

**Heterodinuclear Complexes Containing S<sub>2</sub>CPR<sub>3</sub> as  
Asymmetric Bridges between Cobalt and Metals of Group 7  
(Manganese, Rhenium) or Group 6 (Molybdenum,  
Tungsten): Selective Cobalt-Carbon Bond Formation.  
X-ray Structures of [MnCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] and  
[MoCo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)]·CH<sub>2</sub>Cl<sub>2</sub>**

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The reaction of [M(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (M = Mn, Re) with Co<sub>2</sub>(CO)<sub>8</sub> produces the heterobinuclear complexes [MCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] (2). An X-ray determination of the derivative with M = Mn, and R = Cy [2a, triclinic, space group P $\bar{1}$ , *a* = 11.074(3) Å, *b* = 11.156(3) Å, *c* = 11.769(3) Å, α = 74.64(1)°, β = 85.36(1)°, γ = 83.44(2)°, *Z* = 2, *R* = 0.042, *R<sub>w</sub>* = 0.043] showed the formation of a Mn-Co bond, and the presence of the S<sub>2</sub>CPR<sub>3</sub> ligand coordinated as a η<sup>2</sup>(S,S') chelate to Mn and as a η<sup>3</sup>(S,C,S') pseudoallyl to Co. The structure of 2a, and the spectroscopic data of all derivatives 2a-d indicate that the central carbon of the S<sub>2</sub>CPR<sub>3</sub> ligand shows a definite preference for attachment to cobalt rather than to manganese or rhenium and that the reaction produces specifically the compounds with the carbon bonded to the cobalt atom. Although the reactions could be considered as involving the disproportionation of Co<sub>2</sub>(CO)<sub>8</sub> into Co<sup>I</sup> and Co<sup>II</sup>, it is noticeable that the direct reaction of the starting [M(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] with Co(CO)<sub>4</sub><sup>-</sup> gives complexes 2 only for M = Re, but not for M = Mn. The method can be extended to prepare complexes containing Mo-Co and W-Co bonds. Thus, Co<sub>2</sub>(CO)<sub>8</sub> reacts with [M(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (3; M = Mo, W) to produce [MCo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] (4a-d) in moderate yields. An X-ray structure determination of the derivative with M = Mo, R = Cy [4a·CH<sub>2</sub>Cl<sub>2</sub>, triclinic, space group P $\bar{1}$ , *a* = 10.301(1) Å, *b* = 11.347(7) Å, *c* = 15.723(2) Å, α = 90.08(2)°, β = 102.46(4)°, γ = 112.84(1)°, *Z* = 2, *R* = 0.062, *R<sub>w</sub>* = 0.070] established the existence of a direct Mo-Co bond, and the presence of the S<sub>2</sub>CPCy<sub>3</sub> ligand bonded as η<sup>2</sup>(S,S') chelate to Mo and as a η<sup>3</sup>(S,C,S') pseudoallyl to Co, in the same fashion observed for the structure of the Mn-Co derivative 2a. Again there is a selective formation of a C-Co bond, which indicates a definite preference of the central carbon to bind cobalt rather than molybdenum. In this case, the formal oxidation states are Mo<sup>I</sup> and Co<sup>0</sup> and the preference observed is consistent with our previous observations, which can be rationalized assuming that the central carbon of S<sub>2</sub>CPR<sub>3</sub> prefers to bind the metal atom with the lower oxidation state. A common feature of the structures of 2a and 4a is the occurrence of a Co(CO)<sub>2</sub> fragment which is bonded to a MSCS' ring which donates formally 5 e. In this sense, the molecules of 2a and 4a are isoelectronic to CpCo(CO)<sub>2</sub>. Some geometric parameters of the structures of 2a and 4a compare well with those in CpCo(CO)<sub>2</sub>, suggesting that there is a close analogy between the two types of molecules.

### Introduction

The synthesis of complexes containing heteronuclear metal-metal bonds and the study of their reactivity are areas of continuing interest in organometallic chemistry.<sup>1,2</sup> It has been frequently found that the presence of one or more bridging ligands can help to keep the two metal atoms together, avoiding the fragmentation of the bimetallic unit, and thus permitting a wider range of reactivity studies. In this respect, diphosphines or diphosphites have been often

used as binucleating ligands.<sup>3</sup> We have recently reported synthetic ways to prepare homo and heterobinuclear complexes containing trialkylphosphine-carbon disulfide adducts, S<sub>2</sub>CPR<sub>3</sub>, as bridging ligands between two metals with or without a direct metal-metal interaction,<sup>4-8</sup> and we wish to report here the preparation of complexes containing Mn-Co, Re-Co, Mo-Co, or W-Co bonds. They

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constitute the first examples in which the  $S_2CPR_3$  ligand are coordinated as pseudoallyl to cobalt. It is remarkable that the reactions leading to the preparation of these heterobinuclear complexes involve the specific formation of a bond between cobalt and the central carbon of the  $S_2CPR_3$  ligand, which shows a definite preference to bind cobalt rather than manganese, rhenium, molybdenum, or tungsten.

There are only a few examples of complexes containing cobalt and a metal of group 7, namely the parent carbonyls  $[MCo(CO)_9]$  ( $M = Mn,^{9,10} Tc,^{11} Re^{10}$ ), the derivatives  $[MCo(CO)_5(\mu-CO)(\mu-DAB)]$  ( $M = Mn, Re$ ;  $DAB = PrN=CHCH=NPr$ ),<sup>12</sup> or  $[CpCo(\mu-NO)_2Mn(Cp)(PMe_3)]$ ,<sup>13</sup> and the recently reported dppm complexes  $[CoM(CO)_5(\mu-dppm)_2]$  ( $M = Mn, Re$ ).<sup>14</sup> On the other hand, while there are a fairly good number of tri- and polymetallic clusters<sup>15</sup> containing a Mo-Co or W-Co bonds, bimetallic complexes are much scarcer. Some examples are the heptacarbonyls  $[CpMCo(CO)_7]$  ( $M = Mo, W$ ),<sup>16</sup> their derivatives  $[CpMoCo(CO)_5(\mu-\eta^2-CF_3C\equiv CF_3)]$ ,<sup>17</sup> or  $[CpMCo(CO)_4(\mu-\eta^4-CPh=CPh-CPh=CPh)]$ ,<sup>18</sup> the complex with bridging hydride  $[Cp_2Mo(\mu-H)(\mu-CO)Co(CO)_3]$ ,<sup>19</sup> and complexes with bridging carbyne ligands such as  $[MCo(\mu-CC_6H_4Me-4)(CO)_2(\eta^4-C_4Me_4)(\eta^6-C_2B_{10}H_{10}Me_2)]$ .<sup>20</sup>

## Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of instrumentation and experimental procedures have been given elsewhere.<sup>7b</sup> 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.

