Table I. Positional, Thermal, and Anisotropic Thermal Parameters for $Ni[CH_2P(S)Ph_2]Cl(PPh_3)$

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C2A	0.6997 (7)	0.6682 (5)	0.0083 (3)	3.7 (2)	C1AA	0.3579 (7)	0.8179 (5)	0.1479 (2)	3.6 (2)
C2B	0.8390 (7)	0.5422 (5)	0.0556 (2)	3.4 (2)	C1AB	0.4050 (7)	0.8237 (5)	0.2179 (2)	3.2 (2)
C2AA	0.6950 (9)	0.7586 (6)	−0.0613 (3)	5.4 (2)	C1AC	0.3075 (8)	0.8830 (5)	0.2232 (3)	4.0 (2)
C2AB	0.6126 (8)	0.6485 (6)	−0.0196 (6)	4.8 (2)	C1AD	0.2627 (8)	0.8769 (5)	0.1541 (3)	4.2 (2)
C2AC	0.6103 (9)	0.6943 (6)	−0.0556 (3)	5.8 (2)	C1AE	0.2400 (8)	0.9085 (5)	0.1909 (3)	4.0 (2)
C2AD	0.7788 (8)	0.7778 (6)	−0.0343 (3)	5.1 (2)	C1BA	0.4841 (8)	0.5973 (5)	0.2260 (3)	4.7 (2)
C2AE	0.7874 (8)	0.7327 (5)	0.0024 (3)	4.6 (2)	C1BB	0.6463 (8)	0.6872 (5)	0.2508 (3)	3.9 (2)
C2BA	0.9473 (9)	0.5687 (5)	0.0736 (3)	5.0 (2)	C1BC	0.4759 (9)	0.5581 (6)	0.2642 (3)	5.7 (2)
C2BB	0.0522 (9)	0.5151 (7)	0.0725 (3)	6.1 (2)	C1BD	0.5573 (8)	0.5831 (6)	0.2935 (3)	4.8 (2)
C2BC	0.0452 (9)	0.4353 (6)	0.0554 (3)	5.2 (2)	C1BE	0.6381 (8)	0.6476 (6)	0.2874 (3)	4.8 (2)
C2BD	0.9389 (9)	0.4092 (6)	0.0381 (3)	5.2 (2)	C1CA	0.8142 (7)	0.7623 (5)	0.1768 (2)	3.6 (2)
C2BE	0.8332 (8)	0.4620 (6)	0.0384 (3)	5.1 (2)	C1CB	0.7785 (8)	0.9310 (5)	0.1551 (3)	4.8 (2)
C1A	0.4296 (6)	0.7908 (4)	0.1798 (2)	2.3 (1)	C1CC	0.8957 (8)	0.8994 (6)	0.1598 (3)	4.8 (2)
C1B	0.5693 (6)	0.6619 (4)	0.2187 (2)	2.6 (1)	C1CD	0.6761 (7)	0.8769 (5)	0.1603 (3)	3.6 (2)
C1C	0.6925 (6)	0.7918 (4)	0.1710 (2)	2.5 (1)	C1CE	0.9134 (8)	0.8164 (6)	0.1716 (3)	4.4 (2)
atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.54206 (8)	0.63786 (6)	0.11801 (3)	25 (1)	26 (3)	27 (13)	−1 (1)	1 (2)	−1 (3)
P(1)	0.5595 (2)	0.7190 (1)	0.17139 (6)	20 (1)	25 (3)	27 (13)	0 (1)	0 (2)	0 (3)
P(2)	0.7027 (2)	0.6096 (1)	0.05570 (7)	31 (1)	33 (3)	36 (13)	−2 (1)	4 (2)	−3 (3)
S	0.5443 (2)	0.5458 (1)	0.06494 (7)	35 (1)	37 (3)	40 (13)	−5 (1)	4 (2)	−5 (3)
Cl	0.3517 (2)	0.5940 (1)	0.13275 (6)	27 (1)	44 (3)	36 (13)	−4 (1)	1 (2)	0 (3)
C	0.7042 (7)	0.6802 (5)	0.0974 (3)	39 (4)	39 (4)	45 (13)	−6 (2)	9 (2)	−8 (3)

