(10) K. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974).
(11) E. R. Dockal, L. L. Diaddario, M. D. Glick, and D. B. Rorabacher, *J. Am. Chem. Soc.*, **99**, 4530 (1977).
(12) T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7163 (1975).
(13) P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, **14**, 1753 (1975).
(14) J. T. Spence, *Coord. Chem. Rev.*, **4**, 475 (1969).
(15) W. G. Zumft and L. E. Mortenson, *Biochim. Biophys. Acta*, **416** 1 (1975).
(16) R. C. Bray and J. C. Swann, *Struct. Bonding (Berlin)*, **11**, 107 (1972).
(17) L. A. Ochrymowycz, C. P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974).
(18) T. Tighe and R. E. DeSimone, *J. Inorg. Nucl. Chem.*, **38**, 1623 (1976).
(19) R. E. DeSimone, unpublished results.
(20) (a) R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **97**, 942 (1975); (b) R. E. DeSimone and M. D. Glick, *J. Coord. Chem.*, **5**, 181 (1976).
(21) R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **98**, 762 (1976).
(22) E. H. Abbott, F. Schoenenolf, Jr., and T. Backstrom, *J. Coord. Chem.*, **3**, 255 (1974).
(23) We have chosen at this point to adopt the commonly used nomenclature of Busch.
(24) F. A. Cotton et al., *J. Coord. Chem.*, **5**, 217 (1976).
(25) (a) Local versions of the following programs were used: (1) TRACER II, S. L. Lawton's cell reduction program; (2) SYNCOR, W. Schmonsees' program for data reduction; (3) NEWES, W. Schmonsees' program for generation of normalized structure factors; (5) FORDAP, A. Zalkin's Fourier program; (6) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (7) H-FINDR, A. Zalkin's program for H-atom positions; (8) ORTEP, C. K. Johnson's program for drawing crystal models. (b) Neutral atom scattering factors for Mo, S, F, O, C, and H were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., The Kynoch Press, Birmingham England, 1974.
(26) R. E. DeSimone, unpublished observations.
(27) See paragraph at end of paper regarding supplementary material.
(28) B. Spivak, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975).
(29) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1851 (1971).
(30) D. H. Brown and J. A. B. Jeffreys, *J. Chem. Soc., Dalton Trans.*, 732 (1973).
(31) G. Bunzey and J. H. Enemark, *Inorg. Chem.*, **17**, 682 (1978).
(32) B. Spivak, A. P. Gaughan, and Z. Dori, *J. Am. Chem. Soc.*, **93**, 5265 (1971).
(33) L. A. Ochrymowycz, personal communication.
(34) J. T. Huneke and J. H. Enemark, *Inorg. Chem.*, in press.
(35) R. E. DeSimone and M. D. Glick, *Inorg. Chem.*, in press.
(36) R. E. DeSimone, J. Cragel, Jr., W. H. Ilsley, and M. D. Glick, *J. Coord. Chem.*, in press.

Contribution from the Department of Chemistry,
University of Oklahoma, Norman, Oklahoma 73019

Crystal and Molecular Structures of Two Molybdenum Complexes with Tetraphenylborate As a π-Bonding Ligand: (I) Cycloheptatrienyl(tetraphenylborato)molybdenum and (II) Tetraethylammonium Tricarbonyl(tetraphenylborato)molybdate

M. BILAYET HOSSAIN and DICK VAN DER HELM*

Received February 3, 1978

The crystal and molecular structures of (I) cycloheptatrienyl(tetraphenylborato)molybdenum, $Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5B(C_6H_5)_3)$, and (II) tetraethylammonium tricarbonyl(tetraphenylborato)molybdate, $[(C_2H_5)_4N][Mo(CO)_3(\eta^6\text{-}C_6H_5B(C_6H_5)_3)]$ have been determined from three-dimensional X-ray diffraction data. The compounds crystallize in the triclinic space group $P\bar{1}$ with the following crystal data. Complex I: $a = 9.93$ (1) Å, $b = 11.15$ (1) Å, $c = 10.92$ (1) Å, $\alpha = 97.6$ (1)°, $\beta = 90.4$ (1)°, $\gamma = 106.1$ (1)°, $V = 1150$ (4) Å^3, $Z = 2$, $D_x = 1.461$ g cm^{-3}. Complex II: $a = 10.58$ (1) Å, $b = 12.454$ (8) Å, $c = 11.831$ (7) Å, $\alpha = 101.32$ (5)°, $\beta = 96.88$ (7)°, $\gamma = 90.59$ (7)°, $V = 1517$ (4) Å^3, $Z = 2$, $D_x = 1.378$ g cm^{-3}. In each case intensity data were collected at -135 ± 2 °C on an automatic diffractometer using zirconium-filtered Mo radiation. Both structures were solved by the heavy-atom method and refined by least-squares techniques. The final R value for all 4737 reflections of complex I is 0.063, and for the 6246 reflections of complex II it is 0.066. In compound I, the molybdenum atom is sandwiched between, and directly bonded to, a cycloheptatrienyl ring and one of the phenyl rings of the BPh_4 group. Mo–C distances for the C_7H_7 ring are considerably shorter (average value 2.274 Å) than the corresponding distances for the phenyl ring. In both complexes, the distance of the metal to ring carbon bonded to the boron atom is significantly longer (0.089 Å in complex I and 0.060 Å in complex II) than the average of the rest of the five Mo–C(phenyl) distances (2.341 Å in complex I and 2.372 Å in complex II). All C–H bonds in the two rings forming the sandwich in complex I are significantly bent toward the metal atom. In complex II, the phenyl ring and the three carbonyl ligands form a near-staggered geometry around the molybdenum. In this complex, part of the tetraethylammonium group was found to be disordered.

Introduction

The two molybdenum complexes under investigation, $Mo(\eta^7\text{-}C_7H_7)(\eta^6\text{-}C_6H_5B(C_6H_5)_3)$—complex I—and $[(C_2H_5)_4\text{-}N][Mo(CO)_3(\eta^6\text{-}C_6H_5B(C_6H_5)_3)]$—complex II—were prepared[1] as a part of a program to synthesize and characterize derivatives of the transition metals with tetraphenylborate as a π-bonding ligand and to study the feasibility of using these compounds as oxidation–reduction catalysts. Structural features of metal–arene complexes, particularly the distortion of arene rings by π complexation, have drawn wide attention.[2-5] Although there are several structure reports of molybdenum complexes with η^5-cyclopentadienyl[6-9] and η^7-cycloheptatrienyl[10-12] ligands, complexes of benzene or benzene derivatives with molybdenum are rare.[13] Complex I, which shows a remarkable number of oxidation states (it undergoes three reversible oxidation–reduction reactions,[1] is the only reported sandwich structure of molybdenum with an η^7-C_7H_7 ligand and a phenyl ring. The structural details of such a sandwich complex would be helpful in understanding the dependence of metal-to-ring atom distance on the size of the ring.

Experimental Section

Crystal Data. The crystals of the two compounds were kindly supplied to us by Dr. D. A. Owen of the University of Oklahoma.

The crystals of complex I are fairly well-developed plates. The deep green crystals get a dark dusty coating after several days of

0020-1669/78/1317-2893$01.00/0

Table I. Crystal Data

	complex I	complex II
formula	$C_{31}H_{27}MoB$	$C_{35}H_{40}NMoBO_3$
fw	506.3	629.5
crystal system	triclinic	triclinic
a, Å	9.93 (1)	10.58 (1)
b, Å	11.15 (1)	12.454 (8)
c, Å	10.92 (1)	11.831 (7)
α, deg	97.6 (1)	101.32 (5)
β, deg	90.4 (1)	96.88 (7)
γ, deg	106.1 (1)	90.59 (7)
V, Å^3	1150 (4)	1517 (4)
space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_x, g cm^{-3}	1.461	1.378
μ(Mo Kα), cm^{-1}	5.8	4.1
no. of independent reflcns	4737	6246
max 2θ, deg	53	53
T, °C	−135 ± 2	−135 ± 2
radiation	Mo K$\bar{\alpha}$ (0.7121 Å) for intensity data Mo Kα_1 (0.70926 Å) for cell parameters	

exposure to air. In general, the crystals showed a rather high mosaic spread ranging from 1.4 to 3.0°. A plate fragment of dimensions 0.53 × 0.30 × 0.11 mm with a mosaicity of about 1.4° was selected for all crystallographic measurements. The crystals of complex II are large, transparent, light-yellow prismatic blocks which on long exposure to air turn darker and opaque. A prismatic block of size 0.44 × 0.26 × 0.18 mm was used for cell parameters and data collection.

