distances are well within the accepted range of values with an average of 1.959 ± 0.017 Å.

The extensive hydrogen-bonded network is shown in the packing diagram, Figure 3, and important distances are listed in Table IV. While three of the coordinating carboxyl oxygen atoms, O(1), O(5), and O(7), are not involved in any significant hydrogen bonding (i.e., O···O > 3.2 Å), all other carboxyl oxygen atoms participate in the formation of hydrogen bonds. The two water molecules of crystallization, represented by oxygen atoms O(12) and O(13), also serve to extend the network; in fact, O(12) is involved in a total of four hydrogen bonds. The three water molecules bound to the lithium ion, O(9), O(10), and O(11), play an important role in binding the structural units together. Each of these water molecules is hydrogen bonded to a carboxyl oxygen atom on an adjacent $[Cr(EDDDA)]^-$ anion. This extensive three-dimensional network may account for good-quality crystals produced with the lithium counterion. Counterions such as K^+ do not yield useful crystals in the purification process.[4,10] The Li(I) ion may be of optimum size for the development of the strongly interacting three-dimensional structure.

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Registry No. $(-)_D$-Li[Cr(EDDDA]·$5H_2O$, 63301-38-2.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Molecular Structure of μ-Diphenylacetylene-[1-{carbonyl(η⁴-tetraphenylcyclobutadiene)molybdenum(0)}-2-{dicarbonyl-μ-(η⁴-tetraphenylcyclopentadienone)-molybdenum(0)}], $(OC)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(C_4Ph_4)(CO)$, a Complex with a Mo=Mo Bond and a Bridging Cyclopentadienone Group

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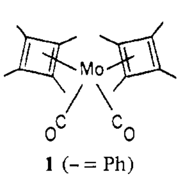
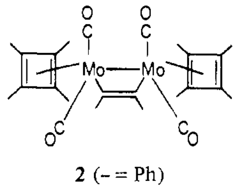
The crystal structure of the title compound, formed from the reaction of $Mo(CO)_6$ and Ph_2C_2 at elevated temperature and pressure, has been determined by a single-crystal x-ray diffraction study. The structure consists of binuclear molybdenum units bonded to three terminal carbonyls and one diphenylacetylene, one tetraphenylcyclobutadiene, and one tetraphenylcyclopentadienone ligand. The Mo–Mo distance [2.772 (4) Å] is consistent with the assignment of a Mo–Mo double bond. Diphenylacetylene acts as a bridging ligand with the C–C bond almost perpendicular (83°) to the Mo–Mo bond axis, while the tetraphenylcyclobutadiene group bonds axially to one of the molybdenum atoms; neither of these modes of attachment is unusual. An exceptional feature of the structure is the attachment of the tetraphenylcyclopentadienone ligand: all five cyclopentadienone carbon atoms are bonded to Mo(2) [Mo(2)–C = 2.30 (2)–2.39 (2) Å] while the oxygen atom is bonded to Mo(1) [Mo(1)–C = 2.06 (1) Å], demonstrating that the ligand is bridging. Crystallographic data are as follows: space group $P2_1/a$; $a = 23.96$ (2), $b = 22.14$ (3), $c = 12.49$ (2) Å; $\beta = 110.24$ (2)°; $Z = 4$. The structure was solved by a combination of heavy-atom and direct methods and refined to a conventional R value of 0.111 for 4811 independent reflections.

Introduction

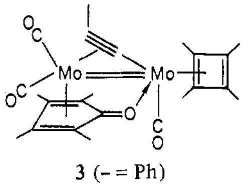
In 1964, Hübel and Merényi[2a] reported the formation of several molybdenum complexes from the reaction of diphenylacetylene with either $Mo(CO)_6$ or $(diglyme)Mo(CO)_3$. Particularly noteworthy are the complexes with assigned structures **1** and **2**. The structure of **1**, the only known complex with a dicyclobutadiene geometry, has been confirmed recently by a single-crystal x-ray analysis.[2b] The structure originally proposed for the green, diamagnetic binuclear complex **2** suggests the presence of metal atoms with 16-electron configurations and is further characterized by an unusual bridging geometry for the diphenylacetylene ligand. Here, we present a crystallographic study of this complex, detailing its structure as **3** rather than **2**.



1 (– = Ph)



2 (– = Ph)



3 (– = Ph)

