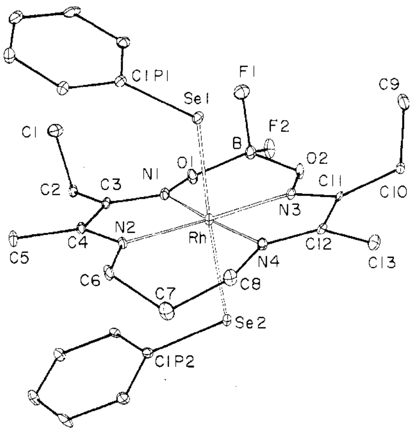

Figure 1. Perspective view of $Rh[C_2(DO)(DOBF_2)](SeC_6H_5)_2$ (5% probability ellipsoids) showing atomic numbering scheme. The hydrogen atoms have been omitted for clarity.

Table II. Bond Distances and Angles with Corresponding Estimated Standard Deviations

Distances, Å			
Rh-Se1	2.510 (1)	Rh-N3	1.952 (5)
Rh-Se2	2.544 (1)	Rh-N4	1.978 (5)
Rh-N1	1.957 (5)	Se1-C1P1	1.927 (6)
Rh-N2	2.013 (5)	Se2-C1P2	1.926 (7)

Angles, Deg			
Se1-Rh-Se2	174.69 (3)	N2-Rh-N4	102.83 (23)
N1-Rh-N2	79.04 (21)	N3-Rh-N4	79.74 (23)
N1-Rh-N3	98.35 (22)	Rh-Se1-C1P1	107.63 (24)
N1-Rh-N4	177.34 (22)	Rh-Se2-C1P2	105.01 (24)
N2-Rh-N3	177.08 (24)		

Description of the Structure

The crystal structure consists of discrete $Rh[C_2(DO)(DOBF_2)](SeC_6H_5)_2$ molecules with the configuration shown in Figure 1. Pertinent bond distances and angles are summarized in Table II.

The rhodium is surrounded by an octahedral ligand field and lies in the center of the plane of the four nitrogen atoms in the macrocycle, similar to the geometric environment observed in $[Co(CH_3)(H_2O)\{(DO)(DOH)\}]ClO_4$[6] and $Rh[C_2(DO)(DOBF_2)](CH_3)I$.[7] The Rh-N bond distances and angles in **2** are almost identical with those found for other $Rh[(DO)(DOBF_2)]$ related complexes[7,8] and are consistent with those in rhodium(III)-bis(dimethylglyoximato) complexes.[9] The Rh^{III}-N bond distances exceed those for the corresponding Co^{III}-N bond by an average of 0.1 Å.

The propylene bridge (C(6), C(7), C(8)) takes on a configuration such that C(7) lies below the plane of the macrocycle. Along a line diagonally projected through C(7) and Rh on the opposite side of the plane from C(7) lies the boron of the borate bridge. The overall conformation defined by C(7), B, and the four nitrogens resembles that of the "chair" conformer of cyclohexane.

The rigorous geometric demands of the square-planar, macrocyclic ligand give rise to the expected trans addition of the diselenide. This is borne out by the observed Se(1)-Rh-Se(2) bond angle of 174.69 (3)°. The constraint of the rhodium-selenium bonds to linearity by the chelating $C_2(DO)(DOBF_2)$ ligand indicates that this system offers a promising route toward the synthesis of one-dimensional intermetallic oligomers. In fact, we have more recently completed the synthesis of two larger, related oligomers, $Rh[C_2(DO)(DOBF_2)][XGe(C_6H_5)_3]_2$, X = S, Se.[10]

This is the first reported x-ray crystal structure of a rhodium complex containing an Rh-Se coordination bond. The Rh-Se distances in this complex are 2.510 (1) and 2.544 (1) Å, which may be compared with 2.49 Å, the sum of the covalent radii[11] for Rh (1.32 Å) and Se (1.17 Å). Rhodium-sulfur distances in tris(dithioacetylacetonato)rhodium(III)[12] and tris(*S*-methylethene-1,2-dithiolato)rhodium(III)[13] fall in the range 2.31-2.37 Å.

