Journal of Organometallic Chemistry, 145 (1978) 315—327

MOLECULAR STRUCTURE AND MASS SPECTRUM OF DICARBONYLBIS(TETRAPHENYLCYCLOBUTADIENE)MOLYBDENUM

A. EFRATY *, J.A. POTENZA, L. ZYONTZ, J. DAILY, M.H.A. HUANG and B. TOBY

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, N.J. 08903 (U.S.A.)

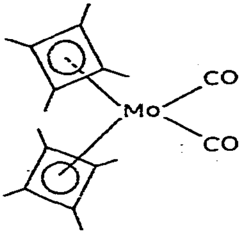
(Received August 6th, 1976)

Summary

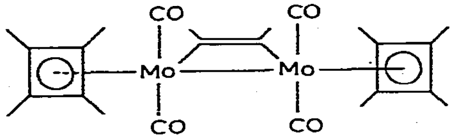
The crystal structure of dicarbonylbis(tetraphenylcyclobutadiene)molybdenum has been determined from three-dimensional X-ray data collected by counter methods. The structure consists of monomeric units with each Mo atom bonded to two carbonyl and two Ph_4C_4 groups. Excluding phenyl substituents, the local symmetry about Mo is very nearly C_{2v}. Both cyclobutadiene (CBD) groups are asymmetrically bonded to Mo, and the spread in Mo—C(CBD) distances (2.26 to 2.38 Å) is significantly larger than that found with other structures containing substituted cyclobutadiene groups. The carbonyl groups show several short intramolecular C···C contacts with the cyclobutadiene C atoms (2.68 to 3.03 Å) and with each other (2.63 Å). They appear to be wedged between the Ph_4C_4 groups and to be responsible for the asymmetric bonding of the cyclobutadiene groups. The mass spectrum, which shows the characteristic fragmentation pattern of cyclobutadienemetal complexes, suggests a relatively high thermal stability for the title compound. Crystallographic data are as follows: space group $P2_1/n$; unit cell a 20.15(2), b 18.82(3), c 11.03(1) Å, β 91.59(6)°; V 4181 Å^3; d_{calc} for $Z = 4$ is 1.380 and d_{obs} is 1.365(7) g/cm^3. A total of 1659 reflections with $F^2 \geqslant 2\sigma$ were used to refine the structure to final values of $R_F = 0.063$ and $R_{wF} = 0.041$.

Introduction

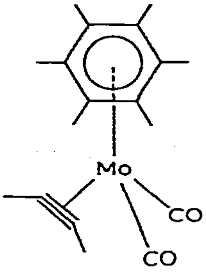
Reactions of metal carbonyls with acetylene derivatives have received considerable attention during the last two decades [1]. These reactions are known to yield a wide variety of organometallic and organic products. For example, reaction [2] of $Mo(CO)_6$ or (diglyme)$Mo(CO)_3$ with Ph_2C_2 in benzene at elevated temperature and under pressure yielded as products hexaphenylbenzene, a diketone of formula $(Ph_2C_2)_3(CO)_2$, and five different organometallic complexes. Proposed structures for two of these complexes are shown below with phenyl substituents indicated by dashes. Of these reaction products, I is particularly interesting since it is the only known complex for which a dicyclobutadiene geometry has been proposed *. The lack of structural data for dicyclobutadiene-metal complexes, coupled with the possibility of formulating the complex as III instead of I, prompted the present structural investigation of I.



(I)



(II)



(III)

Experimental

Synthesis. A sample of I was prepared by a modification of the Hübel and Merényi procedure [2]. 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 a temperature of 127(1)°C for a period of 19 h **. The product mixture was dried under reduced pressure (~1 mmHg, 30°C) and unreacted $Mo(CO)_6$ was removed by sublimation (0.05 mmHg, 80°C). The residue obtained was dissolved in benzene (~30 ml) and the resulting yellow solution was chromatographed on a neutral alumina column (3.5 × 75 cm). A yellow band eluted with a 5/1 v/v mixture of benzene/light petroleum ether (30—60°C) gave, upon drying, ~0.5 g of impure I (m.p. 238—241°C). Further purification of I was accomplished by repeated column chromatography as described above. Recrystallization from methylene chloride/hexane gave finally ~0.1 g of a deep yellow sample of I (m.p. 256—260°C, lit. [2] 255—262°C). Selected analytical and spectroscopic data of I include: Anal.: Found: C, 80.52; H, 4.78; O, 3.99; mol. wt., 861 (Osmometric, $CHCl_3$). $C_{58}H_{40}O_2Mo$ calcd.: C, 80.60; H, 4.64; O, 3.71%; mol. wt., 865. Infrared spectrum (2200—1600 cm^{-1} region, recorded in CH_2Cl_2 solution) $\nu(CO)$, 2008 and 1956 (lit. [2] 2004 and 1961 cm^{-1}). Mass spectrum (80 eV; inlet temperature, 200°C; chamber temperature, 200°C; recorded on a Hitachi RMU-7E mass spectrometer); $(Ph_4C_4)_2Mo(CO)_2^+$ (*M/Z* 866, relative intensity 54); $(Ph_4C_4)_2Mo(CO)^+$ (*M/Z* 838, relative intensity 3); $(Ph_4C_4)_2Mo^+$ (*M/Z* 810, relative intensity 100); $(Ph_4C_4)(Ph_2C_2)Mo^+$ [*M/Z* 632, relative intensity 63); $Ph_4C_4Mo^+$ (*M/Z* 454, relative intensity 98); (Ph_2C_2)-Mo^+ (*M/Z* 276, relative intensity 21); $PhCMo^+$ (*M/Z* 187, relative intensity 12);

---

* Complex II, which has also been characterized structurally in our laboratory, is more correctly formulated as $(CO)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(Ph_4C_4)CO$. The complex contains a Mo=Mo bond and a bridging cyclopentadienone group [3].