Experimental Section

Synthesis. A sample of the title compound was prepared by a modification of the Hübel and Merényi procedure. A mixture consisting of $Mo(CO)_6$ (10.8 g, 41 mmol) and Ph_2C_2 (10.8 g, 61 mmol) in 90 mL of benzene was charged into a 300 mL autoclave and heated with stirring to 120 (1) °C for 17 h. The product mixture was filtered, and the filtrate was concentrated to dryness under reduced pressure (~1 mm; 30 °C). Unreacted $Mo(CO)_6$ was removed by sublimation (0.05 mm; 80 °C). The residue was dissolved in benzene–petroleum ether (bp 30–60 °C) (1/10, v/v), and the resulting solution was chromatographed on a neutral alumina column (3.5 × 75 cm). Four distinct bands (yellow, orange-red, green, yellow) were obtained upon elution with the same solvent mixture. The green band was collected, concentrated, and resubjected to the same procedure to yield two bands (yellow, blue-green). The fraction corresponding to the blue-green band was, in turn, collected, concentrated, and resubjected to the same chromatographic procedure, this time using benzene–petroleum ether (bp 30–60 °C) (7/1, v/v). The green band which separated was collected and concentrated to dryness yielding 0.1 g of impure **3**. Recrystallization from chloroform–hexane yielded ~0.08 g of green needles (mp 205–210 °C dec, uncor). Selected analytical data for **3** follow. Anal. Calcd for $(Ph_4C_4)(Ph_4C_5O)(Ph_2C_2)Mo_2(CO)_3 \cdot CHCl_3$: C, 68.53; H, 3.91; Mo, 14.60; Cl, 8.09; mol wt 1195 (neglecting $CHCl_3$). Found: C, 68.90; H, 4.02, Mo, 15.35; Cl, 6.26; mol wt 1191 (osmometric, $CHCl_3$). For comparison, the product reported in the original paper was claimed to be the disolvated complex $(Ph_4C_4)_2(Ph_2C_2)Mo_2(CO)_4 \cdot 2CHCl_3$ (dec pt 170 °C), and the chloroform-free complex (mp 200–205 °C dec) was obtained by vacuum drying at 100 °C. The analytical data reported for the chloroform-free complex were shown to be consistent with the calculated values, except for the molecular weight for which the experimental values (1430 in $CHCl_3$ and 818 in C_6H_6) were quite different from the expected value (1195). The infrared spectrum of the green binuclear complex prepared during the course of the current investigation was essentially identical with that reported by Hübel and Merényi.

Crystal Data and Data Collection. A single crystal of dimensions 0.47 × 0.16 × 0.16 mm, obtained by slow evaporation from a chloroform–hexane solution, was mounted in a sealed glass capillary parallel to the long axis (a). Preliminary Weissenberg photographs showed no signs of disorder; systematic absences for $h0l$, $h = 2n + 1$, and for $0k0$, $k = 2n + 1$, fixed the space group as $P2_1/a$. Unit cell parameters $a = 23.96$ (2) Å, $b = 22.14$ (3) Å, $c = 12.49$ (2) Å, and $\beta = 110.24$ (1)° were determined from a least-squares fit of 36 moderately intense reflections obtained using graphite-monochromated Mo Kα radiation (λ 0.71069 Å) and an Enraf-Nonius CAD-3 automated diffractometer. The density, measured by flotation of several crystals in aqueous zinc iodide solution, was found to vary between 1.25 (1) and 1.40 (1) g/cm^3. Since the osmometric molecular weight (1191), determined in chloroform, compared well with that expected for $(Ph_4C_4)(Ph_4C_5O)(Ph_2C_2)Mo_2(CO)_3$ and since elemental analysis indicated the presence of chlorine, it was assumed that the crystals contained varying amounts of chloroform of solvation. (The elemental analysis is consistent with an average of approximately 0.8 $CHCl_3$ per unit of **3** while the calculated densities for zero and one molecule of solvation are 1.27 and 1.40, respectively.) In view of the sharpness of the diffraction pattern of the solvated product and the difficulties encountered in obtaining suitable crystals of the chloroform-free complex, data were collected and analyzed using these crystals.

Data were collected at room temperature (22 ± 2 °C) using a θ–2θ scan ($2 < \theta < 20°$). Graphite-monochromated Mo Kα radiation was detected with a scintillation counter and a pulse height analyzer set to admit approximately 90% of the Kα peak. Additional aspects of the data collection procedure have been given previously.[3] At the end of the data collection period (ca. 4 weeks), the crystal showed no sign of decomposition. A standard reflection, measured at 50 reflection intervals, was consistent to ±5% and showed no significant trends.

After correction for Lorentz and polarization effects, 4811 reflections with $F^2 \geq 3\sigma(F^2)$ were considered observed and used in the structure solution and refinement. Here, $\sigma(F^2) = (\mathrm{Lp})^{-1}(N_t + (0.03N_n)^2)^{1/2}$; the various terms have been defined previously.[3] For the determination of the trial structure and in the initial stages of refinement, 2404 low-angle reflections were used. With μ(Mo Kα) = 5.0 cm^{-1}, maximum and minimum absorption factors were calculated[4] to be 1.06 and 1.05, respectively, for the crystal used to collect the data. The maximum effect of absorption is, therefore, expected to be less than 1% of F. Absorption corrections were not applied.

Structure Determination. The structure was solved by a combination of heavy-atom and direct methods.[5] The rigid-body refinement was accomplished using a local modification of program GROUP, developed[6] by LaPlaca and Ibers. Approximate molybdenum coordinates were obtained from a normal sharpened Patterson map. The Patterson map, however, did not reveal the presence of chlorine atoms. A difference Fourier calculation, based on phases determined by the molybdenum coordinates, gave a complex electron density map which contained an extremely large number of maxima, few of which made chemical sense. To expedite the structure determination, an E map was prepared on the basis of the phases, determined by reiterative application of Sayre's equation, for 358 reflections with $|E| \geq 1.5$. Light atoms were then added to the trial structure if they appeared on both maps, yielded vectors of appropriate weight with the molybdenum atoms, and made chemical sense. A series of structure factor–difference Fourier calculations revealed the remaining nonhydrogen atoms except for those of the chloroform of solvation. On several electron density maps, peaks were located which had the approximate geometry of a chloroform molecule but not the expected intensity. Since the electron density map indicated approximately 0.4 $CHCl_3$ unit per asymmetric unit, chloroform atoms were added to the trial structure with atom multipliers of 0.4.

