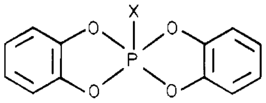
even smaller change between the isoelectronic fluoro[26] and chloro[27] phosphoranes **5** and **6**. The latter structures are displaced 65% (F) and 72% (Cl) based on the dihedral angle method[9,19] using actual bond distances.



5, X = F
6, X = Cl

For the fluorosilicate **7**, it is evident that crystal packing[24] also is of some importance. As we have shown by taking proper cognizance of intermolecular effects, e.g., those due to steric terms[28] or hydrogen bonding,[29] structural changes due to substituent effects may be reliably ascertained. In view of these studies, and the absence of large intermolecular steric effects indicated for the structures compared here, **1**–**7**, it is felt that the substituent effects mentioned are the main factors responsible for structural placement in this series.

Thus far, the pentacoordinate stereochemistry for main group 4 elements displays a marked similarity to that for phosphoranes[9,19] and follows the general structural principles developed for phosphoranes. It seems reasonable that nonrigid behavior typified by intramolecular ligand exchange should be found for some anionic pentacoordinated members of group 4[30] like that observed for phosphoranes[9] and that reaction mechanisms of group 4 compounds based on pentacoordinate transition states should follow the general features developed for mechanisms postulated for related phosphorus reactions.[31]

Acknowledgment. The support of this research by the National Science Foundation (Grant No. CHE7910036) is greatly appreciated as is the generous allocation of computing time by the University of Massachusetts Computing Center.

Registry No. **3**, 76375-58-1; **4**, 79769-92-9.

Supplementary Material Available: Anisotropic thermal parameters (Tables A and B, respectively, for **3** and **4**), bond lengths and angles for the $MePPh_3^+$ cation and acetonitrile solvent for **4** (Table C), and a listing of observed and calculated structure factor amplitudes for **3** and **4** (27 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Bis(dimethylamine)tetrakis(*tert*-butyl mercaptido)di-μ-sulfido-dimolybdenum(IV)

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$Mo_2(NMe_2)_6$ (M≡M) reacts with *t*-BuSH (≥6 equiv) in hydrocarbon solvents at room temperature to give the green crystalline compound $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, which has been characterized by a single-crystal X-ray diffraction study. Each molybdenum atom is in a distorted trigonal-bipyramidal environment with respect to the atoms to which it is directly bonded. The halves of the molecule are joined together by a pair of sulfido bridges, which form alternately long (axial), 2.327 (1) Å, and short (equatorial), 2.238 (1) Å, bonds. The Mo–Mo distance is 2.730 (1) Å, indicative of M–M bonding, which, in a formal sense, may be viewed as a double bond, $\sigma^2\pi^2$. The *tert*-butyl mercaptido groups occupy equatorial sites (Mo–S = 2.325 (2) Å), and the dimethylamino ligands, the remaining axial positions (Mo–N = 2.368 (2) Å). These results are compared with related molybdenum compounds. Crystal data for $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$: space group *A*2/*m*, a = 11.392 (2) Å, b = 17.291 (3) Å, c = 9.304 (1) Å, and β = 103.96 (1)°.

Introduction

The reactions between $Mo_2(NMe_2)_6$ and alcohols give dinuclear alkoxides $Mo_2(OR)_6$ with retention of the molybdenum–molybdenum triple bond when the alkyl group is bulky, e.g., R = *t*-Bu, *i*-Pr, and CH_2CMe_3.[1] With less bulky alkoxy ligands such as EtO and MeO, polymeric and as yet not well-characterized compounds of empirical formula $Mo(OR)_3$ are formed.[1] As part of a general program aimed at elucidating the coordination chemistry of the $(Mo{\equiv}Mo)^{6+}$ unit,[2,3] we investigated the reactions between $Mo_2(NMe_2)_6$ and bulky thiols RSH (R = *t*-Bu, *i*-Pr, and CH_2Ph). We herein report our findings of these studies.