** At this temperature, the major organometallic product found was I with trace amounts of II.

$Ph_2C_2^+$ (M/Z 178, relative intensity 47) and Mo^+ (M/Z 98, relative intensity 6). Here M/Z is given in terms of the most abundant isotopic species of each element.

Crystal data and data collection. Crystals of I, suitable for X-ray analysis, were obtained by slow evaporation from a toluene/hexane (1/1, v/v) solution. A single crystal of approximate dimensions 0.21 × 0.20 × 0.14 mm was mounted on the end of a glass rod. Preliminary Weissenberg photographs revealed systematic absences for $h0l$, $h + l = 2n + 1$ and for $0k0$, $k = 2n + 1$, fixing the space group as $P2_1/n$. Unit cell parameters a 20.15(2), b 18.82(3), c 11.03(1) Å, β 91.59(6)° were determined from a least-squares analysis of 12 reflections obtained using graphite monochromated Mo-K_α radiation (λ 0.71069 Å) and an Enraf-Nonius CAD-3 automated diffractometer. The calculated volume of the unit cell was 4181 Å^3, leading to a density of 1.380 g/cm^3 with $Z = 4$. The observed density, determined by flotation, was 1.365(7) g/cm^3.

Using a $\theta - 2\theta$ scan ($2 < \theta < 20°$), 4465 reflections were collected at room temperature (22 ± 2°C). Graphite monochromated Mo-K_α radiation was detected with a scintillation counter and a pulse height analyzer set to admit approximately 90% of the K_α peak. The scan range was a function of θ chosen according to $S = (0.8 + 0.9 \tan \theta)°$. A circular aperture 1.3 mm in diameter was placed 4.1 cm from the crystal. Each reflection was scanned rapidly before being recorded and Zr foil attenuators were inserted automatically if the diffracted beam intensity exceeded 6000 cps. Background measurements were made at the beginning and end of each scan with the total time for background counting equal to the scan time. The scan rate was 1/6° per second and each reflection was scanned a maximum of six times or until 6000 total counts were obtained. Relative intensities were determined by dividing the total counts by the number of scans. A standard reflection, recorded at fifty reflection intervals, remained consistent to ±3% throughout the data collection period.

After correction for Lorentz and polarization effects, 1659 reflections with $F^2 \geqslant 2\sigma(F^2)$ were used to elucidate and refine the structure. Here, $\sigma(F^2) = (Lp)^{-1}(N_t + (0.02N_n)^2)^{1/2}$, where N_t is the total count (scan plus background), N_n is the net count (scan minus background), and 0.02 is an estimate of instrumental instability. With μ(Mo-K_α) = 3.6 cm^{-1}, maximum and minimum absorption factors A^* were calculated [4] to be 1.07 and 1.05, respectively, for the crystal used to collect the data; consequently, absorption corrections were not applied.

Structure determination

The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques. Approximate coordinates for the unique Mo atom were obtained by analysis of a normal sharpened Patterson map. The remaining non-hydrogen atoms were located in the usual way via a series of structure factor, difference Fourier calculations, each successive difference map being phased by an increasing number of atoms.

In the initial stages of refinement, all phenyl rings were treated as rigid groups of D_{6h} symmetry with C—C and C—H bond distances of 1.392 and 0.95 Å [5], respectively. The rigid body refinement was accomplished using a local modification of program GROUP, developed by LaPlaca and Ibers [6]; the remaining