The structure was refined by full-matrix least-squares techniques. All phenyl rings were treated as rigid groups of D_{6h} symmetry. Positions of the carbon and hydrogen atoms were calculated to give C–C and C–H bond distances of 1.390 and 0.93 Å, respectively. These rings were placed initially such that the carbon atoms coincided, as closely as possible, with the carbon atom peaks obtained from the difference Fourier maps. Except for hydrogen,[7] atomic scattering factors were obtained from the compilations of Cromer and Waber,[8] and all atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion corrections[7] were applied to molybdenum and chlorine atoms.

Refinement was based on F and weights were set according to $w = 1/\sigma^2(F)$, where $\sigma^2(F) = (N_t + (0.03N_n)^2)/LpN_n$. All portions of the structure refined smoothly except for one acetylene phenyl group [ring 6, C(101)–C(106)] and the chloroform molecule. On electron density maps, this phenyl group appeared roughly as a torus of electron density with only small peaks near the nuclear positions. Attempts to refine the isotropic temperature factors of this group gave large values, in agreement with the electron density distribution. Because of this, the temperature factors of these atoms were set equal to 10 and were not refined.

With the chloroform group, all four atoms were located on difference electron density maps and their inclusion led to the decrease in the weighted R factor. An attempt was made to refine the chloroform atom multipliers; this led to an increase in all values and a subsequent increase in the temperature factors to unrealistic values. Consequently, these atom multipliers were reset to 0.4 and the chloroform atom temperature factors were then refined.

Several cycles of refinement, the last three of which utilized anisotropic thermal parameters for the molybdenum atoms, gave final values of $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.111 and $R_{wF} = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}$, the quantity minimized, of 0.150. For the final refinement cycle, all parameter changes were less than their associated estimated standard deviation. The final standard deviation of an observation of unit weight was 1.47. While the final value of R_F appears high by current standards, we note that the structure is large (82 nonhydrogen atoms in the asymmetric unit) and that similar values of R_F have been reported[9] for structures of comparable size where thermal motion caused similar problems.

Final parameters are given in Table I while derived parameters for the group atoms are given in Table II. A list of observed and calculated structure factors is available.[10]

Description of the Structure

A view of the complex **3**, showing the atom-numbering scheme, is given in Figure 1 with phenyl groups omitted for clarity. A stereoview of **3**, including all nonhydrogen atoms, is given in Figure 2. Selected interatomic distances are listed in Table III while the results of least-squares planes calculations are given in Table IV.

The structure consists of discrete molecules of **3** with each binuclear molybdenum unit bonded to three terminal carbonyls (as indicated by the M–C–O angles) and one diphenylacetylene (DPA), one tetraphenylcyclobutadiene (CBD), and one tetraphenylcyclopentadienone (CPD) ligand. The chloroform molecules appear to fill holes in the structure and play no role in bonding.

The Mo–Mo distance in **3** [2.772 (4) Å] lies between those reported for Mo–Mo bonds of single[11] and triple[12] multiplicity. This distance, in conjunction with the diamagnetism of **3**, is

Table I. Final Parameters[a] for $(OC)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(C_4Ph_4)(CO)\cdot 0.4CHCl_3$

Atom	x	y	z	B, Å^2
Mo(1)	0.36803 (7)	0.25305 (8)	0.7852 (2)	*b*
Mo(2)	0.27753 (8)	0.26396 (7)	0.5755 (2)	*b*
Cl(1)	0.0875 (16)	0.3475 (16)	0.225 (3)	11.9 (9)
Cl(2)	0.1573 (13)	0.4007 (13)	0.134 (3)	9.5 (7)
Cl(3)	0.0651 (14)	0.4675 (14)	0.151 (3)	10.5 (8)
O(1)	0.2558 (9)	0.2563 (10)	0.859 (2)	6.8 (5)
O(2)	0.1612 (9)	0.3082 (9)	0.610 (2)	5.5 (4)
O(3)	0.2588 (9)	0.3622 (9)	0.384 (2)	5.9 (5)
O(4)	0.3698 (6)	0.1672 (6)	0.724 (1)	3.0 (3)
C(1)	0.2973 (9)	0.2524 (10)	0.824 (2)	3.2 (4)
C(2)	0.2048 (10)	0.2916 (10)	0.599 (2)	3.4 (4)
C(3)	0.2658 (10)	0.3278 (10)	0.456 (2)	3.2 (5)
C(4)	0.3260 (9)	0.1730 (9)	0.617 (2)	2.4 (4)
C(5)	0.2634 (9)	0.1591 (9)	0.600 (2)	2.7 (4)
C(6)	0.2313 (9)	0.1748 (9)	0.485 (2)	2.3 (4)
C(7)	0.2727 (9)	0.1933 (8)	0.428 (2)	2.2 (3)
C(8)	0.3324 (9)	0.1919 (9)	0.517 (2)	2.4 (4)
C(9)	0.3592 (8)	0.3233 (8)	0.665 (2)	2.0 (3)
C(10)	0.3136 (9)	0.3367 (9)	0.706 (2)	2.7 (4)
C(11)	0.4518 (9)	0.2958 (9)	0.912 (2)	2.6 (4)
C(12)	0.4115 (9)	0.2838 (9)	0.972 (2)	2.4 (4)
C(13)	0.4225 (9)	0.2171 (9)	0.964 (2)	2.7 (4)
C(14)	0.4639 (9)	0.2296 (9)	0.907 (2)	2.8 (4)
C(15)	0.101 (4)	0.395 (4)	0.160 (7)	6.7 (19)