Results and Discussion

Syntheses. Hydrocarbon solutions of $Mo_2(NMe_2)_6$ react readily with the thiols RSH, where R = *t*-Bu, *i*-Pr, and CH_2Ph (≥6 equiv), at room temperature to produce very sparingly soluble precipitates. Reactions involving *t*-BuSH yielded dark green crystals of the title compound in close to quantitative yields based on molybdenum. The reactions involving *i*-PrSH and $PhCH_2SH$ yielded finely divided, microcrystalline products, which were not suitable for single-crystal X-ray studies.

The new compounds are air sensitive and readily hydrolyzed in the atmosphere. They are thermally unstable above 60 °C in vacuo and cannot be sublimed. They are very sparingly soluble in benzene and toluene, barely soluble enough to allow

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Table I. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for the $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ Molecule

atom	x	y^c	z	B_{iso}, Å^2
Mo(1)	8884.2 (2)	0*	9042.0 (2)	8
S(2)	9352 (1)	0*	1618 (1)	10
S(3)	−2214.5 (4)	−1145.1 (3)	−1242.8 (5)	12
C(4)	7485 (2)	8323 (1)	373 (2)	13
C(5)	6665 (2)	7653 (1)	9673 (3)	18
C(6)	−1340 (2)	−1993 (1)	1352 (2)	18
C(7)	−3196 (2)	−1162 (1)	1230 (2)	16
N(8)	8100 (2)	0*	6442 (2)	13
C(9)	−1617 (2)	693 (1)	−4352 (2)	18
C(10)	−5026 (4)	0*	−3529 (5)	35
C(11)	−5019 (2)	−690 (2)	−4280 (3)	30
H(12)	−405 (2)	−221 (2)	−92 (3)	18 (5)
H(13)	−294 (2)	−266 (2)	−83 (3)	17 (5)
H(14)	−353 (3)	−265 (2)	42 (3)	31 (6)
H(15)	−86 (2)	−157 (2)	175 (3)	25 (6)
H(16)	−158 (3)	−231 (2)	214 (3)	24 (6)
H(17)	−91 (2)	−231 (2)	70 (3)	20 (5)
H(18)	−391 (2)	−95 (2)	60 (3)	14 (5)
H(19)	−275 (2)	−78 (2)	172 (3)	20 (5)
H(20)	−349 (2)	−145 (2)	198 (3)	16 (5)
H(21)	730 (4)	0*	638 (4)	20 (8)
H(22)	−206 (2)	64 (1)	−546 (3)	16 (5)
H(23)	−180 (3)	119 (2)	−400 (4)	48 (8)
H(24)	−72 (2)	72 (2)	−422 (3)	17 (5)
H(25)	−517 (5)	0*	−235 (6)	51 (12)
H(26)	502 (4)	877 (3)	637 (4)	71 (11)

[a] Fractional coordinates are $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are ×10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609. [c] Parameters marked by an asterisk were fixed by space group symmetry.

Table II. Bond Distances (Å) for the $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(1)″	2.730 (1)	S(3)	C(4)	1.863 (2)
Mo(1)	S(2)″	2.238 (1)	N(8)	C(9)	1.484 (2)
Mo(1)	S(2)	2.327 (1)	C(4)	C(5)	1.532 (3)
Mo(1)	S(3)	2.323 (1)	C(4)	C(6)	1.528 (3)
Mo(1)	N(8)	2.368 (2)	C(4)	C(7)	1.525 (3)

characterization by ^1H NMR spectroscopy. They are essentially insoluble in aliphatic hydrocarbons and insufficiently soluble in THF, CH_2Cl_2, and $CHCl_3$ to allow recrystallization from these solvents. They are decomposed by (react with) Me_2SO.

The low solubility of these compounds has prevented detailed characterization studies, and the benzyl and isopropyl compounds could have quite different solid-state structures from the *tert*-butyl compound.

The reaction pathway leading to oxidation of molybdenum from the +3 to the +4 state is not known. In reactions involving *t*-BuSH, isobutylene and *tert*-butyldimethylamine were identified along with dimethylamine in the volatile organic products. Similarly in reactions involving *i*-PrSH, propene and isopropyldimethylamine were formed; in reactions with $PhCH_2SH$, benzyldimethylamine was identified in the volatiles.

