# Heterobinuclear Complexes of Manganese and Molybdenum Containing Amino Acidato and Related O,N and S,N Bridges

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*Received March 4, 2002*

The addition of NaOMe to [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-Br)] (**1**) produces [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-OMe)] (**2**), containing a methoxide bridge between Mn and Mo. Compound **2** reacts with α-amino acids to yield, upon elimination of MeOH, the complexes [MnMo(CO)$_5$-($\mu$-S$_2$CPCy$_3$){$\mu$-OC(O)CR$^1$R$^2$NR$^3_2$}] (**3a**−**f**), in which the oxygen atom of the carboxylato group acts as a bridge between Mn and Mo, while the amino function coordinates the molybdenum atom, displacing one carbonyl ligand. In a similar reaction, the addition of ethanolamine to **2** affords the $\mu_2(O)$-$\eta^2(O,N)$-aminoethanolato complex [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$)($\mu$-OCH$_2$CH$_2$-NH$_2$)] (**4**). Reaction of **2** with cysteine methyl ester hydrochloride and NaOMe affords [MnMo-(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$-SCH$_2$C(COOMe)NH$_2$}] (**5**), with the sulfur atom in the bridging position. The new complexes have been characterized by analytical and spectroscopic methods, and their structures have been determined by X-ray crystallography for **2, 3e** (2,2-dimethylaminobutyrato), and **4**.



## Introduction

The use of natural, proteinogenic amino acids as ligands have attracted the interest of chemists from the early days of coordination chemistry,[1] and this has resulted in the preparation of many complexes of transition metals. Moreover, the use of amino acids and other biogenic ligands in organometallic chemistry has experienced a very rapid growth in recent years,[2] mostly due to the potential use of readily available amino acids as chiral auxiliaries. Amino acidato ligands usually coordinate the metal in an O,N chelate fashion, although some examples of monodentate O or N coordination are also known. In comparison, there are not many examples of amino acidato ligands acting as bridges, most cases corresponding to homopolynuclear complexes containing multidentate ethylenediaminetetraacetato and related poly(amino acidato) ligands. Only a few organometallic complexes containing amino acidato bridges have been reported. Some representative examples are [Os$_3$(CO)$_9$($\mu$-XCH$_2$(CO$_2$Et)NH$_2$] (X = O, S)[3] and [Ru$_3$(CO)$_9$($\mu$-H)($\mu$-SCH$_2$(CO$_2$Et)NH$_2$].[4] In both cases the amino ester uses the O or S atom of the pendant chain to bridge two atoms of the same metal. Sometimes, the amino acidato (Aa) ligand coordinated as a chelate can use the uncoordinated oxygen atom of the carboxylate function to bind a second metal atom, thus acting as $\mu$-$\eta^2$(N,O):$\eta^1$(O′), as in the trimers [{($\eta$-ring)M-(Aa)$_3$}](BF$_4$)$_3$.[5] Reported structures in which an amino acidato ligand serves as a bridge between two different metals are even more scarce,[6] and none of them are organometallic. This might be a consequence of the paucity of appropriate precursor complexes, and the lack of knowledge of general trends for the chemistry of heteropolymetallic complexes. In the course of previous works, we have developed synthetic methods for homo- and heterodinuclear complexes containing $\eta^2(S,S')$:$\eta^3$-($S,C,S'$)-S$_2$CPR$_3$ and halide bridges which can be prepared in good yields and constitute convenient starting

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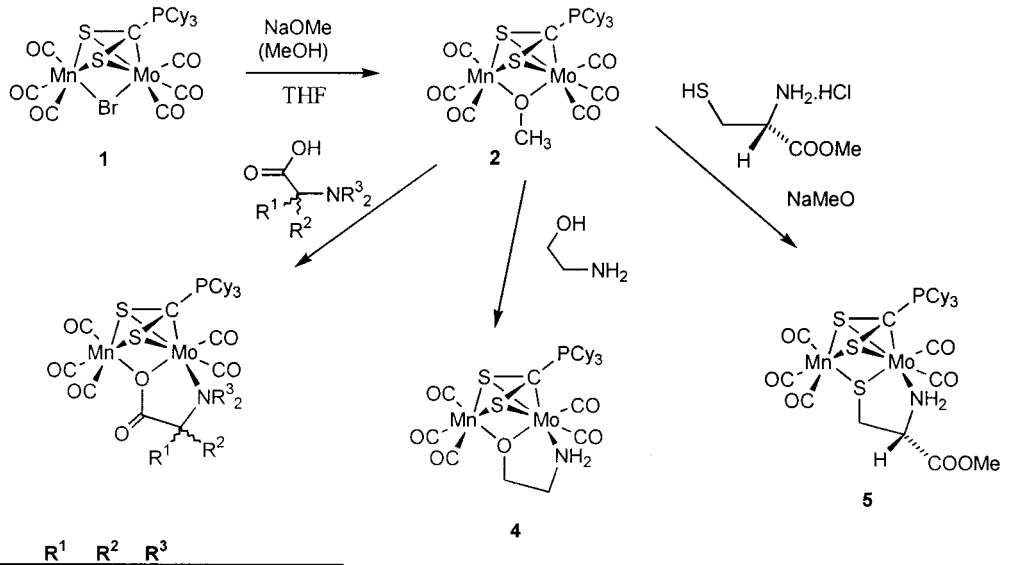
10.1021/om020180g CCC: $22.00 
Publication on Web 06/13/2002

**Scheme 1**




| | $R^1$ | $R^2$ | $R^3$ | |
|---|---|---|---|---|
| **3a** | H | H | H | glycine |
| **3b** | H | Me | H | alanine |
| **3c** | H | Ph | H | phenylglycine |
| **3d** | H | Bz | H | phenylalanine |
| **3e** | Me | Me | H | aminoisobutyric acid |
| **3f** | H | H | Me | N,N-dimethylglycine |



materials for the synthesis of new derivatives.[7] In this paper, we wish to report the easy replacement of the halide bridge by methoxide and the use of the resulting methoxo complex to obtain a family of compounds containing amino acidato and other related ligands as bridges in a heterobimetallic Mn/Mo system.