Group	x_c[c]	y_c	z_c	δ	ϵ	η
Ring 1, C(51)-C(56)	0.2143 (6)	0.0955 (5)	0.7451 (10)	2.53 (2)	−2.29 (1)	−2.95 (2)
Ring 2, C(61)-C(66)	0.1125 (6)	0.1325 (6)	0.3586 (10)	1.95 (1)	2.91 (1)	−3.06 (1)
Ring 3, C(71)-C(76)	0.2382 (4)	0.1975 (4)	0.1872 (8)	1.58 (3)	1.865 (8)	−2.33 (3)
Ring 4, C(81)-C(86)	0.4422 (4)	0.2101 (4)	0.4757 (8)	−1.411 (9)	2.610 (8)	0.68 (1)
Ring 5, C(91)-C(96)	0.4387 (6)	0.3855 (5)	0.5786 (10)	−0.94 (1)	2.48 (1)	−3.00 (1)
Ring 6, C(101)-C(106)	0.2658 (7)	0.4447 (8)	0.7672 (21)	0.41 (1)	−2.77 (2)	−1.76 (2)
Ring 7, C(111)-C(116)	0.5273 (5)	0.4007 (5)	0.9422 (9)	−0.630 (8)	3.13 (1)	−2.77 (1)
Ring 8, C(121)-C(126)	0.3684 (4)	0.3502 (4)	1.1244 (8)	0.56 (1)	−2.238 (9)	−0.40 (1)
Ring 9, C(131)-C(136)	0.4033 (4)	0.1153 (4)	1.0893 (8)	3.00 (1)	−2.487 (7)	−1.22 (1)
Ring 10, C(141)-C(146)	0.5479 (5)	0.1611 (5)	0.8436 (9)	−2.25 (1)	2.61 (1)	−2.78 (1)

[a] Estimated standard deviations, justified to the last significant figure of the preceding number, are given in parentheses. [b] Anisotropic thermal parameters × 10^5 are as follows: for Mo(1), $\beta_{11} = 115$ (4), $\beta_{22} = 96$ (3), $\beta_{33} = 371$ (13), $\beta_{12} = -13$ (3), $\beta_{13} = 95$ (5), $\beta_{23} = -19$ (6); for Mo(2), $\beta_{11} = 99$ (4), $\beta_{22} = 97$ (4), $\beta_{33} = 423$ (14), $\beta_{12} = -4$ (3), $\beta_{13} = 103$ (6), $\beta_{23} = -11$ (6). The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The group variables have been defined previously; see ref 6.

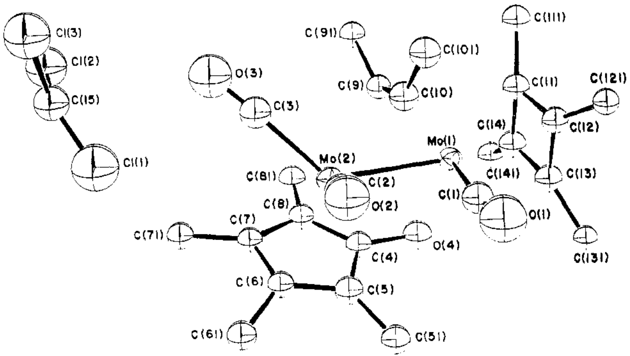


Figure 1. View of $(OC)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(C_4Ph_4)(CO)\cdot 0.4CHCl_3$ showing the atom-numbering scheme. Phenyl groups have been omitted for clarity.

consistent with the assignment of a Mo–Mo double bond in the complex. The complex **3** is a unique example of a complex with a nominal molybdenum–molybdenum bond order of 2. In a sense, its characterization completes a series for molybdenum since structurally characterized molybdenum complexes with bond orders of 1, 3, and 4[13] are already known.

The CBD ligand is axially bonded to Mo(1) as indicated by the Mo(2)–Mo(1)–CL(CBD) angle (172.6°) (CL = center ligand). It shows average bonding parameters [Mo(1)–C(CBD) = 2.31 ± 0.02 Å; C(CBD)–C(CBD) = 1.47 ± 0.04 Å] which closely resemble those reported for other cyclobutadiene–molybdenum complexes such as $[Ph_4C_4Mo(CO)_2Br]_2$[11a] and $(Ph_4C_4)_2Mo(CO)_2$.[2b] The carbon atoms C(11) through C(14) are planar to within ±0.01 Å while the phenyl groups, which are exo to Mo(1), are bent and twisted from the cyclobutadiene plane to various degrees, as indicated

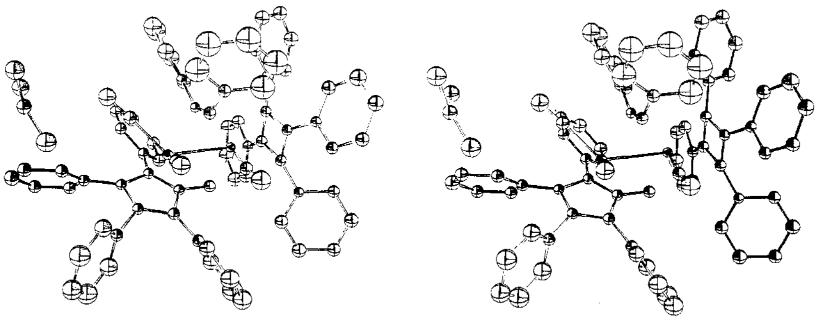


Figure 2. Stereoview of **3** including all nonhydrogen atoms.

