# Syntheses and Structures of the Seven-Coordinate Molybdenum Carbonyl Complexes Containing both Dithiocarbamate and the Uninegative Nitrogen-Tripod Ligand

**Kom-Bei Shiu* and Jean Y. Lee**

Department of Chemistry, National Cheng Kung University,
Tainan, Taiwan 70101, ROC

**Yu Wang and Ming-Chu Cheng**

Department of Chemistry, National Taiwan University,
Taipei, Taiwan 10764, ROC

*Received February 8, 1993*

The metal carbonyl derivatives containing a metal–sulfur bond have recently been shown to afford a variety of novel products through oxidative decarbonylation.[1–4] In particular, [{HB(Me$_2$pz)$_3$}W(CO)$_2$($\eta^2$-(S,S))] (Me$_2$pz = 3,5-dimethylpyrazol-1-yl; (S,S)$^-$ = dithiocarbamato) was confirmed by Young, et al.[3] to be the important intermediate for the reaction between Et$_4$N[{HB(Me$_2$pz)$_3$}W(CO)$_3$] and tetraalkylthiuram disulfide, (S,S)$_2$. This tungsten intermediate cannot be obtained either from substitution of [{HB(Me$_2$pz)$_3$}W(CO)$_3$I] with (S,S)$^-$ or from oxidation of [{HB(Me$_2$pz)$_3$}W(CO)$_3$] with (S,S)$_2$, because either the anion, [{HB(Me$_2$pz)$_3$}W(CO)$_3$]$^-$,[3c] or [{HB(Me$_2$pz)$_3$}WO$_2$($\mu$-O)WO(CO){HB(Me$_2$pz)$_3$}][5] is produced. Quite unexpectedly, the only isolated product from the reaction of Et$_4$N[{HB(Me$_2$pz)$_3$}Mo(CO)$_3$] with (S,S)$_2$ is not the intermediate carbonyl complex but [{HB(Me$_2$pz)$_3$}Mo($\eta^2$-(S,S))($\eta^1$-(S,S))],[3a,b] although in the related cyclopentadienyl (Cp) system both analogues [CpM(CO)$_2$($\eta^2$-(S,S))] (M = Mo, W) can be prepared.[6] However, we wish to report that the reaction between [(N-N-N)Mo(CO)$_3$I] and silver dithiocarbamate, Ag$^+$(S,S)$^-$, can give successfully and cleanly all of the desired compounds [(N-N-N)Mo(CO)$_2$($\eta^2$-(S,S))] ((N-N-N)$^-$ = HBpz$_3^-$, HBtz$_3^-$, PhBtz$_3^-$; pz = pyrazol-1-yl; tz = 1,2,4-triazolyl; (S,S)$^-$ = *N,N*-diethyldithiocarbamato, pyrrolidine-1-carbodithioato) with satisfactory yields (eq 1). When the reaction between [(HBtz$_3$)Mo(CO)$_3$I] and bis(triphenylphosphine)nitrogen(1+) dithiocarbamate, PPN$^+$-(S,S)$^-$, was carried out in CH$_2$Cl$_2$, both PPN[(HBtz$_3$)Mo(CO)$_3$] and [(HBtz$_3$)Mo(CO)$_2$($\eta^2$-(S,S))] were obtained in an approximate ratio of 1:1. Apparently, the less electron-releasing and the smaller ligand (HBpz$_3$)$^-$, (HBtz$_3$)$^-$, or (PhBtz$_3$)$^-$ relative to {HB(Me$_2$pz)$_3$}-[7] can help to stabilize [(N-N-N)Mo(CO)$_2$($\eta^2$-(S,S))].

$$[(\text{N-N-N})\text{Mo(CO)}_3\text{I}] + \text{Ag}^+(\text{S,S})^- \rightarrow [(\text{N-N-N})\text{Mo(CO)}_2(\eta^2\text{-(S,S)})] + \text{CO} + \text{AgI} \quad (1)$$

