Registry No. 1, 79839-04-6; 2, 79816-41-4; 4, 81141-83-5; 5, 81141-84-6; 6, 81141-85-7; 7, 81141-86-8; 8, 81141-87-9; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Tables of X-ray data for compounds **5**, **6**, and **7** and bond lengths and bond angles for compounds **5**, **6**, and **7** (8 pages). Ordering information is given on any current masthead page.

Basic Cluster Reactions. 1. Reversible Unfolding of $FeCO_2Mo$ and $FeCO_2W$ Clusters

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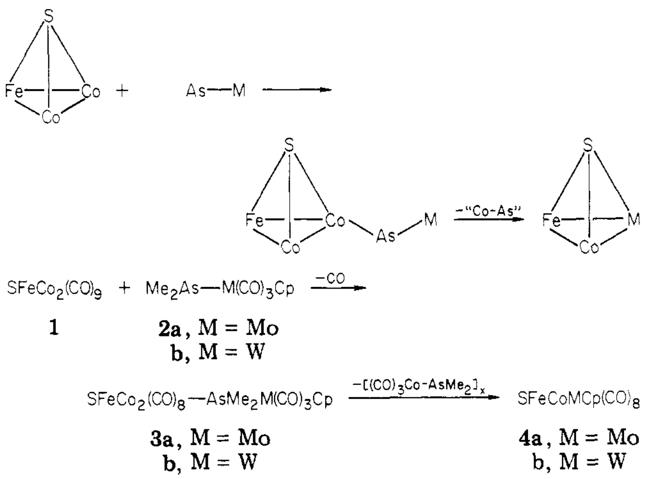
Summary: The tetrahedral clusters $FeCo_2MSAsMe_2Cp(CO)_8$ (M = Mo, W) which are obtained from $FeCo_2S(CO)_9$ and $Cp(CO)_3MAsMe_2$ reversibly add 2 mol of CO to form the clusters $FeCo_2MSAsMe_2Cp(CO)_{10}$ with a $MCo_2(\mu\text{-}AsFe)$ core.

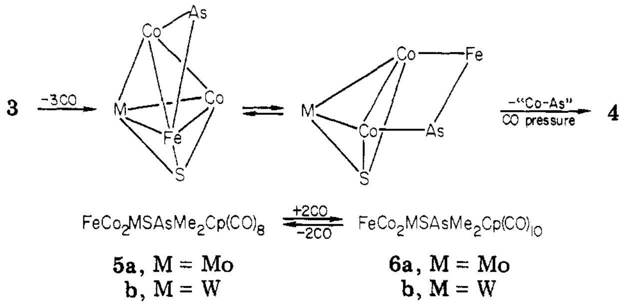
Despite the fact that organotransition-metal clusters are frequently cited as models for topical physical as well as chemical phenomena,[1] their practical utility is as yet unproved,[1,2] and the chemistry of basic cluster reactions is neither well understood nor well developed. One such basic cluster reaction which is not accessible to mononuclear complexes is the formation of active coordination sites by breaking of metal–metal bonds. The significance of this reaction which does not require ligand dissociation and need not lead to complete rupture of the polymetallic unit has been demonstrated for dinuclear[3] as well as trinuclear[4] complexes. We now report such a reaction which reversibly provides two coordination sites by opening up of tetranuclear clusters.

We had previously found[5] that warming of cobalt-containing clusters such as **1**[6] and organometal dimethylarsenides such as **2**[7] under nitrogen leads to metal exchange, forming mixed-metal clusters such as **4** via the intermediates **3** (Scheme I). We have now observed that heating under vacuum leads to aggregation rather than fragmentation, yielding the tetrahedral clusters **5** (Scheme II). Thus, cyclohexane solutions of **3a** or **3b**, evacuated and heated to 80 °C for 15 h, are converted to **5a**[8] (77%) and **5b**[9] (61%), isolated by column chromatography (silica gel) as black crystals. This reaction seems to be a general method for converting trimetal to tetrametal clusters.