Table II. Derived Parameters for the Group Atoms

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(51)	0.2378	0.1294	0.6772	2.8 (4)	C(142)	0.5035	0.1321	0.8722	4.7 (6)
C(52)	0.1876	0.1496	0.6980	4.3 (5)	C(143)	0.5451	0.0984	0.8430	5.3 (6)
C(53)	0.1641	0.1156	0.7659	6.2 (7)	C(144)	0.5894	0.1274	0.8144	5.6 (7)
C(54)	0.1908	0.0616	0.8130	6.8 (8)	C(145)	0.5923	0.1900	0.8150	5.1 (6)
C(55)	0.2411	0.0414	0.7921	8.1 (9)	C(146)	0.5507	0.2237	0.8442	4.1 (5)
C(56)	0.2645	0.0753	0.7242	5.4 (6)	H(52)	0.169	0.185	0.668	5.6
C(61)	0.1685	0.1549	0.4210	2.7 (4)	H(53)	0.131	0.131	0.778	5.6
C(62)	0.1201	0.1937	0.3837	5.2 (6)	H(54)	0.176	0.041	0.855	5.6
C(63)	0.0640	0.1713	0.3213	7.1 (8)	H(55)	0.260	0.006	0.822	5.6
C(64)	0.0564	0.1101	0.2962	6.4 (7)	H(56)	0.298	0.060	0.712	5.6
C(65)	0.1049	0.0713	0.3336	7.3 (8)	H(62)	0.132	0.235	0.399	6.5
C(66)	0.1610	0.0936	0.3960	6.3 (7)	H(63)	0.033	0.199	0.298	6.5
C(71)	0.2561	0.1977	0.3056	2.5 (4)	H(64)	0.022	0.096	0.258	6.5
C(72)	0.2095	0.2345	0.2418	3.1 (4)	H(65)	0.102	0.030	0.319	6.5
C(73)	0.1915	0.2343	0.1233	3.6 (4)	H(66)	0.192	0.066	0.419	6.5
C(74)	0.2202	0.1974	0.0688	4.5 (5)	H(72)	0.189	0.260	0.275	4.2
C(75)	0.2669	0.1606	0.1326	3.4 (4)	H(73)	0.160	0.259	0.084	4.2
C(76)	0.2848	0.1608	0.2511	3.1 (4)	H(74)	0.209	0.197	−0.004	4.2
C(81)	0.3896	0.2015	0.4972	2.7 (4)	H(75)	0.287	0.135	0.100	4.2
C(82)	0.3923	0.2447	0.4183	2.9 (4)	H(76)	0.316	0.136	0.290	4.2
C(83)	0.4449	0.2533	0.3968	3.0 (4)	H(82)	0.360	0.269	0.378	3.9
C(84)	0.4948	0.2187	0.4541	4.5 (5)	H(83)	0.445	0.282	0.344	3.9
C(85)	0.4920	0.1756	0.5330	4.3 (5)	H(84)	0.527	0.224	0.441	3.9
C(86)	0.4394	0.1670	0.5545	3.7 (5)	H(85)	0.524	0.152	0.573	3.9
C(91)	0.3995	0.3563	0.6213	2.3 (4)	H(86)	0.439	0.138	0.608	3.9
C(92)	0.4542	0.3303	0.6336	4.1 (5)	H(92)	0.466	0.294	0.670	6.7
C(93)	0.4934	0.3595	0.5909	5.7 (7)	H(93)	0.529	0.341	0.601	6.7
C(94)	0.4778	0.4147	0.5358	8.6 (10)	H(94)	0.502	0.323	0.510	6.7
C(95)	0.4231	0.4407	0.5235	7.1 (8)	H(95)	0.411	0.477	0.487	6.7
C(96)	0.3840	0.4115	0.5662	5.2 (6)	H(96)	0.348	0.430	0.556	6.7
C(101)	0.2888	0.3911	0.7419	2.9 (6)	H(102)	0.313	0.378	0.914	10.0
C(102)	0.2942	0.4042	0.8539	10	H(103)	0.276	0.465	0.955	10.0
C(103)	0.2713	0.4577	0.8793	10	H(104)	0.229	0.531	0.808	10.0
C(104)	0.2430	0.4983	0.7926	10	H(105)	0.219	0.511	0.620	10.0
C(105)	0.2376	0.4852	0.6805	10	H(106)	0.256	0.425	0.580	10.0
C(106)	0.2605	0.4317	0.6551	10	H(112)	0.566	0.310	1.028	4.4
C(111)	0.4908	0.3501	0.9195	3.0 (4)	H(113)	0.625	0.392	1.064	4.4
C(112)	0.5496	0.3458	0.9926	3.8 (5)	H(114)	0.586	0.482	0.979	4.4
C(113)	0.5860	0.3964	1.0153	4.8 (6)	H(115)	0.489	0.491	0.857	4.4
C(114)	0.5637	0.4514	0.9650	4.9 (5)	H(116)	0.430	0.410	0.820	4.4
C(115)	0.5050	0.4557	0.8919	4.3 (5)	H(122)	0.329	0.255	1.067	4.5
C(116)	0.4686	0.4050	0.8692	2.9 (4)	H(123)	0.296	0.308	1.186	4.5
C(121)	0.3888	0.3174	1.0505	2.2 (4)	H(124)	0.336	0.403	1.244	4.5
C(122)	0.3456	0.2930	1.0887	2.8 (4)	H(125)	0.408	0.445	1.182	4.5
C(123)	0.3252	0.3258	1.1626	3.2 (4)	H(126)	0.440	0.392	1.063	4.5
C(124)	0.3480	0.3830	1.1983	4.2 (5)	H(132)	0.447	0.202	1.184	4.2
C(125)	0.3912	0.4073	1.1601	5.1 (6)	H(133)	0.436	0.123	1.286	4.2
C(126)	0.4116	0.3749	1.0862	3.7 (5)	H(134)	0.392	0.036	1.191	4.2
C(131)	0.4100	0.1646	1.0261	2.2 (3)	H(135)	0.360	0.028	0.994	4.2
C(132)	0.4292	0.1681	1.1444	3.1 (4)	H(136)	0.371	0.108	0.892	4.2
C(133)	0.4224	0.1189	1.2077	4.3 (5)	H(142)	0.475	0.111	0.891	5.5
C(134)	0.3965	0.0660	1.1526	3.8 (5)	H(143)	0.542	0.057	0.844	5.5
C(135)	0.3773	0.0625	1.0342	4.3 (5)	H(144)	0.615	0.107	0.797	5.5
C(136)	0.3841	0.1118	0.9709	3.9 (5)	H(145)	0.621	0.211	0.797	5.5
C(141)	0.5064	0.1948	0.8728	2.7 (4)	H(146)	0.554	0.265	0.844	5.5