Acknowledgment. We thank Tom Eccles and Marguerite Yevitz for their assistance in the structural analysis. We wish to acknowledge the support of E. I. du Pont de Nemours and Co. and the National Science Foundation through Grant MPS75-17018.

Registry No. 1, 60224-26-2; **2**, 60224-27-3; diphenyl diselenide, 1666-13-3.

Supplementary Material Available: Listings of structure factors (Table III) and the positional and thermal parameters from the final refinement (Table IV) (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. A. Little, *Phys. Rev.* [*Sect.*] *A*, **134**, 1416 (1964).
(2) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974).
(3) J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Am. Chem. Soc.*, **95**, 2687 (1973).
(4) All computations were done on a PDP 11/45 computing system. The basic programs (supplied by Enraf-Nonius, Inc.) included a full-matrix least-squares program, Fourier programs, a modified version of ORFFE (Busing and Levy's function and error program) and Johnson's ORTEP. A local program, ENXDR, was used for data reduction.
(5) Supplementary material.
(6) S. Bruckner, M. Calligavis, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **3**, 278 (1969).
(7) J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmittou, and K. O. Hodgson, *Inorg. Chem.*, **15**, 223 (1976).
(8) J. P. Collman, E. B. Fleischer, D. Y. Jester, and D. W. Murphy, unpublished results.
(9) (a) F. A. Cotton and J. G. Norman, *J. Am. Chem. Soc.*, **93**, 80 (1971); (b) A. A. Dvorkin, Y. A. Simoner, A. V. Ablov, O. A. Bologa, and T. I. Malinovskii, *Dokl. Akad. Nauk SSR*, **217**, 833 (1974).
(10) J. P. Collman, R. K. Rothrock, and R. A. Stark, unpublished results.
(11) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, pp 136, 149.
(12) R. Beckett and D. F. Hoskins, *Inorg. Nucl. Chem. Lett.*, **8**, 683 (1972).
(13) R. Richter, J. Kaiser, J. Sieler, and L. Katschabsky, *Acta Crystallogr., Sect. B*, **31**, 1642 (1975).

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Oxidation of 7-Thia-*nido*-undecaborate(2−) by Silver Ion to Give Arylthiaboranes

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Until it was shown that certain closo borane anions actually formed stable complexes[1] it was generally accepted that reduction of silver ion to silver metal was a useful confirmation of B-H bonds.[2] Even so, little is known regarding the fate of the borane moiety after oxidation by silver ion. Our work with boranes and heteroboranes and the redox nature of their interconversions[3-5] suggests oxidation by silver ion as a possible synthetic strategy. Here we report that oxidation of 7-$SB_{10}H_{10}^{2-}$ [6] by Ag^+ in benzene and toluene leads to coupled polyhedra and attack upon the solvent to give arylthiaboranes.[7]

Experimental Section

Reactions were carried out under a nitrogen atmosphere. Solvents were dried prior to use and were distilled in vacuo or under nitrogen. Toluene was dried under nitrogen by percolation through NaH using a Soxhlet extraction apparatus.

Synthesis of 2-(*p*-$CH_3C_6H_4$)-7-$SB_{10}H_{11}$. Thia-*nido*-undecaborate(2−) was generated in cyclohexane from 0.460 g (3.03 mmol) of 7-$SB_{10}H_{12}$ by addition of methyllithium according to the procedure