TABLE 1

FINAL PARAMETERS[a] FOR $(Ph_4C_4)_2Mo(CO)_2$

Atom	x	y	z	B (Å^2)
Mo	0.25726(5)	0.00526(7)	0.0957(1)	b
O(1)	0.2606(4)	0.1568(5)	−0.0199(8)	5.0(3)
O(2)	0.2358(4)	0.0884(5)	0.3370(7)	5.2(3)
C(1)	0.2582(6)	0.1026(7)	0.0260(11)	4.4(4)
C(2)	0.2428(6)	0.0559(6)	0.2487(11)	3.1(4)
C(10)	0.1839(5)	−0.0788(6)	0.0091(9)	1.3(3)
C(20)	0.1592(5)	−0.0540(6)	0.1271(10)	1.5(3)
C(30)	0.1442(5)	0.0144(6)	0.0703(9)	1.6(3)
C(40)	0.1729(4)	−0.0094(7)	−0.0427(9)	1.5(3)
C(50)	0.3476(5)	−0.0737(6)	0.0642(10)	1.4(3)
C(60)	0.3659(4)	−0.0014(8)	0.0378(9)	1.4(2)
C(70)	0.3628(5)	0.0188(6)	0.1682(10)	1.9(3)
C(80)	0.3427(5)	−0.0550(6)	0.1911(10)	1.5(3)
C(11)	0.1912(5)	−0.1479(6)	−0.0520(10)	1.9(3)
C(12)	0.2151(6)	−0.1514(7)	−0.1692(11)	3.5(4)
C(13)	0.2141(6)	−0.2155(7)	−0.2344(11)	3.2(3)
C(14)	0.1885(6)	−0.2761(7)	−0.1809(12)	4.0(4)
C(15)	0.1665(5)	−0.2736(7)	−0.0616(11)	2.8(3)
C(16)	0.1674(5)	−0.2094(6)	0.0010(10)	2.1(3)
C(21)	0.1370(6)	−0.0934(6)	0.2348(10)	2.0(3)
C(22)	0.1783(5)	−0.1392(6)	0.3019(10)	2.8(3)
C(23)	0.1539(6)	−0.1761(6)	0.3997(11)	3.5(4)
C(24)	0.0876(6)	−0.1667(7)	0.4346(12)	4.7(4)
C(25)	0.0476(6)	−0.1220(6)	0.3646(11)	3.2(4)
C(26)	0.0695(6)	−0.0843(6)	0.2664(11)	2.9(4)
C(31)	0.0964(5)	0.0710(6)	0.1005(10)	1.6(3)
C(32)	0.0858(6)	0.0923(6)	0.2164(12)	3.6(4)
C(33)	0.0377(6)	0.1451(6)	0.2436(11)	3.4(3)
C(34)	−0.0004(6)	0.1707(6)	0.1471(12)	3.4(3)
C(35)	0.0080(6)	0.1518(6)	0.0322(11)	3.4(4)
C(36)	0.0593(5)	0.1030(6)	0.0048(11)	2.8(3)
C(41)	0.1612(5)	0.0083(7)	−0.1744(9)	2.1(3)
C(42)	0.1031(5)	−0.0179(6)	−0.2304(10)	2.6(3)
C(43)	0.0929(5)	−0.0114(7)	−0.3579(10)	3.1(3)
C(44)	0.1394(6)	0.0214(6)	−0.4246(11)	4.0(4)
C(45)	0.1971(5)	0.0474(6)	−0.3699(11)	2.8(3)
C(46)	0.2069(5)	0.0441(6)	−0.2431(12)	3.0(3)
C(51)	0.3545(5)	−0.1428(6)	0.0042(10)	1.9(3)
C(52)	0.3246(5)	−0.2035(6)	0.0469(10)	2.5(3)
C(53)	0.3371(6)	−0.2708(6)	−0.0074(11)	2.7(3)
C(54)	0.3793(6)	−0.2736(7)	−0.1035(12)	5.0(4)
C(55)	0.4091(6)	−0.2140(7)	−0.1470(11)	4.3(4)
C(56)	0.3974(5)	−0.1486(6)	−0.0958(11)	2.5(3)
C(61)	0.3948(5)	0.0346(5)	−0.0696(10)	1.4(3)
C(62)	0.3763(5)	0.0201(6)	−0.1888(10)	2.0(3)
C(63)	0.4035(5)	0.0538(6)	−0.2867(11)	3.0(3)
C(64)	0.4512(6)	0.1067(6)	−0.2625(12)	3.8(4)
C(65)	0.4710(5)	0.1234(6)	−0.1433(12)	3.3(4)
C(66)	0.4419(5)	0.0864(6)	−0.0502(11)	2.8(4)

(continued)

Table 1 (continued)

Atom	x	y	z	B (Å²)
[illegible]	[illegible]	[illegible]	0.9491(10)	1.4(3)
[illegible]	[illegible]	[illegible]	0.9307(10)	2.1(3)
[illegible]	[illegible]	[illegible]	0.9969(11)	2.6(3)
[illegible]	[illegible]	[illegible]	[illegible]	3.6(4)
[illegible]	[illegible]	[illegible]	[illegible]	3.2(3)
[illegible]	[illegible]	[illegible]	[illegible]	2.7(3)
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

Refinement was based on F and weights were set according to $w = 1/\sigma^2(F)$; the quantity minimized was $\Sigma w(F_o - F_c)^2$. Several cycles of refinement, the last two of which utilized anisotropic temperature factors for molybdenum and isotropic temperature factors for all carbon, oxygen and group atoms, led to convergence with $R_f = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.070$ and $R_{wF} = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2} = 0.057$. Hydrogen atom temperature factors B_H were set equal to 3.2 Å^2 and were not refined. At this point, an attempt was made to refine the non-group atoms anisotropically. The anisotropic temperature factors for the light atoms were not very well-defined. All had relatively large errors which, for several atoms, were large enough to cause cofactors of the β matrix to be negative, yielding non-positive definite temperature factors.