**[MnCo(CO)<sub>5</sub>( $\mu$ -S<sub>2</sub>CPCy<sub>3</sub>)] (2a).**  $[Mn(CO)_3(S_2CPCy_3)Br]$  (**1a**; 0.43 g, 0.75 mmol)<sup>21</sup> and  $Co_2(CO)_8$  (0.19 g, 0.57 mmol) were dissolved in a mixture of  $CH_2Cl_2/THF$  (1:1, v/v; 50 mL), and the solution was stirred for 8 h. The solvent was evaporated in vacuo, and the residue was extracted with the minimum amount of  $CH_2Cl_2$ , and filtered. The filtrate was concentrated to ca. 5 mL. Addition of hexane gave compound **2a** as a red-brown solid, which was recrystallized from  $CH_2Cl_2$ /hexane. Yield: 0.36 g, 83% (based

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on the starting Mn compound). Anal. Calcd for  $C_{24}H_{33}CoMnO_5PS_2$ : C, 47.22; H, 5.45. Found: C, 46.91; H, 5.44.

**[MnCo(CO)<sub>5</sub>( $\mu$ -S<sub>2</sub>CPPr<sub>3</sub>)] (2b).** Compound **2b** was prepared by the same method as described for **2a** from  $[Mn(CO)_3(S_2CPPr_3)Br]$  (**1b**; 0.12 g, 0.25 mmol) and  $Co_2(CO)_8$  (0.07 g, 0.19 mmol). Yield: 0.08 g, 64%. Anal. Calcd for  $C_{15}H_{21}CoMnO_5PS_2$ : C, 36.75; H, 4.32. Found: C, 36.87; H, 4.49.

**[ReCo(CO)<sub>5</sub>( $\mu$ -S<sub>2</sub>CPCy<sub>3</sub>)] (2c).** **Method A.** A mixture of  $[Re(CO)_3(S_2CPCy_3)Br]$  (**1c**, 0.41 g, 0.58 mmol)<sup>4</sup> and  $Co_2(CO)_8$  (0.15 g, 0.44 mmol) in THF (50 mL) was stirred for 23 h. The solvent was evaporated to dryness in vacuo, and the residue redissolved in a mixture of  $CH_2Cl_2$ /hexane (3:2, v/v) and then filtered. Slow concentration in vacuo produced **2c** as a microcrystalline solid which was washed repeatedly with hexane until the hexane extract was colorless. Yield: 0.37 g, 86%. Anal. Calcd for  $C_{24}H_{33}CoO_5PReS_2$ : C, 38.86; H, 4.48. Found: C, 39.02; H, 4.63.

**Method B.** A solution of  $Na[Co(CO)_4]$  (ca. 0.29 mmol) in THF (20 mL) was prepared by stirring  $Co_2(CO)_8$  (0.05 g, 0.15 mmol) with sodium amalgam (1%, 2g, excess) for 30 min. This solution was transferred with a cannula onto solid  $[Re(CO)_3(S_2CPCy_3)Br]$ <sup>4</sup> (**1c**; 0.18 g, 0.25 mmol) and the mixture was refluxed for 1 h. The solvent was evaporated in vacuo, and the residue was extracted with the minimum amount of  $CH_2Cl_2$  and filtered. The filtrate was concentrated to ca. 5 mL. Addition of hexane (20 mL) gave compound **2c** as a red-brown solid, which was recrystallized from  $CH_2Cl_2$ /hexane. Yield: 0.10 g, 53%. Anal. Calcd for  $C_{24}H_{33}CoO_5PReS_2$ : C, 38.86; H, 4.48. Found: C, 38.64; H, 4.55.

**[ReCo(CO)<sub>5</sub>( $\mu$ -S<sub>2</sub>CPPr<sub>3</sub>)] (2d).** **Method A.** Compound **2d** was prepared as described above for **2a** from  $[Re(CO)_3(S_2CPPr_3)Br]$  (**1d**; 0.45 g, 0.77 mmol)<sup>4</sup> and  $Co_2(CO)_8$  (0.20 g, 0.57 mmol). Yield: 0.36 g, 76%. Anal. Calcd for  $C_{15}H_{21}CoO_5PReS_2$ : C, 28.99; H, 3.41. Found: C, 28.75; H, 3.36.

**Method B.** Compound **2d** was prepared by the same method as described for **2c** from  $Na[Co(CO)_4]$  (ca. 0.29 mmol) and  $[Re(CO)_3(S_2CPPr_3)Br]$  (**1d**; 0.15 g, 0.26 mmol).<sup>4</sup> Yield: 0.07 g, 46%. Anal. Calcd for  $C_{15}H_{21}CoO_5PReS_2$ : C, 28.99; H, 3.41. Found: C, 28.62; H, 3.48.

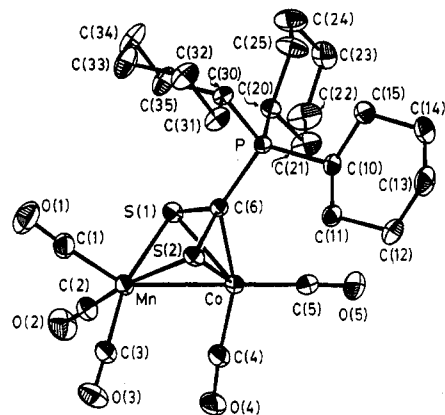
**[MoCo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>( $\mu$ -S<sub>2</sub>CPCy<sub>3</sub>)] (4a).** A mixture of  $Co_2(CO)_8$  (0.49 g, 1.42 mmol) and  $[Mo(\eta^3-C_3H_5)(CO)_2(S_2CPCy_3)Br]$  (**3a**, 1.19 g, 1.89 mmol)<sup>8</sup> in THF (40 mL) was stirred for 12 h. The solvent was evaporated in vacuo, and the residue was extracted with a mixture of  $CH_2Cl_2$ /hexane (1:1, 3 × 10 mL). The extracts were collected and filtered. Slow evaporation in vacuo gave compound **4a** as red-brown microcrystalline solid. Yield: 0.47 g, 33%. Anal. Calcd for  $C_{26}H_{38}CoMoO_4PS_2 \cdot CH_2Cl_2$ : C, 43.27; H, 5.38. Found: C, 43.52; H, 5.23.

**[MoCo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>( $\mu$ -S<sub>2</sub>CPPr<sub>3</sub>)] (4b).** Compound **4b** was prepared as described above for **4a**, from  $Co_2(CO)_8$  (0.49 g, 1.42 mmol) and  $[Mo(\eta^3-C_3H_5)(CO)_2(S_2CPPr_3)Br]$  (**3b**, 0.96 g, 1.89 mmol).<sup>8</sup> Yield: 0.21 g, 20%. Anal. Calcd for  $C_{17}H_{26}CoMoO_4PS_2$ : C, 37.51; H, 4.81. Found: C, 37.28; H, 4.73.

