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Crystal and Molecular Structure of Bis-μ-(benzoato)-1,2-dibromo-1,2-bis(tri-*n*-butylphosphine)dimolybdenum(II), $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$

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Received March 4, 1976

AIC601737

The crystal structure of the title compound has been determined by a single-crystal three-dimensional x-ray diffraction study. The structure consists of discrete centrosymmetric $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ units, each with a short Mo–Mo bond length [2.091 (3) Å] indicative of a strong bond. Each Mo atom is also bonded to a bromine atom, to a phosphorus atom, and to two bridging carboxylate oxygen atoms. The disposition of the former ligands is similar to that reported for $Re_2Cl_6[P(C_2H_5)_3]_2$. Short contacts between the α-methylene atoms of the tri-*n*-butylphosphine ligand and the bromide ligand give rise to relatively large Mo′–Mo–Br and Mo′–Mo–P angles [115.9 (1) and 101.9 (1)°, respectively], and the molybdenum coordination geometry may be described formally as distorted trigonal bipyramidal. It is concluded that these interactions must result in a reduction in the freedom of rotation about the P–Mo bond. This conclusion is sustained by an examination of the ^1H NMR spectrum of the trimethylphosphine analogue, $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$, which exhibits two nonequivalent methyl resonances at ambient temperatures. Short contacts are also observed between the α carbon atoms and the carboxylate oxygen atoms. Several of the α- and β-methylene protons, as well as the ortho phenyl protons, lie in close proximity to the center of the Mo–Mo bond. They are, therefore, in geometrically favorable positions to be influenced strongly by the anisotropic induced magnetic field of the Mo–Mo bond. Crystallographic data are as follows: space group $P2_1/c$; unit cell $a = 12.17$ (1), $b = 11.21$ (1), $c = 17.95$ (1) Å; $\beta = 114.7$ (1)°; $V = 2225$ Å^3; d_{calcd} for $Z = 2$ is 1.49 and d_{obsd} is 1.49 (2) g/cm^3. Diffractometer data (1582 independent reflections with $F^2 \geq 3\sigma$) were used to refine the structure to final values of $R_F = 0.073$ and $R_{wF} = 0.090$.

Introduction

For several years, we have maintained a continuing interest in compounds with metal-to-metal bonds, with particular emphasis on the chemistry of dinuclear molybdenum(II) complexes.[1-6] Physical–chemical studies of these compounds, aimed at clarifying the nature of ligand substitution processes and geometric isomerism[3] as well as the origin of certain spectroscopic features,[3] are currently in progress. Before embarking upon this undertaking, however, we deemed it desirable to firmly establish the structures of several key complexes.

Cotton and co-workers[7] have reported the x-ray structures of a number of dimolybdenum(II) complexes including $Mo_2Cl_8^{4-}$, $Mo_2(CH_3)_8^{4-}$, and several μ-carboxylato and μ-sulfanato species. Our work has centered around the di- and tetrahalo complexes of Mo_2^{4+}, and for these, definitive structural data are unavailable. The structure of a bromo complex would be particularly interesting since the parent species, $Mo_2Br_8^{4-}$, is unknown. These facts, together with our inability to otherwise assign the structure of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ unambiguously, prompted the present investigation.

Experimental Section

The preparation of the complex is described in the previous paper.[6] Crystals suitable for x-ray analysis were obtained by slow evaporation from acetone. A crystal approximately 0.18 × 0.20 × 0.35 mm was mounted in a sealed glass capillary parallel to the crystal axis *b*. Weissenberg photographs indicated space group $P2_1/c$ with systematic absences of $h0l$ when $l = 2n + 1$ and of $0k0$ when $k = 2n + 1$. Unit cell parameters $a = 12.17$ (1) Å, $b = 11.21$ (1) Å, $c = 17.95$ (1) Å, and $\beta = 114.7$ (1)° were obtained from a least-squares fit of 12 reflections using graphite-monochromated Mo Kα radiation (λ 0.710 69 Å) and an Enraf-Nonius CAD-3 automated diffractometer. The unit cell volume is 2225 Å^3. A density of 1.49 g/cm^3 was calculated for $Z = 2$, and this agreed with that of 1.49 (2) g/cm^3 measured by flotation in aqueous ZnI_2 solution.