Scheme I



Scheme II



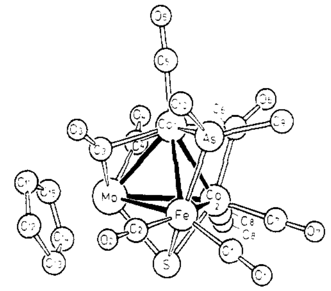


Figure 1. Molecular structure of $FeCo_2MoSAsMe_2Cp(CO)_8$ (**5a**).

Table I. Important Bond Lengths (pm) and Angles (Deg) in 5a and 6a

5a		6a	
Mo-Co1	257.1 (2)	Mo-Co1	277.7 (1)
Mo-Co2	280.5 (2)	Mo-Co2	274.9 (2)
Mo-Fe	282.1 (3)	Co1-Co2	247.4 (2)
Co1-Co2	249.9 (3)	Co2-Fe	274.4 (2)
Co1-Fe	260.8 (3)	Co1-As	231.4 (1)
Co2-Fe	255.8 (3)	Fe-As	236.0 (2)
Co1-As	225.7 (3)	Mo-S	236.0 (2)
Fe-As	228.5 (3)	Co1-S	217.1 (2)
Mo-S	233.6 (4)	Co2-S	217.7 (2)
Co2-S	219.5 (4)	Co1-Mo-Co2	53.19 (4)
Fe-S	217.5 (5)	Mo-Co1-Co2	62.83 (4)
Co1-As-Fe	70.10 (9)	Mo-Co2-Co1	63.98 (5)
Mo-S-Co2	76.4 (1)	Co2-Co1-As	79.54 (5)
Mo-S-Fe	77.3 (1)	Co1-Co2-Fe	95.06 (5)
Co2-S-Fe	71.7 (1)	Co2-Fe-As	73.38 (5)
		Co1-As-Fe	111.08 (6)

The reaction chemistry of the $FeCo_2Mo$ and $FeCo_2W$ clusters **5** should be rich and varied due to their polar

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[1] The P. Chini memorial volume 213/1 of *J. Organomet. Chem.* gives ample evidence of this fact.

[2] Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

[3] Langenbach, H. J.; Vahrenkamp, H. *Chem. Ber.* **1979**, *112*, 3390, 3773. Langenbach, H. J.; Keller, E.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *171*, 259.

[4] Huttner, G.; Schneider, J.; Müller, H. D.; Mohr, G.; v. Seyerl, J.; Wohlfahrt, L *Angew. Chem.* **979**, *91*, 82; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 76. Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27.

[5] Richter, F.; Vahrenkamp, H. *Angew. Chem.* **1978**, *90*, 916; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 684.

[6] Khattab, S. A.; Marko, L.; Bor, G.; Marko, J. *J. Organmet. Chem.* **1964**, *1*, 373.

[7] Malisch, W.; Kuhn, M. *Angew. Chem.* **1974**, *86*, 51; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 84.

[8] $FeCo_2MoSAsMe_2Cp(CO)_8$ (**5a**): mp 155 °C; IR (cyclohexane) 2050 (m), 2015 (s), 2010 (vs), 1992 (vs), 1958 (m), 1864 (w), 1839 (w), 1782 (w) cm^{-1}; ^1H NMR (benzene) 1.48 (3 H), 1.64 (3 H), 4.70 (5 H) ppm. Anal. Calcd for $[C_{15}H_{11}AsCo_2FeMoO_8S]$: C, 25.89; H, 1.59; S, 4.61. Found: C, 26.17; H, 1.47; S, 4.38.