For both crystals, preliminary photographic investigations showed no evidence of monoclinic or any higher symmetry. Diffractometry studies in each case showed the crystals to be triclinic. Crystal data for the two complexes are listed in Table I.

In both cases, the unit cell dimensions and intensity data were obtained at −135 ± 2 °C with a CAD-4 counter diffractometer (Enraf-Nonius) controlled by a PDP8/e computer and fitted with a low-temperature apparatus.

The cell parameters were obtained by a least-squares fit of $+2\theta$ and -2θ values of a number of reflections (34 in the case of complex I and 28 in the case of complex II).

Collection and Reduction of Intensity Data. In each case intensities of all reflections with $2\theta \leq 53°$ were measured at −135 ± 2 °C on the above-mentioned diffractometer using θ–2θ scan techniques with variable scan rates (v) using zirconium-filtered Mo Kα radiation. The angular scan width was also variable and was obtained from $(A + B \tan \theta)°$ for each reflection, where A and B for the two complexes were taken as 1.4 and 1.1 and 0.14 and 0.11, respectively. A receiving aperture with a variable width of $(3.50 + 0.86 \tan \theta)$ mm and a constant height of 6 mm was located at a distance of 173 mm from the crystal. The maximum scan time for a reflection in the case of complex I was 60 s and in the case of complex II, 50 s. For each reflection two-thirds of the scan time was spent scanning the peak (P) and one-sixth of the time spent scanning each of the left and right backgrounds (LB and RB). The unscaled intensity was calculated as $I = (P - 2(\text{LB} + \text{RB}))$. These were then scaled according to their scan rate.

In the case of complex I, reflection ($1\bar{4}2$) was used as a standard reflection and its intensity was monitored every 25 reflections. Fluctuations in the standard were within 1% for most of the data (88%). For about 600 reflections measured on the last day, the monitor intensity decreased as much as 10%. Three orientation control reflections were centered after every 100 observations. In case of any angular change greater than 0.1°, a new orientation matrix was automatically determined from a list of 11 reflections. In all, 4737 independent reflections were measured out of which 768 were considered indistinguishable from the background ($I \leq 2\sigma(I)$) and were assigned an intensity equal to $1.0T^{1/2}$, where $T = P + 2(\text{LB} + \text{RB})$.

For complex II, the reflection ($0\bar{3}5$) was taken as the standard reflection. During the entire measurement of 6246 independent reflections, the standard intensity did not vary more than 1.5%. Out of the total number, 1286 reflections were considered "unobserved" on the basis described above and were left out of least-squares calculations. The intensities of unobserved reflections were assigned a value of $1.0T^{1/2}$ during the refinement.

For both compounds, the structure factors for each reflection were assigned a weight given by $w_F = 1/\sigma_{F^2}$, where σ_F is defined by

$$\sigma_F = \tfrac{1}{2}\left[\frac{\sigma^2 + (0.04Iv)^2}{(Lp)(Iv)}\right]$$

and $\sigma = T^{1/2}v$ and Lp is the Lorentz and polarization factor. All intensity data were scaled by a standard reflection and Lorentz and polarization corrections were applied. No absorption correction was made.

Structure Determination and Refinement

Complex I. The position of the molybdenum atom was determined from a three-dimensional Patterson map. Structure factors calculated with Mo parameters gave an R factor ($R = \sum||kF_o| - |F_c||/\sum|kF_o|$) of 0.350 for all reflections. The parameters of the molybdenum atom were refined and a difference Fourier map was calculated using the heavy-atom phases. From the difference map, all nonhydrogen atoms were easily located. These atoms were refined first isotropically and then anisotropically with thermal parameters to an R factor of 0.086 for all 4737 reflections by using a block-diagonal least-squares program.[14] A difference Fourier map calculated at this stage revealed all hydrogen atom positions. Besides the hydrogen peaks, the difference map contained several other peaks around the molybdenum atom. Hydrogen parameters were refined isotropically. The effect of anomalous dispersion by the molybdenum atom was included in F_o by using $\Delta f'$ and $\Delta f''$ from ref 15. Refinement was discontinued when the maximum parameter shift for all nonhydrogen atoms was less than one-sixth of the corresponding standard deviation. The final R factor is 0.045 for the 3938 reflections that were included in least-squares calculations and is 0.063 for all 4737 reflections. The final difference map was almost featureless except around the molybdenum atom, where several peaks of height ranging from 0.5 to 1.0 e Å^{-3} still persisted.

Complex II. The molybdenum atom position was obtained from a three-dimensional Patterson map. Successive difference Fourier syntheses revealed the positions of three carbonyl ligands and the tetraphenylborate group. The difference map indicated considerable disorder in the tetraethylammonium group. Atoms C(42) and C(43) of phenyl ring 4 (Figure 2) also showed rather extended peaks. The structure was first refined leaving out all disordered parts. At a later stage, the disordered atoms C(55), C(56), C(57), and C(58) were included in the least-squares calculations. Each disordered atom was given fractional occupancies of 0.55 and 0.45 for the two disordered positions. The occupancy factors were estimated on the basis of peak heights in the difference map. The structure was refined to an R factor of 0.088 for all 6246 reflections. All hydrogens except those attached to disordered atoms were located. Hydrogens attached to C(42) and C(43) were also left out. The effect of anomalous dispersion by the molybdenum atom was corrected for and the structure was further refined until the maximum parameter shift was less than one-third of its corresponding standard deviation. The final R factor for 4939 reflections included in least-squares calculations is 0.043 and is 0.065 for all 6246 reflections.

In all least-squares refinements the quantity $\sum w_F(|kF_o| - |F_c|)^2$ was minimized, where w_F is as defined earlier. The scattering factors for Mo, C, N, O, and B atoms were taken from ref 16 and those for hydrogen atoms from Stewart, Davidson, and Simpson.[17] An analysis of the function $w_F(k|F_o| - |F_c|)^2$ vs. $|F_o|$ and $\sin^2 \theta$ in each case showed no significant variation of the average values of $\sum w_F \Delta F^2$ for various ranges of F_o and $\sin^2 \theta$, indicating the validity of the weighting scheme used.

The final atomic parameters (both positional and thermal) for complexes I and II are listed in Tables II and III, respectively. Atom numbering schemes followed in the two structures are shown in Figures 1 and 2. Hydrogen atoms are numbered according to the atoms to which they are bonded. As all the hydrogens in complex II could not be located with certainty due to the disordered part of the molecule, the 28 hydrogens included in the structure factor calculations were omitted from Table III. However, these hydrogens are shown in a stereoview of the single molecule of complex II. Interatomic bond distances calculated on the basis of the final parameters are given in Table IV (complex I) and in Table V (complex II). Corresponding bond angles for the two molecules are shown in Figure 1 and Figure 2, respectively. Tables VI and VII contain the description of various least-squares planes in the two molecules along with the relevant

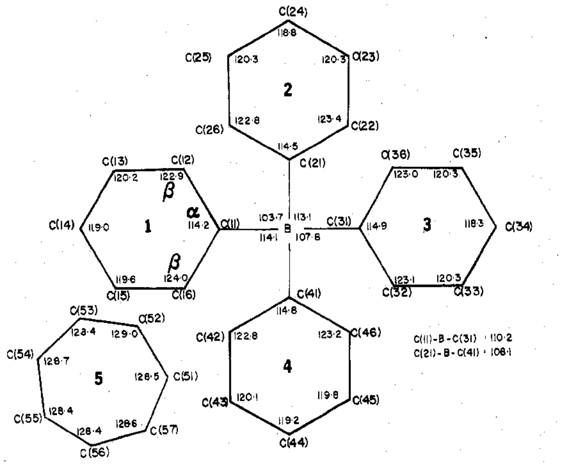

Figure 1. Atom numbering scheme and bond angles in complex I. The standard deviation for bond angles is 0.2–0.4°.