Solid-State Structure of $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$. In the space group $A2/m$, there are two centrosymmetric molecules in the unit cell. An ORTEP view of the molecule is shown in Figure 1. Fractional coordinates and isotropic thermal parameters are given in Table I. Bond distances and bond angles are given in Tables II and III, respectively.

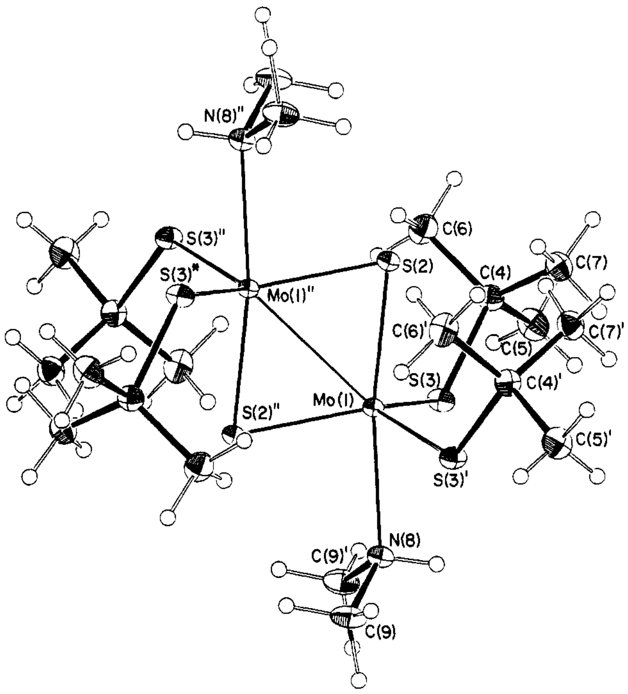

Figure 1. ORTEP diagram of the $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ molecule viewed down (approximately) the C_2 axis of symmetry and giving the atom numbering scheme. Nonhydrogen atoms are represented by ellipsoids drawn at the 50% probability level; hydrogen atoms have been given an artificial thermal parameter. The molecule has rigorous C_{2h} symmetry. Atoms denoted by a double prime are related to unprimed atoms by the C_2 axis of symmetry, e.g., Mo(1) and Mo(1)″, and the mirror plane of symmetry relates primed and unprimed atoms, e.g., S(3) and S(3)′, and double primed and asterisked atoms, e.g., S(3)″ and S(3)*, respectively.

Table III. Bond Angles (Deg) for the $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ Molecule

A	B	C	angle
Mo(1)	Mo(1)″	S(2)	54.8 (1)
Mo(1)″	Mo(1)	S(2)	51.8 (1)
Mo(1)″	Mo(1)	S(3)	117.8 (1)
Mo(1)″	Mo(1)	N(8)	136.8 (1)
S(2)	Mo(1)	S(2)″	106.5 (1)
S(2)	Mo(1)	S(3)	95.8 (1)
S(2)″	Mo(1)	S(3)	117.6 (1)
S(2)″	Mo(1)	N(8)	82.1 (1)
S(2)	Mo(1)	N(8)	171.4 (1)
S(3)	Mo(1)	S(3)′	116.9 (1)
S(3)	Mo(1)	N(8)	79.8 (1)
Mo(1)	S(2)	Mo(1)″	73.5 (1)
Mo(1)	S(3)	C(4)	121.8 (1)
Mo(1)	N(8)	C(9)	115.8 (1)
C(9)	N(8)	C(9)′	107.8 (2)
S(3)	C(4)	C(5)	104.0 (1)
S(3)	C(4)	C(6)	110.6 (1)
S(3)	C(4)	C(7)	110.5 (1)
C(5)	C(4)	C(6)	109.8 (2)
C(5)	C(4)	C(7)	109.2 (2)
C(6)	C(4)	C(7)	112.3 (2)

Each molybdenum atom is five-coordinate, and the central $Mo_2S_2S'_4N_2$ skeleton may be viewed as two trigonal-bipyramidal units, fused along a common equatorial–axial edge through the agency of a pair of sulfido bridges. The *tert*-butyl mercaptido ligands occupy the terminal equatorial positions and the dimethylamino ligands axial positions.

