THE CRYSTAL STRUCTURE OF DI-μ-BROMOBIS(π-TETRAPHENYL-CYCLOBUTADIENE)TETRACARBONYLDIMOLYBDENUM(I)

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SUMMARY

The crystal structure of di-μ-bromobis(π-tetraphenylcyclobutadiene)tetra-carbonyldimolybdenum(I) has been determined by X-ray diffraction techniques using diffractometer data. The red crystals are triclinic with $a = 11.306(4)$, $b = 13.681(4)$, $c = 17.561(10)$ Å and α 105.58(1), β 91.14(2) and γ 108.50(5)°. The space group indicated by the intensity statistics is $P\bar{1}$ and, with two dimer molecules per cell, no molecular symmetry is required (D_m 1.59 g/cm^3 and D_c 1.585 g/cm^3). The structure was solved by the heavy atom method and refined by least-squares methods to a final R of 0.056 for 8089 observed reflections (2θ limit of 135° with copper radiation) used in the analyses. The average Mo–Br distance in the bromine bridged dimer is 2.637 Å, with a Mo–Mo distance of 2.954 Å. The mean Mo–C (cyclobutadiene ring) is 2.253 Å and the Mo–C (carbonyl) is 2.008 Å. The average C–C distance in the planar cyclobutadiene rings is 1.469 Å.

INTRODUCTION

Longuet–Higgins and Orgel[1] predicted that cyclobutadienemetal complexes should be fairly stable even though the parent cyclobutadiene was considered to be unstable. Subsequently, the preparation of di-μ-chlorodichlorobis(π-tetramethyl-cyclobutadiene)dinickel(II)[2] and the confirmation of the structure by an X-ray crystal study[3] stimulated the preparation of other cyclobutadiene complexes[4].

A number of tetraphenylcyclobutadiene–transition metal complexes were prepared by ligand-transfer reactions using tetraphenylcyclobutadienepalladium iodide or bromide. The reactions with molybdenum hexacarbonyl gave compounds which were formulated as $[(C_6H_5C)_4Mo(CO)_3X]_2$, X = Br or I, where an unsupported Mo–Mo bond was present in the dimer[5]. Because of the unusual nature of the postulated Mo–Mo bond and the paucity of data on cyclobutadiene complexes, we undertook an X-ray crystal structure of the above bromo compound. Our preliminary report[6] showed that the compound was correctly formulated as di-μ-bromobis-(π-tetraphenylcyclobutadiene)tetracarbonyldimolybdenum(I) and did not contain an unsupported Mo–Mo bond. We now present the results of our completed investigation.

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EXPERIMENTAL

Crystal data and intensity measurement

The sample was kindly supplied by Dr. A. Efraty. The preliminary precession and Weissenberg photographs indicated triclinic symmetry, with the possible space groups $P1$ or $P\bar{1}$. The space group $P\bar{1}$ was indicated by the intensity statistics and confirmed by the structure analysis.

A small, equidimensional crystal, 0.10 mm on an edge, was used for the intensity measurements. The crystal was mounted on a General Electric XRD-6 diffractometer, and the 2θ values for 25 reflections in the range of 20–50° for the Cu–K_β X-radiation (λ 1.39217 Å) were measured carefully. These data were used in a least-squares procedure to obtain the unit cell dimensions. The values and their estimated standard deviations were $a = 11.306(4)$, $b = 13.681(4)$, $c = 17.561(4)$ Å and α 105.58(1), β 91.14(2) and γ 108.50(5)° The density calculated for two dimers ($Mo_2Br_2C_{60}H_{40}O_4$, mol.wt. 1176.68) per unit cell was 1.585 g/cm³, in good agreement with the value of 1.59 g/cm³ measured by flotation.

The intensity data were measured on the same instrument with the same crystal, using the stationary-crystal–stationary-counter technique with Cu–K_{α_1} X-radiation (λ 1.54051 Å). Reasonable monochromatization was achieved by using a nickel filter (0.7 mil) at the counter window, together with a pulse height analyzer. All reflections were measured for 20 seconds. The unique set with $2\theta \le 135°$ was measured first and then the reflections with $2\theta \le 80°$ were remeasured, for a total of 13725 measurements. Four standard reflections which were measured after every 100 reflections were used to calculate a small correction (maximum 5 %) for the variation of the standards with time. Before the crystal was removed from the orienter, a background curve was derived by the systematic measurement of regions of reciprocal space which were known to contain no reflections or streaks. After averaging reflections which were equivalent by symmetry, 8851 independent reflections were obtained of which the 8089 which were greater than 1.2 times the appropriate background were considered observed and used in the analysis. The remaining 762 reflections were considered unobserved and flagged with a minus sign. After a correction for the $\alpha_1-\alpha_2$ splitting was applied, the reflections were reduced to structure amplitudes in the usual way. Although the value of μ is 68.8 cm^{-1} for Cu–K_α-radiation, no absorption corrections were applied. The value of μr will vary from 0.34 to 0.59 which could produce a maximum error of 20 % in F. However, the variations in the intensity as a function of φ at $\chi = 90°$ suggests that the error is much less. Finally, absorption errors tend to be taken up in the thermal parameters and produce only slight effects in positional parameters[7].