## Results and Discussion

When a solution of $[MnMo(CO)_6(\mu\text{-}Br)(\mu\text{-}S_2CPCy_3)]$ (**1**) in dichloromethane is mixed with a methanol solution of NaOMe, the color of the reaction mixture changes from red-brown to deep green, and the successive IR spectra in solution show a new set of five bands in the $\nu$(CO) region which are shifted to lower frequencies when compared to those of the starting **1**.

Analytical and spectroscopic data obtained for **2** (see Experimental Section) are consistent with its formulation as a methoxide-bridged complex, as presented in Scheme 1, and this has been confirmed by an X-ray determination. Crystal data and refinement details are given in Table 1, a perspective view is presented in Figure 1, and selected bond lengths and angles are collected in Table 2. The clean substitution of bromide by methoxide that yielded **2** came not without surprise, given that the reaction of **1** with phosphines was found to afford products of CO substitution.[7] Moreover, attack of anionic nucleophiles at the central carbon of $S_2CPR_3$ is a well-known reaction.[7] If the reaction mixture is stirred with an excess of sodium methoxide, significant decomposition of **2** can be observed. A careful monitoring by IR spectroscopy is thus necessary to detect the final point of the reaction and quickly isolate the product, as described in the Experimental Section.

(7) See: Galindo, A.; Miguel, D.; Pérez, J. *Coord. Chem. Rev.* **1999**, *193−195*, 643 and references therein.

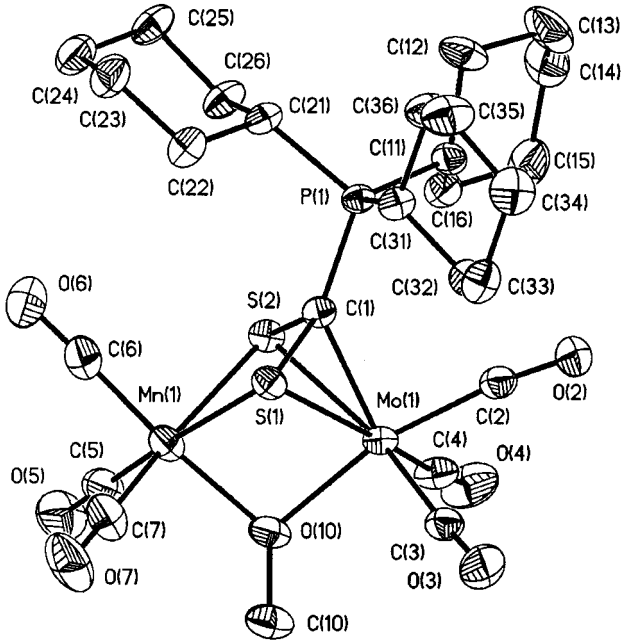



**Figure 1.** Perspective view of the molecule of $[MnMo(CO)_6(\mu\text{-}S_2CPCy_3)(\mu\text{-}OCH_3)]$ (**2**), showing the atom numbering.

The overall structure of **2** is reminiscent of that of the starting bromo complex **1**, having an approximate $C_s$ symmetry with all atoms positioned in a fairly symmetrical arrangement on both sides of the plane defined by Mn, Mo, C(1), and O(10). The methoxide group acts as a symmetric bridge between the two metals, the distances Mo(1)−O(10) = 2.142(2) Å and Mn(1)−O(10) = 2.042(4) Å reflecting the larger covalent radius of Mo as compared to Mn. The intermetallic Mo···Mn distance of 3.149(1) Å is slightly shorter than that observed for the starting bromo complex **1**, both being close to those

**Table 1. Crystal Data and Refinement Details for [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-OCH$_3$)] (2), [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)C(CH$_2$)$_2$NH$_2$}] (3e), and [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OCH$_2$CH$_2$NH$_2$}] (4)**

| | 2 | 3e | 4 |
|---|---|---|---|
| formula | $C_{26}H_{36}MnMoO_7PS_2$ | $C_{28}H_{41}MnMoNO_7PS_2 \cdot 0.25CH_2Cl_2$ | $C_{30}H_{41}MnMoNO_6PS_2$ |
| fw | 706.32 | 770.82 | 792.51 |
| cryst syst | triclinic | monoclinic | orthorhombic |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P2_12_12_1$ (No. 19) |
| *a*, Å | 10.4330(1) | 15.505(4) | 9.829(1) |
| *b*, Å | 10.760(1) | 20.234(5) | 12.895(2) |
| *c*, Å | 14.424(2) | 11.910(3) | 26.883(4) |
| α, deg | 78.61(1) | 90 | 90 |
| *β*, deg | 88.48(1) | 102.18(1) | 90 |
| *γ*, deg | 77.34(1) | 90 | 90 |
| V, Å$^3$ | 1548.6(3) | 3652(2) | 3407.5(8) |
| *Z* | 2 | 4 | 4 |
| *T*, K | 296 | 296 | 296 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.52 | 1.40 | 1.56 |
| *F*(000) | 724 | 1586 | 1624 |
| $\lambda$(Mo Kα), Å | 0.710 73 | 0.710 73 | 0.710 73 |
| cryst size, mm; color | 0.4 × 0.3 × 0.15; deep green | 0.2 × 0.04 × 0.02; green brown | 0.32 × 0.12 × 0.10; red-brown |
| $\mu$, mm$^{-1}$ | 1.039 | 0.923 | 1.104 |
| scan range, deg | $2 \le \theta \le 23.3$ | $1.34 \le \theta \le 23.36$ | $1.51 \le \theta \le 23.27$ |
| abs cor | SADABS | SADABS | SADABS |
| cor factors (min, max) | 1.000, 0.807 | 1.000, 0.708 | 1.000, 0.789 |
| no. of measd rflns | 6943 | 15951 | 15761 |
| no. of indep rflns | 4352 | 5274 | 4888 |
| no. of obsd rflns, $I \ge 2\sigma(I)$ | 3670 | 1779 | 4471 |
| GOF on $F^2$ | 1.154 | 0.805 | 0.915 |
| no. of params | 344 | 396 | 370 |
| residuals R1, wR2 | 0.0398, 0.0973 | 0.0601, 0.1062 | 0.0317, 0.0773 |