Comparison with Other Structures. Within the last few years, a number of Mo_2-containing compounds have been discovered in which each molybdenum atom is five-coordinate and the common structural feature is two trigonal bipyramids fused along a common equatorial–axial edge. These include $Mo_2(i\text{-}PrO)_8$,[4] $Mo_2(i\text{-}PrO)_6(NO)_2$,[5] $Mo_2(t\text{-}BuO)_4(NC_7H_7)_2$-

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(μ-NC_7H_7)$_2$, where C_7H_7 = *p*-tolyl,[6] Mo_2Me_4(*t*-BuN)$_2$(μ-*t*-BuN)$_2$,[7] and now $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$. In all of these molecules, there are unsymmetrical bridges with the axial bond distances being longer than the equatorial. The difference in distance between axial and equatorial bridges is particularly large in the $Mo_2(i\text{-}PrO)_6(NO)_2$ and $Mo_2X_4(NR)_2(\mu\text{-}NR)_2$ molecules (X = Me, *t*-BuO; R = *t*-Bu, *p*-tolyl), where the axial bridging group is trans to either a linear Mo–NO or Mo–NR group, both of which exert a high trans influence.[8] In $Mo_2(i\text{-}PrO)_8$, where all the ligands are the same, the difference between axial and equatorial bridging distances is 0.15 Å. In $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, the axial Mo–S bond distance is longer by only 0.09 Å than the equatorial Mo–S bridge. This is the smallest difference yet seen in a molecule of this general type but is entirely consistent with the view that the $HNMe_2$ ligand exerts a very weak trans influence. The Mo–N distance is certainly long, 2.368 (2) Å, which may be compared with Mo–N = 2.219 (4) and 2.282 (4) Å found in $Mo(OSiMe_3)_4(HNMe_2)_2$[9] and $Mo_2(OSiMe_3)_6(HNMe_2)_2$,[10] respectively. In $Mo_2(OSiMe_3)_6(HNMe_2)_2$, the dimethylamine is readily lost upon heating in vacuo, but $Mo(OSiMe_3)_4(HNMe_2)_2$ sublimes (100 °C, 10^{-4} torr) without loss of amine. It is thus not unreasonable to expect that $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, with its exceedingly long Mo–N bonds, would not be thermally stable.

Within this series of Mo_2-containing fused trigonal bipyramids, the Mo–Mo distance correlates with the involvement of molybdenum d_{xz}, d_{yz} atomic orbitals (the *z* axis is chosen to be coincident with the Mo axial bonds). In $Mo_2(i\text{-}PrO)_6(NO)_2$, the $(d_{xz}, d_{yz})^4$ configuration allows for extensive Mo to NO π^* back-bonding in the absence of any Mo–Mo bond, whereas in $Mo_2(i\text{-}PrO)_8$, which is a d^2–d^2 dimer, the $(d_{xz}, d_{yz})^2$ configuration allows for the formation of a Mo═Mo bond, $\sigma^2\pi^2$. This simple bonding picture readily accounts for the Mo–Mo bond distances of 3.325 (2) Å in $Mo_2(i\text{-}PrO)_6(NO)_2$ and 2.523 (1) Å in $Mo_2(i\text{-}PrO)_8$. In $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, which is a d^2–d^2 dimer, the d_{xz}, d_{yz} orbitals are available for metal–metal bonding and a $\sigma^2\pi^2$ Mo═Mo bond is possible. This is readily reconcilable with the diamagnetic nature of the compound and the observed Mo–Mo distance, 2.730 (1) Å. Of course, whenever there are bridging groups, there is uncertainty in assigning M–M bond orders, since there can be extensive mixing of metal–ligand and metal–metal bonding interactions.[11] It should be noted that the increase in Mo–Mo distance of ca. 0.2 Å in going from $Mo_2(i\text{-}PrO)_8$ to $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ is consistent with a change from oxygen to sulfur bridging groups. For example, in triangulo Mo_3-containing compounds, which have six electrons involved in Mo–Mo bonding, the Mo–Mo distances are ca. 2.53 and 2.73 Å in the presence of oxygen and sulfur ligands, respectively.[12] A similar Mo–Mo distance (2.705 (2) Å) is seen in the compound $Mo_2(\mu\text{-}S)_2(n\text{-}Pr_2SCN)_2(n\text{-}Pr_2S_2CN)_2$.[13]