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the two molybdenum and two bromine atoms were determined from the sharpened three-dimensional Patterson function. A Fourier synthesis phased with these four atoms revealed the positions of all the remaining non-hydrogen atoms. A difference Fourier synthesis at this point, $R = \Sigma |F_o - |F_c||/\Sigma F_o$ was 0.18, did not indicate the presence of any additional carbonyl groups or solvent molecules.

Four, full matrix, least-squares calculations with individual isotropic thermal

TABLE 1

THE FINAL PARAMETERS OF ATOMS

The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$. All values are $\times 10^4$ except for Mo and Br atoms which are $\times 10^5$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	7738(4)	34031(3)	24656(2)	485(3)	309(2)	175(1)	209(5)	23(3)	188(3)
Mo(2)	26403(4)	55283(3)	32878(2)	470(3)	336(2)	153(1)	195(5)	−4(3)	188(2)
Br(1)	8928(5)	52106(4)	21508(3)	619(5)	383(3)	216(2)	280(6)	−96(5)	253(4)
Br(2)	31219(5)	40503(5)	21470(4)	580(5)	484(4)	277(2)	409(7)	166(5)	165(5)
C(1)	420(5)	1804(4)	1514(3)	61(5)	29(3)	21(2)	21(6)	−3(5)	9(4)
C(2)	−18(5)	2509(4)	1177(3)	51(4)	39(3)	18(2)	27(6)	−4(4)	10(4)
C(3)	−1030(5)	2432(4)	1697(3)	56(5)	33(3)	20(2)	24(6)	−3(5)	14(4)
C(4)	−592(5)	1706(4)	2022(3)	55(5)	37(3)	22(2)	29(6)	1(5)	17(4)
C(5)	3154(5)	7321(4)	3568(3)	55(5)	31(3)	24(2)	19(6)	6(5)	21(4)
C(6)	3830(5)	6935(4)	2914(3)	51(4)	37(3)	21(2)	26(6)	5(4)	21(4)
C(7)	4618(5)	6716(4)	3477(3)	60(5)	35(3)	19(2)	15(6)	−4(5)	20(4)
C(8)	3924(5)	7077(4)	4126(3)	53(4)	43(3)	18(2)	20(6)	7(4)	16(4)
C(9)	1330(6)	2754(5)	3247(4)	93(6)	50(4)	28(2)	25(8)	−21(6)	34(5)
O(9)	1562(6)	2367(5)	3699(4)	179(8)	93(5)	48(3)	64(10)	−46(7)	79(6)
C(10)	−444(5)	3723(5)	3225(3)	70(5)	46(4)	23(2)	20(7)	35(5)	14(4)
O(10)	−1160(5)	3902(4)	3626(3)	96(5)	71(4)	39(2)	33(7)	47(5)	15(4)
C(11)	3426(6)	4882(5)	3979(4)	78(6)	56(4)	28(2)	31(8)	−12(6)	39(5)
O(11)	3894(6)	4525(5)	4346(4)	153(7)	84(4)	51(3)	63(9)	−52(7)	69(5)
C(12)	1446(5)	5768(5)	4087(3)	57(5)	65(4)	20(2)	20(8)	8(5)	16(5)
O(12)	793(5)	5958(5)	4543(3)	86(5)	100(4)	33(2)	37(7)	38(5)	16(5)
C(1a)	1230(5)	1140(4)	1258(4)	49(5)	39(3)	32(2)	29(6)	−4(5)	15(4)
C(2a)	1397(7)	838(6)	449(4)	95(7)	62(5)	33(3)	69(9)	−8(7)	−6(6)
C(3a)	1988(7)	93(7)	163(5)	103(8)	84(6)	41(3)	108(11)	−24(8)	−28(7)
C(4a)	2422(7)	−363(6)	673(5)	84(7)	56(5)	60(4)	61(10)	−18(8)	−1(7)
C(5a)	2283(6)	−70(6)	1454(5)	65(6)	63(5)	66(4)	54(9)	16(8)	55(7)
C(6a)	1691(6)	690(5)	1762(4)	69(6)	61(5)	41(3)	62(8)	11(6)	42(6)
C(1b)	255(5)	2964(4)	500(3)	76(5)	43(4)	17(2)	34(7)	4(5)	13(4)
C(2b)	1413(7)	3164(6)	217(4)	100(7)	73(5)	25(2)	51(10)	19(6)	32(5)
C(3b)	1634(8)	3578(8)	−431(5)	126(9)	121(8)	37(3)	83(14)	57(9)	67(8)
C(4b)	670(9)	3777(9)	−797(5)	180(12)	155(10)	41(3)	193(19)	65(11)	103(10)
C(5b)	−506(9)	3573(8)	−527(5)	144(10)	129(8)	40(3)	149(15)	55(9)	88(9)
C(6b)	−711(7)	3167(6)	128(4)	99(7)	81(5)	27(2)	97(10)	9(6)	45(6)
C(1c)	−2294(5)	2517(4)	1632(3)	54(4)	42(3)	18(2)	35(6)	7(4)	16(4)
C(2c)	−2536(6)	3486(5)	1760(4)	74(6)	52(4)	42(3)	54(8)	−13(6)	16(6)
C(3c)	−3761(7)	3471(6)	1663(5)	82(7)	67(5)	54(3)	74(9)	−4(7)	13(7)
C(4c)	−4751(6)	2521(6)	1424(4)	73(6)	86(6)	35(3)	73(9)	2(6)	11(6)
C(5c)	−4524(6)	1573(6)	1302(4)	61(6)	73(5)	40(3)	23(9)	3(6)	27(6)
C(6c)	−3310(6)	1557(5)	1416(4)	63(5)	54(4)	33(2)	27(8)	8(6)	22(5)
C(1d)	−1233(5)	878(4)	2403(3)	61(5)	40(3)	28(2)	26(7)	−8(5)	27(4)
C(2d)	−1919(8)	1099(5)	3046(4)	131(8)	50(4)	35(3)	21(10)	50(8)	28(6)
C(3d)	−2554(8)	309(7)	3375(5)	138(9)	72(6)	38(3)	1(12)	26(9)	33(7)
C(4d)	−2515(8)	736(6)	3067(5)	117(8)	57(5)	57(4)	1(10)	−14(9)	70(7)
C(5d)	−1907(7)	−977(6)	2410(6)	86(7)	57(5)	73(4)	47(9)	31(9)	76(8)
C(6d)	−1263(6)	−179(5)	2079(5)	71(6)	49(4)	54(3)	32(8)	12(7)	45(6)
C(1e)	2307(5)	7953(4)	3663(3)	64(5)	40(4)	29(2)	37(7)	5(5)	16(4)
C(2e)	2045(7)	8425(7)	4418(5)	108(8)	92(6)	40(3)	118(12)	20(8)	9(7)
C(3e)	1273(9)	9064(9)	4488(6)	173(12)	132(9)	49(4)	210(19)	9(11)	−3(9)