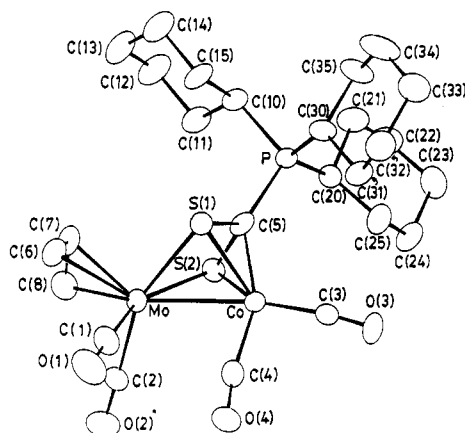
**[WCo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>( $\mu$ -S<sub>2</sub>CPCy<sub>3</sub>)] (4c).** Compound **4c** was prepared as described above for **4a**, from  $Co_2(CO)_8$  (0.25 g, 0.73 mmol) and  $[W(\eta^3-C_3H_5)(CO)_2(S_2CPCy_3)Br]$  (**3c**, 0.70 g, 0.98 mmol).<sup>8</sup> Yield: 0.30 g, 40%. Anal. Calcd for  $C_{26}H_{38}CoO_4PS_2W$ : C, 41.50; H, 5.09. Found: C, 41.37; H, 4.91. <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  3.97 [m, 1 H, CH of allyl], 3.00 [d (6), 2 H, H syn of allyl], 2.47 [m, 3 H, CH of Cy], 2.04–1.32 [m, 32 H, CH<sub>2</sub> of Cy and CH anti of allyl].

**[WCo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>( $\mu$ -S<sub>2</sub>CPPr<sub>3</sub>)] (4d).** Compound **4d** was prepared as described above for **4a**, from  $Co_2(CO)_8$  (0.27 g, 0.80 mmol) and  $[W(\eta^3-C_3H_5)(CO)_2(S_2CPPr_3)Br]$  (**3d**, 0.64 g, 1.1 mmol).<sup>8</sup> Yield: 0.23 g, 34%. Anal. Calcd for  $C_{17}H_{26}CoO_4PS_2W$ : C, 32.29; H, 4.14. Found: C, 31.94; H, 4.06. <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  3.96 [m, 1 H, CH of allyl], 3.00 [d (7), 2 H, H syn of allyl], 2.78 [m, 3 H, CH of Pr<sup>i</sup>], 1.44 [m, 18 H, CH<sub>3</sub> of Pr<sup>i</sup>], 1.23 [d (8), 2 H, CH anti of allyl].

**X-ray Diffraction Study of 2a and 4a.** Crystals suitable for an X-ray determination were grown by slow diffusion of hexane into concentrated solutions of the compounds (**2a** and **4a**) in



**Figure 1.** Perspective view (ORTEP)<sup>23</sup> of the structure of [MnCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (**2a**), showing the atom numbering.



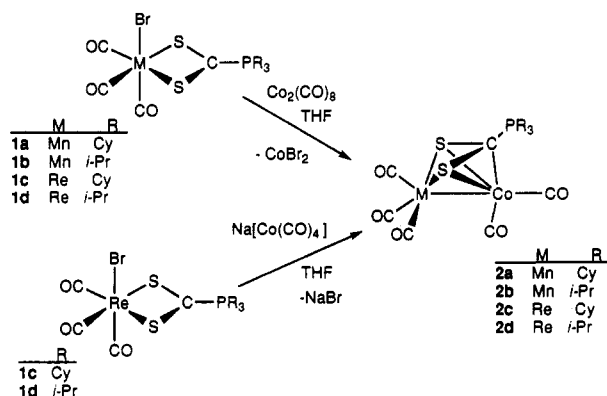
**Figure 2.** Perspective view (CAMERON)<sup>24</sup> of the structure of [MoCo(CO)<sub>4</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (**4a**), showing the atom numbering.

CH<sub>2</sub>Cl<sub>2</sub> at -20 °C. Relevant crystallographic details are given in Table 3. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections in the range 18 ≤ θ ≤ 19. Structure was solved by direct methods and subsequent Fourier maps. An absorption correction was applied with DIFABS.<sup>22</sup> Hydrogen atoms were found on difference maps, and their positions were refined. All H atoms were given a common isotropic temperature factor which was refined. All non-hydrogen atoms were refined anisotropically. Refinements were carried out by least squares methods, in three blocks. Structure solution and refinements were made with CRYSTALS.<sup>23</sup> Torsion angles and least squares planes calculations were made with PARST.<sup>24</sup> Drawings were made with ORTEP<sup>25</sup> (**2a**, Figure 1), and CAMERON<sup>26</sup> (**4a**, Figure 2).

## Results and Discussion

Compounds [M(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (M = Mn,<sup>21</sup> Re;<sup>4</sup> **1a–d** in Scheme 1) react with Co<sub>2</sub>(CO)<sub>8</sub> in CH<sub>2</sub>Cl<sub>2</sub>/THF to afford brown solutions from which binuclear pentacarbonyl complexes of formula [MCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] (**2a–d**) have been isolated as crystalline solids in good yields (64–90%), and characterized by analytical (see Experimental part) and spectroscopic methods (Tables 1 and 2). To fully

## Scheme 1



establish the structure of these compounds, an X-ray determination was carried out on a crystal of the derivative **2a** (M = Mn, R = Cy). Crystal data and refinement details are presented in Table 3, and the results are presented in Figure 1, Table 4 (atomic parameters), and Table 5 (selected distances and angles). It can be seen in Figure 1 that the molecule of **2a** consists of the fragments Mn(CO)<sub>3</sub> and Co(CO)<sub>2</sub>, with the S<sub>2</sub>CPCy<sub>3</sub> ligand acting as an unsymmetric bridge, bonded as η<sup>2</sup>(S,S') to manganese, and as η<sup>3</sup>(S,C,S') to cobalt, donating four electrons to each metal. The Mn–Co distance of 2.599(1) Å is consistent with the existence of a direct bond between the metal atoms,<sup>9,10,12,14</sup> as required by the EAN rule. Additionally, the electron counting leads to the assignment of formal oxidation states Mn<sup>0</sup> and Co<sup>0</sup>.

Complex **2a** appears as the only product in the reaction, and no significant amount of the other possible isomer, with the central carbon of the S<sub>2</sub>CPCy<sub>3</sub> bonded to manganese, has been detected in the final mixtures. The reaction occurs, therefore, with the specific formation of a carbon–cobalt bond, showing that the central carbon of S<sub>2</sub>CPCy<sub>3</sub> prefers, in this case, to get bonded to cobalt rather than to manganese. We have observed before such kind of preference of the central carbon of S<sub>2</sub>CPR<sub>3</sub> when confronted to two different metals.<sup>4–8</sup> In fact, we have found so far that, when the two metals have different formal oxidation states, the central carbon prefers to bind the metal with the lower oxidation state. As is occurred with [MnRe(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)],<sup>4</sup> the two metals atoms in **2a** have the same oxidation number, and there is not a simple reason to explain the observed preferences. From orbital overlap arguments,<sup>27</sup> it has been predicted that the central carbon of the S<sub>2</sub>CPR<sub>3</sub> ligand would bind the metal atom which offered the more diffuse orbital. Attending to the orbital exponents currently used in EHMO calculations,<sup>28</sup> it is manganese (smaller exponents) which offers the more diffuse orbitals and, on the basis of orbital overlap considerations, it should be manganese the preferred metal atom to form the bond with carbon. In the structure of **2a**, the central carbon shows a definite preference, however, to bind cobalt instead of manganese. We shall present below other complexes containing Mo and Co in which the experimental evidence (specific formation again of a Co–C bond) goes opposite to the preference predicted by the orbital overlap arguments, which would favor Mo (smaller exponents). It seems that