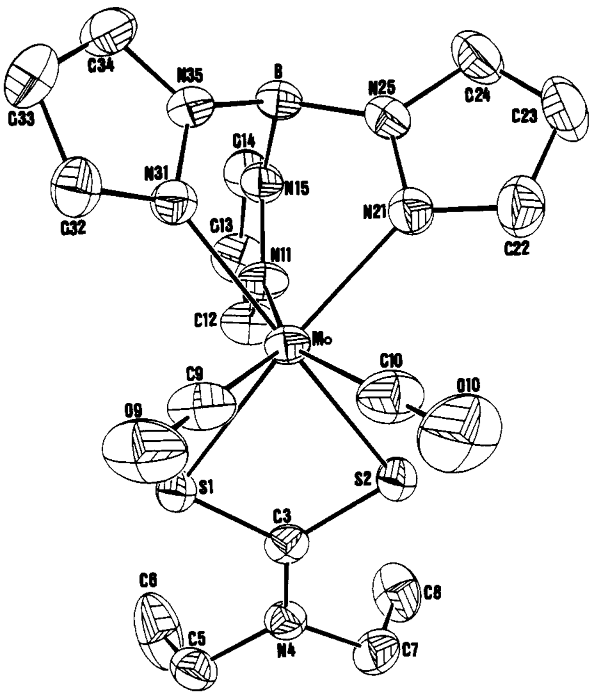

**Figure 1.** ORTEP drawing of complex **1** (50% probability ellipsoids).

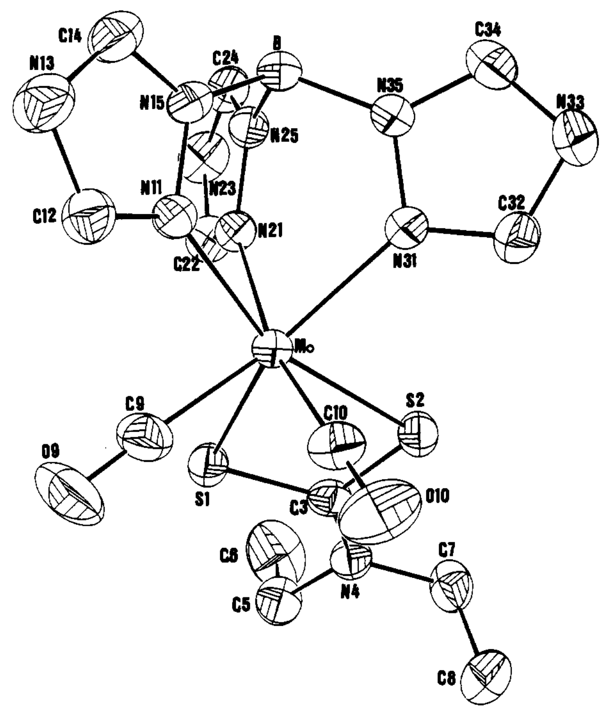

**Figure 2.** ORTEP drawing of complex **2** (50% probability ellipsoids).

The crystal structures of [(HBpz$_3$)Mo(CO)$_2$($\eta^2$-S$_2$CNEt$_2$)] (**1**) (Figure 1) and [(HBtz$_3$)Mo(CO)$_2$($\eta^2$-S$_2$CNEt$_2$)] (**2**) (Figure 2) were also determined by X-ray crystallography to confirm the dihapticity of (S-S)$^-$, which is independent of the identity of (N-N-N)$^-$, either (HBpz$_3$)$^-$ or (HBtz$_3$)$^-$. Like [{HB(Me$_2$pz)$_3$}W(CO)$_2$($\eta^2$-S$_2$CNEt$_2$)],[3c] **1** and **2** adopt the "four-legged piano stool" or 3:4 structures[8] or the distorted pentagonal bipyramidal geometry.[3c] Comparison of the angles of ∠OC–

---

[1] (a) Herrick, R. S.; Templeton, J. L. *Organometallics*, **1982**, *1*, 842. (b) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Ibid.* **1985**, *4*, 745.