Examination of the correlation matrix revealed 26 correlation coefficients with magnitudes >0.50; the largest of these (-0.99, 0.89 and 0.88) were between group variables and did not appear to be due to a poor choice of group axes. Because of the large correlation between group variables, full-matrix refinement was initiated. Beginning with the isotropically converged group parameters, three cycles of refinement utilizing anisotropic temperature factors for Mo and isotropic temperature factors for C and O atoms gave final values of $R_F = 0.063$ and $R_{wF} = 0.041$. Because the ratio of the number of observations (N_o) to the number of variables (N_v) was not large (6.63), no further attempt was made to refine the light atoms anisotropically. For the final cycle, the average parameter shift was 0.06 σ, where σ is the esd obtained from the inverse matrix. The final value for the error in an observation of unit weight, $[\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$, was 1.29. The Mo residual appeared as the largest peak (0.4 e/Å^3) on a final difference map. Final atomic parameters are listed in Table 1; hydrogen coordinates are given in Table 2. A list of observed and calculated structure factors is available *.

Description of the structure and discussion

The structure consists of discrete monomers of I, verifying the original assignment of Hübel and Merényi. In the crystal, the shortest non-hydrogen intermolecular contact is C(45)···O(2′) (3.43(1) Å). Neither this nor any remaining contact is short enough to indicate intermolecular interactions significantly stronger than those arising from Van der Waals forces.

Two views of the molecule showing the numbering scheme are given in Fig. 1 and 2. The phenyl groups are labeled such that carbon atoms C(N1) through C(N6) and hydrogen atoms H(N2) through H(N6) form the phenyl ring attached to the cyclobutadiene carbon atom C(N0). Selected interatomic distances and angles are given in Table 3, short intramolecular contacts are listed in Table 4, while the results of least-squares planes calculations are presented in Table 5.

The structure clearly reveals a tilted dicyclobutadiene geometry with each

(Continued on p. 323)

---

* The table of structure factors has been deposited as NAPS Document No. 03175 (10 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

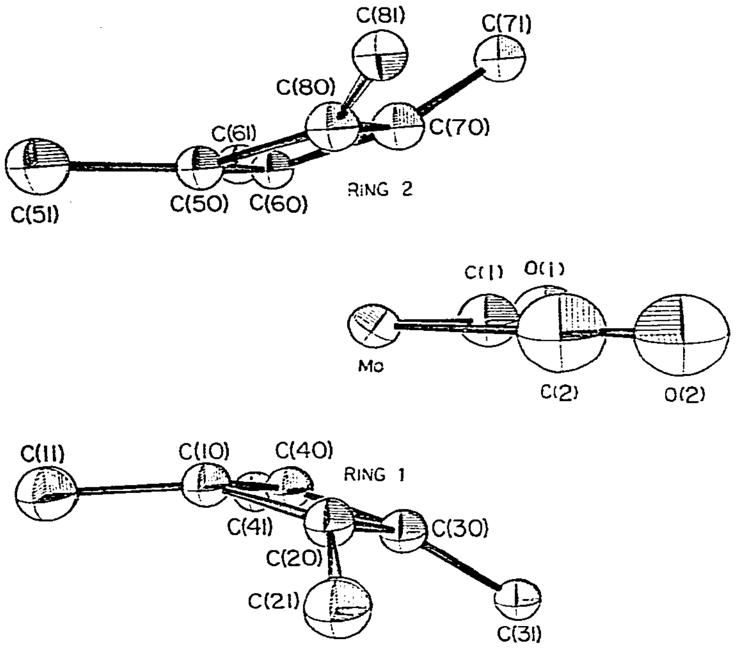


Fig. 1. View of I along the plane of the carbonyl groups showing the atom numbering scheme; phenyl groups have been omitted for clarity.

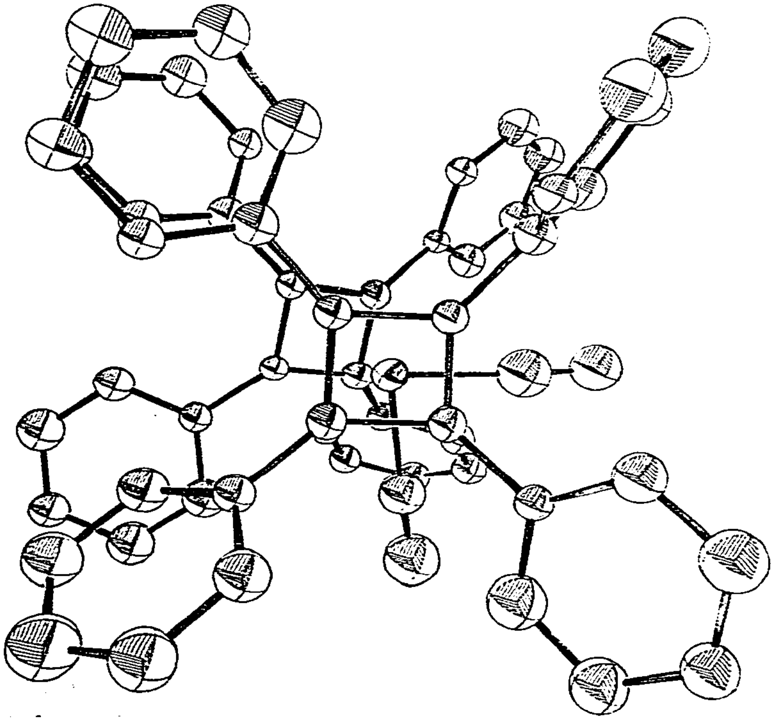


Fig. 2. View of I approximately perpendicular to the plane of the carbonyl groups.

