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Crystal and Molecular Structure of Carbonylbis(*N*,*N*-dimethyldithiocarbamato)(*o*-phenylenebis(dimethylarsine))molybdenum(II) and Preparation of Some Related Compounds

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The Mo(II) complexes $[(NO)Mo(S_2CNR_2)_2diars](BF_4)$ and $(CO)Mo(S_2CNR_2)_2diars$ (R = Me or Et) have been prepared and characterized, and the crystal and molecular structure of $(CO)Mo(S_2CNMe_2)_2diars$ determined. Crystals are triclinic, space group $P\bar{1}$ with two molecules in a unit cell of dimensions a = 9.634 (3) Å, b = 14.986 (4) Å, c = 8.882 (3) Å, α = 94.82 (2)°, β = 104.37 (2)°, and γ = 95.18 (2)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters. R = 0.038 for 2712 "observed" reflections measured by diffractometer. The crystal structure contains discrete molecules separated by normal van der Waals distances. The Mo atom has a slightly distorted pentagonal-bipyramidal geometry, with the CO group and one S atom axial. Principal dimensions are Mo–As = 2.583 (1) and 2.569 (1), Mo–S (equatorial–equatorial) = 2.554 (1) and 2.568 (1), Mo–S (equatorial–axial) = 2.613 (1) and 2.510 (1), Mo–C = 1.889 (5), and C–O = 1.176 (6) Å. $(CO)MO(S_2CNMe_2)diars$ also has an anomalously low carbonyl stretching frequency (1762 cm^{-1}).

Introduction

The wide variety of stereochemistries and oxidation states found for molybdenum has led to its coordination chemistry being described as the most complex and challenging of the transition elements.[1] Because of this, certain classes of molybdenum coordination compounds have therefore received much attention, particularly in efforts to understand the role of molybdenum in living systems. For example, the chemistry of dithiocarbamates of molybdenum in its higher oxidation states relates to that of molybdoenzymes.[1-5] The carbonyl dithiocarbamates of molybdenum(II) are also of interest since they are known to act as reversible carbon monoxide carriers,[6] to be readily oxidized in solution,[6b] and to allow facile replacement of the labile carbon monoxide with other groups.[7] In studying the substitution reaction of the latter complexes with the widely studied chelating arsine *o*-phenylenebis(dimethylarsine) (diars),[8,9] we report the structural characterization of a new compound having an anomalously low carbonyl stretching frequency for a terminal carbonyl group.

Experimental Section

The ^1H NMR spectra were obtained on a Bruker WP 60 spectrometer in $CDCl_3$ solvent with tetramethylsilane as internal standard. IR spectra were measured on a Perkin-Elmer 180 spectrometer (4000–180 cm^{-1}) as CsI pellets, $CHCl_3$ solutions between KBr windows, or as Nujol mulls between CsI plates. Melting and decomposition points were determined with a Gallenkamp melting point apparatus in unsealed capillaries and are uncorrected.

All chemicals were of analytical grade and were used without purification. Solvents, reagent or spectroanalyzed grade, were saturated with dinitrogen gas for 20–30 min prior to use. All operations were performed under an atmosphere of dinitrogen in a polyethylene glovebag or with the use of Schlenk techniques. Reaction intermediates were prepared by slight modifications of published procedures[10,11] but were not isolated.