(continued)

TABLE 1 *(contd.)*

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(4e)	719(9)	9171(8)	3838(7)	128(10)	108(8)	74(5)	144(15)	7(12)	31(10)
C(5e)	934(7)	8677(6)	3093(5)	93(7)	80(6)	53(4)	94(11)	5(8)	42(7)
C(6e)	1733(6)	8059(5)	2992(4)	74(6)	56(4)	39(3)	46(8)	2(6)	41(6)
C(1f)	4022(5)	7182(4)	2145(3)	50(4)	48(4)	22(2)	23(6)	2(5)	33(4)
C(2f)	3824(8)	6403(6)	1413(4)	141(9)	83(6)	22(2)	65(12)	24(7)	35(6)
C(3f)	4107(9)	6724(8)	725(5)	169(11)	122(8)	29(3)	80(16)	40(9)	62(8)
C(4f)	4539(9)	7783(9)	756(6)	152(11)	138(9)	48(4)	112(16)	51(10)	114(10)
C(5f)	4750(8)	8565(7)	1486(6)	124(9)	94(7)	61(4)	74(13)	47(10)	106(9)
C(6f)	4469(6)	8262(5)	2167(4)	79(6)	62(5)	43(3)	29(8)	21(7)	66(6)
C(1g)	5819(5)	6521(4)	3445(3)	59(5)	40(3)	24(2)	28(6)	9(5)	28(4)
C(2g)	6489(7)	6551(7)	4134(4)	86(7)	109(7)	34(3)	92(11)	−3(7)	56(7)
C(3g)	7662(8)	6430(9)	4096(6)	96(8)	159(9)	50(4)	139(15)	7(9)	71(10)
C(4g)	8226(7)	6314(7)	3393(5)	85(7)	93(6)	52(4)	89(11)	16(8)	39(8)
C(5g)	7556(7)	6290(6)	2725(5)	95(7)	74(5)	43(3)	82(10)	52(8)	38(7)
C(6g)	6364(6)	6374(5)	2734(4)	77(6)	61(4)	29(2)	54(8)	24(6)	27(5)
C(1h)	4316(5)	7517(5)	4993(3)	57(5)	56(4)	23(2)	29(7)	3(5)	16(5)
C(2h)	5236(8)	8525(6)	5253(4)	116(8)	68(5)	29(3)	−1(10)	−12(7)	8(6)
C(3h)	5697(9)	8976(8)	6058(5)	135(10)	96(7)	37(3)	−11(14)	−14(9)	−13(8)
C(4h)	5261(9)	8441(9)	6600(5)	119(9)	150(9)	24(3)	29(15)	5(8)	11(8)
C(5h)	4312(9)	7440(8)	6347(5)	122(9)	131(8)	25(3)	34(14)	14(8)	31(8)
C(6h)	3834(7)	6978(6)	5554(4)	97(7)	89(6)	22(2)	32(10)	1(6)	34(6)