by the deviations of the phenyl substituent carbon atoms from plane 1 (0.15–0.55 Å, Table IV).

The diphenylacetylene group acts as a normal four-electron bridging ligand between the two molybdenum atoms. The angle between the vectors Mo(1)–Mo(2) and C(9)–C(10) (83°) shows that the acetylene carbon atoms are nearly perpendicular to the Mo–Mo bond, a geometry observed previously with $Co_2(CO)_6(Ph_2C_2)$,[14] $Fe_2(CO)_4(C_2(t\text{-}Bu)_2)_2$,[15] and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}EtCCEt)$.[16]

Several structural parameters associated with the CPD ligand are noteworthy. As indicated by the C(CPD)–Mo(2) distances, the cyclopentadienone carbon atoms are bonded to Mo(2). All five carbon atoms C(4) through C(8) are coplanar to within ±0.02 Å, and, as with the CBD ligand, the phenyl groups are bent from this plane, exo to Mo(2). In contrast, the oxygen atom of the CPD ligand is displaced 0.08 Å from the plane of the cyclopentadienone carbon atoms in an *endo* direction. This orientation of the keto oxygen atom suggests a strong Mo(1)–O(4) bonding interaction. This view is supported by the Mo(1)–O(4) distance [2.06 (1) Å] which is equal to the average Mo–O distance in $Mo_2(O_2CCF_3)_4$[17] and which is 0.06 Å shorter than the corresponding average in $Mo_2(O_2CCH_3)_4$.[18] Thus, the CPD ligand is coordinated to both molybdenum atoms with the C–O and Mo–Mo bond axes parallel (the angle between these axes is 0°) and acts as a bridging ligand. The strong coordination of the cyclopentadienone keto group to molybdenum is consistent with the absence[2a] of a ketonic band in the infrared spectrum of **3** and helps to explain why the original formulation of the compound (**2**) did not contain a cyclopentadienone ligand.

Discussion

The cyclooligomerization of substituted acetylenes by transition metal complexes is well known.[19-21] Compound **3** is unusual in that it contains monomer, dimer, and carbonylated dimer ligands all on the same compound. Certain

Table III. Interatomic Distances (Å) and Angles (deg)[a]

Molybdenum-molybdenum			
Mo(1)-Mo(2)	2.772 (4)		
Molybdenum-carbonyl			
Mo(1)-C(1)	1.91 (2)	C(1)-O(1)	1.22 (3)
Mo(2)-C(2)	1.96 (2)	C(2)-O(2)	1.16 (3)
Mo(2)-C(3)	2.01 (2)	C(3)-O(3)	1.14 (3)
Molybdenum-diphenylacetylene			
Mo(1)-C(9)	2.12 (2)	C(9)-C(10)	1.40 (3)
Mo(2)-C(9)	2.30 (2)	C(10)-C(91)	1.46 (3)
Mo(1)-C(10)	2.29 (2)	C(10)-C(101)	1.48 (3)
Mo(2)-C(10)	2.25 (2)		
Molybdenum-cyclobutadiene			
Mo(1)-C(11)	2.29 (2)	C(11)-C(111)	1.50 (3)
Mo(1)-C(12)	2.30 (2)	C(12)-C(121)	1.48 (3)
Mo(1)-C(13)	2.30 (2)	C(13)-C(131)	1.49 (3)
Mo(1)-C(14)	2.33 (2)	C(14)-C(141)	1.46 (3)
C(11)-C(12)	1.44 (3)		
C(11)-C(14)	1.50 (3)		
C(12)-C(13)	1.51 (3)		
C(13)-C(14)	1.43 (3)		
Molybdenum-cyclopentadienone			
Mo(2)-O(4)	3.18 (1)	Mo(1)-O(4)	2.06 (1)
Mo(2)-C(4)	2.30 (2)	Mo(1)-C(4)	2.65 (2)
Mo(2)-C(5)	2.38 (2)	Mo(1)-C(5)	3.46 (2)
Mo(2)-C(6)	2.36 (2)	Mo(1)-C(8)	3.43 (2)
Mo(2)-C(7)	2.39 (2)		
Mo(2)-C(8)	2.34 (2)		
O(4)-C(4)	1.38 (2)	C(5)-C(51)	1.46 (3)
C(4)-C(5)	1.47 (3)	C(6)-C(61)	1.50 (3)
C(5)-C(6)	1.43 (3)	C(7)-C(71)	1.45 (3)
C(6)-C(7)	1.46 (3)	C(8)-C(81)	1.49 (3)
C(7)-C(8)	1.47 (3)		
C(8)-C(4)	1.40 (3)		
Chloroform			
Cl(1)-C(15)	1.43 (9)		
Cl(2)-C(15)	1.50 (9)		
Cl(3)-C(15)	1.81 (9)		
C(phenyl)-C(phenyl)	1.390		