Data were collected at room temperature (23 ± 2 °C) using graphite-monochromated Mo Kα radiation and techniques described previously.[4] The intensity of a standard reflection, measured at 50 reflection intervals, showed a maximum deviation of ±6%, and an average deviation of 2.6%. This rather large deviation was traced primarily to temperature fluctuations in the room beyond the control of the experimenters; it caused slight misalignment of the crystal. The crystal was realigned periodically, and a total of 3180 independent reflections were collected in the range $2 < \theta < 25°$. The data were placed on a common scale by correcting for the above deviation and for Lorentz and polarization effects. Absorption corrections were not applied. For Mo Kα radiation, $\mu = 25.6$ cm^{-1} and calculated transmission coefficients ranged from 0.61 to 0.72. Standard deviations were assigned to F^2 values according to

$$\sigma(F^2) = \frac{1}{Lp}\left[N_t + (0.02N_n)^2\right]^{1/2}$$

where N_t is the total count, N_n is the net count, and 0.02 is an estimate of instrumental instability. Of the measured reflections, 1582 with $F^2 \geq 3\sigma$ were used for the structure solution and refinement.

Table I. Fractional Atomic Coordinates ($\times 10^4$),[a] Anisotropic Thermal Parameters ($\times 10^4$),[b] and Isotropic Thermal Parameters ($\times 10$)

Atom	*x*	*y*	*z*	*B*, Å
Mo	−201 (1)	383 (1)	459 (1)	
Br	1601 (2)	1261 (2)	1686 (1)	
P	−2469 (4)	124 (4)	−114 (3)	
O(1)	−527 (10)	2047 (11)	−130 (7)	28 (2)
O(2)	−46 (9)	1263 (10)	−1075 (6)	23 (2)
C(1)	−351 (14)	2140 (15)	−768 (9)	23 (3)
C(2)	−545 (15)	3334 (10)	−1191 (10)	24 (3)
C(3)	−128 (16)	3523 (16)	−1782 (10)	31 (4)
C(4)	−250 (16)	4627 (20)	−2123 (10)	35 (4)
C(5)	−744 (20)	5553 (22)	−1904 (13)	50 (5)
C(6)	−1137 (19)	5361 (22)	−1281 (13)	48 (5)
C(7)	−1038 (18)	4231 (18)	−931 (12)	38 (5)
C(8)	−2916 (16)	632 (17)	674 (11)	32 (4)
C(9)	−2595 (20)	1898 (21)	936 (13)	48 (5)
C(10)	−3053 (22)	2327 (24)	1576 (15)	59 (6)
C(11)	−2740 (30)	3562 (32)	1904 (20)	90 (9)
C(12)	−3293 (17)	1035 (18)	−1028 (11)	36 (4)
C(13)	−4659 (23)	1174 (24)	−1270 (15)	61 (6)
C(14)	−5277 (25)	1965 (29)	−2069 (17)	75 (7)
C(15)	−4863 (29)	3252 (31)	−1926 (19)	87 (9)
C(16)	−3210 (20)	−1359 (21)	−376 (14)	57 (5)
C(17)	−2766 (32)	−2160 (36)	382 (22)	103 (10)
C(18)	−3493 (41)	−3429 (43)	240 (28)	133 (14)
C(19)	−3064 (44)	−4217 (49)	−61 (30)	151 (17)
H(3)	238	2895	−1950	31
H(4)	33	4747	−2536	35
H(5)	−830	6309	−2163	50
H(6)	−1471	6001	−1097	47
H(7)	−1309	4096	−512	38
H(81)	−2529	72	1189	32
H(82)	−3856	517	470	32
H(91)	−2939	2459	418	48
H(92)	−1650	2006	1173	48
H(101)	−2739	1733	2074	59
H(102)	−4002	2239	1320	59
H(121)	−3166	670	−1528	36
H(122)	−2892	1885	−944	36
H(131)	−4805	1558	−781	61
H(132)	−5077	333	−1356	61
H(141)	−6225	1922	−2288	75
H(142)	−5092	1600	−2545	75
H(161)	−3031	−1767	−843	51
H(162)	−4155	−1273	−626	51
H(171)	−2846	−1694	868	103
H(172)	−1836	−2317	586	103