Preparation of Complexes. Carbonylbis(*N*,*N*-dimethyldithiocarbamato)(*o*-phenylenebis(dimethylarsine))molybdenum(II), $(CO)Mo(S_2CNMe_2)_2diars$. A solution of Br_2 (0.61 g, 3.8 mmol) in CH_2Cl_2 (6.0 cm^3) was added dropwise to a slurry of $Mo(CO)_6$ (1.00 g, 3.8 mmol) in CH_2Cl_2 (20.0 cm^3), cooled in an acetone–dry ice bath. The solution was allowed to warm to room temperature before the solvent was removed in vacuo and the residue was dried under reduced pressure. Methanol (10.0 cm^3) followed by $NaS_2CNMe_2{\cdot}2H_2O$ (1.25 g, 7.6 mmol) dissolved in methanol (10.0 cm^3) was added to the crude $Br_2Mo(CO)_4$ residue. The precipitate was dissolved in CH_2Cl_2 (15.0 cm^3), and the solution was stirred at room temperature for 10–15 min. diars (1.08 g 3.8 mmol) was added to the clear red solution, and the resultant solution was stirred overnight. The solvent was then removed in vacuo, the dried residue was dissolved in CH_2Cl_2 (15.0 cm^3), and the NaBr was separated by filtration. Methanol (ca. 20 cm^3) was added to the filtered solution until incipient crystallization. Chilling for several hours afforded deep red crystals that were separated by filtration and washed with CH_3OH (4 × 15 cm^3) until the washings were colorless. The moderately air-stable crystals were dried in vacuo for 4 h. The yield was 1.30 g (52.7%).

Carbonylbis(*N*,*N*-diethyldithiocarbamato)(*o*-phenylenebis(dimethylarsine))molybdenum(II), $(CO)Mo(S_2CNEt_2)_2diars$. The method reported above was used for this preparation, except that 1.71 g of $NaS_2CNEt_2{\cdot}3H_2O$ was used for the dithiocarbamate. The yield of deep red product was 1.80 g (67.2%).

Nitrosylbis(*N*,*N*-dimethyldithiocarbamato)(*o*-phenylenebis(dimethylarsine))molybdenum(II) Tetrafluoroborate, $[(NO)Mo(S_2CNMe_2)_2diars](BF_4)$. Nitrosonium tetrafluoroborate (0.18 g, 1.5 mmol) was added to a solution of $(CO)Mo(S_2CNMe_2)_2diars$ (0.50 g, 7.7 mmol) in CH_2Cl_2 (20.0 cm^3). Immediately a gas was released and the initially deep red solution turned yellow-orange upon stirring at ambient temperature for 4 h. The solution was passed through a column packed with Florisil, collecting the bright yellow solution. Additon of hexane (30.0 cm^3) and chilling several hours resulted in bright yellow microcrystals. These were separated by filtration, washed with hexane, and dried in vacuo. The yield was 0.37 g (65.1%).

Nitrosylbis(*N*,*N*-diethyldithiocarbamato)(*o*-phenylenebis(dimethylarsine))molybdenum(II) Tetrafluoroborate, $[(NO)Mo(S_2CNEt_2)_2diars](BF_4)$. An analogous procedure to the one reported above using $(CO)Mo(S_2CNEt_2)_2diars$ (0.50 g) was successful for this synthesis. However, upon addition of hexane, an oil sometimes formed.

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Table I. Final Fractional Coordinates (Mo and As $\times 10^5$, others $\times 10^4$)

atom	*x*	*y*	*z*
Mo	22075 (5)	24305 (3)	32878 (5)
As(1)	30082 (6)	32409 (4)	11363 (6)
As(2)	44592 (6)	17095 (4)	29921 (7)
S(1)	2959 (2)	1460 (1)	5539 (2)
S(2)	189 (2)	2050 (1)	4606 (2)
S(3)	813 (5)	885 (3)	6769 (5)
S(4)	3260 (2)	3846 (1)	5314 (2)
O(1)	700 (2)	3704 (1)	2735 (2)
N(1)	1784 (5)	5250 (3)	4567 (6)
N(2)	400 (5)	1020 (3)	676 (5)
C(1)	1235 (6)	1388 (4)	5777 (6)
C(2)	1808 (7)	358 (4)	7731 (7)
C(3)	−674 (6)	812 (4)	6870 (6)
C(4)	1910 (6)	4376 (4)	4252 (6)
C(5)	720 (7)	5702 (4)	3530 (7)
C(6)	2790 (7)	5780 (4)	5905 (8)
C(7)	3540 (7)	4546 (4)	1322 (8)
C(8)	1579 (7)	3071 (5)	−871 (7)
C(9)	6123 (7)	1753 (6)	4766 (8)
C(10)	4127 (9)	422 (4)	2328 (9)
C(11)	4695 (6)	2810 (4)	558 (6)
C(12)	5240 (7)	3129 (4)	−579 (7)
C(13)	6494 (8)	2838 (5)	−860 (8)
C(14)	7178 (8)	2214 (5)	1 (8)
C(15)	6609 (8)	1862 (5)	1142 (9)
C(16)	5333 (6)	2164 (4)	1407 (6)
C(17)	1115 (6)	1547 (4)	1690 (6)