[9] $FeCo_2WSAsMe_2Cp(CO)_8$ (**5b**): mp 168 °C; IR (cyclohexane) 2048 (m), 2011 (s), 2009 (vs), 1987 (vs), 1953 (m), 1860 (w), 1825 (w), 1775 (w) cm^{-1}; ^1H NMR (benzene) 1.47 (3 H), 1.65 (3 H), 4.73 (5 H) ppm. Anal. Calcd for $[C_{15}H_{11}AsCo_2FeO_8SW]$: C, 22.99; H, 1.41; S, 4.09. Found: C, 23.11; H, 1.25; S, 3.91.

0276-7333/82/2301-0756$01.25/0

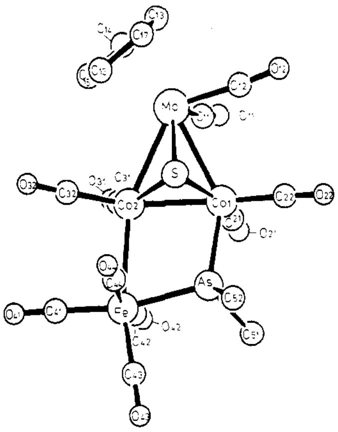

Figure 2. Molecular structure of $FeCo_2MoSAsMe_2Cp(CO)_{10}$ (**6a**).

metal–metal bonds and their additional stabilization by the ligand bridges. One of the simplest such reactions, that with CO, is also depicted in Scheme II. In benzene solution at room temperature under 1 atm of CO, **5a** and **5b** add 2 mol of CO within 1 h. The unfolded clusters **6a**[10] (78%) and **6b**[11] (82%) are obtained as black crystals by recrystallization from hexane. The reconversion of **6a** and **6b** to **5a** and **5b** is equally simple: in benzene solution, in an evacuated flask, after 15 h at 80 °C a small amount (~ 10%) of a precipitate is formed, and from the solution the closed clusters **5** are crystallized in about 70% yield. The ease of these interconversions contrasts sharply with the major changes in the metal and the ligand atom arrangements in the two types of clusters. The reversible opening and closing of the metal tetrahedra model basic steps of substrate activation by cluster catalysts.

The identities of the molybdenum-containing clusters **5a** and **6a** were established by crystal structure analyses[12] Figures 1 and 2 and Table I show the molecular geometries and some bond lengths and angles. Cluster **5a** contains a distorted tetrahedral $FeCo_2Mo$ core with internal angles between 54 and 67°, and the metal framework of **6a** is a $MoCo_2$ triangle with an external iron atom. In both clusters, especially **5a**, ligand bridging is extensive. The metal–metal bond lengths span a considerable range but are within the limits of their variability.[13] The assignment of the iron and cobalt atoms in both structures is somewhat ambiguous because they could not be distinguished crystallographically. But in both cases the positions chosen for iron are plausible: in the ruthenium analogue[14] of **5a** the Ru atom is in the place assigned to the Fe atom here; an external Co–As unit in **6a** is unlikely due to the extreme instability of the known organometallic Lewis base $(CO)_4Co–AsMe_2$ in the free state.[15,16]

By prolonged warming to 50 °C under 1 atm of CO or under 10 atm of CO at room temperature, in benzene solution, the clusters **6** are fragmented to the known FeCoMo and FeCoW clusters **4**,[5] respectively, in 80–90% yield. Thus a full sequence of cluster transformations **1** → **3** → **5** → **6** → **4** is established, which strongly indicates that the originally reported direct conversion of **3** to **4** also proceeds in this way. Whereas the **3** → **4** conversion involves no net change in CO content, the removal of CO on going from **3** to **5** and the addition of CO on going from **5** to **6** to **4** allow us to understand the reaction conditions necessary for these transformations.

The reversible interconversions between **5** and **6**, although being of simple stoichiometry and high yield, must be mechanistically complex. In each of these clusters the sulfur atom bridges a different metal triangle.[17] Thus more than two bonds have to be broken before 2 mol of CO are added to **5** or removed from **6**. This raises the possibility of further intermediates in the cluster reorganization processes which we are currently trying to find.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Rechenzentrum der Universität Freiburg.