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	33.9 (9)	27.3 (11)	16.4 (3)	4.3 (12)	12.3 (2)	0.6 (8)
Br	75 (2)	57 (2)	34 (1)	−6 (2)	19 (1)	−6 (1)
P	49 (3)	53 (4)	24 (1)	−2 (3)	17 (2)	2 (2)

[a] Hydrogen atoms are numbered according to the carbon atom to which they are attached; e.g., H(3) is bonded to C(3); H(81) and H(82) are bonded to C(8), etc. [b] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

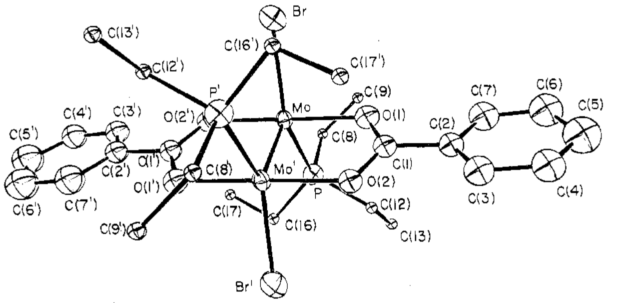

Figure 1. Molecular structure showing the atom-numbering scheme. For clarity, the γ and δ carbon atoms of the butyl groups, have been omitted and the temperature factors of the α and β carbon atoms have been artificially reduced.

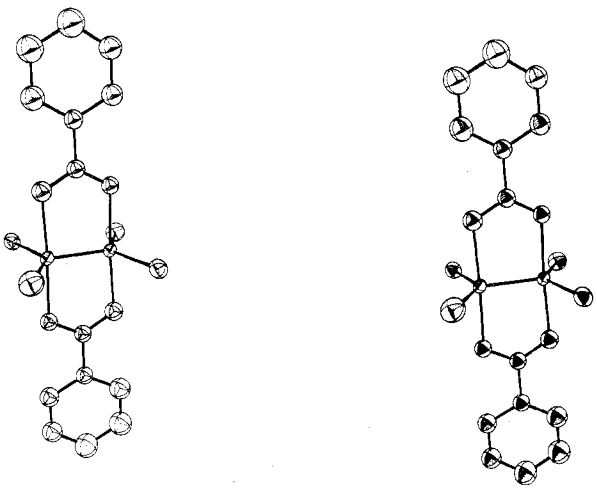

Figure 2. Stereoscopic view of $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$. The butyl groups have been omitted for clarity.

Solution and Refinement of the Structure

The structure was solved by the heavy-atom method and refined by full-matrix techniques using programs described previously.[4] Space group $P2_1/c$ has four general positions, and the presence of two molecules per unit cell requires half of a molecule per asymmetric unit. Approximate coordinates for the unique molybdenum, bromine, and phosphorus atoms were obtained from a normal sharpened Patterson map; oxygen and carbon coordinates were obtained via a series of structure factor difference Fourier calculations. All terminal methyl carbons and one γ-methylene carbon were difficult to locate because their peak intensities were near the level of resolution of the map. No attempt was made to locate hydrogen atoms.

Molybdenum, bromine, and phosphorus thermal parameters were refined anisotropically, while all oxygen and carbon parameters were refined isotropically. Hydrogen coordinates (listed in Table I) were calculated before each refinement cycle using a C–H bond distance of 1.05 Å and tetrahedral angles for all aryl and methylene carbon atoms except C(18). Hydrogen atoms were added as a fixed contribution to the structure factor with temperature factors equal to those of the carbon atom to which they are bonded. All atoms were treated as neutral species, and, except for those of hydrogen,[8a] scattering factors were taken from the compilations of Cromer and Waber.[9] For molybdenum, bromine, and phosphorus, both the real and imaginary components of the anomalous dispersion corrections[8b] were applied. Refinement was based on *F* and the function minimized was $\sum w(F_o - F_c)^2$. Weights, set according to $w = 1/\sigma^2$, were chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. This procedure led to the following assignments: $\sigma(F_o) = 2.52 - 0.021|F_o|$ for $|F_o| \leq 33.5$; $\sigma(F_o) = -0.915 + 0.08|F_o|$ for $|F_o| > 33.5$.