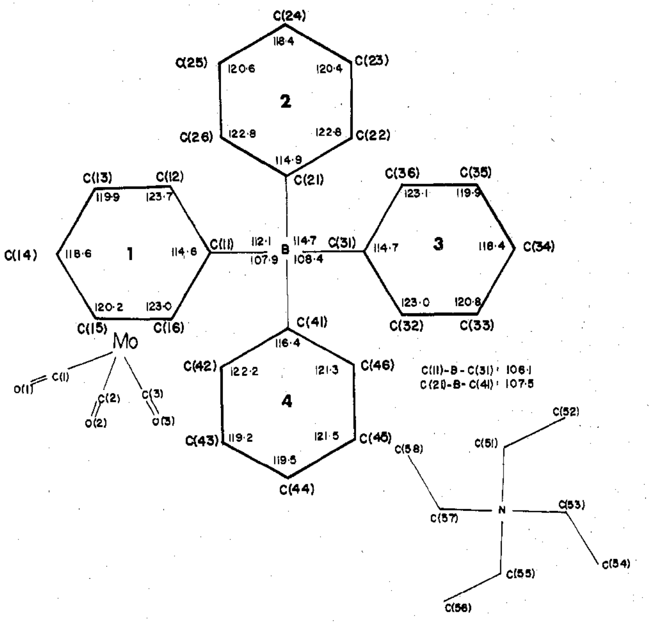

Figure 2. Atom numbering scheme and bond angles in complex II. The standard deviation for bond angles is 0.2–0.5°.

deviations of individual atoms from these planes.

Description of the Structure

Complex I. The molecular structure of cycloheptatrienyl(tetraphenylborato)molybdenum is illustrated by the stereodiagram in Figure 3. The molybdenum atom is sandwiched between the cycloheptatrienyl ring and one of the phenyls (ring 1 in Figure 1) of the tetraphenylborate group.

The metal to ring atom distances suggest that the molybdenum atom is directly bonded to both rings. The distances between the metal atom and the best planes through the seven-membered ring and the phenyl ring are 1.596 and 1.887 Å. The two rings are 3.480 Å away from each other and are nearly parallel (interplanar angle of 4.2°). Figure 4 shows the view of the metal surroundings down the line connecting ring centers. The relative orientation of the two rings shows considerable eclipsing—a phenomenon quite common in sandwich complexes between two similar rings as in ferrocene,[18] ruthenocene,[19] and bis(benzene)chromium.[20] The projection of the molybdenum atom on the plane through phenyl ring 1 is 0.050 Å away from the center of the ring. Similar projection on the seven-membered ring lies only 0.012 Å away from the centroid. Mo–C$_{ring}$ distances for the seven-membered ring range from 2.263 (5) to 2.287 (4) Å with an average value of 2.275 (5) Å. Mo–C$_{ring}$ distances for the phenyl ring are considerably larger than those for the cycloheptatrienyl ring. Five of the six Mo–C$_{ring}$ distances range between 2.326 (5) and 2.351 (4) Å, while the distance between the metal atom and the ring carbon bonded to boron (atom C(11)) has a much larger value of 2.430 (4) Å.

The cycloheptatrienyl ring is found to be almost perfectly symmetrical. The individual C–C distances lie within 2σ of the average value of 1.406 (7) Å. The average C–C–C angle of 128.6° is exactly the value to be expected of a rectangular heptagon. The ring itself is nearly planar, the maximum deviation of a ring carbon from the least-squares plane through the seven atoms being 0.015 Å (Table VI). It would appear from all of these results that the cycloheptatrienyl ring is a fully delocalized planar system. But a significant and distinctive type of distortion is noticed regarding the hydrogen positions. All seven hydrogen atoms in the ring deviate from the least-squares plane of the ring in the direction of the metal atom (last column in Table VI). Such deviations correspond to bending of C–H bonds toward the metal atom by amounts ranging from 2.5 to 10°.

All of the phenyl rings deviate slightly from planarity. The deviations in the case of the ligated ring are comparatively larger than those in the other three phenyl rings. It is interesting to note that a least-squares plane through the atoms C(12), C(13), C(14), C(15), and C(16) of the ligated phenyl ring is perfectly planar with a maximum deviation of only 0.003 Å, and atom C(11) lies nearly 0.04 Å away from this plane. All hydrogen atoms of phenyl ring 1 lie out of the plane and toward the metal atom. The average C–H bending toward the metal atom in the present case is much smaller compared to that in the cycloheptatrienyl ring. Hydrogen atoms in other phenyl rings also deviate from their respective ring planes but in general they lie on either side of the planes. The average C–C distance in ring 1 is 1.412 (6) Å, which is about 3σ larger than the corresponding values in other three rings (1.394 (6),

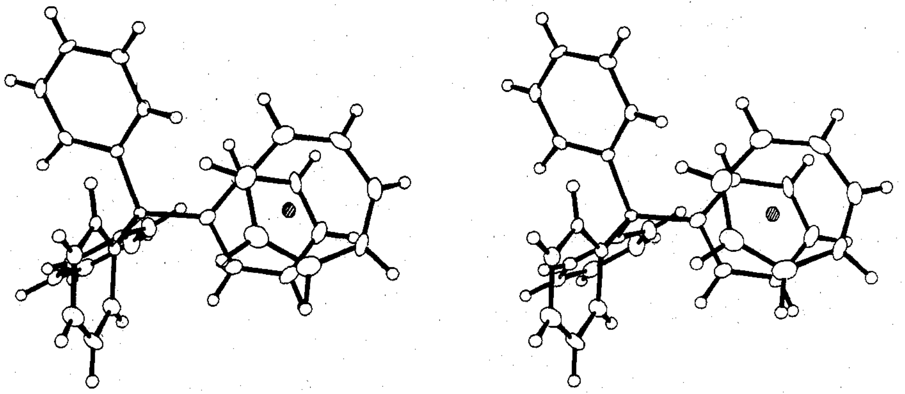

Figure 3. Stereoview of a single molecule of complex I.

Table II

Positional (×10⁴) and Thermal (×10⁴) Parameters for Complex I[a]