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Table 1. IR and <sup>31</sup>P{<sup>1</sup>H} NMR Data for the New Complexes

compound		IR (THF) $\nu(\text{CO})$ , cm <sup>-1</sup>	<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>a</sup> S <sub>2</sub> CP
no.	formula		
2a	[MnCo(CO) <sub>5</sub> (μ-S <sub>2</sub> CPCy <sub>3</sub> )]	2015 s, 1965 vs, 1931 m, 1917 s, 1901 m	30.11
2b	[MnCo(CO) <sub>5</sub> (μ-S <sub>2</sub> CPPr <sub>3</sub> )]	2018 s, 1968 vs, 1926 s, 1920 s, 1901 sh	39.43
2c	[ReCo(CO) <sub>5</sub> (μ-S <sub>2</sub> CPCy <sub>3</sub> )]	2018 s, 1971 vs, 1926 s, 1916 s, 1897 m	41.27
2d	[ReCo(CO) <sub>5</sub> (μ-S <sub>2</sub> CPPr <sub>3</sub> )]	2020 vs, 1972 s, 1919 s, 1917 s, 1895 sh	51.56
4a	[MoCo(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>4</sub> (μ-S <sub>2</sub> CPCy <sub>3</sub> )]	1981 vs, 1933 s, 1857 m	33.07
4b	[MoCo(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>4</sub> (μ-S <sub>2</sub> CPPr <sub>3</sub> )]	1982 vs, 1934 s, 1858 m	42.67
4c	[WCo(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>4</sub> (μ-S <sub>2</sub> CPCy <sub>3</sub> )]	1984 vs, 1932 s, 1845 m	37.23
4d	[WCo(η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> )(CO) <sub>4</sub> (μ-S <sub>2</sub> CPPr <sub>3</sub> )]	1986 vs, 1933 s, 1848 m	47.07

<sup>a</sup> In solutions of CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm) from internal 85% H<sub>3</sub>PO<sub>4</sub>.

Table 2. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR Data for the New Complexes<sup>a</sup>

compd	<sup>1</sup> H NMR, δ, ppm	<sup>13</sup> C{ <sup>1</sup> H} NMR, δ (ppm)
2a	2.46 [m, 3H, CH of Cy], 2.05–1.19 [m, br, 30 H, CH <sub>2</sub> of Cy]	223.9 [s (br), 3 MnCO], 213.9 [s, CoCO], 203.0 [s, CoCO], 91.2 [d (43), S <sub>2</sub> CP], 32.3 [d (40), C <sup>1</sup> of Cy], 27.4 [s, C <sup>2</sup> and C <sup>6</sup> of Cy], 27.0 [d (12), C <sup>3</sup> and C <sup>5</sup> of Cy], 25.5 [s, C <sup>4</sup> of Cy]
2b	2.76 [m, 3H, CH of Pr <sup>i</sup> ], 1.48 [dd (16 and 7), 18 H, CH <sub>3</sub> of Pr <sup>i</sup> ]	223.4 [s (br), 3 MnCO], 211.7 [s, CoCO], 202.7 [s, CoCO], 89.8 [d (46), S <sub>2</sub> CP], 22.3 [d (42), CH of Pr <sup>i</sup> ], 17.5 [d (3), CH <sub>3</sub> of Pr <sup>i</sup> ]
2c	2.47 [m, 3H, CH of Cy], 2.03–1.32 [m, br, 30 H, CH <sub>2</sub> of Cy]	207.7 [s, CoCO], 202.7 [s, CoCO], 196.0 [s, 3 ReCO], 93.7 [d (43), S <sub>2</sub> CP], 32.1 [d (40), C <sup>1</sup> of Cy], 27.2 [s, C <sup>2</sup> and C <sup>6</sup> of Cy], 27.0 [d (12), C <sup>3</sup> and C <sup>5</sup> of Cy], 25.8 [s, C <sup>4</sup> of Cy]
2d	2.81 [m, 3H, CH of Pr <sup>i</sup> ], 1.47 [dd (16 and 7), 18 H, CH <sub>3</sub> of Pr <sup>i</sup> ]	207.5 [s, CoCO], 202.2 [s, CoCO], 195.6 [s, ReCO], 93.0 [d (47), S <sub>2</sub> CP], 22.4 [d (42), CH of Pr <sup>i</sup> ], 17.5 [s, CH <sub>3</sub> of Pr <sup>i</sup> ]
4a	3.97 [m, 1 H, CH of allyl], 3.00 [d (7), 2 H, H <sub>syn</sub> ], 2.47 [m, 3H, CH of Cy], 2.04–1.32 [m, br, 32 H, CH <sub>2</sub> of Cy and H <sub>anti</sub> of allyl]	233.8 [s, 2 MoCO], 215.1 [s, CoCO], 202.8 [s, CoCO], 95.3 [d (45), S <sub>2</sub> CP], 66.7 [s, C <sup>2</sup> of allyl], 49.0 [s, C <sup>1</sup> and C <sup>3</sup> of allyl], 32.4 [d (40), C <sup>1</sup> of Cy], 27.4 [d (2), C <sup>2</sup> and C <sup>6</sup> of Cy], 27.0 [d (12), C <sup>3</sup> and C <sup>5</sup> of Cy], 25.8 [s, C <sup>4</sup> of Cy]
4b	3.96 [m, 1 H, CH of allyl], 3.00 [d (7), 2 H, H <sub>syn</sub> ], 2.78 [m, 3H, CH of Pr <sup>i</sup> ], 1.44 [m, 18 H, CH <sub>3</sub> of Pr <sup>i</sup> ], 1.23 [d (8), 2H, H <sub>anti</sub> ]	233.7 [s, 2 MoCO], 215.1 [s, CoCO], 203.1 [s, CoCO], 94.5 [d (46), S <sub>2</sub> CP], 66.9 [s, C <sup>2</sup> of allyl], 49.2 [s, C <sup>1</sup> and C <sup>3</sup> of allyl], 22.8 [d (42), CH of Pr <sup>i</sup> ], 17.5 [d (3), CH <sub>3</sub> of Pr <sup>i</sup> ]

<sup>a</sup> From CD<sub>2</sub>Cl<sub>2</sub> solutions. Coupling constants, in Hz, in parentheses. <sup>b</sup> The low solubility of the W-Co complexes 4c,d precluded the acquisition of informative <sup>13</sup>C{<sup>1</sup>H} NMR spectra for them. Their <sup>1</sup>H NMR spectral data are given in the Experimental Section.