parameters reduced R to 0.091. The refinement was continued with anisotropic thermal parameters by using a block approximation $(3 \times 3$ and $6 \times 6)$ to the full matrix. After seven least-squares cycles, the shifts in all the parameters were less than $\frac{1}{5}$ of the corresponding estimated standard deviations, and the refinement was terminated. The final R was 0.056 for the 8081 non-zero weight reflections used in the refinement. No attempt to locate the 40 hydrogen atoms was made although this would probably lead to a reduction in the R value. The final positional and thermal parameters are given in Table 1*.

The quantity minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$, where $\sqrt{w} = 1$ if $F(\text{low}) \leqslant F(\text{obs}) \leqslant F(\text{upper})$, $\sqrt{w} = F(\text{obs})/F(\text{low})$ if $F(\text{obs}) < F(\text{low})$ and $\sqrt{w} = F(\text{upper})/F(\text{obs})$ if $F(\text{obs}) > F(\text{upper})$ where $F(\text{low}) = 11.0$ and $F(\text{upper}) = 33.0$. The scattering factors were taken from the usual source[8], with the values for Mo and Br corrected for the real part of the anomalous dispersion factor[9]. All calculations were carried out on an IBM-360/75 computer with programs written or modified by one of us (G.J.P.).

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal consists of discrete dimeric molecules of di-μ-bromobis(π-tetraphenylcyclobutadiene)tetracarbonyldimolybdenum(I). Therefore, the earlier for-

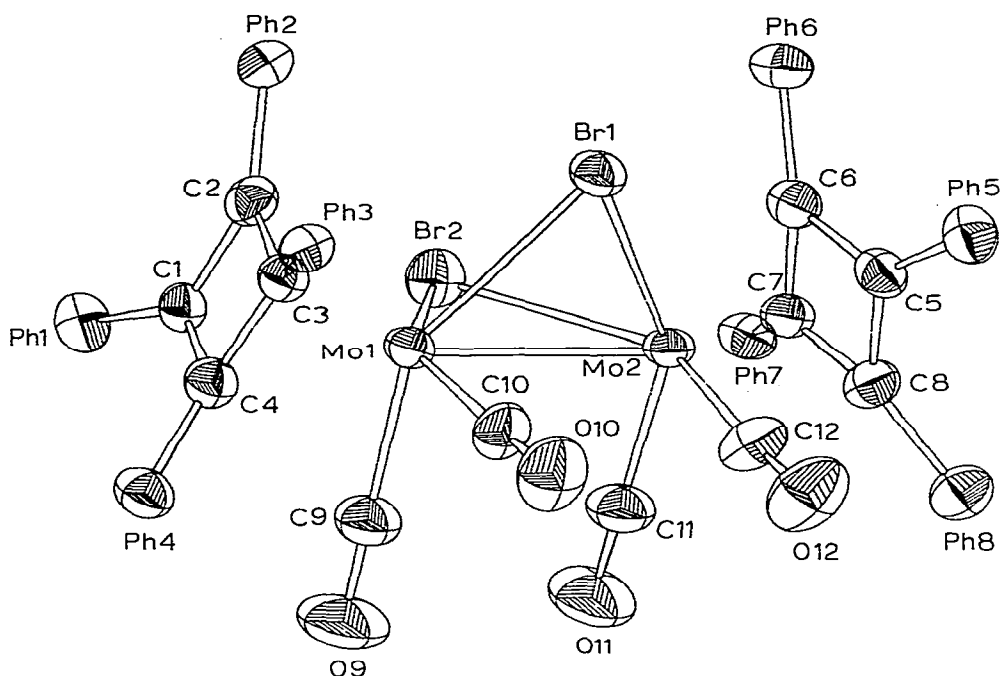Fig. 1. An ORTEP drawing of di-μ-bromobis(π-tetraphenylcyclobutadiene)tetracarbonyldimolybdenum-(I) illustrating the thermal ellipsoids and the atomic numbering. Only the first atom of each phenyl ring is shown in the Figure. The numbering of the phenyl rings from Ph(1) to Ph(8) corresponds to the rings a to h in the text. The angles of bend and twist of the phenyl rings are given in Table 3.

mulation involving three carbonyls per molybdenum is incorrect; an unsupported Mo–Mo bond does not exist in the molecule. The main skeleton of the dimeric unit is illustrated in Fig. 1, together with the atomic numbering. The bond distances and bond angles in the molecule are tabulated in Tables 2 and 3. Assuming a bromide ion, the molybdenum atom is in a formal oxidation state of $+1$ and requires 13 electrons to reach an inert gas configuration. This is achieved by obtaining 2 electrons from each of the two carbonyls and from each of the two bridging bromide ions, 4 electrons from the π-tetraphenylcyclobutadiene group and 1 electron from the other molybdenum atom.