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	2482.4 (4)	2470.2 (3)	2083.3 (3)	98 (1)	136 (1)	131 (1)	27 (1)	1 (1)	17 (1)
C(51)	2154 (5)	982 (4)	375 (4)	274 (24)	169 (22)	197 (23)	2 (18)	27 (18)	−51 (18)
C(52)	2905 (5)	624 (4)	1287 (4)	212 (23)	108 (21)	305 (25)	9 (17)	45 (19)	−6 (18)
C(53)	2644 (5)	596 (4)	2548 (4)	305 (26)	127 (21)	276 (25)	33 (19)	−43 (20)	55 (18)
C(54)	1542 (5)	890 (4)	3201 (4)	317 (26)	186 (23)	231 (24)	25 (19)	64 (20)	97 (19)
C(55)	428 (4)	1294 (4)	2762 (4)	84 (20)	221 (23)	312 (25)	7 (17)	74 (17)	53 (19)
C(56)	168 (4)	1532 (4)	1560 (4)	104 (20)	185 (22)	321 (25)	2 (17)	−2 (18)	25 (19)
C(57)	949 (5)	1403 (4)	498 (4)	232 (23)	214 (23)	186 (23)	4 (19)	−100 (18)	−2 (18)
C(11)	4894 (4)	3793 (4)	2326 (4)	134 (20)	94 (19)	156 (21)	−8 (15)	26 (16)	−13 (15)
C(12)	4231 (4)	3785 (4)	3481 (4)	167 (21)	196 (22)	129 (21)	12 (17)	16 (16)	−14 (17)
C(13)	2981 (5)	4154 (4)	3680 (4)	212 (20)	225 (21)	191 (20)	14 (17)	72 (16)	−38 (17)
C(14)	2333 (4)	4522 (4)	2722 (4)	163 (22)	156 (22)	332 (26)	54 (17)	84 (19)	3 (19)
C(15)	2928 (4)	4511 (4)	1549 (4)	102 (20)	136 (21)	309 (25)	55 (16)	−30 (17)	53 (18)
C(16)	4164 (4)	4142 (4)	1379 (4)	141 (20)	178 (21)	133 (20)	40 (17)	21 (16)	36 (17)
C(21)	7508 (4)	4994 (4)	2855 (4)	132 (20)	186 (21)	75 (18)	12 (15)	27 (15)	16 (16)
C(22)	7250 (4)	6142 (4)	2723 (4)	153 (21)	206 (23)	272 (24)	51 (18)	−24 (18)	23 (19)
C(23)	8157 (5)	7306 (4)	3191 (5)	205 (24)	205 (24)	377 (28)	60 (19)	14 (20)	48 (21)
C(24)	9403 (4)	7376 (4)	3817 (4)	161 (22)	203 (22)	202 (23)	−18 (17)	33 (17)	−50 (18)
C(25)	9712 (4)	6273 (4)	3968 (4)	108 (20)	260 (23)	156 (21)	10 (17)	15 (16)	−24 (18)
C(26)	8784 (4)	5108 (4)	3494 (4)	136 (20)	216 (22)	111 (20)	56 (17)	18 (15)	35 (17)
C(31)	6603 (4)	2447 (4)	2954 (4)	66 (18)	166 (20)	134 (20)	3 (15)	−5 (15)	24 (16)
C(32)	6566 (4)	1263 (4)	2327 (4)	73 (18)	215 (22)	136 (20)	42 (16)	17 (15)	26 (16)
C(33)	6588 (4)	247 (4)	2927 (4)	150 (21)	193 (22)	200 (22)	67 (17)	7 (17)	25 (17)
C(34)	6643 (5)	374 (4)	4214 (4)	221 (23)	244 (24)	240 (24)	41 (19)	2 (18)	146 (19)
C(35)	6693 (4)	1538 (4)	4871 (4)	169 (22)	283 (25)	169 (22)	44 (18)	−46 (17)	96 (18)
C(36)	6700 (4)	2548 (4)	4250 (4)	142 (20)	154 (21)	181 (21)	−5 (16)	−28 (16)	11 (17)
C(41)	6949 (4)	3326 (4)	797 (4)	120 (19)	152 (20)	115 (19)	47 (16)	24 (15)	42 (16)
C(42)	8368 (4)	3691 (4)	516 (4)	148 (20)	172 (21)	137 (20)	48 (17)	−24 (16)	39 (16)
C(43)	8844 (4)	3353 (4)	−644 (4)	93 (19)	155 (21)	234 (23)	47 (16)	48 (16)	79 (17)
C(44)	7904 (4)	2661 (4)	−1581 (4)	182 (21)	193 (22)	117 (20)	69 (17)	63 (16)	0 (16)
C(45)	6485 (4)	2293 (4)	−1354 (4)	173 (21)	198 (22)	134 (21)	18 (16)	−19 (16)	12 (17)
C(46)	6035 (4)	2620 (4)	−189 (4)	77 (18)	200 (22)	171 (21)	23 (16)	27 (15)	48 (17)
B	6480 (4)	3613 (4)	2225 (4)	87 (20)	144 (22)	88 (20)	25 (17)	−5 (16)	−1 (17)

Hydrogen Parameters

atom	10^3x	10^3y	10^3z	*B*, Å²	atom	10^3x	10^2y	10^3z	*B*, Å²
H(51)	261 (5)	100 (4)	−41 (4)	1.2 (9)	H(24)	1010 (5)	818 (4)	420 (4)	1.5 (9)
H(52)	377 (5)	49 (5)	99 (5)	2.9 (12)	H(25)	1059 (4)	631 (4)	440 (4)	1.1 (9)
H(53)	336 (5)	42 (5)	305 (5)	2.4 (11)	H(26)	904 (4)	435 (4)	358 (4)	0.7 (8)
H(54)	164 (5)	96 (5)	411 (5)	2.8 (12)	H(32)	665 (4)	117 (4)	145 (4)	0.9 (8)
H(55)	−23 (4)	153 (4)	341 (4)	0.6 (8)	H(33)	661 (4)	−49 (4)	248 (4)	0.6 (8)
H(56)	−43 (6)	196 (5)	143 (5)	3.3 (13)	H(34)	659 (4)	−32 (4)	462 (4)	1.1 (9)
H(57)	63 (6)	167 (5)	−18 (5)	3.2 (12)	H(35)	674 (5)	162 (5)	573 (5)	2.4 (11)
H(12)	461 (5)	344 (4)	419 (4)	2.0 (10)	H(36)	676 (5)	334 (4)	468 (4)	1.4 (9)
H(13)	260 (5)	406 (4)	442 (4)	1.2 (9)	H(42)	915 (4)	421 (4)	115 (4)	0.9 (9)
H(14)	152 (5)	472 (4)	285 (4)	1.3 (9)	H(43)	971 (4)	363 (4)	−82 (4)	1.1 (9)
H(15)	250 (5)	473 (4)	91 (4)	1.8 (10)	H(44)	820 (4)	242 (4)	−234 (4)	1.1 (9)
H(16)	448 (4)	411 (4)	65 (4)	0.7 (8)	H(45)	584 (5)	180 (4)	−199 (4)	1.7 (10)
H(22)	642 (5)	611 (5)	225 (4)	2.2 (11)	H(46)	513 (4)	230 (4)	1 (4)	1.3 (9)
H(23)	804 (5)	812 (5)	304 (5)	2.3 (11)					

[a] Calculated standard deviations for the last digit are in parentheses. Anisotropic thermal parameters in this table and also in Table III are of the form $\exp\{-2\pi^2(U_{11}h^2a^* + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$.

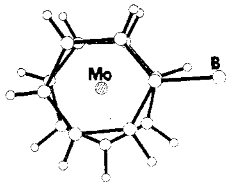

Figure 4. View of the metal surroundings in complex I down the line joining the ring centers.

1.393 (6), and 1.392 (6) Å). The two largest bond lengths, C(11)–C(12) and C(11)–C(13), involve atom C(11). Figure 5 shows the stereoview of the contents of one unit cell for complex I. All intermolecular interactions seem to be of van der Waals type.

Complex II. In this molecule the molybdenum atom is found bonded to the three carbonyl ligands and phenyl ring 1 (Figure 2) of the tetraphenylborate group. The stereoview of the molecule is shown in Figure 6. The metal atom is 1.916 Å away from the mean plane through the six ring atoms. The projection of the metal atom on the ring plane lies 0.11 Å away from the center. The Mo–C_{ring} distances in complex II are systematically larger than those found in the case of the phenyl ring in complex I, and they show the similar asymmetry as has already been noted for complex I. The distances of the metal atom to ring carbon bonded to boron is significantly larger (2.432 (3) Å) than the other five Mo–C distances which range from 2.364 (4) to 2.381 (4) Å. All phenyl rings of the tetraphenylborate group are nearly planar with mean deviations of less than 0.005 Å. The nonplanarity in the ligated phenyl ring is far less than that observed in complex I. The average C–C distance in the ligated phenyl ring is about 3σ larger than those in other rings (1.415 (6) Å compared with 1.396 (6), 1.394 (6), and 1.394 (7) Å). Figure 7 shows the metal surroundings for complex II looking down the ring center. The positions of the three carbonyl ligands relative