Refinement proceeded smoothly except that C(18) and C(19) consistently showed large temperature factors and unusual C–C distances. Examination of several electron density maps calculated at various stages during the refinement revealed a number of small peaks in the vicinity of C(17) at about the level of resolution of the map. It was assumed that the ethyl group C(18)–C(19) was disordered, and several promising combinations were refined. None of these combinations led to significant improvement in the weighted *R* factor or in the calculated bond distances. Remarkably similar difficulties with phosphine alkyl groups were encountered[10] in elucidating the structure of $Re_2Cl_6[P(C_2H_5)_3]_2$ which is similar to that of the title compound. With the rhenium complex, the apparent disorder was attributed to absorption (μ_{Cu} = 265 cm^{-1}). In the present structure, this explanation appears less likely. In view of the essential correctness of the structure and the cost involved for additional refinement and/or data collection, this problem was not examined further.

Several refinement cycles led to final error indices of $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.073$ and $R_{wF} = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.090$. For the final cycle all parameter changes were less than σ, except those for C(18) and C(19) which were within 2σ. Here σ is the estimated standard deviation obtained from the inverse matrix. The

Table II. Intermolecular Contacts <4 Å

Br· · ·C(4)–2[a]	3.83 (2)	C(11)· · ·O(2)–2	3.74 (3)
C(8)· · ·C(4)–2	3.94 (2)	C(11)· · ·C(2)–2	3.96 (3)
C(9)· · ·C(3)–2	3.97 (2)	C(11)· · ·C(3)–2	3.86 (3)
C(9)· · ·C(4)–2	3.86 (3)	C(19)· · ·C(6)–200	3.85 (7)
C(10)· · ·C(2)–2	3.96 (3)	C(19)· · ·C(7)–200	3.84 (7)
C(10)· · ·C(3)–2	3.67 (3)	Br· · ·C(11)–203	3.81 (3)
C(10)· · ·C(4)–2	3.90 (2)	C(4)· · ·O(2)–403	3.86 (2)

[a] The symmetry transformations are defined as follows: 2 = $(x, \frac{1}{2} - y, \frac{1}{2} + z)$; 200 = $(x, y - 1, z)$; 203 = $(-x, y - \frac{1}{2}, \frac{1}{2} - z)$; 403 = $(-x, \frac{1}{2} + y, -\frac{1}{2} - z)$.

Table III. Interatomic Distances (Å) and Angles (deg)