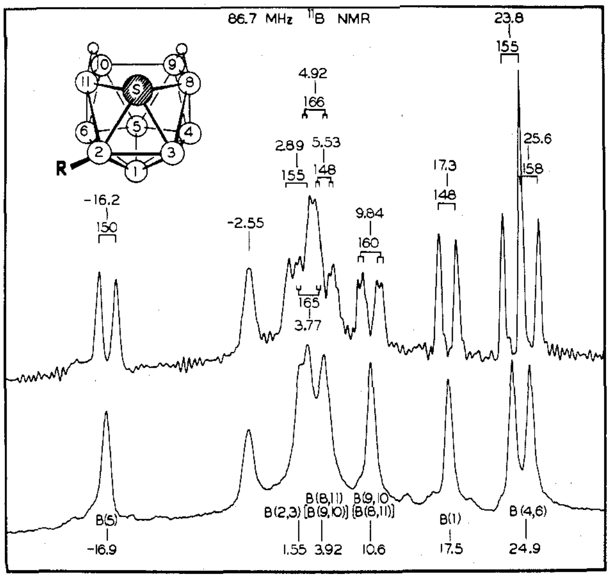

Figure 1. The 86.7-MHz ^{11}B NMR spectrum of 2-R-7-$SB_{10}H_{11}$ (R = *p*-tolyl) in $CDCl_3$: top, line narrowed; bottom, normal ^1H decoupled. The chemical shifts and assignments of the unsubstituted 7-$SB_{10}H_{12}$ are shown at the bottom. The chemical shifts of the *p*-tolyl derivative ($BF_3 \cdot OEt_2$ = 0) and coupling constants (Hz) are on the top.

of Muetterties et al.[6] Evaporation, in vacuo, of cyclohexane left $Li_2SB_{10}H_{10}$ as a white solid to which 150 ml of dry toluene was added by syringe technique to the 250-ml, three-necked flask while under nitrogen. Slow addition of 1.18 g (6.06 mmol) of $AgBF_4$ using a tip-up tube caused immediate darkening of the solution with formation of a silver mirror. After being stirred for 3 h at room temperature the solution was rapidly filtered through a glass frit and the filtrate rotary-evaporated to a yellow oil. The oil was placed in a sublimator and sublimed at 60 °C in vacuo (0.1 mm) giving 161 mg of 7-$SB_{10}H_{12}$. Continued sublimation at 100–105 °C gave 42 mg of impure 2-(*p*-$CH_3C_6H_4$)-7-$SB_{10}H_{11}$ contaminated with 7-$SB_{10}H_{12}$. Repeated fractional sublimation of the above mixture left behind pure *p*-tolyl-substituted material later confirmed by spectral data.

Reaction of silver ion with 7-$SB_{10}H_{10}^{2-}$ in benzene, *tert*-butylbenzene, or *n*-propylbenzene results in aromatically substituted derivatives on the basis of mass spectral data; however, attempts to obtain the pure aryl derivatives by fractional sublimation were unsuccessful.

Results and Discussion

In benzene[9] good yields of 7-$SB_{10}H_{12}$ (40%) and C_6H_5-$SB_{10}H_{11}$ (10%) as well as small amounts of $(SB_{10}H_{11})_2$ (<2%) are obtained by silver ion oxidation of 7-$SB_{10}H_{10}^{2-}$. The new aromatically substituted thiaborane is more subject to hydrolysis than is the parent *nido*-7-$SB_{10}H_{12}$ as evidenced by attempts to obtain infrared spectra in KBr [prominent peaks (cm^{-1}): 2540 (vs), 1960 (w), 1892 (w), 1825 (w), 1786 (w), 1070 (m), 1038 (m), 1011 (s), 992 (s), 880 (m), 645 (m), 601 (m), 582 (m), 564 (m), 513 (s), 470 (s), 344 (s)]. Gas chromatography indicates that decomposition of the substituted thiaborane occurs at temperatures greater than 150 °C while *nido*-7-$SB_{10}H_{12}$ is stable to above 250 °C. Although, it is difficult to separate the arylthiaboranes from 7-$SB_{10}H_{12}$, we have been able to purify a sufficient quantity of the tolyl compound for NMR and mass spectral analysis by fractional sublimation from 60 to 105 °C in vacuo. The ^{11}B NMR spectrum of the tolyl derivative (Figure 1) generally shows less 7-$SB_{10}H_{12}$ impurity than that of the corresponding phenyl derivative.