**Table 2. Selected Interatomic Distances (Å) and Angles (deg) in [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$}($\mu$-OCH$_3$)] (2)**

| | | | |
|---|---|---|---|
| Mn(1)−S(2) | 2.428(2) | S(1)−C(1) | 1.779(5) |
| Mo(1)−S(1) | 2.533(1) | C(2)−O(2) | 1.174(7) |
| Mo(1)−C(3) | 2.012(6) | C(5)−O(5) | 1.156(7) |
| Mn(1)−C(6) | 1.774(8) | C(10)−O(10) | 1.385(7) |
| Mn(1)−O(10) | 2.042(4) | Mo(1)−S(2) | 2.511(1) |
| C(1)−P(1) | 1.806(5) | Mo(1)−C(2) | 1.943(6) |
| C(4)−O(4) | 1.134(7) | Mn(1)−C(5) | 1.800(7) |
| C(7)−O(7) | 1.138(8) | Mo(1)−O(10) | 2.142(4) |
| Mn(1)−S(1) | 2.435(2) | S(2)−C(1) | 1.772(5) |
| Mo(1)−C(1) | 2.148(5) | C(3)−O(3) | 1.140(7) |
| Mo(1)−C(4) | 2.015(7) | C(6)−O(6) | 1.164(8) |
| Mn(1)−C(7) | 1.808(8) | Mo(1)···Mn(1) | 3.149(1) |
| Mn(1)−O(10)−Mo(1) | 97.59(15) | C(2)−Mo(1)−S(1) | 112.06(17) |
| C(3)−Mo(1)−S(1) | 94.21(18) | C(4)−Mo(1)−S(1) | 161.53(18) |
| O(10)−Mo(1)−S(1) | 80.35(12) | S(2)−Mo(1)−S(1) | 69.68(4) |
| C(2)−Mo(1)−S(2) | 111.21(16) | C(3)−Mo(1)−S(2) | 163.32(18) |
| C(4)−Mo(1)−S(2) | 92.77(18) | O(10)−Mo(1)−S(2) | 78.91(11) |
| C(2)−Mo(1)−O(10) | 165.84(19) | C(3)−Mo(1)−O(10) | 94.57(19) |
| C(4)−Mo(1)−O(10) | 90.9(2) | C(3)−Mo(1)−C(1) | 126.0(2) |
| C(4)−Mo(1)−C(1) | 125.7(2) | O(10)−Mo(1)−C(1) | 105.73(17) |
| C(6)−Mn(1)−O(10) | 173.0(2) | C(7)−Mn(1)−S(2) | 167.2(2) |
| O(10)−Mn(1)−S(2) | 82.82(11) | C(5)−Mn(1)−S(1) | 172.6(2) |
| S(2)−C(1)−S(1) | 108.5(3) | O(2)−C(2)−Mo(1) | 172.2(5) |
| O(3)−C(3)−Mo(1) | 175.3(5) | O(4)−C(4)−Mo(1) | 175.2(5) |
| O(5)−C(5)−Mn(1) | 179.4(6) | O(6)−C(6)−Mn(1) | 175.5(6) |
| O(7)−C(7)−Mn(1) | 178.6(8) | C(10)−O(10)−Mn(1) | 122.6(4) |
| C(10)−O(10)−Mo(1) | 122.7(4) | | |

observed in complexes in which a direct Mn−Mo bond is assumed.[8] However, since both the bridging bromide (in **1**) and methoxo group (in **2**) donate three electrons, a direct bond between the two metals is not required for an 18-electron count at each metal center. Although many alkoxo complexes are known, the structure of **2** is among the first examples containing alkoxo bridges between Mn and Mo. The only precedents available for comparison are the mixed carbonyl/oxide polymetallic [*n*Bu$_4$N][Mo$_2$O$_5$(OMe)$_5${Mn(CO)$_3$}$_2$], [Mo$_2$O$_4$(OMe)$_6${Mn(CO)$_3$}$_2$], and related complexes.[9]

Methoxide complex **2** has proven to be a very useful starting material to obtain new derivatives by displacement reactions with substances containing active hydrogen atoms. Thus, reaction of **2** with different amino acids leads to the elimination of methanol and the introduction of an amino acidato ligand to give complexes [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$-OC(O)CR$^1$R$^2$NR$^3_2$}] (**3a**−**f**), as shown in Scheme 1. The spectroscopic features of complexes **3a**−**f** (see Experimental Section) are consistent with their formulation as pentacarbonyl complexes in which, besides the substitution of the methoxide by the carboxylate oxygen in the bridging position, the amino function has displaced one CO ligand on the molybdenum atom, and this has been confirmed by an X-ray determination for compound **3e** (see below). IR monitoring of the reaction shows the emergence of a set of bands for the final complex and the simultaneous disappearance of those of the starting methoxide. The possible hexacarbonyl intermediate containing the amino acidato bonded as a bridge through oxygen, with the amino function uncoordinated, has not been detected.

An X-ray determination was carried out on a crystal of **3e** containing a nonchiral aminoisobutyrato ligand. Crystal and refinement data are presented in Table 1, a perspective view is given in Figure 2, and selected distances and angles are collected in Table 3.

As in the structure of the parent methoxide **2**, the bridging oxygen atom is placed in a fairly symmetrical position between the two metals, taking into account the different sizes of Mo and Mn (distances Mn(1)−O(1) = 2.117(7) Å and Mo(1)−O(1) = 2.195(7) Å). Again, the electron counting does not require the existence of a

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(9) Villanneau, R.; Delmont, R.; Proust, A.; Gouzerh, P. *Chem. Eur. J.* **2000**, *6*, 1184.