[2] Feng, S. G.; Luan, L.; White, P.; Brookhart, M.; Templeton, J. L.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 2582.

[3] (a) Young, C. G.; Roberts, S. A.; Enemark, J. H. *Inorg. Chim. Acta*, **1986**, *114*, L7. (b) *Idem. Inorg. Chem.* **1986**, *25*, 3667. (c) Young, C. G.; Bruck, M. A.; Wexler, P. A.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 587. (d) Young, C. G.; Bruck, M. A.; Enemark, J. H. *Ibid.* **1992**, *31*, 593.

[4] Abrahamson, H. B.; Freeman, M. L.; Hossain, M. B.; Van Der Helm, D. *Inorg. Chem.* **1984**, *23*, 2286.

[5] Young, C. G.; Gable, R. W.; Mackay, M. F. *Inorg. Chem.* **1990**, *29*, 1777.

[6] (a) Abel, E. W.; Dunster, M. O. *J. Chem. Soc., Dalton Trans.* **1973**, 98. (b) Glass, W. K.; Shiels, A. *J. Organomet. Chem.* **1974**, *67*, 401. (c) Cotton, F. A.; McCleverty, J. A. *Inorg. Chem.* **1964**, *3*, 1398. (d) Abrahamson, H. B.; Freeman, M. L. *Organometallics* **1983**, *2*, 679.

[7] (a) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588. (b) Shiu, K.-B.; Lee, J. Y.; Wang, Y.; Cheng, M.-C.; Wang, S.-L.; Liao, F.-L. *J. Organomet. Chem.* **1993**, in press. (c) Frauendorfer, E.; Brunner, H. *J. Organomet. Chem.* **1982**, *240*, 371. (d) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

[8] (a) Kubacek, P.; Hoffmann, R.; Halvas, Z. *Organometallics*, **1982**, *1*, 180. (b) Chaudhuri, P.; Wieghardt, K.; Tsai, Y.-H.; Kruger, C. *Inorg. Chem.* **1984**, *23*, 427. (c) Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213.

0020-1669/93/1332-3565$04.00/0

**Table I.** Crystal Data for Complexes 1 and 2

| | complex | | | complex | |
|---|---|---|---|---|---|
| | 1 | 2 | | 1 | 2 |
| formula | $C_{16}H_{20}BMoN_7O_2S_2$ | $C_{13}H_{17}BMoN_{10}O_2S_2$ | γ, deg | 106.53(4) | 90 |
| $M_r$ | 513.26 | 516.21 | $V$, Å$^3$ | 1046.0(7) | 2112.4(9) |
| cryst syst | triclinic | monoclinic | $Z$ | 2 | 4 |
| space group | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) | $D_{calc}$, g cm$^{-3}$ | 1.629 | 1.623 |
| cell params at 296 K | | | λ | 0.709 30 | 0.709 30 |
| $a$, Å | 8.344(3) | 12.347(3) | μ(Mo, Kα), mm$^{-1}$ | 0.83 | 0.83 |
| $b$, Å | 9.206(5) | 13.572(3) | $T_{min}$–$T_{max}$ | 0.971–0.999 | 0.918–0.994 |
| $c$, Å | 15.226(4) | 13.209(4) | no. of unique obsd data | 3427 | 3335 |
| α, deg | 107.13(4) | 90 | $R$, $R_w$ | 0.022, 0.024 | 0.023, 0.023 |
| β, deg | 96.585(23) | 107.364(21) | | | |