Finally, we note that the Mo–S bond length to the *t*-BuS ligands, 2.323 (1) Å, is considerably shorter than the Mo(IV)–S single bond distances (2.419–2.576 Å) found in $MoO(S_2CN(C_3H_7)_2)_2(TCNE)$,[14] $Cp_2Mo(o\text{-}S_2C_6H_4)$,[15] Cp_2Mo(toluene-3,4-dithiolate),[16] and $Mo(S_2CNEt_2)_4$[17] but somewhat longer than that found in $Mo(t\text{-}BuS)_4$ (2.235 (3) Å).[18] In both $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$ and $Mo(t\text{-}BuS)_4$, there is likely significant M–S π bonding.

Concluding Remarks. The reaction between $Mo_2(NMe_2)_6$ and *t*-BuSH failed to yield the target molecule $Mo_2(t\text{-}BuS)_6$. This should not be taken to imply that mercaptido analogues of the well-known $Mo_2(OR)_6$ compounds will not be accessible (though this could ultimately prove to be the case). We note, for example, that the preparation of $Mo(t\text{-}BuS)_4$ was recently achieved[18] from the reaction between $MoCl_4$ and *t*-BuSLi (4 equiv) in 1,2-dimethoxyethane in good yields, whereas the reaction between $Mo(NMe_2)_4$ and *t*-BuSH (4 equiv) gave the same compound in only low yield (<15% based on Mo).

Experimental Section

General Procedures. All preparations and operations were carried out under a dry and oxygen-free nitrogen atmosphere by using either standard Schlenk techniques or a Vacuum Atmospheres Co. Dri-Lab apparatus. Solvents were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, and sodium and were then stored over molecular sieves.

Physical and Analytical Methods. Elemental analyses were performed by Canadian Microanalytical Service Ltd. ^1H NMR spectra were obtained on Varian Associates A60, EM 390, and HR220 spectrometers with use of C_6D_6, $C_6D_5CD_3$, and $CDCl_3$ as solvents. Infrared spectra were obtained from Nujol mulls between CsI plates by using a Perkin-Elmer 283 spectrophotometer.

Materials. $Mo_2(NMe_2)_6$ was prepared as previously described.[19] *tert*-Butyl mercaptan (from Matheson Coleman and Bell) and isopropyl mercaptan (from City Chemical Corp.) were distilled and stored over molecular sieves under a nitrogen atmosphere. Benzyl mercaptan (from Aldrich) was similarly purified, except that distillation was carried out at reduced pressure.