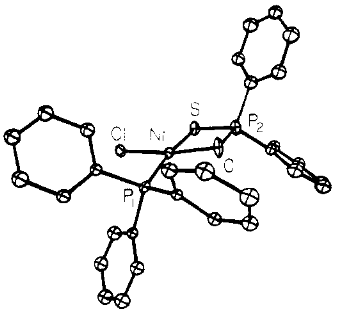

Figure 1. The molecular structure of $Ni[CH_2(S)PPh_2]Cl(PPh_3)$. Bond lengths: Ni–C = 1.999 (8) Å, Ni–S = 2.284 (2) Åa, Ni–P(1) = 2.197 (2) Å, Ni–Cl = 2.216 (2) Å, P(2)–S = 1.999 (3) Å, P(2)–C = 1.776 (8) Å, S···CH_2 = 2.922 (8) Å. Bond angles: S–P(2)–CH_2 = 101.3 (3)°, S–Ni–Cl = 89.3 (2)°, Cl–Ni–P(1) = 94.4 (2)°, S–Ni–C = 86.0 (3)°, P(1)–Ni–C = 90.9 (3)°.

yielded $R = 0.070$ and $R_w = 0.071$ for 2817 independent data with Ni, S, Cl, P, and CH_2 carbon atoms refined anisotropically. The structure is presented in Figure 1.

The NiSPCCl atom core of $Ni(mtp)PPh_3Cl$ is nearly planar (root mean square deviation 0.097 Å). The P(2)–CH_2 distance of 1.776 (8) Å is close to the distance observed in other phosphorus ylide complexes.[1,2] The chelate bite distance of 2.922 (8) Å is not unusually short, and consequently the S–Ni–C angle of 86.0 (3)° is only a few degrees smaller than ideal for a square-planar complex. The S–P(2)–CH_2 angle of 101.3 (3)° is the same internal angle as found[10] in $Ni(S_2PPh_2)_2$. In $\{Ni[(CH_2)_2P(CH_3)_2]_2\}$ the internal CH_2–P–CH_2 angle is[11] 97.7°.

The air stability of crystalline $Ni(mtp)(PPh_3)Cl$ is exceptional for an organometallic alkyl complex of nickel(II). Solution reactivity with various solvents, olefins, and other species is being examined. Exploratory studies have shown that other transition-metal complexes of mtp can be synthesized readily. These results will be reported later.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, Grant CHE-8013141, are gratefully acknowledged for support.

Registry No. $Ni(mtp)(PPh_3)Cl$, 80925-78-6; $NiCl_2(PPh_3)_2$, 14264-16-5; triphenylphosphine sulfide, 3878-45-3; methyllithium, 917-54-4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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[9] Crystal data: $C_{31}H_{27}P_2SClNi$: mol wt 587.74, crystal dimensions of disk ca. 0.2 mm diameter × 0.1 mm thick, orthorhombic, space group *Pbca* (No. 61), $a = 10.672$ (2) Å, $b = 15.617$ (6) Å, $c = 33.425$ (8) Å, $V = 5516$ (3) Å^3, $\rho_{calcd} = 1.40$ g/cm^3, $\rho_{obsd} = 1.40$ (3) g/cm^3, $Z = 8$, μ(Mo Kα) = 10.0 cm^{-1}. Intensity data (5692 reflections, $2.0 \leq 2\theta \leq 55°$, h,k,l) were recorded on a Syntex $P2_1$ four-circle diffractometer at ambient temperature (ca. 22 °C) with graphite-monochromated Mo Kα radiation. The 2870 reflections with $I > 3.0\sigma(I)$ were corrected[12] for Lorentz, decay, and polarization effects (not corrected for absorption—transmission factors range from 0.8 to 0.9). The number of parameters read including phenyl hydrogen atoms was 673, of which 180 were varied. The final difference map contained a peak intensity corresponding to 0.7 e/Å^3.

[10] Porta, P.; Sgamellotti, A.; Vinciguerra, N. *Inorg. Chem.* **1968**, *7*, 2625.