Registry No. 1, 22364-22-3; **2a**, 52456-34-5; **2b**, 52456-36-7; **3a**, 68185-54-6; **3b**, 68212-39-5; **4a**, 68185-55-7; **4b**, 68185-56-8; **5a**, 80926-04-1; **5b**, 80939-28-2; **6a**, 70576-10-2; **6b**, 80939-29-3.

Supplementary Material Available: Listings of the complete crystallographic details, all positional and anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors for both structures (51 pages). Ordering information is given on any current masthead page.

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(10) $FeCo_2MoSAsMe_2Cp(CO)_{10}$ (**6a**): mp 106 °C; IR (cyclohexane) 2068 (m), 2031 (vs), 2008 (s), 2000 (m), 1984 (w), 1970 (w) cm^{-1}; ^1H NMR (benzene) 1.40 (3 H), 1.56 (3 H), 4.53 (5 H) ppm. Anal. Calcd for $[C_{17}H_{11}AsCo_2FeMoO_{10}S]$: C, 27.16; H, 1.47; S, 4.26. Found: C, 27.35; H, 1.47; S, 4.56.

(11) $FeCo_2WSAsMe_2Cp(CO)_{10}$ (**6b**): mp 120 °C; IR (cyclohexane) 2065 (m), 2035 (vs), 2008 (s), 1997 (m), 1983 (w), 1967 (w); ^1H NMR (benzene) 1.47 (3 H), 1.63 (3 H), 4.50 (5 H) ppm. Anal. Calcd for $[C_{17}H_{11}AsCo_2FeO_{10}SW]$: C, 24.31; H, 1.32; S. 3.82. Found: C, 24.31; H, 1.14; S, 3.46.

(12) Crystals of **5a** and **6a** were obtained from hexane. The crystal quality was checked by Weissenberg photographs, all other measurements were done on a Nonius CAD4 diffractometer. **5a**: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 908.5$ (3) pm, $b = 1464.2$ (5) pm, $c = 862.0$ (4) pm, $\alpha = 90.47$ (3)°, $\beta = 101.45$ (3)°, $\gamma = 72.70$ (3)°. **6a**: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 1576.1$ (7) pm, $b = 1136.9$ (2) pm, $c = 1346.0$ (4) pm, $\beta = 93.91$ (3)°. The structures were solved by Patterson and Fourier methods. Anisotropic full matrix refinement for all nonhydrogen atoms using unit weights resulted in R values of 0.069 for **5a** and 0.041 for **6a**. All details of the crystallographic work are documented in the supplementary material: Table A contains all crystallographic data; Tables B and C list all atomic parameters for **5a** and **6a**; Tables D and E list all bond lengths and angles for **5a** and **6a**; Tables F and G give the F_o/F_c listings.

(13) Bruce, M. I. *J. Organomet. Chem.* **1980**, *196*, 295 and previous papers in that series.

(14) Richter, F.; Roland, E.; Beurich, H.; Müller, M.; Vahrenkamp, H., unpublished results.

(15) Müller, R.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 3517.

(16) A structure determination of the ruthenium analogue of **6a** could provide support for the given assignment. This compound, however, could not be obtained as yet.[14]

(17) After each step in the **3** → **5** → **6** → **4** sequence the three metal atoms bridged by the sulfur atom have changed.

Silanes in Organic Synthesis. 15. Silicon-Directed Hydride Abstraction from (2-(Trimethylsilyl)-1,3-cyclohexadiene)iron Tricarbonyl Complexes and Nucleophilic Addition to the Derived Cations[1]

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Summary: Several (2-(trimethylsilyl)-1,3-cyclohexadiene)iron tricarbonyl complexes were prepared and treated with triphenylcarbenium cation. In all cases, hydride abstraction proved to be completely regiospecific to

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(1) For part 14, see: Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron Lett.* **1982**, 263.

(2) Presidential Fellow, 1981.