Preparation of $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$. $Mo_2(NMe_2)_6$ (0.281 g, 0.616 mmol) was dissolved in hexane (25 mL) in a 50-mL round-bottomed flask, and the solution was cooled to −78 °C. *t*-BuSH (0.49 mL, 4.3 mmol) was added via syringe, and the resulting mixture was allowed to warm to room temperature slowly. A series of color changes occurred: yellow → orange → red → green → dark green. After the mixture was allowed to stand for 12 h, the dark green crystals that had formed were collected by filtration and dried in vacuo. The dark green filtrate was also collected and the volume of solution reduced to ca. 10 mL at reduced pressure. The resulting solution was then cooled to ca. −10 °C in the freezer section of a refrigerator. More dark green crystals formed, which were collected by filtration and dried in vacuo. The total quantity of dark green crystals collected in this way was 0.373 g: 86% yield of $Mo_2(S)_2(t\text{-}BuS)_4(HNMe_2)_2$ based on Mo. Anal. Calcd for $Mo_2(S)_2(t\text{-}BuS)_4(HNMe_2)_2C_6H_6$: C, 39.99; H, 7.23; N, 3.59; S, 24.63. Found: C, 39.92; H, 8.11; N, 4.00; S, 25.45. (Analytical data were performed on crystals obtained from a reaction performed in benzene, which yielded the sample used for X-ray studies.) ^1H NMR data obtained in benzene-d_6 at 34 °C: δ(*t*-BuS) 1.18 (singlet) and $\delta(HNMe_2)$ 2.15 in the integral ratio 3:1. Infrared data: 3250 w, 1020 m, 890 w, 670 m, 560–570 broad m, 490 m, 420 m, 370 m, 330 w cm^{-1}.

X-ray Structural Determination of $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$. General operating procedures and computational techniques have been described previously.[20]

A crystal of dimensions 0.25 × 0.25 × 0.20 mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cold-stream of the diffractometer. The cell parameters, determined from 30 reflections at −166 °C with Mo Kα radiation, λ = 0.71069

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Å, were $a = 11.392$ (2) Å, $b = 17.291$ (3) Å, $c = 9.340$ (1) Å, $\beta = 103.96$ (1)°, $V = 1778.6$ (1) Å^3, $Z = 2$, $d_{\text{calcd}} = 1.458$ g cm^{-3}, and space group $A2/m$.

A total number of 4168 reflections were collected, including redundancies, and were reduced to 2578 unique reflections. Standard moving-crystal, moving-detector techniques were used with the following values: scan speed = 4.0°/min, scan width = 2.0 + dispersion, single background at extremes of scan = 4 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. The number of reflections with $F > 2.33\sigma(F)$ was 2411.

The structure was solved by a combination of direct methods and Fourier techniques. Two molecules of benzene were located in the unit cell. All hydrogen atoms were located and refined isotropically; all other atoms were refined anisotropically, with use of full-matrix techniques. The final residuals are $R(F) = 0.025$ and $R_w(F) = 0.033$. The goodness of fit for the last cycle was 0.904 and the maximum Δ/σ was 0.05. The final difference Fourier map was essentially featureless, with the largest peak being 0.35 e/Å^3.

Acknowledgment. We thank the National Science Foundation for financial support and the Marshal H. Wrubel Computing Center for computing facilities.

Registry No. $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(HNMe_2)_2$, 79681-95-1; $Mo_2(NMe_2)_6$, 51956-20-8; t-BuSH, 75-66-1.

Supplementary Material Available: A table of anisotropic thermal parameters and a listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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[*o*-Phenylenebis(dimethylarsine)]heptacarbonyldiiron. Preparation, Crystal Structure, and Fluxionality in Solution

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The reaction of $Fe_2(CO)_9$ with *o*-phenylenebis(dimethylarsine), diars, in an atmosphere of CO gives yellow (diars)$Fe_2(CO)_8$ and red (diars)$Fe_2(CO)_7$, separable by chromatography on silica. The red compound crystallizes in space group $P\bar{1}$ with $Z = 2$ and the following unit cell dimensions: $a = 9.706$ (4) Å; $b = 11.876$ (3) Å; $c = 9.576$ (3) Å; $\alpha = 92.41$ (2)°; $\beta = 104.81$ (2)°; $\gamma = 91.25$ (2)°; $V = 1066$ (1) Å^3. The structure consists of dinuclear molecules in which diars is chelated on one iron atom (Fe(1)) to which are also bound two terminal CO groups. Fe(1) also forms a metal–metal bond, 2.566 (1) Å, to Fe(2), which bears three strictly terminal CO groups. Of the remaining two CO groups, one forms a nearly symmetrical bridge while the other is semibridging with its short bond, 1.894 (7) Å, to Fe(2) and its long bond, 2.103 (7) Å, to Fe(1). The ^{13}C NMR spectrum is highly temperature dependent, changing from a five-line spectrum (1:2:2:1:1) at −132 °C to a single-line spectrum at 11 °C. A three-stage process for equivalencing all of the CO's is proposed.

