{OH}_2\cdots\text{nmp})$. This molecule is closely related to the known species $\text{Cu}_4\text{OCl}_6\text{L}_4$ (**2**),¹² having the "basic