Distances			
Mo–Mo′	2.091 (3)	C(7)–C(2)	1.35 (3)
Mo–Br	2.566 (2)	P–C(8)	1.81 (2)
Mo–P	2.526 (5)	P–C(12)	1.83 (2)
Mo–O(1)	2.10 (1)	P–C(16)	1.86 (2)
Mo′–O(2)	2.11 (1)	C(8)–C(9)	1.50 (3)
Mo· · ·O(2)	3.02 (1)	C(9)–C(10)	1.55 (4)
O(1)–C(1)	1.25 (2)	C(10)–C(11)	1.49 (4)
O(2)–C(1)	1.26 (2)	C(12)–C(13)	1.54 (3)
C(1)–C(2)	1.51 (2)	C(13)–C(14)	1.58 (4)
C(2)–C(3)	1.37 (3)	C(14)–C(15)	1.51 (4)
C(3)–C(4)	1.36 (3)	C(16)–C(17)	1.53 (4)
C(4)–C(5)	1.34 (3)	C(17)–C(18)	1.64 (6)
C(5)–C(6)	1.41 (4)	C(18)–C(19)	1.26 (7)
C(6)–C(7)	1.40 (3)		
Selected Intramolecular Contacts			
Br· · ·P′	3.739 (2)	C(12)· · ·C(1)	3.63 (3)
Br· · ·C(8′)	5.54 (2)	C(12)· · ·O(2)	3.99 (2)
Br· · ·C(12′)	3.78 (2)	C(16)· · ·O(1′)	4.32 (3)
Br· · ·C(13′)	4.92 (2)	C(16)· · ·C(1′)	4.04 (3)
Br· · ·C(16′)	3.64 (2)	C(16)· · ·O(2′)	3.72 (3)
Br· · ·C(17′)	4.61 (3)	C(17)· · ·O(2′)	3.27 (3)
C(12)· · ·O(1)	3.27 (2)	C(17)· · ·C(1′)	3.56 (4)
Angles			
Br–Mo–P	142.1 (1)	C(2)–C(3)–C(4)	119.0 (19)
Br–Mo–O(1)	90.3 (3)	C(3)–C(4)–C(5)	123.4 (23)
Br–Mo–O(2′)	90.1 (3)	C(4)–C(5)–C(6)	117.4 (22)
Br–Mo–Mo′	115.9 (1)	C(5)–C(6)–C(7)	120.2 (23)
P–Mo–O(1)	87.3 (3)	C(6)–C(7)–C(2)	121.0 (18)
P–Mo–Mo′	101.9 (1)	Mo–P–C(8)	106.3 (5)
P–Mo–O(2′)	90.3 (3)	Mo–P–C(12)	113.3 (7)
O(1)–Mo–O(2′)	176.6 (5)	Mo–P–C(16)	122.6 (8)
O(1)–Mo–Mo′	91.4 (4)	P–C(8)–C(9)	114.9 (17)
O(2)–Mo′–Mo	91.4 (4)	C(8)–C(9)–C(10)	113.6 (22)
O(1)–C(1)–O(2)	122.0 (16)	C(9)–C(10)–C(11)	118.0 (28)
C(1)–O(1)–Mo	117.7 (11)	P–C(12)–C(13)	115.5 (18)
C(1)–O(2)–Mo′	117.3 (11)	C(12)–C(13)–C(14)	111.1 (25)
O(1)–C(1)–C(2)	119.0 (16)	C(13)–C(14)–C(15)	112.5 (22)
O(2)–C(1)–C(2)	119.0 (17)	P–C(16)–C(17)	110.4 (18)
C(1)–C(2)–C(3)	120.0 (17)	C(16)–C(17)–C(18)	113.9 (27)
C(1)–C(2)–C(7)	119.0 (19)	C(17)–C(18)–C(19)	112.5 (53)

only significant feature revealed by a final difference electron density map was a small peak (1.0 e/Å^3) in the vicinity of C(18). A list of observed and calculated structure factors is available.[11] Final atomic parameters are listed in Table I. A view of the molecule showing the numbering scheme is given in Figure 1, while a stereoscopic view is given in Figure 2.

Description of the Structure and Discussion

The structure consists of discrete, centrosymmetric $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ dimers. Intermolecular contacts shorter than 4 Å are listed in Table II; none of these is short enough to indicate intermolecular interactions significantly stronger than those arising from van der Waals forces.

Within each dimer, crystallographically equivalent molybdenum atoms are separated by 2.091 (3) Å (Table III); as expected, this short distance is indicative of a strong, nominally quadruple Mo–Mo bond. A number of dimolybdenum complexes with Mo–Mo bond orders of 4 have been studied[7] crystallographically and Mo–Mo bond distances ranging from 2.090 (1) Å in $Mo_2[N_2C(C_6H_5)_3]_4$ to 2.183 (2) Å in $Mo_2(C_3H_5)_4$ have been reported. Thus, the Mo–Mo bond in the present structure is among the shortest known. Each molybdenum atom is bonded to a bromine atom, a tri-*n*-butylphosphine phosphorus atom, and two bridging carboxylate oxygen atoms which complete the coordination. The bromine and phosphorus atoms are bent significantly from a plane containing the molybdenum atom and perpendicular to the Mo′–Mo bond [Mo′–Mo–Br = 115.9 (1)°; Mo′–Mo–P = 101.9 (1)°], while the oxygen atoms lie very nearly in this plane [Mo′–Mo–O(1) = 91.4 (4)°; Mo–Mo′–O(2) = 91.4 (4)°]. Thus, the immediate coordination around each molybdenum atom may be described formally as distorted trigonal bipyramidal with the oxygen atoms of the carboxylate group occupying the axial positions. Both the "equatorial" bromine and phosphorus atoms have suffered substantial displacement from the nearly square-planar disposition of ligands observed about the metal center in a number of dinuclear complexes of molybdenum(II) and rhenium(II) and -(III). A similar distortion, observed[12] in $Re_2I_4(O_2CC_6H_5)_2$ [average Re′–Re–I = 110 (1)°], has been ascribed to nonbonded repulsions between bulky iodine atoms.