[11] Brauer, D. J.; Kruger, D.; Roberts, P. J.; Tsay, U.-H. *Chem. Ber.* **1974**, *107*, 3706–3715.

[12] See: Chen, H.-W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 22, for a description of crystallographic procedures and computer programs used.

Heteronuclear Organotransition-Metal Clusters: Rational Syntheses and Fluxional Behavior

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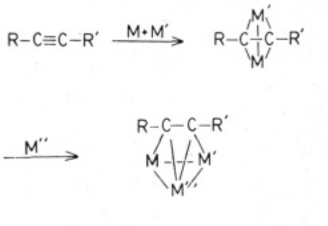
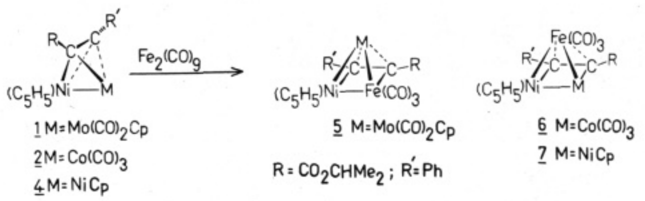
Received December 8, 1981

Summary: Chiral organotransition-metal tetrahedral clusters of the type $(RC{\equiv}CR')MM'$, where M = $(C_5H_5)Ni$

Scheme I



Scheme II



and M′ = $(C_5H_5)Mo(CO)_2$, $Co(CO)_3$, or $(C_5H_5)Ni$ react with $Fe_2(CO)_9$ to give square-pyramidal chiral clusters of general formula $(RC{\equiv}CR')MM'Fe(CO)_3$. When M′ = $Co(CO)_3$, 6, or $(C_5H_5)Ni$, 7, the $Fe(CO)_3$ moiety caps the basal plane whereas when M′ = $(C_5H_5)Mo(CO)_2$, 5, the latter moiety caps the basal plane comprised of $\overline{\text{C–C–Ni–Fe}}$ atoms.

The current burgeoning interest in the synthesis of mixed organotransition-metal clusters may be attributed not only to their potential use as catalysts but also to their low symmetry—an undoubted advantage in ligand stereolability studies.[2a] Only very recently, however, have nonserendipitous routes to tri- or tetrametallic clusters appeared. One general approach is to add metal fragments to unsaturated moieties such as metal–metal multiple bonds[2b,c] or metal–carbyne linkages.[3] The Geoffroy–Gladfelter approach, viz., the addition of metal carbonyl anions to formally coordinatively saturated precursors, also shows great promise for future generalization.[4,5] A preparative strategy[6] based upon the possible interchangeability of cluster skeletal components (using structurally and electronically similar moieties) has been applied to chiral clusters; however, it would appear that stepwise combination of the required metal fragments provides an alternative synthetic method for heteronuclear trimetallic clusters.

We report here several examples of a designed synthetic procedure (Scheme I) in which an alkyne is used as the bridging ligand for the metal centers.

Results and Discussion. We have reported that a series of mixed dimetal–alkyne complexes (e.g., $(RC_2R')[CpNi–Mo(CO)_2Cp]$, **1**, $(RC_2R')[CpNi–Co(CO)_3]$, **2**, $(RC_2R')[CpNiMn(CO)_4]$, **3**) is readily accessible in reasonable yields (~40%) by heating at 100 °C the alkyne, nickelocene, and the appropriate metal carbonyl complex $Cp_2Mo_2(CO)_6$, $Co_2(CO)_8$, or $Mn_2(CO)_{10}$.[7] When treated with $Fe_2(CO)_9$, these compounds (as do the related $(RC_2R')[CpNi–NiCp]$ derivatives, **4**) yield heterotrimetallic species[8] as typified in Scheme II.