Table III. Positional (×10⁴) and Thermal (×10⁴) Parameters for Complex II[a]

atoms	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	7569.1 (3)	1118.0 (3)	−192.3 (3)	347 (2)	269 (2)	205 (1)	169 (1)	146 (1)	120 (1)
C(1)	8862 (4)	1968 (4)	−718 (4)	287 (21)	595 (28)	403 (23)	247 (20)	159 (18)	299 (21)
C(2)	6336 (3)	2119 (3)	−751 (3)	303 (20)	259 (18)	147 (16)	16 (16)	76 (14)	33 (14)
C(3)	7336 (5)	280 (3)	−1779 (3)	736 (32)	260 (20)	306 (21)	239 (21)	275 (21)	141 (17)
C(11)	7216 (4)	1721 (3)	1825 (3)	341 (21)	362 (20)	168 (17)	208 (17)	132 (15)	161 (15)
C(12)	8521 (4)	1527 (3)	1766 (3)	354 (22)	389 (22)	243 (19)	205 (18)	117 (16)	177 (16)
C(13)	8989 (4)	509 (3)	1247 (3)	401 (23)	414 (23)	289 (20)	246 (19)	155 (17)	184 (17)
C(14)	8135 (4)	−369 (3)	739 (3)	459 (23)	355 (22)	283 (19)	249 (19)	166 (18)	196 (17)
C(15)	6807 (4)	−213 (3)	766 (3)	449 (24)	290 (20)	290 (19)	142 (18)	170 (18)	175 (16)
C(16)	6374 (4)	804 (3)	1285 (3)	371 (22)	339 (20)	232 (18)	170 (17)	142 (16)	168 (16)
C(21)	5303 (3)	3195 (3)	2055 (3)	300 (20)	321 (20)	116 (15)	172 (16)	67 (14)	50 (14)
C(22)	4267 (4)	2510 (3)	2143 (3)	357 (21)	340 (20)	183 (17)	162 (17)	113 (16)	59 (15)
C(23)	3015 (4)	2698 (3)	1739 (3)	306 (21)	368 (22)	273 (19)	80 (18)	119 (17)	19 (17)
C(24)	2729 (4)	3618 (3)	1268 (3)	315 (22)	410 (23)	265 (19)	169 (18)	52 (17)	35 (17)
C(25)	3720 (4)	4330 (3)	1199 (3)	371 (22)	343 (21)	236 (19)	169 (18)	35 (17)	89 (16)
C(26)	4971 (3)	4123 (3)	1589 (3)	277 (20)	324 (21)	181 (17)	121 (16)	43 (15)	63 (15)
C(31)	7856 (4)	3832 (3)	2456 (3)	290 (20)	346 (20)	157 (17)	196 (17)	9 (15)	−25 (15)
C(32)	8814 (4)	4250 (3)	3374 (3)	405 (24)	418 (23)	226 (19)	245 (19)	−57 (17)	−51 (17)
C(33)	9811 (4)	4929 (4)	3258 (4)	357 (24)	515 (27)	326 (22)	212 (21)	−136 (18)	−139 (20)
C(34)	9904 (4)	5252 (3)	2215 (4)	242 (21)	376 (23)	471 (26)	97 (18)	−37 (18)	−135 (20)
C(35)	8973 (4)	4866 (3)	1281 (3)	308 (21)	325 (21)	293 (20)	55 (17)	46 (17)	−48 (16)
C(36)	7984 (3)	4166 (3)	1410 (3)	243 (20)	347 (20)	166 (17)	81 (16)	−16 (14)	−45 (15)
C(41)	6775 (4)	2833 (4)	3922 (3)	264 (21)	681 (29)	171 (17)	209 (20)	55 (15)	161 (19)
C(42)	6317 (6)	3725 (6)	4681 (4)	1086 (48)	1578 (61)	189 (22)	1057 (47)	215 (25)	195 (30)
C(43)	6436 (5)	3795 (6)	5897 (4)	535 (31)	1505 (57)	140 (20)	511 (34)	62 (20)	39 (27)
C(44)	7001 (4)	2960 (4)	6361 (3)	293 (22)	815 (33)	148 (18)	−224 (22)	−5 (16)	151 (20)
C(45)	7431 (4)	2081 (4)	5638 (3)	592 (30)	513 (27)	233 (20)	−295 (33)	−113 (20)	210 (19)
C(46)	7313 (4)	2010 (3)	4427 (3)	260 (20)	398 (22)	227 (19)	−89 (17)	−6 (15)	141 (17)
C(51)	7027 (4)	7014 (3)	2996 (3)	396 (22)	171 (17)	168 (16)	67 (16)	50 (15)	6 (14)
C(52)	7376 (4)	7291 (3)	1899 (3)	465 (25)	306 (21)	334 (21)	136 (18)	214 (19)	124 (17)
C(53)	7001 (4)	8972 (3)	4020 (4)	299 (22)	209 (19)	469 (24)	−42 (16)	138 (19)	−107 (17)
C(54)	5605 (4)	9061 (4)	3700 (4)	401 (25)	413 (24)	341 (22)	201 (20)	−32 (19)	−33 (19)
O(1)	9633 (3)	2473 (3)	−1029 (3)	344 (18)	1027 (29)	812 (26)	121 (18)	238 (17)	587 (23)
O(2)	5624 (2)	2719 (2)	−1078 (2)	351 (15)	309 (14)	234 (13)	131 (12)	0 (11)	65 (11)
O(3)	7221 (4)	−194 (2)	−2738 (2)	1122 (30)	338 (17)	269 (15)	251 (18)	276 (17)	67 (13)
N(1)	2559 (3)	2165 (3)	5897 (3)	410 (21)	453 (21)	305 (18)	282 (17)	−146 (15)	−153 (16)
B(1)	6761 (4)	2918 (4)	2541 (3)	347 (24)	372 (24)	148 (19)	204 (20)	58 (17)	68 (17)

atoms	*x*	*y*	*z*	*B*, Å²	atoms	*x*	*y*	*z*	*B*, Å²
C(55)[b]	971 (7)	1853 (6)	5944 (6)	1.37 (12)	C(57)	2734 (7)	2334 (6)	4839 (6)	1.65 (12)
C(55′)	1260 (7)	2390 (6)	5490 (6)	2.44 (12)	C(57′)	3470 (6)	2641 (5)	4963 (5)	1.46 (10)
C(56)	396 (9)	958 (7)	4935 (8)	2.85 (16)	C(58)	1933 (8)	3259 (7)	4462 (7)	2.57 (15)
C(56′)	788 (8)	1838 (6)	4216 (7)	3.33 (15)	C(58′)	3170 (7)	3786 (6)	4747 (6)	2.88 (13)

[a] Calculated standard deviations for the last digit are in parentheses. [b] Disordered atoms: atoms with primed numerals have 0.45 occupancy; others, 0.55 occupancy.

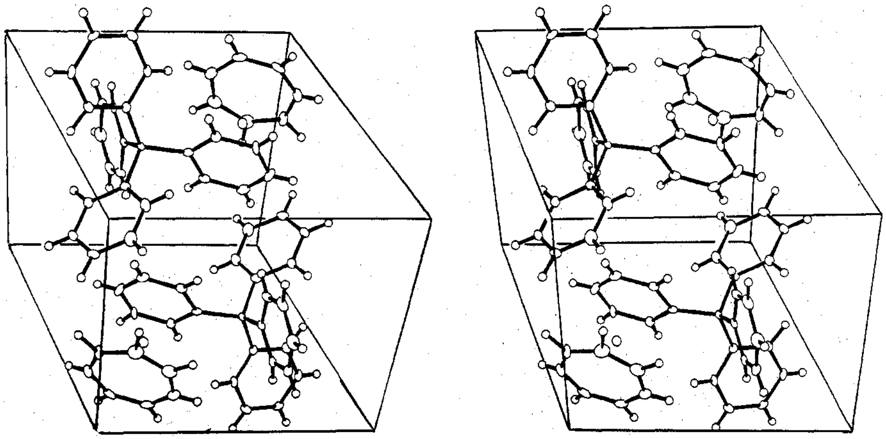

Figure 5. Stereoview of the contents of one unit cell in the complex I structure.

to the phenyl ring give a near-staggered geometry. The three carbonyl ligands lie almost symmetrically about the metal atom as can be seen from the following dimensions: C(1)–Mo–C(2) = 86.4°, C(1)–Mo–C(3) = 85.6°, C(2)–Mo–C(3) = 86.1°; C(1)–C(2) = 2.680 (5) Å, C(1)–C(3) = 2.653 (5) Å, C(2)–C(3) = 2.668 (5) Å. The carbonyl ligands are linear with Mo–C–O angles of 179.8 (4), 179.0 (3), and 177.7 (4)°. The metal–carbon distances of 1.953 (4) Å [Mo–C(1)], 1.960 (4) Å [Mo–C(2)], and 1.946(4) Å [Mo–C(3)] are very similar to those found in strongly interacting carbonyl complexes of molybdenum as tabulated by Clark and Palenik[10] and also by Rajaram and Ibers.[8] The C–O distances of 1.161 (6), 1.153 (4), and 1.163 (5) Å in the present structure compare well with those listed in the above-mentioned tabulations.