     Figure 2 presents a view down the Mo–Mo bond and clearly shows the almost eclipsed nature of the various groups on the Mo atoms. The Mo–Mo bond distance of 2.954(1) Å is within the range of Mo–Mo distances reported in other compounds; 2.09 Å in molybdenum(II) trifluoroacetate[10], 2.11 Å in molybdenum(II) acetate[11], 2.38 Å in trirubidium octachlorodimolybdenum[12], 2.89 Å in bis(π-cyclopentadienyl)-oxomolybdenum sulphide[13], 3.090 Å in di-μ-dimethylphosphidodi(triethylphosphine)hexacarbonyldimolybdenum(0)[14] and 3.26 Å in μ-hydrido-μ'-dimethylphosphidobis(π-cyclopentadienyl)tetracarbonyldimolybdenum[15]. The latter compound is very similar to the present one. The Mo–Mo bond distance is suggestive of some double bond character since the shorter values are indicative of multiple Mo–Mo bonds[10,16]. In addition, the Mo–Mo distance of 3.22 Å in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ is

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) WITH THE ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bond lengths (Å) involving Mo atoms

Mo(1)–Br(1)	2.639(1)	Mo(2)–Br(1)	2.629(1)
Mo(1)–Br(2)	2.642(1)	Mo(2)–Br(2)	2.639(1)
Mo(1)–C(1)	2.279(5)	Mo(2)–C(5)	2.243(6)
Mo(1)–C(2)	2.270(5)	Mo(2)–C(6)	2.240(6)
Mo(1)–C(3)	2.225(6)	Mo(2)–C(7)	2.264(6)
Mo(1)–C(4)	2.256(6)	Mo(2)–C(8)	2.247(6)
Mo(1)–C(9)	2.011(7)	Mo(2)–C(11)	2.019(7)
Mo(1)–C(10)	2.002(6)	Mo(2)–C(12)	2.002(6)

(b) Angles (°) around Mo atoms[a]

CR(1)–Mo(1)–Br(1)	111.3(3)	CR(2)–Mo(2)–Br(1)	110.0(3)
CR(1)–Mo(1)–Br(2)	111.7(3)	CR(2)–Mo(2)–Br(2)	115.2(3)
CR(1)–Mo(1)–Mo(2)	161.6(3)	CR(2)–Mo(2)–Mo(1)	163.0(3)
CR(1)–Mo(1)–C(9)	103.3(4)	CR(2)–Mo(2)–C(11)	102.0(4)
CR(1)–Mo(1)–C(10)	103.2(4)	CR(2)–Mo(2)–C(12)	101.0(4)
Br(1)–Mo(1)–Br(2)	79.51(2)	Br(1)–Mo(2)–Br(2)	79.74(2)
Br(1)–Mo(1)–Mo(2)	55.74(2)	Br(1)–Mo(2)–Mo(1)	56.06(2)
Br(1)–Mo(1)–C(9)	145.4(2)	Br(1)–Mo(2)–C(11)	147.5(2)
Br(1)–Mo(1)–C(10)	85.9(2)	Br(1)–Mo(2)–C(12)	89.1(2)
Br(2)–Mo(1)–Mo(2)	55.96(2)	Br(2)–Mo(2)–Mo(1)	56.04(2)
Br(2)–Mo(1)–C(9)	88.3(2)	Br(2)–Mo(2)–C(11)	81.7(2)
Br(2)–Mo(1)–C(10)	145.0(2)	Br(2)–Mo(2)–C(12)	143.8(2)
C(9)–Mo(1)–C(10)	86.0(3)	C(11)–Mo(2)–C(12)	90.3(3)

(c) Dimensions of carbonyl groups

C(9)–O(9)	1.133(9)	Mo(1)–C(9)–O(9)	175.3(6)
C(10)–O(10)	1.125(8)	Mo(1)–C(10)–O(10)	177.1(6)
C(11)–O(11)	1.119(9)	Mo(2)–C(11)–O(11)	177.5(6)
C(12)–O(12)	1.135(8)	Mo(2)–C(12)–O(12)	176.5(6)

(d) Dimensions of the cyclobutadiene groups
Bond lengths (Å)