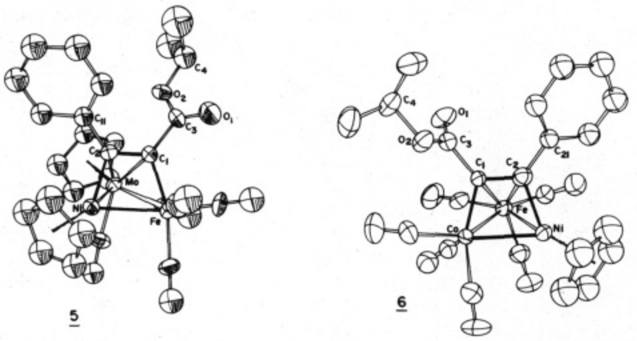


Figure 1. ORTEP diagrams showing structures of molecules **5** and **6**.

The molecules $(RC_2R')(CpNiFe(CO)_3M)$ have been characterized crystallographically[9] (see Figure 1) for M = $Mo(CO)_2Cp$, **5**, $Co(CO)_3$, **6**, and CpNi, **7**, but we wish to focus not on the detailed structures but rather on the overall geometries and fluxional behavior of these systems. In **6** and **7** the final structural component, viz., the $Fe(CO)_3$ unit, caps the basal plane comprising the four original cluster vertices. In contrast, **5** has the $Fe(CO)_3$ in the basal plane which is capped by the $CpMo(CO)_2$ group. Furthermore, in **5** if all the carbonyls are regarded as terminal, the EAN formalism is not appropriate since the Fe, Ni, and Mo atoms would possess 17-, 18-, and 19-electron counts, respectively. The molecule attempts to alleviate the situation via a weak semibridging interaction between a carbonyl on Mo (Mo–C = 1.97 (2) Å) and the basal Fe atom (Fe–C = 2.96 (2) Å). All other bond distances are normal. Formally, the observed structure could have arisen

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(1) (a) Ecole Nationale Supérieure de Chimie. (b) Université de Rennes I. (c) Institut de Recherche sur la Catalyse. (d) McMaster University.

(2) (a) Geoffroy, G. L. *Acc. Chem. Res.* **1980**, *13*, 469–476. (b) Cirjak, L. M.; Huang, J. S.; Zhu, Z. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6623–6626. (c) Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430–2431.

(3) (a) Stone, F. G. A. *Inorg. Chim. Acta* **1981**, *50*, 33. (b) Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 966. (c) Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318.

(4) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207–273.

(5) Johnson, B. F. G. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley-Interscience: New York, 1980; p 1.

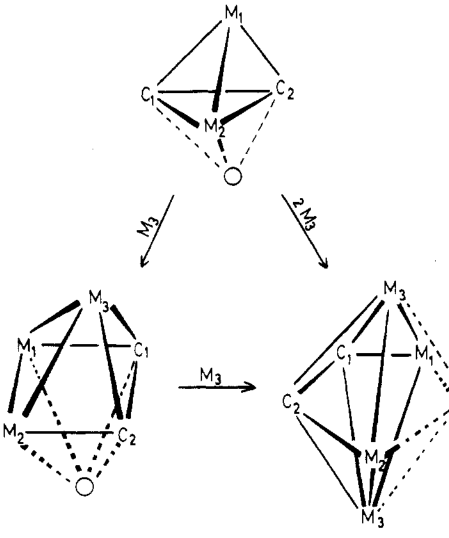
(6) Richter, F.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 864; **1980**, *19*, 65.

(7) Jaouen, G.; Marinetti, A.; Saillard, J. Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1982**, *1*, 225.

(8) Among other products, an (alkyne)$FeNi_2$ cluster was isolated almost 20 years ago: Tilney-Bassett, J. F. *J. Chem. Soc. A*, **1963**, 4784.