At 86.7 MHz the ^{11}B NMR spectrum of the phenyl or the analogous tolyl derivative is found to be a perturbed version of that of the parent 7-$SB_{10}H_{12}$. The nine clearly discernible boron resonances of unit intensity confirm substitution at other than the symmetric B(1) or B(5) boron positions (see Figure 1 for numbering convention[10]). The singlet at −2.55 or −1.91 ppm for the tolyl- or phenyl-substituted product, respectively, was confirmed by $\{^{11}B\}^1H$ proton decoupling as characteristic of the new boron site.

Relaxation time measurements led Garber[11] to propose the following partial assignment of the ^{11}B NMR spectrum of 7-$SB_{10}H_{12}$ (ppm): B(5), −16.9; B(2,3), 1.55; B(1), 17.5; B(4,6), 24.9. Because the remaining B(8,11) and B (9,10) both show bridge hydrogen coupling, no further assignment was proposed.

In the arylthiaborane (Figure 1) the boron resonance at 10.6 ppm (either B(8,11) or B(9,10)) has been shifted downfield upon substitution leaving an intensity 1 signal at 9.84 ppm. The lack of bridge hydrogen coupling on the singlet at −2.55 ppm (shifted from 1.55 ppm in 7-$SB_{10}H_{12}$ upon substitution), with other resonances being accounted for, implies that the derivative is substituted at the B(2) position, i.e., 2-(*p*-$CH_3C_6H_4$)-7-$SB_{10}H_{11}$. Recent observations[15] of the relationship between chemical shifts and the location of bridge hydrogens provide additional support that the highest field borons, B(4) and B(6), are related to the two bridging hydrogens on the open face between B(8)–B(9) and B(10)–B(11), both in the parent and in the substituted thiaboranes. Thus, lack of bridge hydrogen coupling on the singlet, the supporting evidence for the bridge hydrogens (vide supra), and observation of at least three open-face boron resonances with bridge hydrogen coupling provide good evidence that substitution is not on the open face but rather at the B(2) position adjacent to sulfur.

The proton NMR of the tolyl derivative shows a AA′BB′ quartet at τ 2.8 (intensity 4) and a singlet at τ 7.7 (intensity 3) indicative of para substitution on toluene.[16]

Isolation of *nido*-7-$SB_{10}H_{12}$ was unexpected since initial generation of the dianion from 7-$SB_{10}H_{12}$ has been shown to be complete[17] and no protonic solvents were used which might be expected to reprotonate the dianion. Use of benzene-d_6 as the solvent established the source of hydrogen atoms in regeneration of the starting material, 7-$SB_{10}H_{12}$, as being other thiaboranes and not the aromatic solvent. No evidence of the partially deuterated thia-*nido*-undecaborane(12) was observed by mass spectral analysis. However, the deuterium-substituted 2-$C_6D_5SB_{10}H_{10}D$ was observed indicating a concerted transferal of deuterium to the borane during substitution by the phenyl group.

Oxidation reactions carried out using the monoanion 7-$SB_{10}H_{11}^-$, generated by 1 equiv of alkyllithium, once again gave 7-$SB_{10}H_{12}$ as the major product with small yields of the dimeric species. There was no indication of the aromatically substituted thiaborane. Use of a one-electron oxidant such as silver ion with the thiaborane dianion seems to justify initial formation of a 7-$SB_{10}H_{10}\cdot^-$ radical anion. Radical anions are not unprecedented in borane chemistry, a familiar one being $B_8H_8\cdot^-$.[18] Furthermore, the reaction is inhibited by galvinoxyl.[20] The experimental facts suggest the reaction scheme shown by eq 1–4. Hydrogen abstraction from other thiaboranes by 7-$SB_{10}H_{10}\cdot^-$ affords the known 7-$SB_{10}H_{11}^-$. A second oxidation and abstraction would produce the observed 7-$SB_{10}H_{12}$. The boranes from which hydrogens are abstracted ultimately polymerize giving the observed dark brown, nonvolatile residue. Coupling of the radical 7-$SB_{10}H_{11}\cdot$ moieties may produce the observed $(SB_{10}H_{11})_2$ dimers. Since oxidation starting from 7-$SB_{10}H_{11}^-$ (step 3) produced no aryl-substituted