Table II. Interatomic Distances (Å) and Angles (Deg) with Estimated Standard Deviation in Parentheses

Bond Distances

Mo-As(1)	2.583 (1)	S(3)-C(4)	1.708 (6)
Mo-As(2)	2.569 (1)	S(4)-C(4)	1.724 (5)
Mo-S(1)	2.568 (1)	N(1)-C(1)	1.321 (7)
Mo-S(2)	2.554 (1)	N(1)-C(2)	1.454 (7)
Mo-S(3)	2.613 (1)	N(1)-C(3)	1.452 (7)
Mo-S(4)	2.510 (1)	N(2)-C(4)	1.338 (7)
Mo-C(17)	1.889 (5)	N(2)-C(5)	1.456 (7)
As(1)-C(7)	1.959 (6)	N(2)-C(6)	1.454 (7)
As(1)-C(8)	1.944 (6)	C(11)-C(12)	1.350 (8)
As(1)-C(11)	1.967 (6)	C(11)-C(16)	1.374 (8)
As(2)-C(9)	1.940 (6)	C(12)-C(13)	1.393 (10)
As(2)-C(10)	1.943 (7)	C(13)-C(14)	1.369 (10)
As(2)-C(16)	1.949 (5)	C(14)-C(15)	1.385 (10)
S(1)-C(1)	1.720 (6)	C(15)-C(16)	1.414 (9)
S(2)-C(1)	1.707 (5)	C(17)-O(1)	1.176 (6)

Bond Angles

As(1)-Mo-As(2)	75.8 (1)	C(7)-As(1)-C(11)	100.2 (2)
As(1)-Mo-S(1)	145.7 (1)	C(8)-As(1)-C(11)	101.5 (3)
As(1)-Mo-S(2)	147.0 (1)	Mo-As(2)-C(9)	120.6 (2)
As(1)-Mo-S(3)	90.4 (1)	Mo-As(2)-C(10)	114.8 (2)
As(1)-Mo-S(4)	72.7 (1)	Mo-As(2)-C(16)	114.9 (2)
As(1)-Mo-C(17)	87.6 (2)	C(9)-As(2)-C(10)	100.2 (4)
As(2)-Mo-S(1)	71.5 (1)	C(9)-As(2)-C(16)	101.9 (3)
As(2)-Mo-S(2)	135.2 (1)	C(10)-As(2)-C(16)	101.7 (3)
As(2)-Mo-S(3)	103.6 (1)	Mo-S(1)-C(1)	90.0 (2)
As(2)-Mo-S(4)	147.4 (1)	Mo-S(2)-C(1)	90.7 (2)
As(2)-Mo-C(17)	87.5 (2)	Mo-S(3)-C(4)	86.3 (2)
S(1)-Mo-S(2)	67.2 (1)	Mo-S(4)-C(4)	89.4 (2)
S(1)-Mo-S(3)	87.6 (1)	C(1)-N(1)-C(2)	120.8 (4)
S(1)-Mo-S(4)	136.8 (1)	C(1)-N(1)-C(3)	120.7 (4)
S(1)-Mo-C(17)	100.7 (2)	C(2)-N(1)-C(3)	118.5 (4)
S(2)-Mo-S(3)	91.7 (1)	C(4)-N(2)-C(5)	121.3 (5)
S(2)-Mo-S(4)	77.4 (1)	C(4)-N(2)-C(6)	119.8 (5)
S(2)-Mo-C(17)	83.6 (2)	C(5)-N(2)-C(6)	118.8 (4)
S(3)-Mo-S(4)	68.9 (1)	S(1)-C(1)-S(2)	111.7 (3)
S(3)-Mo-C(17)	167.9 (2)	S(1)-C(1)-N(1)	122.8 (4)
S(4)-Mo-C(17)	99.2 (2)	S(2)-C(1)-N(1)	125.5 (4)
Mo-As(1)-C(7)	123.2 (2)	S(3)-C(4)-S(4)	115.2 (3)
Mo-As(1)-C(8)	113.2 (2)	S(3)-C(4)-N(2)	123.0 (4)
Mo-As(1)-C(11)	114.9 (2)	S(4)-C(4)-N(2)	121.8 (4)
C(7)-As(1)-C(8)	100.1 (3)	C(14)-C(15)-C(16)	119.0 (6)
C(16)-C(11)-C(12)	120.4 (5)	C(15)-C(16)-C(11)	119.8 (5)
As(1)-C(11)-C(12)	123.5 (5)	As(2)-C(16)-C(11)	118.3 (4)
As(1)-C(11)-C(16)	116.1 (4)	As(2)-C(16)-C(15)	121.9 (5)
C(11)-C(12)-C(13)	120.5 (6)	Mo-C(17)-O(1)	177.5 (5)
C(12)-C(13)-C(14)	120.3 (6)		
C(13)-C(14)-C(15)	119.9 (6)		