Table 3. Crystal Data and Refinement Details for [MnCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (2a) and [MoCo(CO)<sub>4</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(μ-S<sub>2</sub>CPCy<sub>3</sub>)]·CH<sub>2</sub>Cl<sub>2</sub> (4a)

formula	C <sub>24</sub> H <sub>33</sub> CoMnO <sub>5</sub> PS <sub>2</sub>	C <sub>27</sub> H <sub>40</sub> Cl <sub>2</sub> CoMoO <sub>4</sub> PS <sub>2</sub>
fw	610.5	749.5
cryst syst; space group		triclinic; P $\bar{1}$
a, Å	11.074(3)	10.301(1)
b, Å	11.156(3)	11.347(7)
c, Å	11.769(3)	15.723(2)
α, deg	74.64(1)	90.08(2)
β, deg	85.36(1)	102.46(4)
γ, deg	83.44(2)	112.84(1)
V, Å <sup>3</sup>	1391(2)	1646(3)
Z	2	2
T, K	295	295
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.46	1.51
F(000)	632	768
λ(Mo Kα), Å		0.710 69
cryst size, mm; color	0.75 × 0.70 × 0.65; red	0.70 × 0.45 × 0.25; red
μ, cm <sup>-1</sup>	12.6	12.4
method of collcn		ω/2θ scan
scan range, deg	1 ≤ θ ≤ 28	1 ≤ θ ≤ 25
no of reflns measd	6055	5766
no of reflns obsd, I ≥ 3σ(I)	4600	2804
no. of paramrs	409	345
data to param ratio	11.25	8.13
residuals R, R <sub>w</sub> <sup>a</sup>	0.042, 0.043	0.062, 0.070

<sup>a</sup> R = Σ(|ΔF|)/Σ|F<sub>o</sub>|, R<sub>w</sub> = [Σw(ΔF)<sup>2</sup>/Σw|F<sub>o</sub>|<sup>2</sup>]<sup>1/2</sup>, and w = 1.

simple, qualitative arguments do not provide a general explanation for the preference observed when the two metal atoms are in oxidation state zero. In contrast, when the oxidation states of the metals are different, the simple (but unambiguous) formalism based on the oxidation numbers, provides a predictive rule for which exceptions have not been found.

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å<sup>2</sup>) for [MnCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (2a)

atom	x/a	y/b	z/c	U(eq) <sup>a</sup>
Co(1)	0.19973(5)	0.88494(4)	0.71227(5)	0.0330
Mn(1)	0.39245(5)	0.75279(5)	0.80658(5)	0.0348
S(1)	0.28615(9)	0.91278(8)	0.87190(8)	0.0345
S(2)	0.39372(9)	0.92238(8)	0.64327(8)	0.0333
P(1)	0.28496(8)	1.17733(8)	0.69834(8)	0.0268
O(1)	0.6271(3)	0.7577(4)	0.9012(4)	0.0790
O(2)	0.3234(4)	0.5538(3)	1.0142(3)	0.0725
O(3)	0.4683(4)	0.5551(3)	0.6844(3)	0.0669
O(4)	0.1364(4)	0.6425(3)	0.7069(4)	0.0686
O(5)	-0.0268(3)	1.0220(4)	0.6230(4)	0.0679
C(1)	0.5370(4)	0.7518(4)	0.8625(4)	0.0512
C(2)	0.3478(4)	0.6322(4)	0.9341(4)	0.0477
C(3)	0.4405(4)	0.6342(4)	0.7291(4)	0.0461
C(4)	0.1646(4)	0.7361(4)	0.7138(4)	0.0485
C(5)	0.0637(4)	0.9698(4)	0.6572(4)	0.0457
C(6)	0.3041(3)	1.0099(3)	0.7288(3)	0.0276
C(10)	0.2126(3)	1.2494(3)	0.5584(3)	0.0330
C(11)	0.2510(4)	1.1858(4)	0.4585(4)	0.0392
C(12)	0.1747(5)	1.2465(5)	0.3517(4)	0.0491
C(13)	0.1834(5)	1.3851(5)	0.3098(4)	0.0528
C(14)	0.1472(5)	1.4479(5)	0.4078(5)	0.0564
C(15)	0.2223(5)	1.3905(4)	0.5164(4)	0.0477
C(20)	0.1887(3)	1.2122(3)	0.8233(3)	0.0310
C(21)	0.0592(4)	1.1769(6)	0.8254(5)	0.0506
C(22)	-0.0105(5)	1.1914(6)	0.9395(5)	0.0593
C(23)	-0.0112(5)	1.3208(5)	0.9560(5)	0.0534
C(24)	0.1162(5)	1.3577(6)	0.9492(5)	0.0590
C(25)	0.1879(5)	1.3451(4)	0.8354(5)	0.0520
C(30)	0.4345(3)	1.2318(3)	0.6998(3)	0.0317
C(31)	0.5201(4)	1.2161(5)	0.5951(4)	0.0417
C(32)	0.6422(4)	1.2654(5)	0.5997(4)	0.0506
C(33)	0.7014(4)	1.2009(6)	0.7146(5)	0.0588
C(34)	0.6164(5)	1.2194(7)	0.8170(5)	0.0568
C(35)	0.4946(4)	1.1673(5)	0.8158(4)	0.0491

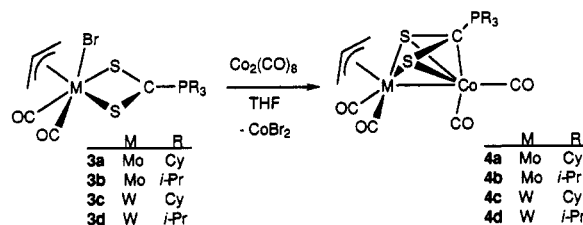
<sup>a</sup> U(eq) defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

**Table 5. Selected Bond Lengths (Å) and Angles (deg) for [MnCo(CO)<sub>5</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (2a)**