A part of the tetraethylammonium group was found to be disordered. From the difference Fourier map it was noticed

Table IV. Bond Distances (in Å) in Complex I

Mo–C Distances

Mo–C(51)	2.282 (5)	Mo–C(11)	2.430 (4)
Mo–C(52)	2.276 (5)	Mo–C(12)	2.334 (4)
Mo–C(53)	2.263 (5)	Mo–C(13)	2.326 (5)
Mo–C(54)	2.267 (5)	Mo–C(14)	2.347 (5)
Mo–C(55)	2.286 (4)	Mo–C(15)	2.347 (4)
Mo–C(56)	2.278 (4)	Mo–C(16)	2.351 (4)
Mo–C(57)	2.267 (5)	mean of last 5	2.341
mean	2.274		

C–C Distances in the C_7H_7 Ring

C(51)–C(52)	1.403 (6)	C(55)–C(56)	1.410 (7)
C(52)–C(53)	1.406 (7)	C(56)–C(57)	1.413 (7)
C(53)–C(54)	1.401 (7)	C(57)–C(51)	1.402 (7)
C(54)–C(55)	1.408 (7)	mean	1.406

B–C Distances

B–C(11)	1.645 (6)	B–C(31)	1.644 (6)
B–C(21)	1.649 (6)	B–C(41)	1.646 (6)

C–C Distances in the Phenyl Rings

bond	*r* = 1	*r* = 2	*r* = 3	*r* = 4
C(*r*1)–C(*r*2)	1.427 (6)	1.399 (6)	1.395 (6)	1.402 (6)
C(*r*2)–C(*r*3)	1.421 (6)	1.387 (7)	1.387 (6)	1.397 (6)
C(*r*3)–C(*r*4)	1.388 (7)	1.388 (7)	1.394 (6)	1.375 (6)
C(*r*4)–C(*r*5)	1.415 (7)	1.377 (7)	1.385 (7)	1.388 (6)
C(*r*5)–C(*r*6)	1.405 (6)	1.398 (6)	1.389 (6)	1.387 (6)
C(*r*6)–C(*r*1)	1.414 (6)	1.408 (6)	1.406 (6)	1.403 (6)
mean	1.412	1.393	1.393	1.392

Hydrogen Distances

C(51)–H	0.97 (4)	C(24)–H	1.00 (5)
C(52)–H	0.96 (5)	C(25)–H	0.98 (5)
C(53)–H	0.97 (5)	C(26)–H	0.96 (4)
C(54)–H	0.99 (5)	C(32)–H	0.95 (4)
C(55)–H	1.02 (4)	C(33)–H	0.90 (4)
C(56)–H	0.88 (6)	C(34)–H	0.94 (4)
C(57)–H	0.92 (6)	C(35)–H	0.93 (5)
C(12)–H	1.03 (5)	C(36)–H	0.93 (5)
C(13)–H	0.90 (4)	C(42)–H	1.02 (4)
C(14)–H	0.90 (5)	C(43)–H	0.86 (4)
C(15)–H	0.91 (5)	C(44)–H	0.92 (4)
C(16)–H	0.86 (4)	C(45)–H	0.94 (5)
C(22)–H	0.96 (5)	C(46)–H	0.91 (4)
C(23)–H	0.97 (5)		

Table V. Bond Distances (in Å) in Complex II

Mo–C_6H_6 Distances			
Mo–C(11)	2.432 (3)	B–C(11)	1.670 (6)
Mo–C(12)	2.368 (4)	B–C(21)	1.644 (5)
Mo–C(13)	2.377 (4)	B–C(31)	1.642 (6)
Mo–C(14)	2.381 (4)	B–C(41)	1.656 (5)
Mo–C(15)	2.369 (4)	Mo–C(1)	1.952 (4)
Mo–C(16)	2.364 (4)	Mo–C(2)	1.960 (4)
mean of last 5	2.372	Mo–C(3)	1.946 (4)
		C(1)–O(1)	1.161 (6)
		C(2)–O(2)	1.153 (4)
		C(3)–O(3)	1.163 (5)

C–C Distances in the Phenyl Rings

bond	*r* = 1	*r* = 2	*r* = 3	*r* = 4
C(*r*1)–C(*r*2)	1.412 (5)	1.409 (5)	1.408 (5)	1.414 (7)
C(*r*2)–C(*r*3)	1.418 (6)	1.391 (6)	1.381 (6)	1.414 (6)
C(*r*3)–C(*r*4)	1.401 (6)	1.391 (6)	1.385 (6)	1.377 (8)
C(*r*4)–C(*r*5)	1.423 (6)	1.386 (6)	1.394 (6)	1.369 (6)
C(*r*5)–C(*r*6)	1.402 (5)	1.392 (5)	1.396 (5)	1.408 (5)
C(*r*6)–C(*r*1)	1.436 (5)	1.406 (5)	1.402 (5)	1.379 (6)
mean	1.415	1.396	1.394	1.394

Table VI. Least-Squares Planes in Complex I

Equation: $m_1x + m_2y + m_3z = d$

plane through atoms	m_1	m_2	m_3	*d*	plane (*P*)
C(11), C(12), C(13), C(14), C(15), C(16)	2.813	8.998	1.438	5.108	1
C(21), C(22), C(23), C(24), C(25), C(26)	4.828	0.041	−9.577	0.915	2
C(31), C(32), C(33), C(34), C(35), C(36)	9.576	−0.150	−0.492	6.153	3
C(41), C(42), C(43), C(44), C(45), C(46)	3.505	−10.643	4.401	−0.758	4
C(51), C(52), C(53), C(54), C(55), C(56), C(57)	3.038	8.964	1.001	1.581	5

Deviations in Å

atom	*P* = 1	*P* = 2	*P* = 3	*P* = 4	*P* = 5
C(*P*1)	+0.017	−0.003	−0.012	+0.005	−0.008
C(*P*2)	−0.011	+0.003	+0.001	−0.009	−0.010
C(*P*3)	−0.002	−0.002	+0.007	+0.006	+0.012
C(*P*4)	+0.009	0.000	−0.005	+0.001	+0.006
C(*P*5)	−0.002	+0.000	−0.007	−0.005	−0.014
C(*P*6)	−0.011	+0.001	+0.015	+0.002	+0.000
C(*P*7)					+0.015
H(*P*1)					+0.068
H(*P*2)	−0.116	+0.049	+0.124	−0.015	+0.106
H(*P*3)	−0.091	+0.086	+0.062	−0.060	+0.126
H(*P*4)	−0.018	−0.024	−0.065	+0.030	+0.187
H(*P*5)	−0.016	+0.014	−0.010	+0.017	+0.067
H(*P*6)	−0.058	+0.040	+0.043	+0.110	+0.189
Mo	−1.887				+1.596
B	+0.287	+0.098	−0.111	+0.163	

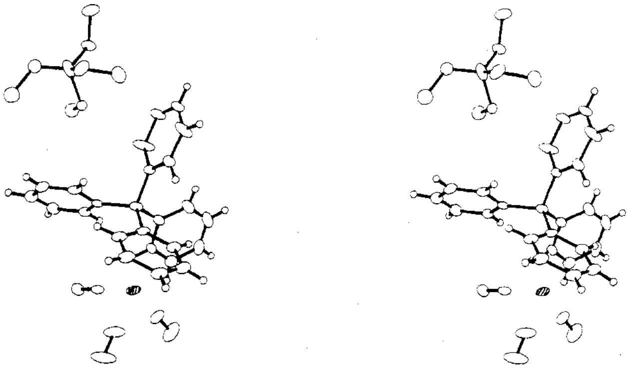

Figure 6. Stereoview of the single molecule of complex II. Only one part (with 55% occupancy) of the disordered tetraethylammonium is shown.