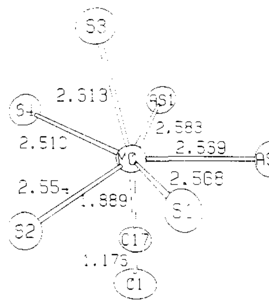

Figure 1. Coordination about Mo in (CO)Mo(S_2CNMe_2)$_2$diars. The standard deviations are 0.001 Å except for Mo–C (0.005 Å) and C–O (0.006 Å). The thermal ellipsoids are shown at the 50% probability level.

This was readily crystallized by vigorous shaking. The yield of yellow solid was 0.40 g (71.1%).

Satisfactory C, H, and N analyses were obtained for all the products (data deposited).

Crystallography. Slow crystallization of (CO)Mo(S_2CNMe_2)$_2$diars from a dichloromethane–methanol solution afforded dark red plate crystals. A crystal of approximate dimensions 0.12 × 0.11 × 0.06 mm was chosen for X-ray analysis. Unit cell and space group data were obtained from various Weissenberg and precession photographs. Accurate unit cell parameters were obtained by a least-squares procedure applied to the setting angles for 12 general reflections measured on a Hilger and Watts diffractometer at 20 °C.

Crystal data: $C_{17}H_{28}As_2MoN_2OS_4$: M_r = 650.45; triclinic; a = 9.634 (3), b = 14.986 (4), c = 8.882 (3) Å; α = 94.82 (2), β = 104.37 (2), γ = 95.18 (2)°; V = 1229.6 Å^3; $F(000)$ = 648; Z = 2; D_c = 1.76 g cm^{-3}; λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 34.1 cm^{-1}; space group $P1$ or $P\bar{1}$, $P\bar{1}$ from analysis.

The intensities of the unique reflections with $2° < \theta < 25°$ were measured on a PDP8I controlled Hilger and Watts Y290 four-circle diffractometer as described previously.[12] Of the 3420 reflections measured, the 2712 with $I > 3\sigma(I)$ were considered observed; the remainder were excluded from the refinement calculations. The data were corrected for Lorentz, polarization, and absorption effects. The transmission coefficients were in the range 0.63–0.71.

Structure Analysis. The structure was solved by the heavy-atom method. The phases were originally derived from the coordinates of the molybdenum and arsenic atoms whose positions in the asymmetric unit were deduced from a three-dimensional Patterson synthesis. Successive Fourier syntheses revealed the positions of all nonhydrogen atoms. These were then refined[13] with isotropic thermal parameters by full-matrix least-squares calculations to R = 0.119. R dropped to 0.072 after four cycles of full-matrix least-squares using anisotropic thermal parameters, and a difference Fourier synthesis revealed the positions of all the hydrogen atoms close to those expected on geometrical grounds. These were then positioned geometrically (with C–H = 0.95 Å), and in subsequent refinement cycles only an overall isotropic thermal parameter was refined for hydrogen atoms. Refinement converged with R = 0.038 and $R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$ = 0.043. In the least-squares calculations, the weights used were based on counting statistics. The scattering factors were from ref 14 and anomalous dispersion corrections were made for Mo and As.[15]