Co(1)–Mn(1)	2.599(1)	Co(1)–S(1)	2.282(1)
Co(1)–S(2)	2.279(1)	Co(1)–C(4)	1.744(4)
Co(1)–C(5)	1.759(4)	Co(1)–C(6)	1.966(3)
Mn(1)–S(1)	2.294(1)	Mn(1)–S(2)	2.313(1)
Mn(1)–C(1)	1.777(5)	Mn(1)–C(2)	1.808(4)
Mn(1)–C(3)	1.807(4)	S(1)–C(6)	1.754(3)
S(2)–C(6)	1.757(3)	P(1)–C(6)	1.797(3)
P(1)–C(10)	1.835(4)	P(1)–C(20)	1.846(4)
P(1)–C(30)	1.830(4)	O(1)–C(1)	1.146(5)
O(2)–C(2)	1.141(5)	O(3)–C(3)	1.143(5)
O(4)–C(4)	1.148(5)	O(5)–C(5)	1.145(5)
S(1)–Co(1)–Mn(1)	55.60(3)	S(2)–Co(1)–Mn(1)	56.14(3)
S(2)–Co(1)–S(1)	76.81(4)	C(4)–Co(1)–Mn(1)	80.2(1)
C(4)–Co(1)–S(1)	119.1(2)	C(4)–Co(1)–S(2)	113.5(2)
C(5)–Co(1)–Mn(1)	176.1(2)	C(5)–Co(1)–S(1)	122.8(1)
C(5)–Co(1)–S(2)	127.6(2)	C(5)–Co(1)–C(4)	98.4(2)
C(6)–Co(1)–Mn(1)	75.9(1)	C(6)–Co(1)–S(1)	48.1(1)
C(6)–Co(1)–S(2)	48.2(1)	C(6)–Co(1)–C(4)	155.8(2)
C(6)–Co(1)–C(5)	105.7(2)	S(1)–Mn(1)–Co(1)	55.18(3)
S(2)–Mn(1)–Co(1)	54.90(3)	S(2)–Mn(1)–S(1)	75.91(4)
C(1)–Mn(1)–Co(1)	147.3(2)	C(1)–Mn(1)–S(1)	100.2(2)
C(1)–Mn(1)–S(2)	101.6(2)	C(2)–Mn(1)–Co(1)	109.7(1)
C(2)–Mn(1)–S(1)	94.5(1)	C(2)–Mn(1)–S(2)	164.5(1)
C(2)–Mn(1)–C(1)	91.9(2)	C(3)–Mn(1)–Co(1)	108.9(1)
C(3)–Mn(1)–S(1)	163.9(1)	C(3)–Mn(1)–S(2)	96.8(1)
C(3)–Mn(1)–C(1)	95.3(2)	C(3)–Mn(1)–C(2)	89.3(2)
Mn(1)–S(1)–Co(1)	69.22(3)	C(6)–S(1)–Co(1)	56.5(1)
C(6)–S(1)–Mn(1)	88.5(1)	Mn(1)–S(2)–Co(1)	68.96(3)
C(6)–S(2)–Co(1)	56.5(1)	C(6)–S(2)–Mn(1)	87.9(1)
O(1)–C(1)–Mn(1)	175.5(4)	O(2)–C(2)–Mn(1)	177.6(4)
O(3)–C(3)–Mn(1)	176.7(4)	O(4)–C(4)–Co(1)	174.6(4)
O(5)–C(5)–Co(1)	177.9(4)	S(1)–C(6)–Co(1)	75.4(1)
S(2)–C(6)–Co(1)	75.2(1)	S(2)–C(6)–S(1)	107.6(2)
P(1)–C(6)–Co(1)	133.4(2)	P(1)–C(6)–S(1)	122.4(2)
P(1)–C(6)–S(2)	126.0(2)		

We have recently shown that the reaction of [Mn(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (1a,b) with pentacarbonyl anions of group 7 metals, [M(CO)<sub>5</sub>]<sup>−</sup> (M = Mn, Re), affords ultimately the binuclear hexacarbonyls [MMn(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] containing a metal–metal bond and a S<sub>2</sub>CPCy<sub>3</sub> ligand acting as η<sup>2</sup>(S,S');η<sup>3</sup>(S,C,S') bridge.<sup>4</sup> This can be viewed as the result of the nucleophilic substitution of Br<sup>−</sup> by Mn(CO)<sub>5</sub><sup>−</sup>, thus creating a metal–metal bond through a salt elimination process. On the other hand, the reaction of the same [Mn(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] with the neutral [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] affords binuclear complexes which contain a bridging bromide in addition to the η<sup>2</sup>(S,S');η<sup>3</sup>(S,C,S') S<sub>2</sub>CPR<sub>3</sub> bridge between the two metals that are not directly bonded.<sup>7</sup> Within this context, the overall reaction of [Mn(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (1a,b) with Co<sub>2</sub>(CO)<sub>8</sub> to give 2a,b (see Scheme 1) may be regarded as a reduction of Mn<sup>I</sup> to Mn<sup>0</sup> as the expense of Co<sup>0</sup>, which is oxidized to Co<sup>II</sup>. Consistently, in the reaction mixture a good amount of blue precipitate appears, which dissolves in water to give a pink solution.

On the other hand, it is well-known that Co<sub>2</sub>(CO)<sub>8</sub> readily undergoes disproportionation in the presence of Lewis bases (B), to give complexes [Co<sup>II</sup>(B)<sub>6</sub>][Co<sup>I</sup>(CO)<sub>4</sub>]<sub>2</sub>,<sup>29</sup> and complexes 1a,b have been shown to behave as Lewis bases, displacing three nitrile ligands from [M(CO)<sub>3</sub>(nitrile)<sub>3</sub>].<sup>7</sup> The reaction of 1a,b with octacarbonyl dicobalt may involve disproportionation to produce [Co(CO)<sub>4</sub>]<sup>−</sup> which would then react with the bromo derivatives 1a,b in the same fashion as do the pentacarbonyl anions [M(CO)<sub>5</sub>]<sup>−</sup> (M = Mn, Re):<sup>4</sup> nucleophilic substitution at the manganese

**Scheme 2**

atom would create a Mn–Co bond, with the formation of a heptacarbonyl intermediate [(S<sub>2</sub>CPR<sub>3</sub>)(CO)<sub>3</sub>Mn–Co(CO)<sub>4</sub>]. Subsequent displacement of two carbonyl groups at cobalt by the S,C,S' donor set of the S<sub>2</sub>CPR<sub>3</sub> ligand would give the final products 2a,b. Although this could be a plausible mechanism,<sup>30</sup> such a path does not provide a useful synthetic method, since the reaction of complexes 1a,b with Na[Co(CO)<sub>4</sub>] produces only small amounts of the desired 2a,b, together with extensive decomposition. In contrast, such reaction works much better for the rhenium derivatives. Thus, [Re(CO)<sub>3</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (1c,d) react with Na[Co(CO)<sub>4</sub>] to give binuclear Re–Co compounds 2c,d in moderate yields (46–53%).