C(1)–C(2)	1.456(8)	C(1)–C(1a)	1.480(8)
C(2)–C(3)	1.473(8)	C(2)–C(1b)	1.479(8)
C(3)–C(4)	1.470(8)	C(3)–C(1c)	1.475(8)
C(4)–C(1)	1.459(8)	C(4)–C(1d)	1.471(8)
C(5)–C(6)	1.465(8)	C(5)–C(1e)	1.466(8)
C(6)–C(7)	1.467(8)	C(6)–C(1f)	1.482(8)
C(7)–C(8)	1.462(8)	C(7)–C(1g)	1.463(8)
C(8)–C(5)	1.468(8)	C(8)–C(1h)	1.480(8)

Bond angles (°)

C(1)–C(2)–C(3)	90.0(4)	C(5)–C(6)–C(7)	89.5(4)
C(2)–C(3)–C(4)	89.5(4)	C(6)–C(7)–C(8)	90.5(4)
C(3)–C(4)–C(1)	90.0(4)	C(7)–C(8)–C(5)	89.5(4)
C(4)–C(1)–C(2)	90.5(4)	C(8)–C(5)–C(6)	90.4(4)
C(4)–C(1)–C(1a)	131.8(5)	C(8)–C(5)–C(1e)	134.0(5)
C(2)–C(1)–C(1a)	134.4(5)	C(6)–C(5)–C(1e)	133.8(5)
C(1)–C(2)–C(1b)	136.1(5)	C(5)–C(6)–C(1f)	131.2(5)

[a] CR(1) and CR(2) are the centers of the cyclobutadiene rings.

TABLE 2 (*contd.*)

Bond angles (°)

C(3)–C(2)–C(1b)	133.0(5)	C(7)–C(6)–C(1f)	133.5(5)
C(2)–C(3)–C(1c)	133.8(5)	C(6)–C(7)–C(1g)	133.5(5)
C(4)–C(3)–C(1c)	129.8(5)	C(8)–C(7)–C(1g)	133.9(5)
C(3)–C(4)–C(1d)	132.2(5)	C(7)–C(8)–C(1h)	130.1(5)
C(1)–C(4)–C(1d)	132.9(5)	C(5)–C(8)–C(1h)	133.7(5)
C(1)–C(1a)–C(2a)	118.6(5)	C(5)–C(1e)–C(2e)	120.3(6)
C(1)–C(1a)–C(6a)	122.5(6)	C(5)–C(1e)–C(6e)	119.8(6)
C(2)–C(1b)–C(2b)	122.1(6)	C(6)–C(1f)–C(2f)	124.0(6)
C(3)–C(1b)–C(6b)	118.2(5)	C(6)–C(1f)–C(6f)	117.3(5)
C(3)–C(1c)–C(2c)	124.6(5)	C(7)–C(1g)–C(2g)	120.9(6)
C(3)–C(1c)–C(6c)	117.1(5)	C(7)–C(1g)–C(6g)	120.6(5)
C(4)–C(1d)–C(2d)	121.7(6)	C(8)–C(1h)–C(2h)	116.6(6)
C(4)–C(1d)–C(6d)	119.7(6)	C(8)–C(1h)–C(6h)	124.4(6)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) INVOLVING PHENYL RINGS

	i							
	a	b	c	d	e	f	g	h
(a) Bond lengths								
C(1i)–C(2i)	1.403(9)	1.380(10)	1.398(9)	1.402(10)	1.392(10)	1.393(9)	1.400(9)	1.388(10)
C(2i)–C(3i)	1.381(12)	1.396(12)	1.386(11)	1.370(12)	1.404(15)	1.401(12)	1.388(13)	1.396(11)
C(3i)–C(4i)	1.382(12)	1.389(15)	1.372(12)	1.402(12)	1.354(15)	1.359(16)	1.396(13)	1.360(14)
C(4i)–C(5i)	1.349(12)	1.389(15)	1.364(11)	1.372(13)	1.367(14)	1.391(14)	1.371(12)	1.395(15)
C(5i)–C(6i)	1.404(11)	1.399(12)	1.390(10)	1.383(11)	1.405(11)	1.379(12)	1.389(11)	1.383(10)
C(6i)–C(1i)	1.384(9)	1.400(9)	1.395(9)	1.393(9)	1.396(9)	1.391(9)	1.398(9)	1.402(9)
(b) Bond angles								
C(6)–C(1)–C(2)	118.4(6)	119.8(6)	118.3(6)	118.4(6)	119.9(6)	118.6(6)	118.4(6)	119.0(6)
C(1)–C(2)–C(3)	120.6(7)	120.6(7)	119.8(7)	121.1(7)	118.6(8)	119.5(8)	119.7(8)	120.1(8)
C(2)–C(3)–C(4)	120.2(8)	119.3(9)	121.4(7)	119.5(8)	121.5(9)	121.2(9)	122.2(9)	121.0(9)
C(3)–C(4)–C(5)	119.9(8)	121.1(9)	119.1(7)	119.9(8)	120.2(9)	119.6(9)	117.2(8)	119.2(9)
C(4)–C(5)–C(6)	121.2(7)	119.1(9)	121.0(7)	120.5(8)	120.5(8)	119.8(9)	122.3(7)	120.9(9)
C(5)–C(6)–C(1)	119.7(7)	120.2(7)	120.3(6)	120.5(7)	119.2(7)	121.2(7)	120.2(6)	119.7(7)
Angle of bend (°)[a]	12.9	7.9	19.3	17.9	11.4	17.3	12.3	18.6
Angle of twist (°)[a]	37.4	24.3	60.6	43.0	14.1	69.3	16.3	85.5