$$SB_{10}H_{10}^{2-} + Ag^+ \rightarrow SB_{10}H_{10}\cdot^- + Ag^0 \quad (1)$$

$$SB_{10}H_{10}\cdot^- + HB_x \rightarrow SB_{10}H_{11}^- + B_x\cdot \quad (2)$$

$$SB_{10}H_{11}^- + Ag^+ \rightarrow SB_{10}H_{11}\cdot + Ag^0 \quad (3)$$

$$SB_{10}H_{11}\cdot + HB_x \rightarrow SB_{10}H_{12} + B_x\cdot \quad (4)$$

product, reaction of the solvent seems to occur with the radical anion or the borane dianion at step 1 or 2.

Para substitution of toluene and the position of substitution on the thiaborane may reflect both steric considerations and a tendency toward electrophilic substitution of the aromatic ring by the borane or, conversely, nucleophilic substitution of the thiaborane by toluene. Substitution on the thiaborane would then be expected at the more positive sites, i.e., B(2,3) or B(8,11).

An alternative proposal is attack on the aromatic system by the radical anion $7\text{-}SB_{10}H_{10}\cdot^-$, a $2n + 3 = 25$ framework electron system. Such a system, one electron short of the 26-electron nido framework requirement,[3] may well seek electrons to achieve the more stable nido configuration. On this basis, electrophilic attack by $7\text{-}SB_{10}H_{10}\cdot^-$ on toluene might be expected to give the exceptionally stable 11-vertex nido thiaborane electron count. Thus, simple radical addition to the aromatic solvent would give $2\text{-}R\text{-}7\text{-}SB_{10}H_{11}\cdot^-$, a $2n + 5 = 27$ electron system. An additional one-electron oxidation by silver ion affords the observed $2\text{-}R\text{-}7\text{-}SB_{10}H_{11}$.

To this time there have been no published reports of an oxidative synthesis technique using silver ion in borane or heteroborane chemistry. However, similar complex reactions involving solvent attack and dimerization have been reported in[19] attempted syntheses of metallocarboranes using other transition metals. In these cases, proposed borane radicals might explain many of the unexpected products observed.

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Registry No. $2\text{-}(p\text{-}CH_3C_6H_4)\text{-}7\text{-}SB_{10}H_{11}$, 60294-95-3; $7\text{-}SB_{10}H_{12}$, 60294-96-4; ^{11}B, 14798-13-1; Ag^+, 14701-21-4.

References and Notes

(1) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Noth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).
(2) L. J. Todd, *Prog. Boron Chem.*, **2**, 11 (1970).
(3) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972).
(4) Vinay Chowdhry, W. R. Pretzer, D. N. Rai, and R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 4560 (1973).
(5) W. R. Pretzer, D. A. Thompson, and R. W. Rudolph, *Inorg. Chem.*, **14**, 2571 (1975).
(6) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).
(7) Preliminary work by S. Wreford (Harvard University) and by these laboratories also indicates a similar chemistry when $B_5H_8^-$ is oxidized by Ag^+. One of the products is $B_{10}H_{14}$.
(8) The dianion is generated from *nido*-$7\text{-}SB_{10}H_{12}$ by removal of bridge hydrogens with 2 equiv of methyl- or *n*-butyllithium.
(9) It had previously been observed[4,12-14] that reactions of 11-vertex boranes and carboranes with electron-pair-donating solvents result in 26-electron nido frameworks. To prevent complexation nondonating aromatic solvents were used in these reactions.
(10) Commission on Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, **30**, 681 (1972).
(11) A. R. Garber, Ph.D. Dissertation, Indiana University, 1974.
(12) (a) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968); (b) C. D. Tsia and W. E. Streib, *ibid.*, **88**, 4413 (1966).
(13) (a) D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.*, **91**, 6002 (1969); (b) D. A. Owen, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1969.
(14) R. W. Rudolph and D. A. Thompson, *Inorg. Chem.*, **13**, 2779 (1974).
(15) W. Hermanek and J. Plesek, *Z. Anorg. Allg. Chem.*, **409**, 115 (1974).
(16) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N. Y., 1969, Appendix D.
(17) Measurement of evolved methane from reaction of $SB_{10}H_{12}$ and methyllithium confirms greater than 95% reaction.
(18) F. Klanburg, D. R. Eaton, L. J. Guggenberger and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).
(19) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973).
(20) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