Molybdenum-carbonyl			
Mo(1)-C(1)-O(1)	173 (2)	Mo(2)-Mo(1)-C(1)	76.5 (6)
Mo(2)-C(2)-O(2)	178 (2)	Mo(1)-Mo(2)-C(2)	109.4 (7)
Mo(2)-C(3)-O(3)	177 (2)	Mo(1)-Mo(2)-C(3)	128.9 (6)
Molybdenum-diphenylacetylene			
Mo(1)-Mo(2)-C(9)	48.4 (5)	Mo(2)-Mo(1)-C(9)	54.1 (5)
Mo(1)-Mo(2)-C(10)	52.9 (5)	Mo(2)-Mo(1)-C(10)	51.6 (5)
Mo(1)-Mo(2)-CL(DPA)	48.0	Mo(2)-Mo(1)-CL(DPA)	50.7
		C(10)-C(9)-C(91)	137 (2)
		C(9)-C(10)-C(101)	137 (2)
Molybdenum-cyclobutadiene			
Mo(2)-Mo(1)-C(11)	146.1 (5)	C(1)-Mo(1)-CL(CBD)	105.4
Mo(2)-Mo(1)-C(12)	149.6 (5)	CL(DPA)-Mo(1)-CL(CBD)	121.9
Mo(2)-Mo(1)-C(13)	160.3 (5)		
Mo(2)-Mo(1)-C(14)	155.2 (5)		
Mo(2)-Mo(1)-CL(CBD)	172.6		
C(11)-C(12)-C(13)	89 (2)	C(12)-C(13)-C(121)	131 (2)
C(12)-C(13)-C(14)	91 (2)	C(14)-C(13)-C(131)	135 (2)
C(13)-C(14)-C(11)	90 (2)	C(11)-C(14)-C(141)	134 (2)
C(14)-C(11)-C(12)	91 (2)	C(13)-C(14)-C(141)	136 (2)
C(11)-C(12)-C(121)	136 (2)	C(12)-C(11)-C(111)	129 (2)
C(13)-C(12)-C(121)	131 (2)	C(14)-C(11)-C(111)	131 (2)
Molybdenum-cyclopentadienone			
Mo(1)-Mo(2)-O(4)	39.7 (3)	Mo(2)-Mo(1)-O(4)	80.9 (4)
Mo(1)-Mo(2)-C(4)	62.3 (5)	C(1)-Mo(1)-O(4)	102.7 (7)
Mo(1)-Mo(2)-C(5)	83.8 (5)	CL(CBD)-Mo(1)-O(4)	105.4
Mo(1)-Mo(2)-C(6)	117.8 (5)	CL(DPA)-Mo(1)-O(4)	126.2
Mo(1)-Mo(2)-C(7)	118.9 (5)	C(3)-Mo(2)-O(4)	143.3 (7)
Mo(1)-Mo(2)-C(8)	84.0 (5)	C(2)-Mo(2)-O(4)	126.7 (7)
Mo(1)-Mo(2)-CL(CPD)	94.0		
C(4)-C(5)-C(6)	106 (2)	C(6)-C(5)-C(51)	125 (2)
C(5)-C(6)-C(7)	110 (2)	C(5)-C(6)-C(61)	124 (2)
C(6)-C(7)-C(8)	106 (2)	C(7)-C(6)-C(61)	124 (2)
C(7)-C(8)-C(4)	108 (2)	C(6)-C(7)-C(71)	123 (2)
C(8)-C(4)-C(5)	110 (2)	C(8)-C(7)-C(71)	129 (2)
C(8)-C(4)-O(4)	128 (2)	C(7)-C(8)-C(81)	126 (2)
C(5)-C(4)-O(4)	122 (2)	C(4)-C(8)-C(81)	126 (2)
C(4)-C(5)-C(51)	129 (2)		
Chloroform			
Cl(1)-C(15)-Cl(2)	126 (6)		
Cl(1)-C(15)-Cl(3)	120 (6)		
Cl(2)-C(15)-Cl(3)	110 (5)		

[a] CL = center ligand.