Atomic coordinates of the nonhydrogen atoms are in Table I. Intramolecular distances and angles are in Table II. Listings of

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Table III. Spectrochemical Data for Mo(II)–diars Complexes

compd	IR, cm^{-1}			NMR	
	ν(CO/NO)	ν(CN)	ν(MoS)	δ(dtc)	δ(diars)
$(CO)Mo(S_2CNMe_2)_2$diars	1762, 1723 sh	1497	352	3.37	1.64
	1762 (soln)				7.66, 7.69
$(CO)Mo(S_2CNEt_2)_2$diars	1760, 1717 sh	1479	356	1.23 (t)	1.56
	1770 (soln)			3.84 (q)	7.62, 7.69
$[(NO)Mo(S_2CNMe_2)_2diars](BF_4)$	1650	1532	353	3.25	1.68
				3.39	1.83
				3.43	2.08
				3.46	2.11
					7.86
$[(NO)Mo(S_2CNEt_2)_2diars](BF_4)$	1653	1508	355	1.18 (t)	1.74
				1.38 (t)	1.86
				3.83 (m)	2.12
					7.87
					7.93

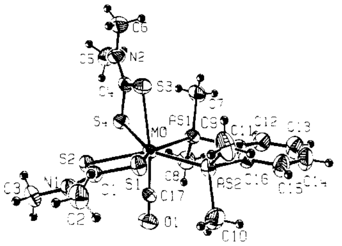

Figure 2. View of $(CO)Mo(S_2CNMe_2)_2$diars with the crystallographic numbering scheme. The thermal ellipsoids are shown at the 50% probability level except for the hydrogen atoms which are shown as spheres of arbitrary radius.

calculated and observed structure factors, calculated hydrogen coordinates, intra- and intermolecular contacts, and mean plane data have been deposited. Figure 1 shows the immediate pentagonal-bipyramidal environment of the molybdenum atom. Figures 2 and 3 show respectively an ORTEP[16] plot of the molecule with our numbering scheme and a stereodiagram of the unit cell contents.

Discussion

We have shown that the reaction between $Mo(CO)_x(S_2CNR_2)_2$ ($x = 2, 3$)[10] prepared in situ and diars replaces not only the labile carbonyl group but also one which was more firmly attached. The possibility of a bridging bidentate ligand, found in $[Mo(S_2CNEt_2)_2(CO)_2]_2N_2H_4$[10] but rarely for the diars ligand,[8] is not realized in this case. The carbonyl complexes are deep red crystals which are air stable for several days as solids but show a marked reduction in stability toward aerobic conditions in solution. Their high decomposition points (150, 188 °C) attest to their thermal stability. This property is further enhanced in the cationic nitrosyl compounds, which show remarkable air stability even as solutions. All of the compounds are diamagnetic, and the important features of their IR and nuclear magnetic resonance spectra are recorded in Table III.

For the carbonyl complexes, the C–O stretching frequencies are the same in $CHCl_3$ solutions, as CsI pellets, or as Nujol mulls. This illustrates that lattice constraints are not important and that no infrared detectable processes occur upon dissolution. Most importantly, however, it is to be noted that these frequencies fall in the range normally associated with bridging carbonyl groups. Such low terminal carbonyl frequencies for molybdenum are rare. They do occur, for example, in complexes such as $Mo(CO)_2EPh_3$(paphy) (E = P, As) where paphy (pyridine-2-carboxaldehyde 2′-pyridylhydrazone) fromulated as terdentate[17] is a nitrogen donor ligand of poor back-bonding capability. Also, recent reports[11,18] indicate that $(CO)Mo(S_2CNEt_2)_2$(diphos) has a similarly low carbonyl stretching frequency. Our crystal structure analysis (vide infra) unambiguously establishes that the CO moiety is terminal.