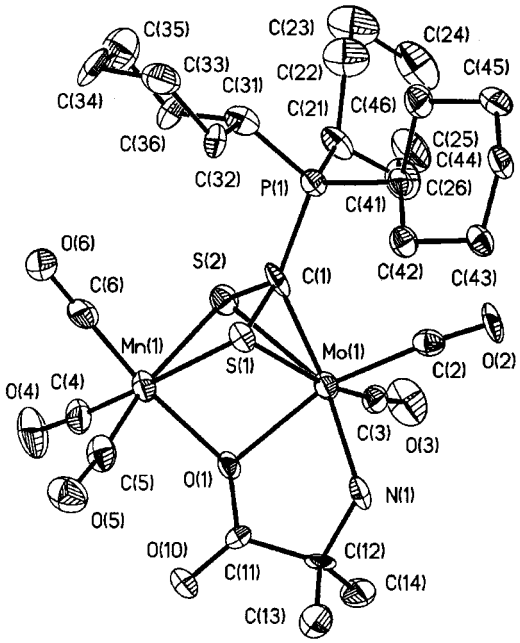


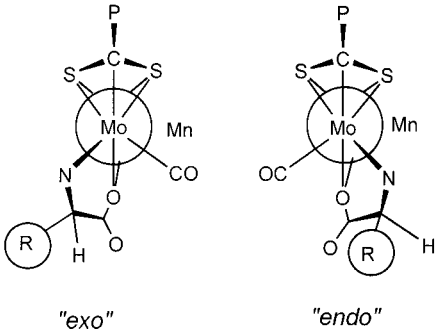

**Figure 2.** Perspective view of the molecule of [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)C(CH$_3$)$_2$NH$_2$}] (**3e**), showing the atom numbering.

**Table 3. Selected Interatomic Distances (Å) and Angles (deg) in [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$)-{$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)C(CH$_2$)$_2$NH$_2$}] (3e)**

| | | | |
|---|---|---|---|
| Mo(1)−S(1) | 2.479(3) | S(1)−C(1) | 1.725(9) |
| Mn(1)−S(2) | 2.439(3) | O(1)−C(11) | 1.292(11) |
| Mn(1)−O(1) | 2.117(7) | C(4)−O(4) | 1.134(11) |
| Mo(1)−C(3) | 1.959(12) | Mn(1)···Mo(1) | 3.205(2) |
| Mn(1)−C(6) | 1.732(14) | Mn(1)−S(1) | 2.428(4) |
| N(1)−C(12) | 1.475(12) | Mo(1)−N(1) | 2.184(8) |
| C(3)−O(3) | 1.156(12) | Mo(1)−C(2) | 1.941(12) |
| C(6)−O(6) | 1.179(12) | Mn(1)−C(5) | 1.771(14) |
| Mo(1)−S(2) | 2.576(3) | S(2)−C(1) | 1.821(10) |
| Mo(1)−C(1) | 2.100(11) | C(2)−O(2) | 1.172(11) |
| Mo(1)−O(1) | 2.195(7) | C(5)−O(5) | 1.182(13) |
| Mn(1)−C(4) | 1.840(12) | | |
| C(6)−Mn(1)−O(1) | 173.2(5) | C(5)−Mn(1)−S(1) | 169.4(4) |
| C(4)−Mn(1)−S(1) | 97.9(4) | O(1)−Mn(1)−S(1) | 81.4(2) |
| C(6)−Mn(1)−S(2) | 90.3(4) | C(5)−Mn(1)−S(2) | 98.0(4) |
| C(4)−Mn(1)−S(2) | 170.9(4) | O(1)−Mn(1)−S(2) | 84.76(18) |
| S(1)−Mn(1)−S(2) | 73.18(11) | C(3)−Mo(1)−C(1) | 121.1(4) |
| C(2)−Mo(1)−N(1) | 92.0(4) | C(3)−Mo(1)−N(1) | 100.4(4) |
| C(1)−Mo(1)−N(1) | 137.6(3) | C(2)−Mo(1)−O(1) | 163.0(4) |
| C(3)−Mo(1)−O(1) | 101.2(4) | C(1)−Mo(1)−O(1) | 105.3(3) |
| N(1)−Mo(1)−O(1) | 72.5(3) | C(2)−Mo(1)−S(1) | 117.6(3) |
| C(3)−Mo(1)−S(1) | 94.3(3) | N(1)−Mo(1)−S(1) | 149.7(2) |
| O(1)−Mo(1)−S(1) | 78.8(2) | C(2)−Mo(1)−S(2) | 108.9(3) |
| C(3)−Mo(1)−S(2) | 163.9(3) | N(1)−Mo(1)−S(2) | 95.3(2) |
| O(1)−Mo(1)−S(2) | 79.99(19) | S(1)−Mo(1)−S(2) | 70.03(10) |
| C(11)−O(1)−Mn(1) | 130.6(7) | C(11)−O(1)−Mo(1) | 119.8(7) |
| Mn(1)−O(1)−Mo(1) | 96.0(3) | S(1)−C(1)−S(2) | 109.8(5) |
| O(3)−C(3)−Mo(1) | 175.1(11) | O(4)−C(4)−Mn(1) | 173.0(13) |
| O(5)−C(5)−Mn(1) | 174.3(13) | O(6)−C(6)−Mn(1) | 176.3(13) |
| O(10)−C(11)−O(1) | 121.6(11) | O(10)−C(11)−C(12) | 122.6(11) |
| O(1)−C(11)−C(12) | 115.8(11) | N(1)−C(12)−C(11) | 106.5(9) |

direct Mn−Mo bond, and the intermetallic distance of 3.205(2) Å is slightly longer than in **2**. The coordination of the NH$_2$ group, replacing one carbonyl, closes a five-membered chelate ring at the Mo atom and breaks the effective $C_s$ symmetry found in the parent **2**. In this way the amino acidato ligand acts as a $\mu$(O)-$\eta^2$(O,N) bridge, which, as mentioned above, is unprecedented in organometallic heterobinuclear complexes. The asymmetry introduced by the chelate ring explains some features

**Chart 1**




of the NMR spectra in solution. For those complexes in which the amino acidato ligand is chiral (alaninato, **3b**; phenyl glycinato, **3c**; phenyl alaninato, **3d**), the $^{31}$P{$^1$H} NMR spectra display two signals at very close frequencies, while only one peak is observed for those containing nonchiral amino acidato (glycinato, **3a**; aminoisobutyrato, **3e**; *N*,*N*-dimethylglycinato, **3f**). This can be explained by taking into account the two possible sites for carbonyl replacement in the second step of the reaction. In the case of nonchiral amino acids this leads to a pair of enantiomers. In contrast, when a chiral amino acid is employed, two diastereomers arise, depending on the orientation ("endo" or "exo") of the bulky (non-H) group on the α-carbon, as summarized in Chart 1. Unfortunately, despite repeated attempts, it has not been possible to separate the two diastereoisomers or to induce the selective formation of one of them by changing the reaction conditions. As estimated from NMR spectra of the crude reaction mixtures, the isomer ratio varies significantly from alanine (90/10, R = Me) to phenylglycine (60/40, R = Ph) and phenylalanine (55/45, R = Bz), following the increasing size of the substituent on the α-carbon. This behavior is somewhat counterintuitive, since it would be expected that the smallest substituent (Me in alanine) would have the smallest effect, thus leading to a distribution closest to 50/50. In any case, several factors might be involved, and additional work is in progress to ascertain this point. Due to the presence of the mixture of isomers, it is difficult to obtain crystalline samples for the complexes containing chiral amino acidato ligands.