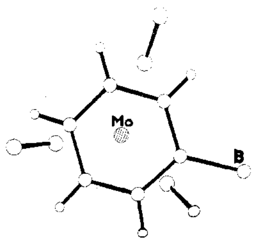

Figure 7. View of the metal surroundings in complex II.

that while the nitrogen atom and two of the ethyl groups are perfectly normal, the other two ethyls are distinctly disordered. The peak arrangement suggested two widely separated positions for each of the disordered ethyl chains. It was also seen that a rotation of about 30° made one disordered ethyl position fall almost on the top of the second position in each of the two disordered ethyl chains. The disordered part of the tetraethylammonium group was refined by assuming 55 and 45% occupancy for each of the four carbon atoms C(55), C(56), C(57), and C(58). Final atomic positions of the disordered atoms led to some ambiguous bond distances and angles. The dimensions of the tetraethylammonium were, therefore, left out of this report. The geometry of the tetraethylammonium group does allow a free rotation of ethyl groups, but it is not clearly understood why only half of the group shows large disorder while the other half appears almost normal. It may

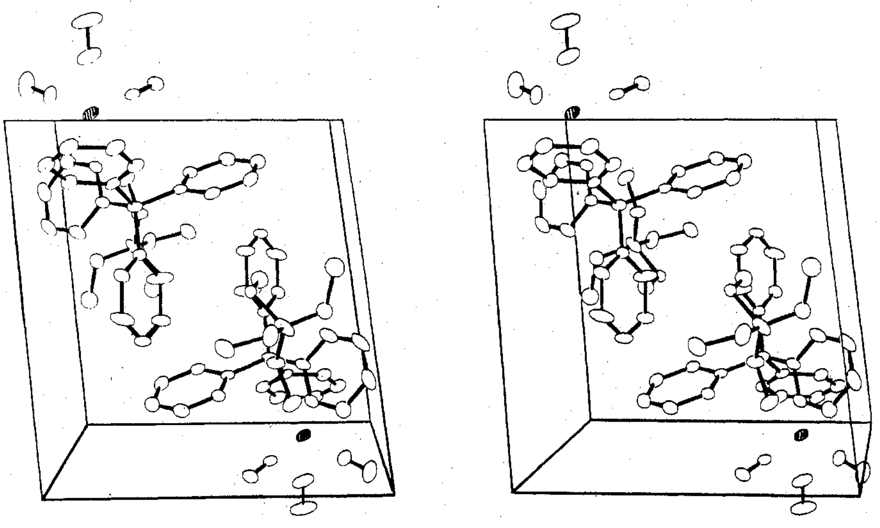

Figure 8. Stereoview of the contents of one unit cell in complex II structure.

Table VII. Least-Squares Planes in Complex II

Equation: $m_1x + m_2y + m_3z = d$

plane through atoms	m_1	m_2	m_3	d	plane (P)
C(11), C(12), C(13), C(14), C(15), C(16)	0.491	6.030	−11.254	−0.654	1
C(21), C(22), C(23), C(24), C(25), C(26)	2.371	−4.392	−9.967	−2.210	2
C(31), C(32), C(33), C(34), C(35), C(36)	6.288	−9.463	−2.312	0.747	3
C(41), C(42), C(43), C(44), C(45), C(46)	9.340	5.602	−1.182	7.441	4

Deviations in Å

atom	$P = 1$	$P = 2$	$P = 3$	$P = 4$
C(P1)	−0.008	+0.016	0.000	+0.011
C(P2)	+0.006	−0.017	−0.005	−0.007
C(P3)	−0.001	+0.006	+0.006	0.000
C(P4)	−0.001	+0.005	−0.001	+0.005
C(P5)	−0.002	−0.005	−0.005	−0.001
C(P6)	+0.006	−0.005	+0.006	−0.007

be mentioned that atoms C(42) and C(43) of phenyl ring 4 show some degree of disorder indicated by their rather large thermal parameters. It is relevant to note that the tetraethylammonium group lies very near phenyl ring 4 with the disordered part lying closer to the atoms C(42) and C(43) and leading to such close contacts: C(42)–C(57′) = 3.37 Å, C(42)–C(58′) = 3.34 Å, and C(43)–C(57′) = 3.40 Å (Figure 8).

Tetraphenylborate Anion. Dimensionally the tetraphenylborate groups in the two complexes are very similar, though there are some conformational differences. The B–C distance of 1.653 (6) Å in complex II is slightly larger than that in complex I (1.647 (6) Å). These values are in fair agreement with those observed in several other tetraphenylborate ligands. In complex I, C–B–C angles deviate quite significantly from normal tetrahedral angles, ranging from 103.7 (3) to 114.1 (3)°. Such deviations in complex II are comparatively smaller, where the angles vary from 106.1 (3) to 114.7 (3)°. Values of interplanar angles between the best planes through the phenyl rings show a much wider spread about the mean value compared with those observed in other structures. The interplanar angles in complex I range from 49.5 to 87.1°, with a mean value of 69.5°. In complex II, the angles vary from 49.8 to 87.0° with a mean value of 72.1°. The average bond lengths in the ligated phenyl rings show enlargements of 0.019 (6) Å in complex I and 0.020 (6) Å in complex II. Bond lengths in other phenyl rings do not vary appreciably from normal values. But all of the phenyl rings in the two structures show very significant and similar angular deviations. In each phenyl ring, the angle at the carbon atom bonded to boron (indicated by angle α in Figure 1) is much smaller than the normal trigonal angle, and the two adjacent angles (indicated by β in Figure 1) are systematically larger. The average value of the angle α in complex I is 114.6 (4)°, while that in complex II is 115.1 (3)°. The average values of β in two molecules are 123.1 (4) and 122.8 (4)°. These values are in excellent agreement with those found (α = 114.5°, β = 123.1°) in Ni(nas)BPh_4 by DiVaira and Orlandini.[21] These authors have extensively examined such angular distortions in tetraphenylborate ligands. From conformational energy calculations they have shown that both the regular phenyl ring and a distorted ring with α = 114.5° and β = 123.1° are energetically quite similar. In addition, they concluded that a wide range of conformations for the tetraphenylborate anion with a much wider spread of interplanar angles, as observed in the present structures, are theoretically viable.