Table IV

Least-Squares Planes[a]

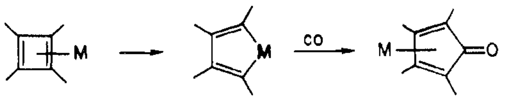
Plane	*A*	*B*	*C*	*D*	Atoms defining plane
1	−0.210	0.946	0.248	4.325	C(4) through C(8)
2	0.475	0.053	0.879	13.014	C(11) through C(14)

Deviations from the Planes, Å

Plane 1		Plane 2	
C(11)	−0.01	C(4)	0.02
C(12)	0.01	C(5)	−0.02
C(13)	−0.01	C(6)	0.02
C(14)	0.01	C(7)	−0.01
C(111)	0.55	C(8)	−0.01
C(121)	0.44	O(4)	0.08
C(131)	0.30	C(51)	−0.22
C(141)	0.17	C(61)	−0.32
Mo(1)	−2.06	C(71)	−0.30
		C(81)	−0.16
		Mo(2)	2.01

[a] Equations have the form $AX_0 + BY_0 + CZ_0 = D$ where X_0, Y_0, and Z_0 are Cartesian axes lying along $b \times c^*$, b, and c^*, respectively.

cyclobutadiene complexes are known to undergo carbonylation to give π-cyclopentadienone complexes, presumably via five-member metallocycles such as **4**–**6**.[22] Our present understanding of the steps in the process leading to **3** is exceedingly primitive; indeed, it is not even known at what stage (i.e., as a mononuclear or binuclear species) carbon monoxide insertion takes place. The observed geometry of **3**, however, does raise the interesting possibility of a reaction pathway involving adjacent metal centers acting on a common substrate.[23,24] If so, **3** may represent a kinetically stable intermediate.



4 5 6

Last, the bonding of the CPD ligand to Mo requires some comment. The line drawing of **3** suggests a cyclopentadienone group coordinated to both metal atoms via the π system. However, on the basis of the present data, it is not possible to distinguish unambiguously between that type of attachment and the other extreme in which the five-membered ring C(4)–C(8) functions as a cyclopentadienyl ligand oxy-bridged to the adjacent molybdenum atom. The O(4)–C(4) distance [1.38 (2) Å] lies between those reported for either aliphatic[25] or aromatic[26] C=O bonds and those for C(aliphatic)–O–X bonds;[27] it most nearly resembles those for oxygen atoms singly bonded to an ethylene fragment[25] or to an aromatic center.[27]

This suggests that an oxy-bridged structure is a contributing factor to the bonding in **3**.

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Registry No. 3, 63181-01-1; $Mo(CO)_6$, 13939-06-5; Ph_2C_2, 501-65-5.

Supplementary Material Available: Listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Molecular Structures of CF_3OOH, CF_3OOF, and CF_3OOCl by Gas-Phase Electron Diffraction

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Structural characteristics of the present molecules are consistent with previous chemical evidence differentiating the substances from each other and from other peroxides. Whereas the hydride and chloride are typical peroxides, the fluoro derivative departs significantly in the direction of the unusual substance FOOF as revealed by the rather short O–O and long O–F and C–O bonds. It was observed that O–O bond lengths in peroxides are strongly correlated with the force constants for internal rotation about the peroxide bonds. The trifluoromethyl groups have unexceptional structures, tilts, and, except for the chloro derivative, conformations. It appears in the case of CF_3OOCl that $CF_3\cdots Cl$ steric interactions introduce a hump in the expected minimum of the CF_3 torsional potential function at the staggered conformation, giving rise to two distinct conformers. Structural parameters ($\pm 3\sigma$) for CF_3OOX (X = H, Cl, F) were determined to be r_g(O–O) = 1.447 (8), 1.447 (15), 1.366 (33) Å; r_g(O–X) = 0.974 (42), 1.699 (6), 1.449 (15) Å; r_g(C–O) = 1.376 (10), 1.372 (22), 1.419 (24) Å; ∠O–O–X = (100.0, assumed), 110.8 (1.2), 104.5 (4.5)°; and ∠O–O–C = 107.6 (0.8), 108.1 (4.0), 108.2 (1.2)°. Values of other structural parameters are tabulated together with observed amplitudes of vibration as well as calculated amplitudes and shrinkage corrections derived with the aid of a normal-coordinate treatment.

Introduction

Highly fluorinated peroxides are a small but most interesting class of compounds.[2] Although the first two examples, CF_3OOCF_3[3] and FOOF,[4] were prepared in 1933, further well-characterized examples did not appear until the 1950's. At present, the number of such compounds is over 100 and some general synthetic methods have been found which could make their number much larger.

It turns out that the first two examples represent extremes in this class of compounds. Both O_2F_2 and $CF_3O_2CF_3$ are unusual compounds, O_2F_2 for its unusual structure, low thermal stability, and extreme reactivity and $CF_3O_2CF_3$ for its high thermal stability, unusual decomposition equilibrium, and rather low reactivity. While both compounds are formally derivatives of H_2O_2, where hydrogen is replaced by an electronegative atom or group, they have little other similarity. The oxygen–oxygen bond in $CF_3O_2CF_3$ closely resembles that in H_2O_2,[5] whereas the bond in O_2F_2 is considerably shorter and not greatly different from that in molecular oxygen.[6] Several rationales have been invoked to account for structural variations among the compounds, but a quantitative treatment has not yet appeared.[7]

Three important compounds that can be viewed as intermediate between H_2O_2 and O_2F_2 are CF_3OOH,[8,9] CF_3OOCl,[10,11] and CF_3OOF.[12,13] These molecules can in principle

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