A preliminary exploration of the reactivity of complexes **3a**−**f** has shown that the amino acidato ligand can be deprotonated reversibly on the nitrogen atom. Thus, reaction of **3e** with LiBu$^n$ in THF shows the formation of an anionic species, according to IR monitoring ($\nu$(CO) 1995 s, 1984 s, 1880 vs, 1765 s, 1605 m, vs 2001 s, 1935 s, 1898 vs, 1789 s, 1691 m cm$^{-1}$ for the parent **3e**). Subsequent addition of trifluoroacetic acid gives back the starting compound **3b**. Since no reaction is observed when LiBu$^n$ is added to complex **3f** (bearing two methyl groups and no proton at the N atom), it can be concluded that the deprotonation is produced at the N atom, not at the α-carbon of the ligand. Further work is now in progress attempting to exploit this reactivity in the formation of a peptidic bond.

The synthetic potential of the methoxide complex **2** is further demonstrated by the reaction with ethanolamine to afford [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OCH$_2$CH$_2$NH$_2$}] (**4**) after deprotonation of ethanolamine and liberation of methanol. Complex **4** was character-

**Table 4. Selected Interatomic Distances (Å) and Angles (deg) in [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$)-{$\mu$(*O*)-$\eta^2$(*O*,*N*)-OCH$_2$CH$_2$NH$_2$}] (4)**

| | | | |
|---|---|---|---|
| Mn(1)−S(2) | 2.4034(14) | S(1)−C(1) | 1.800(4) |
| Mo(1)−S(2) | 2.4714(12) | N(1)−C(11) | 1.481(6) |
| Mo(1)−O(1) | 2.182(3) | C(3)−O(3) | 1.162(6) |
| Mo(1)−C(3) | 1.948(5) | C(6)−O(6) | 1.152(6) |
| Mn(1)−C(6) | 1.801(6) | Mo(1)−S(1) | 2.595(1) |
| O(1)−C(10) | 1.420(5) | Mn(1)−O(1) | 2.084(3) |
| C(2)−O(2) | 1.150(6) | Mo(1)−C(2) | 1.948(5) |
| C(5)−O(5) | 1.152(6) | Mn(1)−C(5) | 1.777(6) |
| Mn(1)−S(1) | 2.4246(15) | S(2)−C(1) | 1.774(5) |
| Mo(1)−C(1) | 2.128(4) | C(10)−C(11) | 1.485(7) |
| Mo(1)−N(1) | 2.221(4) | C(4)−O(4) | 1.160(6) |
| Mn(1)−C(4) | 1.790(6) | Mn(1)···Mo(1) | 3.182(1) |
| C(5)−Mn(1)−O(1) | 174.00(19) | C(6)−Mn(1)−S(2) | 169.47(18) |
| O(1)−Mn(1)−S(2) | 82.76(8) | C(4)−Mn(1)−S(1) | 172.60(17) |
| S(2)−Mn(1)−S(1) | 73.64(4) | C(3)−Mo(1)−O(1) | 162.41(16) |
| C(1)−Mo(1)−O(1) | 105.37(14) | C(2)−Mo(1)−N(1) | 103.78(18) |
| C(1)−Mo(1)−N(1) | 133.55(16) | O(1)−Mo(1)−N(1) | 76.97(13) |
| C(3)−Mo(1)−S(2) | 116.60(14) | O(1)−Mo(1)−S(2) | 79.25(8) |
| N(1)−Mo(1)−S(2) | 153.65(10) | C(3)−Mo(1)−S(1) | 113.01(15) |
| C(2)−Mo(1)−S(1) | 160.72(15) | O(1)−Mo(1)−S(1) | 78.68(9) |
| N(1)−Mo(1)−S(1) | 94.58(10) | S(2)−Mo(1)−S(1) | 69.60(4) |
| C(1)−S(1)−Mn(1) | 88.46(16) | C(1)−S(1)−Mo(1) | 54.33(13) |
| C(11)−N(1)−Mo(1) | 107.0(3) | S(2)−C(1)−S(1) | 108.1(2) |
| C(10)−O(1)−Mn(1) | 119.9(3) | C(10)−O(1)−Mo(1) | 112.3(2) |
| Mn(1)−O(1)−Mo(1) | 96.47(12) | O(2)−C(2)−Mo(1) | 174.1(5) |
| O(3)−C(3)−Mo(1) | 171.8(4) | O(4)−C(4)−Mn(1) | 177.3(5) |
| O(5)−C(5)−Mn(1) | 177.2(6) | O(6)−C(6)−Mn(1) | 176.2(5) |
| O(1)−C(10)−C(11) | 109.6(4) | N(1)−C(11)−C(10) | 107.2(4) |