Discussion

In recent years the structure determination of metal–arene complexes has brought about some intriguing and interesting questions regarding metal to ring atom distance and the nature of ring distortion caused by complexation. From a general survey of results of a series of Mo–C_5H_5 complexes, Churchill and O'Brien[2] observed that the geometry of the metal–arene complexes is dominated by an almost constant metal–ring carbon distance, whereas Clark and Palenik[10] from a similar survey of a few Mo–C_7H_7 structures have concluded that the metal–$C_{\rm ring}$ distance is not expected to be constant but depends on the strength and nature of other interacting groups around the metal atom. It has further been suggested by Mason, Thomas, and Heath[5] that the metal–ring atom distances are independent of the ring size and are determined by the type of associated ligands. The present structures provide some interesting results for metal–arene complexes. Table VIII gives the average Mo–$C_{\rm ring}$ distances for some of the Mo–C_5H_5, Mo–C_6H_6, and Mo–C_7H_7 complexes from earlier structure determinations. The table shows that Mo–C distances in the case of C_7H_7 complexes, with a mean value of 2.312 Å, are systematically shorter than those in the case of Mo–C_5H_5 complexes, where the average Mo–C distance is 2.349 Å. The tabulated results further indicate that Mo–C distances in C_6H_6 complexes lie in the range of those for C_5H_5 complexes. The

Table VIII. Molybdenum–Carbon Distances (A) in Arene Complexes

Mo–C ring distance	complex	ref
	A. Mo–C_7H_7 Complexes	
2.321	$C_7H_7Mo(CO)_2Sn(C_6H_5)_2Cl$	23
2.312	$C_7H_7Mo(CO)_2Sn(C_6H_5)Cl$	11
2.337	$C_7H_7Mo(CO)_2SnCl_3$	11
2.307	$C_7H_7Mo(CO)_2Cl$	12
2.321	$C_7H_7Mo(CO)_2Br$	12
2.314	$C_7H_7Mo(CO)_3BF_4$	10
2.316	$C_7H_7Mo(CO)_2C_6H_5$	2
2.274	complex I	present report
	B. Mo–C_6H_6 Complexes	
2.372	$[C_6H_3(CH_3)_3](CO)_3Mo$	13
2.392	$[C_6(CH_3)_6](CO)_3Mo$	13
2.280	$Mo[P(CH_3)_2C_6H_5]_4$	5
2.341	complex I	present report
2.372	complex II	present report
	C. Mo–C_5H_5 Complexes	
2.333	$(\eta^5\text{-}C_5H_5)Mo(CO)_3C_3F_7$	6
2.345	$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$	23
2.347	$(\eta^5\text{-}C_5H_5)Mo(CO)_2[P(C_6H_5)_3]COCH_3$	7
2.374	$(\eta^5\text{-}C_5H_5)Mo(CO)_3C_2H_5$	24
2.361	$(p\text{-}CH_3C_6H_4CH_2)(\eta^5\text{-}C_5H_5)(CO)_2Mo$	25
2.331	$(C_5H_5)_2MoS_4$	9
2.351	$Tl(Mo(CO)_3(\eta^5\text{-}C_5H_5))_3$	8

only exception is the complex $Mo[P(CH_3)_2(C_6H_5)]_4$[5] where very short Mo–C distances are observed. However, not a very high degree of accuracy was claimed for this particular structure. It can also be seen that all the C_7H_7 complexes in Table VIII contain strongly interacting carbonyl ligands. The results of the present structures are added to this sample (Table VIII). The following observations are clear: (a) the Mo–C_{ring} (C_7H_7) distances in complex I are shorter than any others observed; (b) these distances are significantly shorter than Mo–C_{ring} (C_6H_6) distances in complex I; (c) the latter are in turn shorter than the Mo–C_{ring} distances in complex II. One can conclude from observations (a) and (c) that in the absence of strong π acids, molybdenum interacts more strongly with arene rings. Observations (b) and also (a) and (c) and other results in Table VIII clearly indicate that the molybdenum atom interacts more strongly with C_7H_7 rings than with either C_6H_6 or C_5H_5 rings. In other words, Mo–C_{ring} distances are not independent of the type of the arene ring. A Mo sandwich with C_7H_7 and C_5H_5 rings would have provided additional evidence of such a suggestion but no such structure is reported. However, in a Ti sandwich complex, C_7H_7–Ti–C_5H_5,[26] the metal–carbon distance (average) for the seven-membered ring of 2.194 Å was found to be considerably shorter than the corresponding distance (2.321 Å) for the five-membered ring.

The effect of complexation on the planarity of the arene rings in the present structures seems to be minimal, as indicated by the deviations of ring atoms (Table VI and Table VII). However, both the cycloheptatrienyl ring and the ligated phenyl ring in complex I show significant out-of-plane C–H bending toward the metal atom. Such concave distortion of a ligated ring seems to be a general feature of "sandwich" compounds, as it has been observed in bis(benzene)chromium,[20] ferrocene,[18] and $U(C_8H_4(CH_3)_4)_2$.[4] Similar distortion was also observed in a nonsandwich complex as in (benzene)tricarbonylchromium.[3] It may be noted here that Khoshland, Myers, and Chesick[13] observed bending of methyl carbons away from the metal atom in (hexamethylbenzene)tricarbonylmolybdenum.

The two ligated phenyl rings in the present structures show another very significant deviation from the normally expected values. In both structures, the metal to C(11) distance is significantly larger than the rest of the Mo–C_{ring} (phenyl) distances, where C(11) in each case is the carbon atom bonded to boron. Similar asymmetry in metal–carbon distances in a metal-complexed phenyl ring has been observed in (η^5-cyclopentadienyl)(η^6-tetraphenylborato)ruthenium[27] and in bis(trimethyl phosphite)(tetraphenylborato)rhodium.[28] In the latter compound, the phenyl ring displayed a boatlike distortion with two longer Mo–C_{ring} distances instead of one. The fact that no such asymmetry was noticed in metal complexes either with free benzene, as in bis(benzene)chromium[20] and (benzene)tricarbonylchromium,[3] or with phenyl groups other than tetraphenylborate, as in (dimethylphenylphosphine)molybdenum,[5] is suggestive that this kind of deviation is characteristic of tetraphenylborate ligands.

Complex II has a staggered geometry around the metal atom with the phenyl ring on one side and the three carbonyl ligands on the other. The situation is quite similar to that in (benzene)tricarbonylchromium[3] or (hexamethylbenzene)tricarbonylmolybdenum.[12] But, unlike these complexes, the ligated phenyl ring in complex II does not show any significant symmetry reduction with alternation in the C–C bond lengths.

Acknowledgment. We are thankful to Dr. D. A. Owen for kindly supplying the crystals and to the University of Oklahoma for providing computational facilities.

Registry No. I, 67254-39-1; II, 67226-43-1.

Supplementary Material Available: A listing of structure factor amplitudes for both complexes (44 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. B. Kirkpatrick, R. L. Richey, W. O. Wooden, and D. A. Owen, Abstracts, 32nd Southwest Regional Meeting of the American Chemical Society, Fort Worth, Texas, 1976, p 46.

(2) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1110 (1969).

(3) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2515 (1973).

(4) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **12**, 458 (1973).

(5) R. Mason, K. N. Thomas, and G. A. Heath, *J. Organomet. Chem.*, **90**, 195 (1975).

(6) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(7) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 953 (1968).

(8) R. Rajaram and J. Ibers, *Inorg. Chem.*, **12**, 1313 (1973).

(9) H. D. Block and R. Allman, *Cryst. Struct. Commun.*, **4**, 53 (1975).

(10) G. R. Clark and G. J. Palenik, *J. Organomet. Chem.*, **50**, 185 (1973).

(11) M. L. Zeigler, H.-E. Sasse, and B. Nuber, *Z. Naturforsch., B*, **30**, 22 (1975).

(12) M. L. Zeigler, H.-E. Sasse, and B. Nuber, *Z. Naturforsch., B*, **30**, 26 (1975).

(13) D. E. Khoshland, S. E. Myers, and J. P. Chesick, *Acta Crystallogr., Sect. B*, **33**, 2013 (1977).

(14) R. F. Ahmed, SFLS Program, NCR-10, National Research Council, Ottawa, Canada, 1966.

(15) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 149.

(16) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 72.

(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(18) R. K. Bohn and A. Haaland, *J. Organomet. Chem.*, **5**, 470 (1966).

(19) G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, **12**, 28 (1959).

(20) A. Haaland, *Acta Chem. Scand.*, **19**, 41 (1965).

(21) M. DiVaira and A. B. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972).

(22) H.-E. Sasse and M. L. Zeigler, *Z. Anorg. Allg. Chem.*, **406**, 109 (1973).

(23) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

(24) M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963).

(25) F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

(26) J. D. Zeinstra and J. L. DeBoer, *J. Organomet. Chem.*, **54**, 207 (1973).

(27) G. J. Kruger, A. L. duPreez, and R. J. Haines, *J. Chem. Soc., Dalton Trans.*, 1302 (1974).

(28) M. J. Nolte and G. Gafner, *Acta Crystallogr., Sect. B*, **30**, 738 (1974).