To test the generality of this method for the preparation of heterobinuclear complexes, we tried the reactions of [Co<sub>2</sub>(CO)<sub>8</sub>] with the recently prepared allyl derivatives [M(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(S<sub>2</sub>CPR<sub>3</sub>)Br] (M = Mo, W; 3a,b in Scheme 2). These reactions resulted in the production of binuclear complexes [MCo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] (4a,d in Scheme 2). The isolated yields (20–40%) are much lower than those obtained for the complexes 2a–d containing Mn or Re. Extensive decomposition was observed, together with the production of M(CO)<sub>6</sub>. This may be due to the longer times required by the reactions. The <sup>13</sup>C NMR spectra (Table 2) of complexes containing Mo–Co display the signal of the central carbon of S<sub>2</sub>CPR<sub>3</sub> as a doublet in the region expected for a η<sup>3</sup>-(S,C,S') pseudoallyl coordination of the ligand (δ 95.3 ppm for 4a, δ 94.5 ppm for 4b). Unfortunately, the limited solubility of the complexes containing W and Co (4c,d) precluded the acquisition of good <sup>13</sup>C NMR spectra for them. Nevertheless, although the position of the signal indicates η<sup>3</sup>-coordination for S<sub>2</sub>CPR<sub>3</sub>, it is not possible to distinguish which of the two metals is bonded to the central carbon of the ligand. To ascertain this point, an X-ray determination was carried out on a crystal of the derivative 4a. The relevant crystallographic data are collected in Table 3, and the results are presented in Table 6 (atomic parameters), Table 7 (selected distances and angles), and Figure 2. It can be seen that the structure of compound 4a resembles closely that of compound 2a described above: again a metal–metal bond (distance Mo–Co: 2.719(2) Å)<sup>31</sup> has been produced, and again, the central carbon of S<sub>2</sub>CPR<sub>3</sub> shows a definite preference bond to cobalt rather than to molybdenum. As with the structure of 2a, discussed above, the criteria of compatibility of orbitals<sup>27</sup> would predict in 4a the formation of a bond between the central carbon and the molybdenum atom for which orbital exponents are smaller than those of cobalt.<sup>28</sup> The electron counting in 4a leads to the assignment of oxidation

(30) One reviewer suggests that an other hypothesis for the mechanism of the formation of 2a,b could involve an initial nucleophilic attack of 1a,b on Co<sub>2</sub>(CO)<sub>8</sub>, followed by the elimination of bromine through the transient formation of the unstable BrCo(CO)<sub>4</sub>.

(31) The Mo–Co distance is very close to the sum of covalent radii (2.71 Å) and falls well within the range 2.68–2.9 Å reported for other complexes with a direct bond between the two metals.<sup>15,17–19</sup>

**Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å<sup>2</sup>) for [MoCo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)]-CH<sub>2</sub>Cl<sub>2</sub> (4a)**

Mo(1)	0.4243(1)	0.5838(1)	0.29552(8)	0.0436
Co(1)	0.6897(2)	0.5879(1)	0.2948(1)	0.0385
S(1)	0.4884(3)	0.4623(3)	0.1909(2)	0.0412
S(2)	0.5505(4)	0.4569(3)	0.3796(2)	0.0428
P(1)	0.5908(3)	0.2530(3)	0.2674(2)	0.0363
O(1)	0.407(1)	0.810(1)	0.1907(8)	0.0884
O(2)	0.478(1)	0.791(1)	0.4434(7)	0.0792
O(3)	0.988(1)	0.655(1)	0.2933(7)	0.0664
O(4)	0.763(1)	0.8612(9)	0.3140(9)	0.0783
C(1)	0.410(2)	0.724(1)	0.2255(9)	0.0587
C(2)	0.461(2)	0.714(1)	0.391(1)	0.0557
C(3)	0.868(1)	0.619(1)	0.2946(8)	0.0449
C(4)	0.723(1)	0.752(1)	0.308(1)	0.0558
C(5)	0.570(1)	0.408(1)	0.2789(7)	0.0381
C(6)	0.190(2)	0.520(2)	0.210(1)	0.0742
C(7)	0.201(2)	0.447(2)	0.281(1)	0.0705
C(8)	0.234(2)	0.504(1)	0.363(1)	0.0748
C(10)	0.409(1)	0.122(1)	0.2504(8)	0.0409
C(11)	0.338(2)	0.125(1)	0.3249(9)	0.0587
C(12)	0.187(2)	0.011(2)	0.310(1)	0.0716
C(13)	0.091(2)	0.012(2)	0.223(1)	0.0755
C(14)	0.163(2)	0.008(1)	0.150(1)	0.0684
C(15)	0.310(1)	0.120(1)	0.1616(9)	0.0529
C(20)	0.702(1)	0.234(1)	0.3693(8)	0.0436
C(21)	0.687(2)	0.093(1)	0.377(1)	0.0650
C(22)	0.775(2)	0.086(1)	0.468(1)	0.0718
C(23)	0.932(2)	0.177(2)	0.484(1)	0.0673
C(24)	0.941(2)	0.316(1)	0.4775(9)	0.0580
C(25)	0.861(2)	0.329(1)	0.3871(9)	0.0588
C(30)	0.652(1)	0.248(1)	0.1682(8)	0.0444
C(31)	0.788(1)	0.361(1)	0.1591(9)	0.0571
C(32)	0.814(2)	0.352(1)	0.066(1)	0.0644
C(33)	0.824(2)	0.224(2)	0.047(1)	0.0767
C(34)	0.697(2)	0.118(2)	0.057(1)	0.0904
C(35)	0.663(2)	0.120(1)	0.148(1)	0.0629
Cl(1)	0.6150(9)	0.7451(8)	0.0575(4)	0.1334
Cl(2)	0.8576(7)	0.7091(7)	0.0188(5)	0.1450
C(40)	0.704(2)	0.655(2)	0.050(1)	0.1002

<sup>a</sup> U(eq) defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

numbers 1+ for Mo (which bears a η<sup>3</sup>-allyl group) and 0 for Co. This is consistent with our previous predictions<sup>7,32</sup> stating that the central carbon of S<sub>2</sub>CPR<sub>3</sub> prefers to bind the metal atom with the lower oxidation number. As in the previous examples, a very simple argument based on the oxidation numbers helps to rationalize the experimental facts. However, this can only be applied when the formal oxidation numbers for the two metals are different. A detailed analysis of the bonding in these molecules is necessary to get a definite picture of the factors governing the selective formation of the metal-carbon bond.

The comparison of Figure 1 with Figure 2 reveals some analogy between the structures of **2a** and **4a**. Both structures display Co(CO)<sub>2</sub> fragments which are essentially planar (within 0.027(4) Å in **2a**, and within 0.02(2) Å in **4a**) and not very different from that found in Cp\*Co(CO)<sub>2</sub> (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>).<sup>33</sup> In both **2a** and **4a**, the Co(CO)<sub>2</sub> fragment is coordinated to a four-member, metalladithio-cyclobutene ring, MSCS', which is also essentially planar itself (within 0.057(3) Å in **2a**, within 0.07(1) Å in **4a**). This situation is again reminiscent of that found in the molecule of Cp\*Co(CO)<sub>2</sub>,<sup>33</sup> where the Co(CO)<sub>2</sub> fragment is bonded to a planar pentamethylcyclopentadienyl ring. The analogy of **2a**, **4a**, and Cp\*Co(CO)<sub>2</sub> can be extended to

**Table 7. Selected Bond Lengths (Å) and Angles (deg) for [MoCo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>4</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)]-CH<sub>2</sub>Cl<sub>2</sub> (4a)**