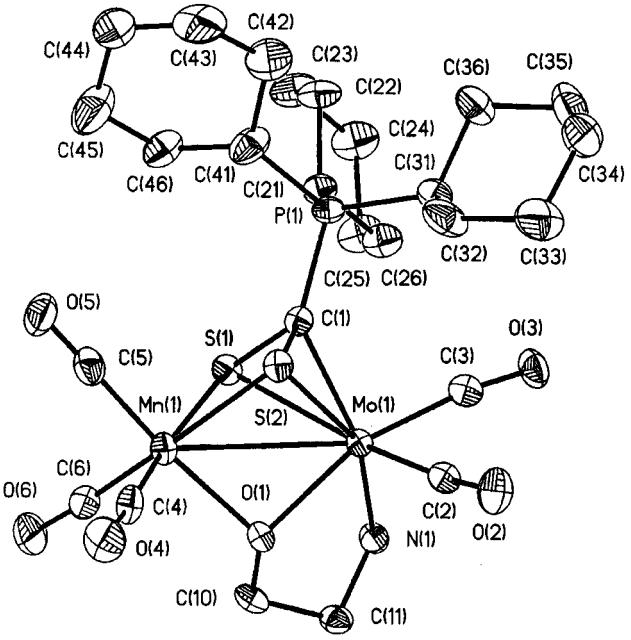



**Figure 3.** Perspective view of the molecule of [MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OCH$_2$CH$_2$NH$_2$}] (**4**), showing the atom numbering.

ized by analytical and spectroscopic methods (see the Experimental Section), and an X-ray determination was carried out to confirm the structure of **4** containing an alkoxo−amino ligand. Relevant data are given in Table 1, and selected distances and angles are summarized in Table 4.

The structure of **4** (see perspective view in Figure 3) is closely related to that of the amino acidato species **3b** discussed above. All three distances in the Mn−O−Mo triangle of **4** are intermediate between those found in the methoxide complex **2** (shorter) and those of the amino acidato **3e** (longer). This can be related to the donor ability of the oxygen atom in the sequence methoxide > ethanolamine > amino acidato. This sequence is confirmed in part by the direct comparison of the $\nu$(CO) bands for the two pentacarbonyls: those of the aminoisobutyric complex **3e** are 8−22 cm$^{-1}$ higher than those of **4**.

There are 42 structures deposited in the Cambridge Structural Database (CSD) containing alkoxoamino bridges. Most of them are polynuclear homometallic complexes. The only one which can be referred to as organometallic is a diiron tetracarbonyl complex containing in fact the bis(alkoxo)−bis(imine) ligand 1,4-bis(*tert*-butylimino)-2,3-dimethylbutane-2,3-diolato ligand.[10] On the other hand, the only related precedent containing an alkoxo−amino bridge in a heterometallic system is [BaCu$_4$(bdmap)$_4$(pyO)$_4$(CF$_3$COO)], in which the 1,3-bis(dimethylamino)-2-propanolato (bdmap) ligand acts as a $\mu_3$(O) bridge bonding two Cu atoms and one Ba atom.[11]

The reaction of the methoxide **2** with cysteine gave a mixture from which we could not isolate any pure compound. However, when **2** is stirred with L-cysteine methyl ester hydrochloride, in the presence of 1 mol equiv of NaOMe, it is possible to isolate [MnMo(CO)$_6$-($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*S*,*N*)-SCH$_2$CH(COOCH$_3$)NH$_2$}] (**5** in Scheme 1), which has been characterized by analytical and spectroscopic methods. In this case the spectroscopic evidence is consistent with the presence of the deprotonated S atom bonded as a bridge between Mn and Mo, while the amino function displaces one carbonyl, closing a chelate ring at the Mo atom, as occurred in the formation of complexes **3**. As with with complexes **3b**,**c** containing chiral amino acidato ligands, the two possible sites of CO substitution at the Mo atom produce two diastereoisomers, depending on the orientation of the pendant group, in this case COOMe, at the chiral carbon. $^1$H, $^{31}$P, and $^{13}$C NMR solution spectra (see the Experimental Section) both of the crude reaction mixture and of the isolated product show the presence of the two diastereoisomers in a ratio close to 50/50.

## Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of the instrumentation and experimental procedures have been given elsewhere.[12] Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

**[MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-OCH$_3$)] (2).** To a solution of [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-Br)] (**1**; 0.5 g, 0.662 mmol) in CH$_2$Cl$_2$ (40 mL) was added a solution of sodium methoxide (9 mL of 0.1 M in MeOH, 0.9 mmol). The mixture was stirred for 10 min, after which the color changes from red-brown to bright green. The end of the reaction was checked by IR monitoring. The solvents were evaporated in vacuo, the residue was redissolved in CH$_2$Cl$_2$, and the solution was filtered through a column of alumina (activity III, 10 × 2.5 cm). The filtrate was concentrated in vacuo to afford compound **2** as a bright green solid. Yield: 0.369 g, 79%. Anal. Calcd for C$_{26}$H$_{36}$MnMoO$_7$PS$_2$: C, 44.20; H, 5.14. Found: C, 44.01; H, 4.95. IR