(9) Equimolar amounts of **2** and $Fe_2(CO)_9$ were heated at 40 °C in heptane for 3 h under nitrogen. $(\mu_3\text{-}PhC_2CO_2\text{-}i\text{-}Pr)[CpNiFe(CO)_3Co(CO)_3]$, **6** (mp 120 °C; m/z 593.9001, calcd 593.896; IR $(CHCl_3)$ ν_{CO} 2060 (s), 2015 (vs), 2000 (s), 1970 (m), 1960 (m), 1950 (m) cm^{-1}) was obtained in 85% yield as the only isolable product after recrystallization from heptane/$CHCl_3$. Similarly, **1** led to $(PhC_2CO_2\text{-}i\text{-}Pr)[Fe(CO)_3NiCpMo(CO)_2Cp]$, **5** (mp 145 °C, m/z 585.929 (M − 3CO), calcd 585.9274; IR (heptane) ν_{CO} 2028 (vs), 1970 (vs), 1876 (w), 1830 (w) cm^{-1}); also $(PhC_2CO_2\text{-}i\text{-}Pr)Ni_2Cp_2$, **4**, led to $(PhC_2CO_2\text{-}i\text{-}Pr)[Cp_2Ni_2Fe(CO)_3]$, **7** (mp 125 °C; m/z 573.9528, calcd 573.9522). Interestingly, the same procedure applied to the $(RC_2R')[Co_2(CO)_6]$ series slowly gave rise to a gray material that decomposed during TLC separation to yield starting material. $(PhC_2CO_2Et)Ni_2Cp_2Fe(CO)_3$ was stirred with an excess of $Fe_2(CO)_9$ in CH_2Cl_2 at 40 °C for 4 h to give the tetrametallic cluster $(PhC_2CO_2Et)Ni_2Cp_2Fe_2(CO)_6$, **8**, in 20% yield: mp 180 °C; mass spectrum, m/z 699.8518, calcd 699.85635; IR $(CHCl_3)$ ν_{CO} 2050 (m), 2020 (m), 2000 (s), 1970 (sh), 1953 (s), 1712 (m) cm^{-1}. The molecular structure of the diethyl analogue of **8**, viz., $(Et_2C_2)Ni_2Cp_2Fe_2(CO)_6$, prepared as in ref 8, has been reported recently: Marinetti, A.; Sappa, E.; Tiripicchio, A.; Tiripicchio-Camelli, M. *Inorg. Chim. Acta* **1980**, *44*, L183. **5**, $FeNiMoO_7C_{27}H_{22}$; M_r = 668.966; triclinic; $P\bar{1}$; a = 8.634 (3) Å, b = 9.879 (2) Å, c = 15.471 (5) Å, α = 90.71 (2)°, β = 100.32 (3)°, γ = 99.16 (2)°, V = 1280.5 $Å^3$, Z = 2. Full-matrix least-squares refinement by the heavy-atom method gave R = 0.053 and R_w = 0.055 for 2608 independent reflections: radiation Ag Kα, θ range 1–21°, refined scale factor 0.267 (3)°; residual electron density after last difference Fourier synthesis, 0.47 e/$Å^3$ near the heavy atoms. **6**, $FeCoNiO_8C_{23}H_{17}$: M_r = 594.88; triclinic; $P\bar{1}$; a = 8.179 (1) Å, b = 11.910 (2) Å, c = 12.512 (4) Å, α = 94.02 (2)°, β = 106.73 (2)°, γ = 90.33 (2)°, V = 1163.9 $Å^3$; d_{calcd} = 1.697 g·cm^{-3} for Z = 2; μ(MoKα = 21.7 cm^{-1}; $F > 3\sigma(F)$; 2θ max 60°; R = 0.046 for 3312 reflections. **7**, $Ni_2FeO_5C_{25}H_{22}$: M_r = 575.715; triclinic; $P\bar{1}$; a = 8.313 (2) Å, b = 9.648 (3) Å, c = 13.149 (3) Å, α = 104.97 (2)°, β = 102.84 (1)°, γ = 93.94 (2)°, V = 1209 $Å^3$; d_{calcd} = 1.58 g·cm^{-3} for Z = 2. For 3122 independent reflections, $(I \geq 2\sigma(I))$, R = 0.041 and R_w = 0.047.

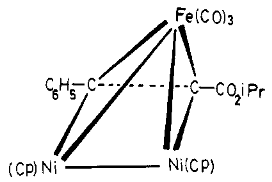
Scheme III



by rotation of the alkyne with respect to the metal triangle in the presumed initial product, viz., with Fe capping the Mo–Ni–C–C plane. This observation parallels that very recently reported by Stone et al.,[10] who showed that in $(R_2C_2)Cp_2W_2Os(CO)_7$ the pyramidal cap of the M_2C_2 plane can be either W or Os.