**Table II.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$)[a] for Complex 1

| | $x$ | $y$ | $z$ | $B_{eq}$ | | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.03691(3) | 0.41695(3) | 0.768464(15) | 2.170(9) | C(13) | 0.3385(4) | 0.8278(3) | 0.68473(21) | 4.04(16) |
| S(1) | –0.03748(8) | 0.29977(8) | 0.59157(4) | 2.61(3) | C(14) | 0.3044(3) | 0.9048(3) | 0.76845(20) | 3.47(14) |
| S(2) | 0.25526(8) | 0.29968(8) | 0.70529(4) | 2.69(3) | N(15) | 0.2155(3) | 0.79349(22) | 0.80146(14) | 2.66(10) |
| C(3) | 0.1459(3) | 0.2498(3) | 0.59248(17) | 2.33(12) | N(21) | 0.1940(3) | 0.56872(24) | 0.91289(14) | 2.82(10) |
| N(4) | 0.19577(25) | 0.18177(23) | 0.51572(14) | 2.56(10) | C(22) | 0.2857(4) | 0.5335(3) | 0.97703(20) | 3.90(15) |
| C(5) | 0.0935(3) | 0.1408(3) | 0.42119(18) | 3.27(14) | C(23) | 0.3770(4) | 0.6723(4) | 1.05324(20) | 4.55(17) |
| C(6) | 0.1534(5) | 0.2630(5) | 0.3757(3) | 6.44(22) | C(24) | 0.3354(4) | 0.7935(3) | 1.03272(18) | 3.91(15) |
| C(7) | 0.3601(3) | 0.1519(3) | 0.52395(19) | 3.49(15) | N(25) | 0.2253(3) | 0.73101(24) | 0.94875(14) | 2.96(10) |
| C(8) | 0.5093(4) | 0.2972(4) | 0.53460(21) | 4.57(18) | N(31) | –0.11960(24) | 0.57597(23) | 0.81337(13) | 2.52(10) |
| C(9) | –0.1892(3) | 0.2588(3) | 0.73554(19) | 3.52(14) | C(32) | –0.2888(3) | 0.5469(3) | 0.79799(19) | 3.31(14) |
| O(9) | –0.32427(25) | 0.15989(23) | 0.71507(15) | 5.03(11) | C(33) | –0.3249(4) | 0.6868(4) | 0.84078(21) | 4.09(17) |
| C(10) | 0.0254(4) | 0.2533(3) | 0.82529(20) | 3.79(15) | C(34) | –0.1693(4) | 0.8020(3) | 0.88211(19) | 3.64(15) |
| O(10) | 0.0206(3) | 0.1540(3) | 0.85801(16) | 6.27(16) | N(35) | –0.0461(3) | 0.73559(23) | 0.86591(14) | 2.76(10) |
| N(11) | 0.1893(3) | 0.64243(23) | 0.74001(14) | 2.79(10) | B | 0.1484(4) | 0.8156(3) | 0.89178(21) | 2.93(14) |
| C(12) | 0.2651(4) | 0.6647(3) | 0.67005(19) | 3.60(14) | | | | | |

[a] $B_{eq}$, equivalent isotropic thermal parameter, is the mean of the principal axes of the thermal ellipsoid.