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(THF): $\nu$(CO) 2025 m, 2002 vs, 1930 s, 1906 m, 1844 m cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 3.71 (s, 3H, OC$H_3$), 2.56 (m, 3H, C$^1H$ of Cy), 2.1−1.2 (m, 33 H, *Cy*). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 35.51(s, SC*P*). $^{13}$C{$^1$H} NMR (acetone-$d_6$): $\delta$ 244.0 (d(5), 2 × Mo*C*O), 221.6 (s, Mo*C*O), 219.18 (m(br), 3 × Mn*C*O), 102.8 (d(37), S*C*P), 69.7 (s, O$CH_3$), 34.1 (d(39), $C^1$ of Cy), 28.3 (s, $C^2$ and $C^6$ of Cy), 27.6 (d(12), $C^3$ and $C^5$ of Cy), 26.3 (s, $C^4$ of Cy).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH$_2$NH$_2$}] (3a).** A mixture of glycine (0.019 g, 0.254 mmol) and MeOH (15 mL) was refluxed for 1 h. The resulting suspension was added to a solution of the methoxo complex **2** (0.15 g, 0.212 mmol) in dichloromethane (20 mL), and the mixture was stirred in the dark for 8 h. After evaporation of the solvents, the residue was dissolved in $CH_2Cl_2$ and chromatographed on a silica column (10 × 2.5 cm). Elution with $CH_2Cl_2$ gave a red band, which was discarded. Further elution with THF/hexane (1:1) gave a reddish yellow band which, after evaporation of the solvents in vacuo, gave **3a** as a microcrystalline green-brown solid. Yield: 0.069 g, 46%. Anal. Calcd for $C_{26}H_{37}MnMoNO_7PS_2$·$CH_2Cl_2$: C, 40.21; H, 4.87; N, 1.74. Found: C, 40.46; H, 5.01; N, 1.57. IR (THF): $\nu$(CO) 2021 m, 1934 m, 1900 vs, 1790 m 1697 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): $\delta$ 5.03 (m(br), 1H, N$H_2$), 4.25 (m(br), 1H, N$H_2$), 2.87 (s, 2H, CC$H_2$NH$_2$), 2.36−1.42 (m, 33H, Cy).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH(CH$_3$)NH$_2$}] (3b).** Compound **3b** was obtained as described above for **3a**, starting from L-alanine (0.023 g, 0.254 mmol) and **2** (0.15 g, 0.212 mmol). Yield: 0.066 g, 42% (isomer ratio 80/20). Anal. Calcd for $C_{27}H_{39}MnMoNO_7PS_2$: C, 44.09; H, 5.34; N, 1.90. Found: C, 44.26; H, 5.39; N, 1.92. IR (THF): $\nu$(CO) 2021 m, 1934 m, 1899 vs, 1789 m, 1694 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): isomer ratio M(ajor)/m(inor) = 85/15; $\delta$ 5.78 (M) and 5.28 (m) (m(br), 1H, N$H_2$), 4.80 (M + m) (m(br), 1H, N$H_2$), 3.47 (M + m) (m, 1H, C$H$(CH$_3$)NH$_2$), 2.72 (m, 3H, C$^1H$ of Cy), 1.62 (m) and 1.48 (M) (d(7), 3H, CH(C$H_3$)NH$_2$), 2.3 (m, 30H, C$H_2$ of Cy). $^{31}$P{$^1$H} NMR ($CH_2Cl_2$/acetone-$d_6$ cap): $\delta$ 35.31 (M), 35.29 (m).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH(C$_6$H$_5$)NH$_2$}] (3c).** Compound **3c** was obtained as described above for **3a**, starting from L-phenylglycine (0.038 g, 0.254 mmol) and **2** (0.15 g, 0.212 mmol). Yield 0.075 g, 45%. Anal. Calcd for $C_{32}H_{41}MnMoNO_7PS_2$·$0.5CH_2Cl_2PS_2$: C, 46.46; H, 5.04; N, 1.67. Found: C, 46.68; H, 4.94; N, 1.69. IR (THF): $\nu$(CO) 2021 m, 1935 m, 1900 vs, 1791 m 1698 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): isomer ratio M(ajor)/m(inor) = 60/40; $\delta$ 7.62−7.34 (M + m) (3 × m, 10H, Ph), 6.22 (M) and 5.74 (m) (m(br), 1H, N$H_2$), 5.51 (m) and 5.24 (M) (m(br), 1H, N$H_2$), 4.60 (M) and 4.53 (m) (m(br), 1H, C$H$(Ph)NH$_2$), 2.74 (M + m) (m, 3H, C$^1H$ of Cy), 2.2 to 1.3 (M + m) (m, 30H, C$H_2$ of Cy). $^{31}$P{$^1$H} NMR ($CH_2Cl_2$/acetone-$d_6$ cap): $\delta$ 36.73 (M), 36.65 (m).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH(CH$_2$C$_6$H$_5$)NH$_2$}] (3d).** Compound **3d** was obtained as described above for **3a**, starting from L-phenylalanine (0.042 g, 0.254 mmol) and **2** (0.15 g, 0.212 mmol). Yield: 0.113 g, 65%. Anal. Calcd for $C_{33}H_{44}MnMoNO_7PS_2$·$0.5CH_2Cl_2$: C, 47.11; H, 5.19; N, 1.64. Found: C, 47.34; H, 5.20; N, 1.79. IR (THF): $\nu$(CO) 2021 m, 1935 m, 1900 vs, 1791 m, 1694 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): isomer ratio M(ajor)/m(inor) = 55/45; $\delta$ 7.51−7.32 (M + m) (3 × m, 10H, Ph), 5.69 (M) and 5.32 (m) (m(br), 1H, N$H_2$), 4.65 (m) and 4.51 (M) (m(br), 1H, N$H_2$), 3.6 to 2.8 (M + m) (m(br), 1H, C$H_2$(Ph)NH$_2$), 2.71 (M + m) (m, 3H, C$^1H$ of Cy), 2.2 to 1.3 (M + m) (m, 30H, C$H_2$ of Cy). $^{31}$P{$^1$H} NMR ($CH_2Cl_2$/acetone-$d_6$ cap): $\delta$ 35.63 (M), 35.57 (m).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH(CH$_3$)$_2$NH$_2$}] (3e).** Compound **3e** was obtained as described above for **3a**, starting from 2-aminoisobutyric acid (0.044 g, 0.425 mmol) and **2** (0.25 g, 0.354 mmol). Yield: 0.111 g, 42%. Anal. Calcd for $C_{28}H_{41}MnMoNO_7PS_2$·$0.25CH_2Cl_2$: C, 44.02; H, 5.43; N, 1.82. Found: C, 43.79; H, 5.21; N, 1.67. IR (THF): $\nu$(CO) 2021 m, 1935 s, 1898 vs, 1789 s, 1691 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): $\delta$ 5.57 (d(10), 1H, N$H_2$), 4.90 (d(10), 1H, N$H_2$), 2.72 (m, 3H, C$^1H$ of Cy), 2.2−1.3 (m, 30H, C$H_2$ of Cy), 1.65 (s, 3H, C$H_3$), 1.50 (s, 3H, C$H_3$). $^{31}$P{$^1$H} NMR (acetone-$d_6$): $\delta$ 36.60. $^{13}$C{$^1$H} NMR (acetone-$d_6$): $\delta$ 237.1 (m, 2 × Mo*C*O), 219 (m, 3 × Mn*C*O), 182,3 (s, OO*C*), 101.2 (d(37), S$_2$*C*PCy$_3$), 55.3 (s, *C*NH$_2$), 34.2 (d(40), $C^1$ of Cy), 32.7 and 28.6 (2 × s, *C*H$_3$), 28.2 (s, $C^2$ and $C^6$ of Cy), 27.8 (d(12), $C^3$ and $C^5$ of Cy), 26.5 (s, $C^4$ of Cy).