TABLE 3. BOND DISTANCES (Å) AND ANGLES (deg)

Atoms	Distance	Atoms	Distance	Atoms	Angle	Atoms	Angle
Mo—C(1)	1.987(13)	O(1)—C(1)	1.14(1)	C(1)—Mo—C(2)	83.6(5)	CR(1)—Mo—C(1)	102.6
Mo—C(2)	1.966(12)	O(2)—C(2)	1.16(1)	CR(1)—Mo—CR(2)	140.8	CR(1)—Mo—C(2)	105.2
Mo—C(10)	2.346(11)	Mo—C(50)	2.377(11)	Mo—C(1)—O(1)	175.9(12)	CR(2)—Mo—C(1)	107.4
Mo—C(20)	2.295(11)	Mo—C(60)	2.291(9)	Mo—C(2)—O(2)	176.9(10)	CR(2)—Mo—C(2)	102.6
Mo—C(30)	2.283(10)	Mo—C(70)	2.255(10)	CR(1)—C(10)—C(11)	163.2	CR(2)—C(50)—C(51)	165.5
Mo—C(40)	2.263(9)	Mo—C(80)	2.287(11)	CR(1)—C(20)—C(21)	166.3	CR(2)—C(60)—C(61)	169.8
C(10)—C(20)	1.48(1)	C(50)—C(60)	1.44(2)	CR(1)—C(30)—C(31)	163.5	CR(2)—C(70)—C(71)	159.0
C(20)—C(30)	1.46(1)	C(60)—C(70)	1.49(1)	CR(1)—C(40)—C(41)	158.7	CR(2)—C(80)—C(81)	165.2
C(30)—C(40)	1.46(1)	C(70)—C(80)	1.47(1)	C(10)—C(20)—C(30)	88.3(8)	C(50)—C(60)—C(70)	91.6(9)
C(40)—C(10)	1.44(1)	C(80)—C(50)	1.45(1)	C(20)—C(30)—C(40)	90.8(10)	C(60)—C(70)—C(80)	86.8(9)
C(10)—C(11)	1.47(2)	C(50)—C(51)	1.47(1)	C(30)—C(40)—C(10)	90.0(10)	C(70)—C(80)—C(50)	92.1(10)
C(20)—C(21)	1.48(1)	C(60)—C(61)	1.50(1)	C(40)—C(10)—C(20)	90.7(9)	C(80)—C(50)—C(60)	89.5(10)
C(30)—C(31)	1.48(1)	C(70)—C(71)	1.45(1)	C(20)—C(10)—C(11)	136(1)	C(80)—C(50)—C(51)	131(1)
C(40)—C(41)	1.50(1)	C(80)—C(81)	1.50(1)	C(40)—C(10)—C(11)	129.4(9)	C(60)—C(50)—C(51)	136(1)
				C(10)—C(20)—C(21)	132(1)	C(50)—C(60)—C(61)	134(1)
				C(30)—C(20)—C(21)	136(1)	C(70)—C(60)—C(61)	133(1)
				C(20)—C(30)—C(31)	132(1)	C(60)—C(70)—C(71)	133(1)
				C(40)—C(30)—C(31)	134(1)	C(80)—C(70)—C(71)	133(1)
				C(30)—C(40)—C(41)	135(1)	C(70)—C(80)—C(81)	128(1)
				C(10)—C(40)—C(41)	127(1)	C(50)—C(80)—C(81)	136(1)

Phenyl group distances

Atoms	N = 1	N = 2	N = 3	N = 4	N = 5	N = 6	N = 7	N = 8
C(N1)—C(N6)	1.39(1)	1.42(1)	1.41(1)	1.38(1)	1.42(1)	1.37(1)	1.39(1)	1.40(1)
C(N5)—C(N6)	1.39(1)	1.38(2)	1.42(2)	1.41(1)	1.38(2)	1.38(2)	1.37(2)	1.38(2)
C(N4)—C(N5)	1.40(2)	1.38(2)	1.33(1)	1.38(1)	1.36(2)	1.40(2)	1.38(1)	1.37(2)
C(N3)—C(N4)	1.39(2)	1.41(1)	1.38(2)	1.35(1)	1.38(2)	1.40(2)	1.40(1)	1.38(2)
C(N2)—C(N3)	1.40(2)	1.38(2)	1.42(2)	1.42(1)	1.43(1)	1.38(1)	1.38(1)	1.40(2)
C(N1)—C(N2)	1.39(1)	1.39(2)	1.36(1)	1.40(1)	1.38(1)	1.38(1)	1.39(1)	1.40(1)