The N–O stretching vibrations (Table III) fall within the range reported for other mononitrosyl complexes.[19,20] This, taken together with the diamagnetism of the complexes, is consistent with their formulation as nitrosonium–molybdenum(II) complexes having linear nitrosyl groups.

In the four complexes, C–N vibrations associated with the partial double-bond character of the $S_2C–NR_2$ bond are normal. There appears to be no splitting of this vibrational frequency in either solution or the solid state. This indicates bidentate coordination for the dithiocarbamate moieties, although a better criterion would be the occurrence of a single band associated with the C–S vibration, usually observed between 950 and 1050 cm^{-1}.[21–25] The assignment of this band was not possible in the four compounds described here. The decreases in the C–N vibrational frequency in going from the S_2CNMe_2 to the S_2CNEt_2 derivatives have been associated with a decrease in the C–N force constant,[25] whereas the increase in the C–N vibrational frequency for a dithiocarbamate ligand on substituting NO for CO in a complex is consistent with an increased double-bond character for the C–N bond.[26] The Mo–S vibrations are in the range assigned for related compounds by Colton and Scollary[6] and show little variation within the series.

Although there is a large ^1H NMR chemical shift difference between the dithiocarbamate methyl resonances in the S_2CNMe_2 and S_2CNEt_2 derivatives, they are in accord with the results of other workers.[10,11,19] The chemical shift of the methyl protons due to the diars ligand are indicative of coordinated diars.[9,27,28] It appears that while the carbonyl

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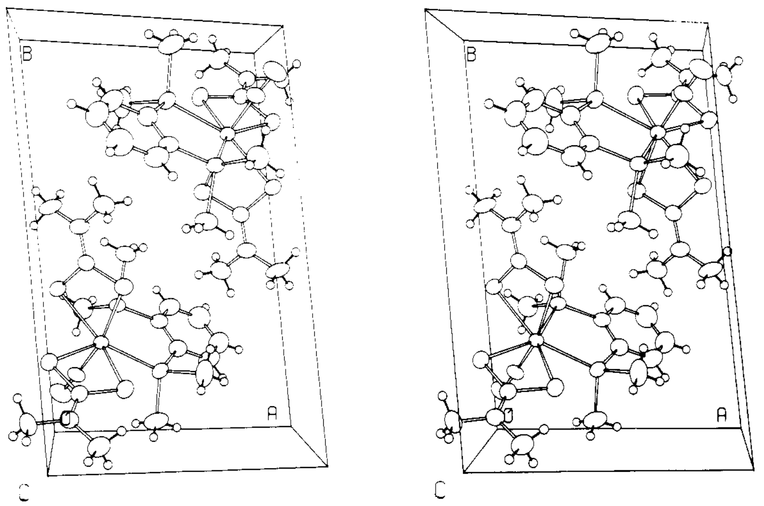

Figure 3. Stereoview of the unit cell of (CO)Mo(S$_2$CNMe)$_2$diars. The thermal ellipsoids are shown at the 50% probability level except for the hydrogen atoms which are shown as spheres of arbitrary radius.

derivatives are fluxional[29-31] at ambient temperatures, the nitrosyl derivatives are static.[20,32]

The structure of (CO)Mo(S$_2$CNMe$_2$)$_2$diars consists of discrete monomeric molecules separated by normal van der Waals distances (Figure 3). No crystallographic symmetry is required of the molecule (Figures 1 and 2), and the S$_2$CNMe$_2$ and diars ligands are bidentate as anticipated. The immediate coordination sphere around molybdenum is a slightly distorted pentagonal bipyramid (Figure 1), with As(1), As(2), S(1), S(2), and S(4) forming the equatorial plane and the carbonyl group and S(3) axial. Intramolecular contacts and geometrical constraints imposed by the axial–equatorial dithiocarbamate ligand cause a slight ruffling of the equatorial plane with deviations ranging from −0.43 (S(2)) to +0.37 Å (S(1)).