[a] Relative to the plane of the appropriate cyclobutadiene ring.

considered to be a pure Mo–Mo single bond. Finally, in the majority of complexes involving multiple metal–metal bonds, an eclipsed configuration similar to that shown in Fig. 2 is usually observed.

We are unaware of any structural data on other bromine-bridged molybdenum complexes for a comparison with our results. As can be seen in Fig. 1 or 2, the Mo₂Br₂ system is not planar but folded so that the angle between the Br(1)–Mo(1)–Br(2) and Br(1)–Mo(2)–Br(2) planes is 93.6°. The angles around the bridging bromine atoms
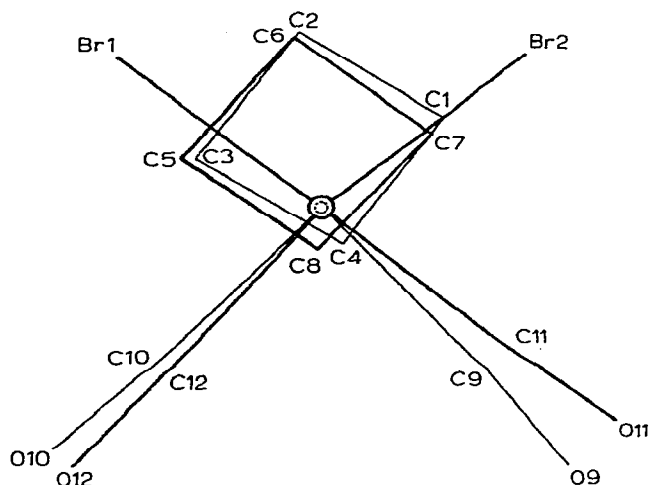
Fig. 2. A view down the Mo–Mo bond which shows the approximately eclipsed nature of the compound.

(Mo(1)–Br(1)–Mo(2) of 68.20(2)° and Mo(1)–Br(2)–Mo(2) of 68.01(2)°) are the smallest reported for any bridging group and are indicative of a strong Mo–Mo interaction. Furthermore, the acute angle at the Br atom is also a consequence of the strong Mo–Mo interaction since for a square-planar Mo_2Br_2 system with sides of 2.64 Å, the Mo–Mo distance of 3.73 Å is too long for appreciable metal–metal interaction. Furthermore, a planar Mo_2Br_2 system with a Mo–Mo distance of 2.954 Å would have a Mo–Br–Mo angle of 68.1°, in good agreement with the observed values of 68.01 and 68.20°. Therefore, the geometry of the Mo_2Br_2 system found in this study appears to be a direct result of the strong Mo–Mo interaction which folds and squeezes the Mo_2Br_2 group into a compact moiety.

The Mo–Br distances vary from 2.629 to 2.642 Å, with a average of 2.637 Å which is only slightly longer than the Mo–Br distance of 2.58 Å in $Mo(CO)_2[P-(C_6H_5)_3]_2Br_2$[17]. Although an increase in the distance is expected for bridging groups, both values are much shorter than the sum of the covalent radii of 2.76 Å (using Mo of 1.62 Å[15] and Br of 1.14 Å[18]) which may indicate significant double bond character in the Mo–Br bonds. Unfortunately, the lack of sufficient structural data on Mo–Br bonds precludes any extensive discussion at this time.

The Mo–C (carbonyl) distances vary from 2.002(6) to 2.019(7) Å, with a mean value of 2.008 Å. This value is long compared to other $Mo(CO)_2$ derivatives which vary from 1.955(13) Å in $(\pi\text{-}C_5H_5)Mo(CO)_2[P(C_6H_5)_3]COCH_3$[19] to 2.017(9) Å in $(\pi\text{-}C_7H_7)(\sigma\text{-}C_6F_5)Mo(CO)_2$[20]. The Mo–C (carbonyl) distances in a variety of compounds have been summarized recently and the variation of this distance with substituents has been discussed[21]. The Mo–C bonds are all long in spite of the fact that the CO groups are *trans* to a bridging bromine atom. Therefore, the suggestion that metal–carbonyl bonds *trans* to bridging bromine atoms are shortened may not be generally applicable to organometallic systems[22].