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OC(O)CH$_2$N(CH$_3$)$_2$}] (3f).** Compound **3f** was obtained as described above for **3a**, starting from *N*,*N*-dimethylglycine (0.026 g, 0.254 mmol) and **2** (0.15 g, 0.212 mmol). Yield: 0.047 g, 30%. Anal. Calcd for $C_{28}H_{41}MnMoNO_7PS_2$: C, 44.86; H, 5.51; N, 1.87. Found: C, 44.53; H, 5.38; N, 1.72. IR (THF): $\nu$(CO) 2023 m, 1937 s, 1902 vs, 1794 s, 1702 w cm$^{-1}$. $^1$H NMR (acetone-$d_6$): $\delta$ 3.77 (d(14), 1H, C$H_2$NMe$_2$), 3.26 (s, 3H, NC$H_3$), 2.88 (d(14), 1H, C$H_2$NMe$_2$), 2.77 (m, 3H, C$^1H$ of Cy), 2.70 (s, 3H, NC$H_3$), 2.3−1.2 (m, 30H, C$H_2$ of Cy). $^{31}$P{$^1$H} NMR (acetone-$d_6$): $\delta$ 37.14.

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*O*,*N*)-OCH$_2$CH$_2$NH$_2$}] (4).** To a solution of [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-OCH$_3$)] (**2**; 0.253 g, 0.357 mmol) in $CH_2Cl_2$ (30 mL) was added ethanolamine (0.026 mL, 0.428 mmol). The mixture was stirred for 2 h at room temperature, and the solvents were evaporated in vacuo. The oily residue was dissolved in $CH_2Cl_2$ and chromatographed through a silica gel column (5 × 2.5 cm) packed with $CH_2Cl_2$. Elution with $CH_2Cl_2$ gave a pink band, which was discarded. Further elution with THF/hexane (1:1) gave an orange-brown band which, upon slow evaporation of the solvents, produced **4** as a brown microcrystalline powder. Yield: 0.121 g, 46%. Anal. Calcd for $C_{26}H_{39}MnMoNO_6PS_2$: C, 44.14; H, 5.56; N, 1.98. Found: C, 43.96; H, 5.34; N, 1.92. IR (THF): $\nu$(CO) 2008 m, 1913 s, 1890 vs, 1778 s cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 4.07 (m, 1H, N$H_2$), 3.57 (m, 1H, N$H_2$), 3.43 (m, 2H, OC$H_2$), 2.94 (m, 2H, OCH$_2$C$H_2$NH$_2$), 2.57 (m, 3H, C$^1H$ of Cy), 2.1 to 1.3 (m, 30H, C$H_2$ of Cy). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 34.60.

**[MnMo(CO)$_5$($\mu$-S$_2$CPCy$_3$){$\mu$(*O*)-$\eta^2$(*S*,*N*)-SCH$_2$CH(COOCH$_3$)NH$_2$}] (5).** To a solution of [MnMo(CO)$_6$($\mu$-S$_2$CPCy$_3$)($\mu$-OCH$_3$)] (**2**; 0.250 g, 0.354 mmol) in $CH_2Cl_2$ (30 mL) were added [HSCH$_2$CH(COOCH$_3$)NH$_3$]Cl (0.062 g, 0.361 mmol) and NaOMe (3.7 mL of a 0.1 M solution in MeOH, 0.37 mmol). The reaction was completed in a few minutes, and the solvents were evaporated in vacuo. The oily residue was dissolved in $CH_2Cl_2$/hexane (1:1) and chromatographed in alox (activity IV, 5 × 2.5 cm column, packed with hexane). Elution with $CH_2Cl_2$/hexane (1:1) gave first a purple band, which was discarded. Further elution gave a red-brown band containing compound **5**, which was isolated as a brown solid upon concentration in vacuo. Yield: 0.116 g, 41%. Anal. Calcd for $C_{28}H_{41}MnMoNO_7PS_3$: C, 43.02; H, 5.29; N, 1.79. Found: C, 43.21; H, 5.37; N, 1.62. IR (THF): $\nu$(CO) 2006 m, 1915 s, 1899 vs, 1794 s, 1746 s cm$^{-1}$. $^1$H NMR (acetone-$d_6$): isomer ratio A/B = 50/50; $\delta$ 5.49, 5.10, 4.99, 4.43 (4 × m, 4H, N$H_2$ (A + B)), 4.38 (pseudo t(12), 1H, C$H$NH$_2$ (A)), 3.77 and 3.76 (2 × s, 6H, C$H_3$ (A + B)), 3.43 (pseudo tt(8.6 and 4), 1H, C$H$NH$_2$ (B)), 3.3 to 2.3 (4 × m, 4H, C$H_2$ (A + B)), 2.85 and 2.83 (2 × m, 3H, C$^1H$ of Cy (A + B)), 2.2 to 1.3 (m, 30H, C$H_2$ of Cy (A + B)). $^{31}$P{$^1$H} NMR ($CH_2Cl_2$/acetone-$d_6$ cap): $\delta$ 37.31 and 37.05 (isomers A and B).

**X-ray Diffraction Study of 2, 3e, and 4.** Crystals were grown by slow difusion of hexane into concentrated solutions of the complexes in THF at −20 °C. Relevant crystallographic details are given in Table 1. A crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromated Mo K$\alpha$ X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to $2\theta$ = 48.6°. Raw frame data were integrated with the SAINT[13] program. The structure was solved by direct methods with SHELXTL.[14] A semiempirical absorption correction was applied with the program SADABS.[15] All non-

(13) SAINT+ SAX Area Detector Integration Program, version 6.02; Bruker AXS, Inc., Madison, WI, 1999.

hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. The absolute structure of **4** (orthorhombic, chiral space group $P2_12_12_1$) was deemed as correct according to the final value of 0.02(3) for the refined Flack parameter. All calculations and graphics were made with SHELXTL.

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**Acknowledgment.** We thank the Spanish DGICYT (PB97-0470-C02-01 and BQU2000-0220), JCyL (VA32/00B), and FICYT (PR-01-GE−4) for financial support and for an FPI grant to B.G.

**Supporting Information Available:** Complete tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the structures of **2**, **3e**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Lists of structure factor amplitudes are available from the authors.

OM020180G