The Mo–C–O moiety is approximately normal to the equatorial coordination plane and trans to S. The dimensions (Mo–C = 1.889 (5) and C–O = 1.176 (6) Å) are comparable with those reported in [ClMo(CO)$_2$(diars)$_2$]$^+$ (Mo–C = 1.87 (6) and 1.92 (5), C–O = 1.18 (7) and 1.23 (8) Å)[33] and in (CO)$_2$Mo(S$_2$CN-*i*-Pr$_2$)$_2$ (Mo–C = 1.902 (8) and 1.919 (8), C–O = 1.175 (7) and 1.180 (8) Å).[34] The C–O stretching frequency found for (CO)Mo(S$_2$CNMe$_2$)$_2$diars (Table III) is more than 80 cm^{-1} lower than those reported for C–O in (CO)$_2$Mo(S$_2$CN-*i*-Pr$_2$)$_2$ (1934 and 1842 cm^{-1})[34] although the actual C–O distances do no differ significantly. The decrease in the carbonyl stretching frequency is expected from synergic theory by the substitution of diars, a ligand of poorer back-bonding capacity than CO, but the magnitude is unusual.

The Mo–S distances in the equatorial–equatorial S$_2$CNMe$_2$ ligand are comparable (2.554, 2.568 (1) Å) but those in the axial–equatorial ligand differ by 0.1 Å (2.613 (1) (ax) 2.510 (1) Å (eq)). Similar variations in Mo–S distances have been noted previously in (NO)Mo(S$_2$CNBu$_2$)$_3$.[35] The S$_2$CNC$_2$ moieties of both dithiocarbamate ligands are individually planar. The plane of the equatorial–equatorial ligand makes an angle of 17.6° with the MoAs$_2$S$_3$ equatorial coordination plane. In the axial–equatorial ligand, as a consequence of the ligand bite, S(4) is 0.32 Å above the coordination plane and axial atom S(3) is bent away from the normal to the coordination plane (S(3)–Mo–C(17) = 167.9, As(2)–Mo–S(3) = 103.6°). The N(1)–C(1) and N(2)–C(4) bond lengths (1.321 (7) and 1.338 (7) Å) reflect the considerable double-bond character of the central C–N bond in the dithiocarbamates; such double-bond character has been noted previously in related molecules.[31,35] The S–C distances (1.707–1.724 (5) Å) and the N–C(methyl) distances 1.452–1.456 (7) Å are also in the same range as previously reported.[31,35]

The Mo–As distances (2.569 and 2.583 (1) Å) are significantly shorter than those found in racemic and meso forms of (CO)$_3$Mo[*o*-C$_6$H$_4$(AsMePh)$_2$] (2.603, 2.663 and 2.595, 2.645 (3) Å)[36] and in [ClMo(CO)$_2$(diars)$_2$]$^+$ (2.614 and 2.617 (5) Å).[33] The diars bite angle is similar in these four complexes (74.8–76.6 (1)°), but the expected relationship[35] between the bite angle and the Mo–As distances is complicated by the difference in coordination geometries and donor atoms in the four complexes. The C$_6$H$_4$As$_2$ moiety is essentially planar, and the As–C distances (1.94–1.97 Å) are in the same range as those reported previously.[33,36] The angles at As(1) and As(2) range from 100.1 to 123.2°; the Mo–As–C angles are much larger than tetrahedral whereas the C–As–C angles are all less than tetrahedral (Table II). Similar results have been observed in other diars[9,33] and related ligand complexes[36] and are indicative of crowding, by other ligands, around arsenic.

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Registry No. (CO)Mo(S$_2$CNMe$_2$)$_2$diars, 80584-30-1; (CO)Mo(S$_2$CNEt$_2$)$_2$diars, 80584-31-2; [(NO)Mo(S$_2$CNMe$_2$)$_2$diars](BF$_4$), 80584-33-4; [(NO)Mo(S$_2$CNEt$_2$)$_2$diars](BF$_4$), 80584-35-6; Mo(CO)$_6$, 13939-06-5.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen coordinates, some intra- and intermolecular contacts, mean plane data, analytical data for Mo(II)–diars complexes, and structure factors (18 pages). Ordering information is given on any current masthead page.

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