One must try to rationalize the facility with which these reactions occur since the tetrahedral precursors are supposedly coordinatively saturated; nevertheless, even the absence of a manifest metal–metal multiple bond in the bimetallic complexes does not prevent the ready addition of organometallic fragments. A useful bonding picture is based on the Wade–Williams–Rudolph–Mingos[11] approach to electron-deficient clusters. This view[12] regards the initial tetrahedral molecules 1 through 4 as nido-trigonal bipyramids and the clusters 5, 6, and 7 as nido-octahedral systems each possessing five vertices and seven electron pairs for cluster skeletal bonding. This delocalized picture not only obviates the EAN requirements of the Fe and Mo atoms in 5 but also provides a vacant coordination site on the cluster surface; thus 5, 6, and 7 should be capable of ready cluster expansion and should also be fluxional as are their tetrahedral precursors.[7] Both of these predictions are valid. Thus, addition of a second $Fe(CO)_3$ unit to $(RC_2R')[Cp_2Ni_2Fe(CO)_3]$, 7, yields $(RC_2R')[Cp_2Ni_2Fe_2(CO)_6]$, 8—a nido-pentagonal bipyramid—as depicted in Scheme III. The general idea of polyhedral expansion was developed by Hawthorne for metallocarboranes[13] and was recently extended to metal–carbido clusters.[14]

The pentanuclear systems 5, 6, and 7 may be regarded as octahedral clusters with a vacant coordination site; this is in accord with the fact that these molecules show fluxional behavior consistent with formal rotation of the alkyne moiety with respect to the metal triangle.[15] Figure 2 shows the ^1H NMR spectra of the C_5H_5 protons of 7 at various temperatures. The Ni atoms (and hence their attached Cp's) are chemically and magnetically different at low temperature but are equilibrated via a process for which $\Delta G^{\ddagger} = 15.1 \pm 0.5$ kcal/mol. Substitution of one of the $Fe(CO)_3$ carbonyl units by triphenylphosphine raises this barrier to 17.5 ± 0.5 kcal/mol. The molecules 5 and 6 also show fluxionality, and this can be probed by the diastereotopic methyl group of the isopropyl ester function.[16] We note that at the high-temperature limit the spectrum shows two doublets, thus demonstrating that the intrinsic chirality of the molecule is never lost, hence ruling out an intermolecular exchange as a mechanistic possibility.



7

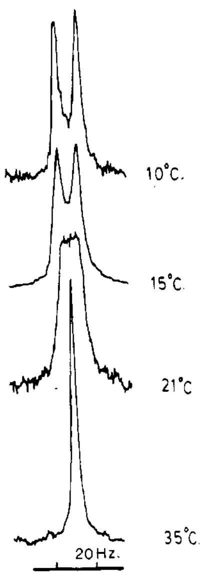


Figure 2. Variable-temperature 80-MHz ^1H NMR spectra of the C_5H_5 protons of 7.

Complete crystallographic data together with extended Hückel molecular orbital calculations of the rotational barriers in these clusters will be presented elsewhere.

In conclusion, it has been shown that nido electron-deficient organotransition-metal clusters allow a synthetic cascade procedure since addition of moieties contributing two skeletal electrons yields nido clusters of higher nuclearity as shown in Scheme III.[17] The vacancy in the coordination polyhedron also allows reversible transformation between isomeric structures detectable by NMR spectroscopy.[18]

Acknowledgment. We thank Dr. G. L. Geoffroy (The Pennsylvania State University) and Professor R. Hoffmann (Cornell University) for helpful comments and for disclosing results prior to publication. Financial support from the CNRS (France) and NSERC (Canada) is gratefully acknowledged.

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[10] Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101.

[11] (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Williams, R. E. *Ibid.* **1976**, *18*, 67. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (d) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1974**, 133.

[12] Wade, K. In ref 5, p 193.

[13] Callahan, K. P.; Hawthorne, M. F. *Adv. Organomet. Chem.* **1976**, *14*, 145.

[14] Tachikawa, M.; Sievert, A. C.; Muetterties, E. L.; Thompson, M. R.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1725.