Phenyl group angles

C(NO)—C(N1)—C(N2)	120(1)	123(1)	123(1)	117(1)	122(1)	124(1)	125(1)	123(1)
C(NO)—C(N1)—C(N6)	120(1)	117(1)	118(1)	123(1)	119(1)	119(1)	117(1)	121(1)
C(N2)—C(N1)—C(N6)	119(1)	120(1)	119(1)	119(1)	119(1)	117(1)	118(1)	116(1)
C(N1)—C(N2)—C(N3)	121(1)	121(1)	122(1)	120(1)	121(1)	123(1)	122(1)	122(1)
C(N2)—C(N3)—C(N4)	119(1)	120(1)	116(1)	120(1)	118(1)	117(1)	120(1)	119(1)
C(N3)—C(N4)—C(N5)	120(1)	118(1)	124(1)	120(1)	122(1)	121(1)	118(1)	120(1)
C(N4)—C(N5)—C(N6)	120(1)	124(1)	119(1)	121(1)	121(1)	118(1)	121(1)	121(1)
C(N5)—C(N6)—C(N1)	121(1)	117(1)	119(1)	119(1)	120(1)	123(1)	121(1)	121(1)

TABLE 4

SELECTED INTRAMOLECULAR CONTACTS SHORTER THAN 3.5 Å

Atoms	Distance	Atoms	Distance
C(1)···C(2)	2.63(2)	C(11)···C(51)	3.23(1)
C(10)···C(50)	3.32(1)	C(11)···C(52)	3.05(2)
C(1)···C(30)	2.88(2)	C(12)···C(51)	3.35(2)
C(1)···C(40)	2.81(2)	C(12)···C(52)	3.34(2)
C(1)···C(60)	2.91(2)	C(15)···C(53)	3.46(2)
C(1)···C(70)	3.03(2)	C(16)···C(52)	3.18(1)
C(2)···C(20)	2.96(2)	C(22)···C(81)	3.42(1)
C(2)···C(30)	2.86(2)	C(22)···C(82)	3.43(2)
C(2)···C(70)	2.68(2)	C(46)···C(62)	3.46(1)
C(2)···C(80)	2.97(2)		

molybdenum atom bonded to two carbonyl and two Ph_4C_4 groups. Excluding the phenyl groups, the local point symmetry about molybdenum is approximately C_{2v} with mirror planes perpendicular to and in the plane of the carbonyl groups. The degree of tilt between the cyclobutadiene (CBD) groups may be gauged by the angle CR(1)—Mo—CR(2) (140.8°) or alternatively by the dihedral angle between least-squares planes of the cyclobutadiene rings (33.5°). Here, CR designates the center of the CBD ring. The cyclobutadiene rings, whose average bond distances closely resemble those found for other cyclobutadiene-metal complexes (Table 6), are nearly eclipsed and are slightly puckered as indicated by the dihedral angles C(20), C(30), C(40)/C(20), C(10), C(40) (5.3°) and C(60), C(70), C(80)/C(60), C(50), C(80) (1.8°). The phenyl groups are twisted from the plane of the associated CBD rings to varying degrees (Table 5) and are bent from the CBD planes, *exo* to molybdenum, by angles ranging from 12.3 to 22.2°. Bending and twisting of this magnitude for phenyl groups is common with tetraphenylcyclobutadienemetal complexes [10—13]. However, two of the phenyl groups, C(1N) and C(5N), which are opposite to the carbonyl groups, are nearly eclipsed, and the shortest contact between them (3.05(2) Å) is indicative of a weak secondary interaction.

Nonbonding intramolecular contacts suggest that the molecule is crowded sterically with the carbonyl groups wedged between the Ph_4C_4 groups. Each C(CO) atom shows four short (2.68 to 3.03 Å) contacts to the CBD carbon atoms (Table 4). In addition, the C(CO)···C(CO) distance is also relatively short (2.63 Å). Thus, an increase or decrease in the C(1)—Mo—C(2) angle from its value of 83.6° is not possible without decreasing an already short C···C contact or without decreasing the CR(1)—Mo—CR(2) angle. A decrease in the latter would increase non-bonding repulsion between the Ph_4C_4 groups, particularly in the vicinity of the phenyl groups C(1N) and C(5N) which are already in fairly close contact.

Both cyclobutadiene groups are bonded asymmetrically to Mo. As seen from the Mo—C(CBD) distances in Table 3, long Mo—C(CBD) distances are associated with the CBD carbon atoms furthest from the C(CO) atoms. Because of this asymmetric bonding, the spread in Mo—C(CBD) distances (2.26 to 2.38 Å) is considerably larger than that found typically with other structures containing substituted cyclobutadiene groups [10—13]. The average Mo—C(CBD) distance

TABLE 5

LEAST-SQUARES PLANES [a] AND DIHEDRAL ANGLES

	Least-squares planes			
	A	B	C	D
Ring 1 [C(10), C(20), C(30), C(40)]	0.904	0.308	0.296	2.944
Ring 2 [C(50), C(60), C(70), C(80)]	0.958	−0.246	0.145	7.130
Phenyl 1 [C(11)—C(16)]	0.907	−0.216	0.361	3.913
Phenyl 2 [C(21)—C(26)]	0.252	0.759	0.600	0.893
Phenyl 3 [C(31)—C(36)]	−0.673	−0.733	0.093	−2.184
Phenyl 4 [C(41)—C(46)]	−0.465	0.876	0.130	−1.629
Phenyl 5 [C(51)—C(56)]	0.758	−0.142	0.636	5.822
Phenyl 6 [C(61)—C(66)]	−0.721	0.692	0.033	−5.326
Phenyl 7 [C(71)—C(76)]	−0.709	−0.003	0.705	−3.764
Phenyl 8 [C(81)—C(86)]	0.919	0.329	0.218	6.456