Bond distances within the coordination polyhedron do not appear to be unusual for their type. The Mo–Br distance [2.566 (2) Å] lies between those reported for $Br_4[(CH_3)_2C_6H_5P]_3Mo^{IV}$ [2.560 (5), 2.425 (7) Å][13] and for several Mo(I),[14] -(II),[15] and -(IV)[16] complexes, of which $[(C_6H_5)_2AsCH_2As(C_6H_5)_2]_2Br_2(CO)_2Mo^{II}$ [2.650 (5), 2.674 (5) Å] is typical. Of these complexes, only the short Mo–Br distance in the seven-coordinated $Br_4[(CH_3)_2C_6H_5P]_3Mo^{IV}$ complex is significantly shorter than that in the present structure. The Mo–P distance [2.526 (5) Å] lies in the range of 2.435–2.618 Å reported[15b,17] for several Mo^{II}–P(phosphine) bonds; only the unusually long linkage in $MoBr_2(CO)_3[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]$ is significantly longer than that in the present structure. Last, the Mo–O distances [2.10 (1), 2.11 (1) Å] compare favorably with those reported[18] for other $Mo_2(O_2CR)_4$ derivatives [2.107 (5)–2.137 (4) Å in

Table IV. Least-Squares Planes[a]

Plane	A	B	C	D	Atoms defining the plane
1	0.812	0.233	0.535	0.000	Mo, Mo′, O(1), O(1′), O(2), O(2′), C(1), C(1′)
2	−0.071	−0.881	0.469	0.000	Mo, Mo′, Br, Br′, P, P′
3	0.672	0.247	0.698	0.267	C(2)–C(7)

Deviations of Atoms from Planes, Å

Plane	Mo	Br	P	O(1)	O(2)	C(1)	C(2)	C(8)
1	0.023			−0.019	0.003	0.012	0.022	
2	0.014	−0.004	−0.004					0.178

Plane	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	O(1)	O(2)	C(1)
3	−0.010	0.010	0.000	0.010	0.010	0.000	0.321	−0.101	0.087

[a] Equations are expressed in 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. Unit weights were employed in the calculation of all planes. The dihedral angle between planes 1 and 2 is 91.1 (15)°.

Table V. Distances (Å) of Selected Atoms from the Origin

C(3)	5.04	H(81)	4.42
C(7)	5.01	H(82)	5.13
C(8)	4.26	H(91)	4.81
C(9)	4.66	H(92)	4.13
C(12)	3.82	H(121)	3.75
C(13)	5.31	H(122)	3.84
C(16)	3.98	H(131)	5.69
C(17)	4.43	H(132)	5.62
H(3)	4.87	H(161)	3.89
H(7)	4.82	H(162)	4.90
		H(171)	4.75
		H(172)	3.84

$Mo_2(O_2CCH_3)_4$, 1.97 (2)–2.14 (2) Å in $Mo_2(O_2CCF_3)_4$, and 2.098 (6)–2.128 (6) Å in $Mo_2(O_2CCF_3)_4 \cdot 2C_6H_5N$].