Mo(1)-Co(1)	2.719(2)	Mo(1)-S(1)	2.493(3)
Mo(1)-S(2)	2.496(3)	Mo(1)-C(1)	1.97(1)
Mo(1)-C(2)	1.97(1)	Mo(1)-C(6)	2.32(1)
Mo(1)-C(7)	2.18(1)	Mo(1)-C(8)	2.30(2)
Co(1)-S(1)	2.289(3)	Co(1)-S(2)	2.285(4)
Co(1)-C(3)	1.73(1)	Co(1)-C(4)	1.76(1)
Co(1)-C(5)	1.91(1)	S(1)-C(5)	1.70(1)
S(2)-C(5)	1.75(1)	P(1)-C(5)	1.87(1)
P(1)-C(10)	1.85(1)	P(1)-C(20)	1.82(1)
P(1)-C(30)	1.81(1)	O(1)-C(1)	1.13(1)
O(2)-C(2)	1.14(1)	O(3)-C(3)	1.15(1)
O(4)-C(4)	1.14(1)	C(6)-C(7)	1.40(2)
C(7)-C(8)	1.35(2)		
S(1)-Mo(1)-Co(1)	51.87(8)	S(2)-Mo(1)-Co(1)	51.75(8)
S(2)-Mo(1)-S(1)	71.2(1)	C(1)-Mo(1)-Co(1)	104.7(4)
C(1)-Mo(1)-S(1)	100.2(4)	C(1)-Mo(1)-S(2)	155.6(4)
C(2)-Mo(1)-Co(1)	104.9(4)	C(2)-Mo(1)-S(1)	156.5(4)
C(2)-Mo(1)-S(2)	98.5(4)	C(2)-Mo(1)-C(1)	80.5(6)
C(6)-Mo(1)-Co(1)	142.6(4)	C(6)-Mo(1)-S(1)	91.6(4)
C(6)-Mo(1)-S(2)	130.9(4)	C(6)-Mo(1)-C(1)	70.6(6)
C(7)-Mo(1)-C(2)	110.5(6)	C(7)-Mo(1)-Co(1)	140.1(4)
C(7)-Mo(1)-S(1)	96.6(5)	C(7)-Mo(1)-S(2)	99.0(5)
C(7)-Mo(1)-C(1)	104.7(6)	C(7)-Mo(1)-C(2)	106.0(6)
C(7)-Mo(1)-C(6)	36.0(6)	C(8)-Mo(1)-Co(1)	143.8(4)
C(8)-Mo(1)-S(1)	127.0(4)	C(8)-Mo(1)-S(2)	92.2(4)
C(8)-Mo(1)-C(1)	110.5(6)	C(8)-Mo(1)-C(2)	73.1(6)
C(8)-Mo(1)-C(6)	61.6(6)	C(8)-Mo(1)-C(7)	35.0(6)
S(1)-Co(1)-Mo(1)	58.95(9)	S(2)-Co(1)-Mo(1)	59.08(9)
S(2)-Co(1)-S(1)	78.8(1)	C(3)-Co(1)-Mo(1)	170.2(4)
C(3)-Co(1)-S(1)	126.5(4)	C(3)-Co(1)-S(2)	127.9(4)
C(4)-Co(1)-Mo(1)	76.9(4)	C(4)-Co(1)-S(1)	116.5(5)
C(4)-Co(1)-S(2)	116.3(5)	C(4)-Co(1)-C(3)	93.4(6)
C(5)-Co(1)-Mo(1)	77.4(4)	C(5)-Co(1)-S(1)	46.8(3)
C(5)-Co(1)-S(2)	48.3(4)	C(5)-Co(1)-C(3)	112.3(5)
C(5)-Co(1)-C(4)	154.2(6)	Co(1)-S(1)-Mo(1)	69.2(1)
C(5)-S(1)-Mo(1)	87.8(4)	C(5)-S(1)-Co(1)	55.0(4)
Co(1)-S(2)-Mo(1)	69.2(1)	C(5)-S(2)-Mo(1)	86.6(4)
C(5)-S(2)-Co(1)	54.7(4)	O(1)-C(1)-Mo(1)	175.1(14)
O(2)-C(2)-Mo(1)	177.2(14)	O(3)-C(3)-Co(1)	171.5(11)
O(4)-C(4)-Co(1)	170.0(12)	S(1)-C(5)-Co(1)	78.2(5)
S(2)-C(5)-Co(1)	76.9(5)	S(2)-C(5)-S(1)	114.3(7)
P(1)-C(5)-Co(1)	138.0(7)	P(1)-C(5)-S(1)	120.4(7)
P(1)-C(5)-S(2)	118.6(6)	C(7)-C(6)-Mo(1)	66.5(8)
C(6)-C(7)-Mo(1)	77.5(9)	C(8)-C(7)-Mo(1)	77.4(10)
C(8)-C(7)-C(6)	118.7(15)	C(7)-C(8)-Mo(1)	67.6(9)

electronic grounds. Thus, the MSCS' rings in **2a** and **4a** donate a total of five electrons (four electrons from the S,C,S' system, plus one electron from the metal) to the Co(CO)<sub>2</sub> fragment, as does the Cp\* ring. It can be concluded, therefore, that the molecules of **2a** and **4a** are both structurally and electronically analogues of Cp\*Co(CO)<sub>2</sub> and CpCo(CO)<sub>2</sub>.<sup>34</sup> We have previously found these kinds of similarities between the dimanganese complexes [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] and CpMn(CO)<sub>3</sub>.<sup>35</sup> Another common feature of the structures of **2a** and **4a** is that both molecules are fairly symmetrical with respect to the plane defined by the M-Co bond and the central carbon of the S<sub>2</sub>CPR<sub>3</sub> ligand. That plane contains the Co(CO)<sub>2</sub> fragment, and this places one of the carbonyl groups *trans* to the metal (angles Mn-Co-C(5) = 176.1(2)° in **2a**, Mo-Co-C(3) = 170.2(4)° in **4a**), and the other CO *trans* to the

(34) The discussion and the analogy has been established for the Cp\* derivative because a very detailed analysis of the X-ray crystal structure determination is available.<sup>33</sup> A less detailed structural analysis derived from electron diffraction data in the gaseous state for (η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> (liquid) has been published, see Beagley, B.; Parrott, C. T.; Albrecht, V.; Young, G. G. *J. Mol. Struct.* 1979, 52, 47. It shows that the derivative with unsubstituted cyclopentadiene is structurally analogous to that of the derivative with Cp\*.

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central carbon of the  $S_2CPR_3$  (angles C(6)-Co-C(4) = 155.8(2)° in **2a**, C(5)-Co-C(4) = 154.2(6)° in **4a**). The two carbonyl groups are therefore nonequivalent, and this situation persists in solution as suggested by the  $^{13}C\{^1H\}$ -NMR spectra of the derivatives **2** and **4**, which show two different signals for the carbonyl groups bonded to cobalt, one of them in the region  $\delta$  215–207 ppm, and the other in the range  $\delta$  203–202 ppm.

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**Supplementary Material Available:** Complete tables of atomic coordinates for hydrogen atoms, anisotropic thermal parameters, bond lengths and angles, torsion angles, and least squares planes for the structures of **2a** and **4a** (16 pages). Ordering information is given on any current masthead page.

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