Deviations of atoms from the planes (Å) [b]

Phenyl rings	N = 1	N = 2	N = 3	N = 4	N = 5	N = 6	N = 7	N = 8
C(N0) *	−0.198	−0.024	0.116	−0.215	0.122	0.012	−0.079	−0.045
C(N1)	−0.010	0.006	0.020	−0.022	0.004	−0.003	0.007	−0.016
C(N2)	0.007	0.000	0.013	0.004	−0.002	0.007	0.019	0.007
C(N3)	0.007	−0.010	−0.030	0.005	0.000	−0.007	−0.025	0.002
C(N4)	−0.016	0.014	0.014	0.005	0.000	0.002	0.006	−0.003
C(N5)	0.013	−0.008	0.019	−0.023	0.002	0.002	0.019	−0.007
C(N6)	0.001	−0.002	−0.036	0.031	−0.004	−0.002	−0.026	0.016

Ring 1	C(10)	−0.024	C(11)*	−0.474
	C(20)	0.023	C(21)*	−0.287
	C(30)	−0.024	C(31)*	−0.476
	C(40)	0.024	C(41)*	−0.480
	Mo*	2.059		
Ring 2	C(50)	0.008	C(51)*	0.382
	C(60)	−0.008	C(61)*	0.243
	C(70)	0.008	C(71)*	0.539
	C(80)	−0.008	C(81)*	0.353
	Mo*	−2.061		

Dihedral angles between planes (deg.)

Ring 1—Ring 2	33.5	Ring 2—Phenyl 7	125.2
Ring 1—Phenyl 1	30.6	Ring 2—Phenyl 8	33.7
Ring 1—Phenyl 2	50.2	Phenyl 1—Phenyl 5	18.5
Ring 1—Phenyl 3	143.8	Phenyl 2—Phenyl 8	52.2
Ring 1—Phenyl 4	96.4	Phenyl 3—Phenyl 7	56.9
Ring 2—Phenyl 5	31.4	Phenyl 4—Phenyl 6	19.0
Ring 2—Phenyl 6	148.9		

[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 bxc^*, b and c^*, respectively. [b] Starred atoms were not used to define the plane.

in I is ~0.05 Å larger than that reported for $[(\mathrm{Ph_4C_4})\mathrm{Mo(CO)_2Br}]_2$ [10]; most of this lengthening is accounted for by the two long Mo—C(CBD) distances in I. Lastly, we note that long Mo—C(10) and Mo—C(50) contacts are consistent with the short C(CBD)···C(CO) contacts mentioned above; i.e., a decrease in either Mo—C(10) or Mo—C(50) would require a corresponding decrease in the

TABLE 6

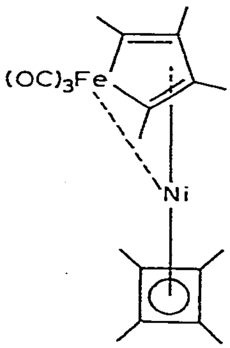
STRUCTURAL PARAMETERS FOR COMPLEXES CONTAINING Ph_4C_4 GROUPS

	I[a]	$[Ph_4C_4)Mo(CO)_2Br]_2$	$(C_5H_5)Nb(CO)(Ph_2C_2)(Ph_4C_4)$	$(C_5H_5)V(CO)_2(Ph_4C_4)$	$(Ph_4C_4)Fe(CO)_3$
C(CBD)—C(CBD) (Å)	1.46(2)	1.465(8)	1.46	1.47	1.459(17)
C—C—C (°)	89.9(15)	90.0(4)	90.0	90.0	90.0(10)
C(phenyl)—C(CBD) (Å)	1.48(2)	1.475(8)	1.48	1.46	1.468(17)
M—C(CBD) (Å)	2.30(4)	2.253(6)	2.38	2.26	2.067(12)
C(CO)—M—C(CO) (°)	83.6(5)	88.2(3)	—	89	97.0(6)
(Ph_4C_4)—M—π-ligand (°)	140.8	—	137	137	—
Reference	this work	10	11	12	13

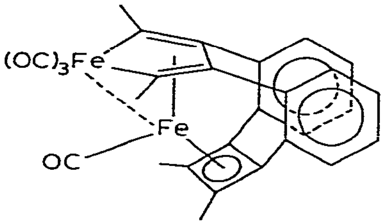
[a] Standard deviations for numbers in this column were calculated using the equation $s = [\Sigma(x_i - \bar{x})^2/(N-1)]^{1/2}$.

already short C(CBD)···C(CO) contacts. Thus, the structural evidence is consistent with asymmetric Ph_4C_4 bonding resulting from steric crowding between C(CBD) and C(CO) atoms.