**Table III.** Fractional Atomic Coordinates and $B_{eq}$ Values (Å$^2$)[a] for the Complex 2

| | $x$ | $y$ | $z$ | $B_{eq}$ | | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.335959(18) | 0.083014(16) | 0.130751(17) | 2.143(9) | N(13) | 0.37350(19) | 0.26030(17) | –0.14043(17) | 3.70(11) |
| S(1) | 0.28894(6) | 0.14629(5) | 0.29347(5) | 2.96(3) | C(14) | 0.28113(22) | 0.20618(20) | –0.18297(20) | 3.23(13) |
| S(2) | 0.31100(6) | –0.05450(5) | 0.25037(5) | 2.86(3) | N(15) | 0.25514(16) | 0.14863(15) | –0.11255(15) | 2.41(9) |
| C(3) | 0.29130(20) | 0.02813(19) | 0.34090(19) | 2.57(11) | N(21) | 0.14514(17) | 0.11320(14) | 0.05761(15) | 2.44(9) |
| N(4) | 0.28013(18) | 0.00456(15) | 0.43429(15) | 2.88(11) | C(22) | 0.05946(22) | 0.14089(20) | 0.09249(21) | 3.23(13) |
| C(5) | 0.25907(24) | 0.07901(22) | 0.50664(21) | 3.65(14) | N(23) | –0.04190(18) | 0.14461(18) | 0.01770(18) | 3.75(12) |
| C(6) | 0.1380(3) | 0.0791(3) | 0.5057(3) | 6.82(23) | C(24) | –0.01658(20) | 0.11726(19) | –0.06887(21) | 3.03(12) |
| C(7) | 0.2925(3) | –0.09819(20) | 0.47144(22) | 3.69(14) | N(25) | 0.09426(16) | 0.09785(14) | –0.04904(15) | 2.42(9) |
| C(8) | 0.4126(3) | –0.12255(24) | 0.5300(3) | 5.76(19) | N(31) | 0.29801(17) | –0.03736(15) | 0.01254(15) | 2.49(9) |
| C(9) | 0.43255(24) | 0.19664(21) | 0.18896(20) | 3.49(13) | C(32) | 0.33689(22) | –0.12873(19) | 0.01416(21) | 3.10(13) |
| O(9) | 0.49704(18) | 0.25920(16) | 0.22133(16) | 5.48(12) | N(33) | 0.29507(19) | –0.17838(16) | –0.07692(17) | 3.45(12) |
| C(10) | 0.48940(22) | 0.03293(20) | 0.17847(20) | 3.17(13) | C(34) | 0.22539(22) | –0.11246(19) | –0.13706(20) | 3.03(12) |
| O(10) | 0.58136(16) | 0.00252(17) | 0.20851(16) | 5.16(11) | N(35) | 0.22449(16) | –0.02809(15) | –0.08771(15) | 2.34(9) |
| N(11) | 0.33619(16) | 0.16400(14) | –0.01678(15) | 2.36(9) | B | 0.1631(3) | 0.06946(21) | –0.12363(23) | 2.58(13) |
| C(12) | 0.40390(21) | 0.23025(19) | –0.03873(20) | 3.04(12) | | | | | |

[a] $B_{eq}$, equivalent isotropic thermal parameter, is the mean of the principal axes of the thermal ellipsoid.

**Table IV.** Selected Bond Lengths (Å) and Angles (deg) for Complexes 1 and 2

| Complex 1 | | | | Complex 2 | | | |
|---|---|---|---|---|---|---|---|
| Mo–S(1) | 2.5154(12) | Mo–S(2) | 2.5137(11) | Mo–S(1) | 2.5374(9) | Mo–S(2) | 2.5228(8) |
| Mo–C(9) | 1.929(3) | C(9)–O(9) | 1.168(3) | Mo–C(9) | 1.961(3) | C(9)–O(9) | 1.155(3) |
| Mo–C(10) | 1.932(3) | C(10)–O(10) | 1.156(3) | Mo–C(10) | 1.933(3) | C(10)–O(10) | 1.161(3) |
| Mo–N(11) | 2.2949(23) | Mo–N(21) | 2.2346(23) | Mo–N(11) | 2.2381(20) | Mo–N(21) | 2.3006(20) |
| Mo–N(31) | 2.2402(22) | C(3)–N(4) | 1.327(3) | Mo–N(31) | 2.2112(20) | C(3)–N(4) | 1.321(3) |
| C(3)–S(1) | 1.7184(25) | C(3)–S(2) | 1.712(3) | C(3)–S(1) | 1.719(3) | C(3)–S(2) | 1.709(3) |
| S(1)–Mo–S(2) | 68.42(3) | C(9)–Mo–C(10) | 67.57(13) | S(1)–Mo–S(2) | 67.56(3) | C(9)–Mo–C(10) | 74.12(12) |
| N(11)–Mo–N(21) | 79.74(8) | N(11)–Mo–N(31) | 79.60(8) | N(11)–Mo–N(21) | 79.29(7) | N(11)–Mo–N(31) | 78.64(7) |
| N(21)–Mo–N(31) | 80.72(8) | S(1)–C(3)–S(2) | 111.04(14) | N(21)–Mo–N(31) | 81.98(7) | S(1)–C(3)–S(2) | 110.34(14) |
| C(5)–N(4)–C(7) | 118.46(19) | Mo–C(9)–O(9) | 178.21(23) | C(5)–N(4)–C(7) | 117.19(20) | Mo–C(9)–O(9) | 174.1(3) |
| Mo–C(10)–O(10) | 178.5(3) | | | Mo–C(10)–O(10) | 179.04(23) | | |