The Mo–C–O group is bent slightly (av. angle is 176.6(1.0)°), but significantly, from linearity. This deviation may be related to the eclipsed nature of the molecule (see Fig. 2) since each CO group on a Mo atom almost eclipses the CO group on the

other Mo atom. Furthermore, the deviations of the CO groups from the plane of the other two CO groups also suggest that the bend may be a steric effect. The average C–O distance of 1.128(7) Å is on the short side but is consistent with the long Mo–C bond lengths.

The two cyclobutadiene rings are planar (see Table 4), with an average C–C distance of 1.469(5) Å. The average C–C distance is similar to the values found in other tetraphenylcyclobutadiene complexes (1.470(4) Å in π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I)[23] and 1.459(7) Å in π-tetraphenylcyclobuta-dienetricarbonyliron[24]) as well as one of the tetramethylcyclobutadiene derivatives (av. 1.463 Å)[25], but not the other (av. 1.431(34) Å)[3]. However, the large e.s.d. in the latter structure suggests that the C–C distances in cyclobutadiene derivatives are approximately constant at 1.46(1) Å. The planar phenyl rings attached to the cyclo-butadiene rings are twisted and bent out of the C₄-ring (see Table 3). Similar bends and twists have been observed in the other two tetraphenyl derivatives and are presumably related to steric factors.

TABLE 4

EQUATIONS OF "BEST" LEAST-SQUARES PLANES FOR THE CYCLOBUTADIENE RINGS AND DISTANCES OF ATOMS FROM THESE PLANES[a,b]

Plane through C(1)–C(4)
0.3341 X + 0.6103 Y + 0.7135 Z − 2.642 = 0

Mo(1)	2005	C(1)	6	C(2)	−6	C(3)	6	C(4)	−6		
C(1a)	−330	C(2a)	−1168	C(3a)	−1667	C(4a)	−1344	C(5a)	−525	C(6a)	2
C(1b)	−202	C(2b)	130	C(3b)	−86	C(4b)	−654	C(5b)	−1006	C(6b)	−773
C(1c)	−488	C(2c)	152	C(3c)	−418	C(4c)	−1623	C(5c)	−2251	C(6c)	−1690
C(1d)	−453	C(2d)	−14	C(3d)	−480	C(4d)	−1407	C(5d)	−1900	C(6d)	−1427

Plane through C(5)–C(8)
0.3657 X + 0.9104 Y + 0.1934 Z − 8.242 = 0

Mo(2)	−1995	C(5)	8	C(6)	−8	C(7)	8	C(8)	−8		
C(1e)	289	C(2e)	549	C(3e)	873	C(4e)	851	C(5e)	548	C(6e)	261
C(1f)	440	C(2f)	−328	C(3f)	222	C(4f)	1478	C(5f)	2255	C(6f)	1726
C(1g)	311	C(2g)	514	C(3g)	881	C(4g)	1102	C(5g)	902	C(6g)	1726
C(1h)	472	C(2h)	1845	C(3h)	2375	C(4h)	1565	C(5h)	188	C(6h)	−362

[a] The orthogonal coordinates XYZ are related to the fractional coordinates by the transformations
$$X(Å) = ax + by \cos \gamma + cz \cos \beta$$
$$Y(Å) = by \sin \gamma - cz \sin \beta \cos \alpha^*$$
$$Z(Å) = cz \sin \beta \sin \alpha^*.$$
[b] Deviations are in Å × 10³.

The Mo–C (to C₄-ring) distances are not equal but vary from 2.225(6) to 2.279(5) Å. This variation also may arise from steric contraints in trying to pack the various groups around the Mo atoms. The planar C₄ rings are not parallel but are tipped away from the carbonyl groups. This can be seen in Fig. 2, where C(2) and C(6) are tipped toward each other, while C(4) and C(8) are tipped away. One result is that the ring centers are not colinear with the Mo–Mo bond. The Mo–C₄-ring-center distances are 1.995 and 2.008 Å, almost identical to the Mo–C₅-ring-center distances

found in various π-cyclopentadienyl compounds, i.e. 2.00 Å in $(\pi\text{-}C_5H_5)_2Mo_2H(CO)_4\text{-}$ $P(CH_3)_2{}^{15}$ or 2.018 Å in $(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}CH_2SCH_3)^{26}$. However, the individual Mo–C (C_5-ring) distances are all about 0.1 Å longer than in the C_4 case (consider 2.329[15] and 2.340 Å[26] as typical). In contrast, the Mo–C (C_7-ring) distances are similar (av. 2.314 Å[21]) but the Mo–C_7-ring-center distance is only 1.658 Å. Apparently, neither of these Mo distances is constant in a series of planar π-type ligands. We might note that we were unable to locate any data on a C_6 system although compounds of this type have been prepared. The significance of the variations of the metal to ring distances is presumably related to the geometry of the ring as well as to the nature of the other ligands attached to the metal atom.

ACKNOWLEDGEMENT

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