An examination of the least-squares planes results given in Table IV shows that the $(MoO_2C)_2$ group is planar to $\sim\pm 0.025$ Å and perpendicular to the plane formed by the molybdenum, bromine, and phosphorus atoms. Thus, the core symmetry is very nearly C_{2h}. The phenyl group atoms are almost strictly coplanar (maximum deviation ±0.01 Å); however, the phenyl ring is bent and twisted from the carboxylate group as indicated by the $O_2C-C_6H_5$ dihedral angle (12°) and the torsional angles O(1)–C(1)–C(2)–C(7) [7 (2)°] and O(2)–C(1)–C(2)–C(3) [15 (2)°]. Dihedral angles of this magnitude (5–17°) between carboxyl and phenyl groups have been reported for $Re_2I_4(O_2CC_6H_5)_2$[12] and $Re_2Cl_2(O_2CC_6H_5)_4 \cdot 2CHCl_3$.[19] In the latter case, deviations of the benzoate group from planarity were ascribed to packing forces; in the present structure, steric crowding may contribute as well.

The central portion of the molecule is crowded sterically, as indicated by the intramolecular contacts in Table III. Both C(12) and C(16) are disposed toward the center of the molecule and show contacts with bromine [C(16′)···Br = 3.64 Å; C(12′)···Br = 3.78 Å] shorter than the sum of the appropriate van der Waals radii [methyl group 2.0 Å, bromine 1.95 Å]. While these short contacts can account for the rather large Mo′–Mo–P and Mo′–Mo–Br angles, they do not account for the asymmetry observed (Mo′–Mo–Br > Mo′–Mo–P). This type of asymmetry has also been reported for $Re_2Cl_6[P(C_2H_5)_3]_2$, and presumably results from the differing electronic requirements of the phosphine and bromide ligands.[10] In addition to those with bromine, there are two short nonbonding contacts between the butyl group carbon atoms and the carboxyl oxygen atoms [C(12)···O(1) = 3.27 Å; C(17)···O(2′) = 3.27 Å]. These contacts are consistent with a twist between the phenyl and carboxylate portions of the benzoate ligand.

A close consideration of the contact distances between bromine and the α-methylene carbon atoms in the adjacent phosphine ligand reveals that the halogen atom is essentially "locked" between the scissoring arms of the carbon chains (cf. Figure 1). This conclusion strongly suggests that the free rotation normally observed about the phosphorus–metal bonds in transition metal–phosphine complexes[20] is unlikely in $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$ and related complexes. In an effort to demonstrate this conclusion, we have examined the ^1H NMR spectra of $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2X_2$ (X = Cl, Br). In contrast to the single doublet typically observed for either free or coordinated (but freely rotating) trimethylphosphine, the methyl protons in the spectrum of $[(CH_3)_3P]_2(C_6H_5CO_2)_2Mo_2Cl_2$ (recorded in $CDCl_3$ at 220 MHz) appear as two overlapping doublets centered (relative to TMS) at δ 1.50 ($J_{CH_3\text{-}P}$ = 9.0 Hz, 6 H) and δ 1.54 ($J_{CH_3'\text{-}P}$ = 9.0 Hz, 3 H). A similar but less well-resolved spectrum was observed for the bromo analogue. It follows that two of the three methyl groups in this complex are equivalent and reside in a different environment from the third. These results provide compelling evidence for the correctness of the crystallographically derived conclusion that the proximity of the vicinal halogen in such complexes prevents the free rotation of the coordinated phosphine about the phosphorus–metal bond. In view of the close structural similarity between the complexes discussed in this paper and a number of other dinuclear complexes of molybdenum and rhenium, including $Mo_2X_4L_4$, $Re_2X_6L_2$, and $Re_2X_4L_4$, it is reasonable to conclude that similar interactions and consequences may be operating in these complexes as well.

Last, Table V shows the proximity of selected hydrogen and hydrogen-bearing carbon atoms to the center of the Mo–Mo bond. It follows that those hydrogen atoms closest to this point (i.e., the ortho hydrogen atoms of the phenyl ring and the α carbon atoms of the tri-*n*-butylphosphine ligand) are subjected to the greatest influence of the diamagnetic anisotropic induced field of the metal–metal bond.[1] On the basis of this effect alone, an enhanced chemical shift difference is expected between these protons and homologous but more remote protons in the same complex.[1] Such behavior is, in fact observed.[1,6]

Acknowledgment. We thank the Center for Computer and Information Services, Rutgers University, for computer time and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

Registry No. $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$, 59493-09-3.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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