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Structure of Tetrakis(benzoato)dimolybdenum(II)

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For some time, we have been interested in molecules containing strong metal to metal bonds, of which many are now known.[1] Among them, a series of carboxylato compounds of the type $Mo_2(O_2CR)_4$, where R is H,[2] CH_3,[3] CF_3,[4] or $CH_2NH_3^+$,[5] have been characterized. Their air stability is variable with the arylcarboxylato compounds being distinctly less stable. To see if there were any differences in the basic structures, we undertook the x-ray study of tetrakis(benzoato)dimolybdenum(II).

Experimental Section

Crystal Data and Structure Determination. A yellow crystal, obtained by recrystallization from diglyme, measuring 0.38 × 0.34 × 0.30 mm was sealed in a capillary containing some solution (since crystals lose solvent readily) and examined on a Syntex $P\bar{1}$ four-circle automated diffractometer. Axial photographs and ω scans of several intense reflections showed that the crystal quality was good and that it was suitable for x-ray diffraction studies. At small scattering angles the peak widths at half-height were about 0.2°. For calculation of lattice parameters, 15 of the strongest reflections in the range $20° < 2\theta < 31°$ were selected to give a variety of crystal orientations. Based on angular settings for these reflections, the refined lattice parameters obtained from the Syntex software package are (Mo Kα, λ 0.710 73 Å) $a = 11.321$ (4) Å, $b = 11.547$ (4) Å, $c = 10.489$ (5) Å, $\alpha = 115.62$ (3)°, $\beta = 98.87$ (3)°, $\gamma = 113.72$ (2)°, and $V = 1038.6$ (7) Å^3. For the triclinic space group $P\bar{1}$ with $Z = 1$ and a molecular weight of 944.71, the calculated density is 1.510 g cm^{-3}.

Intensity data were collected at 22 ± 1 °C using graphite-monochromatized Mo Kα radiation and a θ–2θ scan rate varying from 4 to 24°/min, depending on the intensity of the reflection. Background measurements were made at both limits of each scan. Of the 2399 integrated intensities collected in the range $0° < 2\theta(\text{Mo K}\alpha) < 43°$, 2055 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. Three standard reflections, measured repeatedly every 50 data points, were stable. Since the linear absorption coefficient of this compound is 6.62 cm^{-1} for Mo Kα radiation, for any reflection, the maximum relative error due to absorption is <3% of F_o, and the data were not corrected for absorption.

A three-dimensional Patterson map gave the position of the molybdenum atom (the other molybdenum atom is related by symmetry by an inversion center). A difference Fourier synthesis based on the refined molybdenum position revealed all but one of the nonhydrogen atoms. The missing atom appeared on the next difference map. All atoms were assigned isotropic thermal parameters and least-squares refinement then gave discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.071$$
$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.098$$

Refinement was continued with anisotropic thermal parameters for the molybdenum atom and isotropic thermal parameters for the rest of the nonhydrogen atoms to convergence at $R_1 = 0.052$ and $R_2 = 0.076$, the error in an observation of unit weight being 2.0. No attempt was made to locate the hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $p = 0.06$ was used in the previous defined expression for the weights,[6,7] and the scattering factors were from ref 8. Correction for anomalous scattering by molybdenum were taken from Cromer and Liberman.[9] Programs used have been previously reported.[10] A final difference map was judged to be free of significant features. No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, reflection number, $\lambda^{-1} \sin \theta$, or various classes of indices. A table of observed and calculated structure factor amplitudes is available.[11]

Results

Figure 1 shows the entire contents of one unit cell and defines the atom numbering scheme. Positional and aniso-