Introduction

It has been found that *o*-phenylenebis(dimethylarsine), diars, reacts with $Fe_2(CO)_9$ to produce a variety of products. The course of the reaction is influenced by concentrations, temperature, and the use of a sweep gas (Ar) to remove CO. We previously described the isolation of (diars)$Fe_3(CO)_{10}$ and reported its crystal structure.[2] In an atmosphere of CO the products are (diars)$Fe_2(CO)_8$ and (diars)$Fe_2(CO)_7$. In this paper we report a structural and dynamical study of the second of these compounds, the stoichiometry of which is analogous to that of (bpy)$Fe_2(CO)_7$, a compound prepared and characterized in one of these laboratories several years earlier.[3] This bpy complex was found to have a complicated structure, the interpretation of which was seminal in the development of the concept of semibridging carbonyl groups.[4]

Initially, our intention in the present study was simply to see how the structure of the title compound compared with that of (bpy)$Fe_2(CO)_7$, for whatever further light this might throw on the role of the semibridging carbonyl groups. However, when we examined the ^{13}C NMR spectrum of (diars)$Fe_2(CO)_7$, we found that the dynamic aspects of this molecule were of unusual interest. In fact, it is the reporting and interpretation of the fluxionality, or carbonyl scrambling, behavior of (diars)$Fe_2(CO)_7$ that will be our chief concern here and we shall defer a detailed discussion of the comparative structural chemistry of (diars)$Fe_2(CO)_7$ and (bpy)$Fe_2(CO)_7$ to a future detailed report on the latter structure.

Experimental Section

Preparation. A mixture of 2.07 g (5.7 mmol) of $Fe_2(CO)_9$, 0.59 g (1.9 mmol) of diars, and 50 mL of freshly distilled THF was stirred for 6 h at 25 °C with a slow stream of carbon monoxide bubbling through the reaction mixture. The solvent was removed under vacuum, leaving a dark red residue, which was redissolved in hexane and transferred to a column of silica in hexane. Elution of the column with a 1:1 hexane:benzene solvent gave first a yellow band and then a red band. The yellow fraction yielded a yellow solid, which was recrystallized from dichloromethane and hexane to give crystalline (diars)$Fe_2(CO)_8$. Anal. Calcd: C, 34.76; H, 2.57. Found: C, 34.8; H, 2.56. IR (cm^{-1}): 2040 (s), 1970 (s), 1930 (s).

Evaporation of the eluate of the red band followed by recrystallization from a mixture of dichloromethane and hexane gave red, crystalline (diars)$Fe_2(CO)_7$. Anal. Calcd: C, 34.30; H, 2.69. Found: C, 34.2; H, 2.69. IR (cm^{-1}): 2050 (s), 1980 (s), 1965 (sh), 1785 (sh), 1765 (m).

NMR Spectra. These were measured on ^{13}C enriched samples (vide infra) with use of a JEOL PFT 100/Nicolet 1080 Fourier transform spectrometer operating at 25.036 MHz. A sweep width of 7000 Hz and a repetition rate of 1.1 s were employed. The temperatures were measured with a copper–constantan thermocouple inserted into an NMR tube and read on a Leeds and Northrup Model 913 digital thermometer, with an estimated precision of ±1°. The solvent used at all temperatures was 2-methyltetrahydrofuran with 10% toluene-d_8 added for deuterium lock.

A sample of the diiron complex was enriched in ^{13}C carbon monoxide simply by stirring at room-temperature a tetrahydrofuran solution of this material under an atmosphere of 18% enriched ^{13}CO. The labeled derivative was then purified by chromatography and used immediately for the NMR studies.

X-ray Crystallography. A crystal of approximate dimensions 0.1 × 0.1 × 0.1 mm was attached to the end of a glass fiber and mounted

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