[15] For related phenomena see: (a) Evans, J. *Adv. Organomet. Chem.* **1977**, *16*, 319. (b) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1975**, *97*, C16. (c) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2859. (d) Todd, L. J.; Wilkinson, J. R.; Rausch, M. D.; Dickson, R. S. *J. Organomet. Chem.* **1975**, *101*, 133. (e) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1879. (f) Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 231.

[16] At low temperature the spectrum appears as four doublets but coalesces to two doublets at ~80 °C when interconversion of diastereomers (but not of enantiomers) is rapid on the NMR time scale. The ratios of diastereomers are 88:12 for 5 and 82:18 for 6 at room temperature.

[17] Of course, closo clusters are also known: an example of a closo-pentagonal-bipyramidal organotransition-metal cluster is $(Ph_4C_4)[Ru_3(CO)_8]$: Gambino, O.; Sappa, E.; Manotti-Lonfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1979**, *36*, 190.

[18] Interestingly, a closo hexanuclear chiral cluster has been observed to racemize on the chemical (slow) time scale rather than on the relatively fast NMR time scale: Fox, J. R.; Gladfelter, W. L.; Geoffroy, G. L.; Tavanaiepour, I.; Abdel-Mequid, S.; Day, V. W. *Inorg. Chem.* **1981**, *20*, 3230.

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$_2$Mo and FeCO$_2$W Clusters

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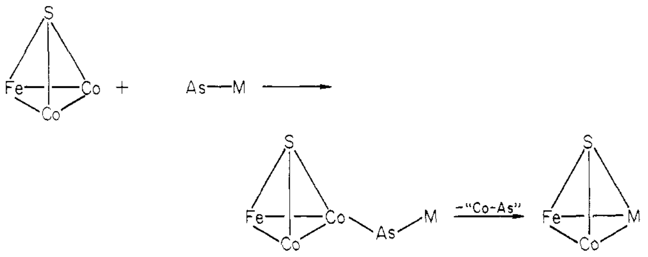
Summary: The tetrahedral clusters $FeCo_2MSAsMe_2Cp(CO)_8$ (M = Mo, W) which are obtained from $FeCo_2S(CO)_9$ and $Cp(CO)_3MAsMe_2$ reversibly add 2 mol of CO to form the clusters $FeCo_2MSAsMe_2Cp(CO)_{10}$ with a $MCo_2(\mu\text{-}AsFe)$ core.

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.

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

Scheme I



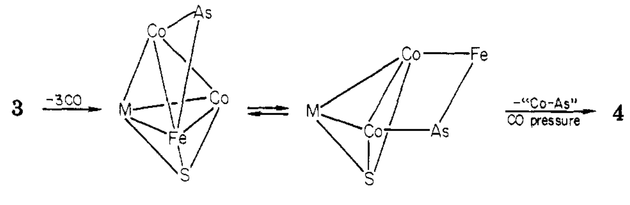
$SFeCo_2(CO)_9$ + $Me_2As—M(CO)_3Cp$ $\xrightarrow{-CO}$

1 **2a**, M = Mo; **b**, M = W

$SFeCo_2(CO)_8—AsMe_2M(CO)_3Cp$ $\xrightarrow{-[(CO)_3Co\text{-}AsMe_2]_x}$ $SFeCoMCp(CO)_8$

3a, M = Mo; **b**, M = W **4a**, M = Mo; **b**, M = W

Scheme II



$FeCo_2MSAsMe_2Cp(CO)_8$ $\underset{-2CO}{\overset{+2CO}{\rightleftharpoons}}$ $FeCo_2MSAsMe_2Cp(CO)_{10}$

5a, M = Mo; **b**, M = W **6a**, M = Mo; **b**, M = W

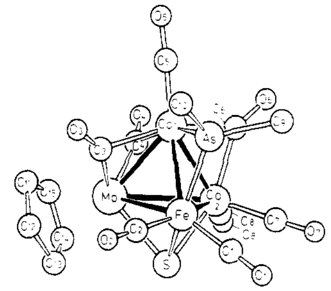


Figure 1. Molecular structure of $FeCo_2MoSAsMe_2Cp(CO)_8$ (**5a**).

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)

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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.

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