Mo–N, ∠N–Mo–S, and ∠OC–Mo–S and that of the Mo–N distances in 1 and 2 (Table IV) further reveals that the pentagaonal bipyramid is best defined by axial donor atoms (C(10) and N(11) in **1** and C(10) and N(21) in **2**) and equatorial donor atoms (C(9), N(21), N(31), S(1), and S(2) in **1** and C(9), N(11), N(31), S(1), and S(2) in **2**). The major difference between the two structures is the orientation of the dithiocarbamato group, as reflected in the dihedral angles of 81.44(17)° in **1** and 89.68(17)° in **2** between the planes defined by Mo, C(9), and C(10) on one hand and S(1), S(2), and C(3) on the other. Since the steric effect can be regarded as similar for $(HBpz_3)^-$ or $(HBtz_3)^-$, the resulted electronic effect caused by the change of the substituent from pz to tz influences somehow unexpectedly not only the observed $\nu_{CO}$ frequencies (1934, 1840 in **1** and 1946, 1856 cm$^{-1}$ in **2**, measured in $CH_2Cl_2$) but also the relative orientation of the dithiocarbamato group with respect to the nitrogen-tripod ligand.

## Experimental Section

The general operations and the spectral measurements were carried out as previously described.[9] The complexes [(N-N-N)Mo(CO)$_3$I] were prepared by following the published procedures.[7b,8c] Since the preparations of the orange red compounds [(N-N-N)Mo(CO)$_2$($\eta^2$-(S,S))] are all similar and straightforward, only a typical preparation for **1** is described. Microanalytical and spectral data for the complexes are deposited as supplementary material.

**Preparation of 1.** To a stirred solution of [(HBpz$_3$)Mo(CO)$_3$I] (0.26 g, 0.50 mmol) dissolved in MeCN (20 mL) was added solid AgS$_2$CNEt$_2$ (0.14 g, 0.55 mmol). After gas evolution had ceased (30 min), the resulted suspension was filtered through a pad of Celite and the solvent was removed from the filtrate under vacuum. Recrystallization from CH$_2$Cl$_2$/hexane gave 0.19 g of the orange product. Yield: 74%.

**X-ray Diffraction Study of 1 and 2.** All the single crystals were grown from CH$_2$Cl$_2$/hexane at room temperature. General procedures and listings of programs were previously given.[9a] An absorption correction was performed on the structures using $\psi$ scans. Related crystal data, final coordinates of the non-hydrogen atoms, and selected bond lengths and bond angles are reported in Tables I–IV.

**Acknowledgment.** We wish to thank the National Science Council of the Republic of China for the financial support of this research.

**Supplementary Material Available:** A listing of microanalytical and spectral data for the dithiocarbamate complexes of molybdenum and tables of fractional atomic coordinates for hydrogen atoms, anisotropic thermal displacement coefficients, and complete bond lengths and angles for complexes **1** and **2** (9 pages). Ordering information is given on any current masthead page.

---

(9) (a) Shiu, K.-B.; Liou, K.-S.; Cheng, C. P.; Fang, B.-R.; Wang, Y.; Lee, G.-H.; Vong, W.-J. *Organometallics* **1989**, *8*, 1219. (b) Shiu, K.-B.; Chou, J. L.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 1989.