Despite the apparent steric crowding in I, which conceivably could lead to relatively weak metal—ligand bonds, the complex appeared to be stable both in air and in solution; also, it exhibited sufficient volatility and thermal stability to permit its mass spectrum to be recorded. Under electron-impact conditions, the molecular ion of I underwent a two-step unimolecular carbonyl dissociation sequence to yield the carbonyl-free ion, which then degraded further to the bare metal ion by consecutive elimination of four neutral Ph_2C_2 fragments. This fragmentation sequence, depicted in Fig. 3, is consistent with those reported previously for other cyclobutadienemetal [14] and tetraphenylcyclobutadienemetal [15] complexes. The presence of the $PhCMo^+$ (*M/Z* 187) ion in the mass spectrum of I suggests an alternative route for the decay of $Ph_2C_2Mo^+$ to Mo^+ via a two-step sequence involving elimination of PhC fragments (Fig. 3); this fragmentation mode has not been observed previously with cyclobutadienemetal complexes. A second feature of interest in the mass spectrum is the rela-



(IV) (–) = CH_3



(V) (–) = C_6H_5

M/Z	Relative intensity	Fragmentation	
		$(Ph_4C_4)_2Mo(CO)_2$	
		$\downarrow$ $+e^-$ $-2e^-$	
866	54	$(Ph_4C_4)_2Mo(CO)_2^+$	
		$\downarrow$ $-CO$	
838	3	$(Ph_4C_4)_2Mo(CO)^+$	
		$\downarrow$ $-CO$	
810	100	$(Ph_4C_4)_2Mo^+$	
		$\downarrow$ $-Ph_2C_2$	
632	63	$(Ph_4C_4)(Ph_2C_2)Mo^+$	
		$\downarrow$ $-Ph_2C_2$	
454	98	$(Ph_4C_4)Mo^+$	
		$\downarrow$ $-Ph_2C_2$	
276	21	$(Ph_2C_2)Mo^+$	
		$\downarrow$ $-PhC$	
187	12	$PhCMo^+$	$-Ph_2C_2$
		$\downarrow$ $-PhC$	
98	6	Mo^+	

Fig. 3. Proposed fragmentation pattern of I under electron impact conditions.

tively high abundance of the molecular ion (54% of the base peak, $(Ph_4C_4)_2Mo^+$). In view of the high molecular weight of the complex *, this implies a high stability for $(Ph_4C_4)_2Mo(CO)_2^+$ (*M/Z* 866) which is consistent with the high thermal stability of the parent molecule. While it is also tempting to infer a high stability for the base peak, $(Ph_4C_4)_2Mo^+$, this could be misleading since the abundance of this ion will depend both on its rate of formation and decay.

Lastly, we comment on the apparent scarcity of dicyclobutadienemetal complexes. Substituted cyclobutadiene ligands are known to form a variety of mixed sandwich complexes with other π-ligands such as tetracyclone [2], ferracyclopentadiene (e.g. IV [17] and V [18]), cyclopentadienyl [19,20], benzene [21], cyclooctatetraene [22] and others [23]. This observation, taken together with the apparent high stability of I, suggests that the scarcity of dicyclobutadienemetal complexes might be due to synthetic complications rather than an inherent instability.

---

* Mass spectra of organometallic compounds with molecular weights greater than 750 are extremely rare [16].

Acknowledgement

We thank the Rutgers Computing Center for computer time, and the Research Council and the School of Chemistry of Rutgers University for partial financial support.

References

1 F.L. Bowden and A.B.P. Lever, Organometal. Chem. Rev., 3 (1968) 227.
2 W. Hübel and R. Merényi, J. Organometal. Chem., 2 (1964) 213.
3 J.A. Potenza, R.J. Johnson, R. Chirico and A. Efraty, Inorg. Chem., 16 (1977) 2354.
4 P. Coppens and R.F. Stewart, ABSORB Program.
5 M.R. Churchill, Inorg. Chem., 12 (1973) 1213.
6 S.J. LaPlaca and J.A. Ibers, Acta Cryst., 18 (1965) 511.
7 J. Potenza, P. Giordano, D. Mastropaolo and A. Efraty, Inorg. Chem., 13 (1974) 2540.
8 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham England, 1974, p. 71—98.
9 Ref. 8, p. 148—151.
10 M. Mathew and G.J. Palenik, J. Organometal. Chem., 61 (1973) 301.
11 A.I. Gusev and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 515.
12 A.I. Gusev, G.G. Aleksandrov and Yu.T. Struchkov, Zh. Strukt. Khim., 10 (1969) 655.
13 R.P. Dodge and V. Schomaker, Acta Cryst., 18 (1965) 614.
14 A. Efraty, M.H.A. Huang and C.A. Weston, J. Organometal. Chem., 91 (1975) 327.
15 R.B. King and A. Efraty, Org. Mass. Spectrom., 3 (1970) 1233.
16 M.I. Bruce, Advan. Organometal. Chem., 6 (1968) 273; M. Cais and M.S. Lupin, ibid., 8 (1970) 211.
17 E.F. Epstein and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 502.
18 E.F. Epstein and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 493.
19 P.M. Maitlis, A. Efraty and M.L. Games, J. Amer. Chem. Soc., 87 (1965) 719; P.M. Maitlis and A. Efraty, J. Organometal. Chem., 4 (1965) 172.
20 R.B. King and A. Efraty, Chem. Commun., (1970) 1370.
21 A. Efraty and P.M. Maitlis, J. Amer. Chem. Soc., 89 (1967) 3744.
22 H.O. Van Oven, J. Organometal. Chem., 55 (1973) 309.
23 P.M. Maitlis, Advan. Organometal. Chem., 4 (1966) 95.