Contribution from the Institut für Anorganische und Analytische Chemie der Universität, D-7800 Freiburg, FRG,
and Institut für Anorganische Chemie der Universität, D-6500 Mainz, FRG

Framework Isomerism of Mixed Tetranuclear Clusters

Manfred Müller,[1] Hans-Thomas Schacht,[1] Klaus Fischer,[1] Jürgen Ensling,[2] Philipp Gütlich,[2]
and Heinrich Vahrenkamp*[1]

The clusters $(\mu_3\text{-S})FeCo_2MCp(CO)_8(AsMe_2)$ (**1**, M = Mo; **2**, M = W) and $(\mu_3\text{-PMe})FeCo_2MCp(CO)_8(AsMe_2)$ (**3**, M = Mo; **4**, M = W) are formed as mixtures of isomers **a** and **b** with ca. 70:30 to 90:10 compositions. The isomers, which differ in color, X-ray powder data, and IR, NMR, and Mössbauer spectra, can be separated and obtained spectroscopically and analytically pure by medium-pressure chromatography. Together with the known structure of **1a** the crystal structure determinations of **1b** [monoclinic, $P2_1/c$, a = 1509.4 (4) pm, b = 849.7 (2) pm, c = 1817.7 (3) pm, β = 115.64 (3)°, V = 2.1017 (3) nm³, Z = 4], **3a** [monoclinic, $P2_1/c$, a = 1595.9 (2) pm, b = 956.7 (1) pm, c = 1585.0 (2) pm, β = 109.68 (1)°, V = 2.2786 (2) nm³, Z = 4], and **3b** [monoclinic, $P2_1/c$, a = 1587.1 (3) pm, b = 983.6 (4) pm, c = 1545.1 (2) pm, β = 110.99 (1)°, V = 2.2520 (3) nm³, Z = 4] reveal that the two isomers each have the same molecular structures but differ in the locations of the iron and cobalt atoms, which cannot be assigned unambiguously, in the cluster core. If one starts with the pure isomers, the equilibrium mixtures are obtained within days in normal solvents (degassed and distilled C_6H_6, C_6H_{12}, or $CDCl_3$) or when small amounts of CO are present, indicating that impurities or cluster breakdown fragments induce isomerization. Correspondingly, under very clean conditions, equilibration does not occur. The equilibrium compositions are temperature independent between 5 and 70 °C. Chemically the isomers cannot be distinguished: CO produces identical degradation products, and PPh_3 reactions lead to identical substitution derivatives.

Introduction

The accessibility of mixed-metal clusters[3] and the beginning investigation of basic cluster reactions[4] have opened the field of cluster stereochemistry. This field should be fertile with respect to basic knowledge (designed cluster growth, heterosite reactivity, mutual site modification) as well as application (multicenter substrate activation, transfer of stereochemical information). A prerequisite for the study of such phenomena is the availability of clusters with similar compositions but different geometries, i.e. cluster core isomerism.

All reported results on cluster core isomerism are very recent, including framework fluxionality,[5] the formation of isomeric products in two different reactions,[6] the production of noninterconvertible isomers in one reaction,[7] and the observation of temperature-dependent isomer mixtures in solution.[8] Simple interconversions of separable isomers by heating[9] or even by recrystallization[10] are so far known just as unique examples.

Our own interest in cluster core isomerism arose from metal-exchange studies[11] and the isolation of optically active clusters,[12] which created questions about the metal-exchange mechanism

and the pathways for cluster core racemization. During these studies reversible opening reactions for trinuclear[13] and tetranuclear clusters[14] were found that may create intermediates for isomerization and reconstitution pathways. Together with the preliminary observation that some of the tetranuclear clusters[14] exist as isomeric mixtures, this caused us to investigate the isomeric situation. Herein we report an extensive study of the isomer separations, interconversions, structures, and reactivities of four pairs of clusters with $FeCo_2M(\mu_3\text{-E})(\mu\text{-AsMe}_2)$ composition for M = Mo, E = S (**1**), M = W, E = S (**2**), M = Mo, E = PMe (**3**), and M = W, E = PMe (**4**).

Experimental Section

All procedures were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk techniques and dry, degassed solvents. ¹H NMR spectra were obtained on a Varian T 60 A machine with Me_4Si as internal standard; IR spectra were recorded in cyclohexane solutions on a Perkin-Elmer 782 spectrometer. EI mass spectra were obtained at 70 eV on a Finnegan 4000 mass spectrometer. X-ray powder data were measured on a Stoe Stadi II/P1 powder diffractometer in glass capillaries by using the Debye-Scherrer technique, Cu Kα radiation, and a graphite monochromator. Single-crystal X-ray data were measured on a Nonius CAD4 diffractometer.

Mössbauer spectra were recorded in transmission geometry by using a 12 mCi $^{57}Co/Rh$ source (The Radiochemical Centre, Amersham, England) kept at 293 K and a conventional spectrometer operating in the constant-acceleration mode. The drive system was calibrated by using the known hyperfine splitting of α-iron. the samples ($\approx$0.1 mg $^{57}Fe/cm^2$) were sealed in poly(methyl methacrylate) containers and placed in a liquid-helium flow cryostat. The temperature was kept at 80 K and measured with a FeRh resistor. The spectra, consisting of a quadrupole doublet, were fitted as a superposition of two independent lines by using the MOSFUN program.[15a]

The medium-pressure chromatography apparatus was self-built from commercial components. Reagents were obtained commercially. The tetranuclear clusters were synthesized according to our published[14] procedures.

Chromatographic Separations. Isomeric mixtures (35-mg portions) of each of the clusters **1–4** were dissolved in 3 mL of benzene/hexane (1:1) and subjected to chromatography with the same mixture as eluent and

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(2) Universität Mainz.
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Table I. Crystallographic Data for **1b** and **3a,b**

	1b	**3a**	**3b**
mol formula	$C_{15}H_{11}AsCo_2FeMoO_8S$	$C_{16}H_{14}AsCo_2FeMoO_8P$	$C_{16}H_{14}AsCo_2FeMoO_8P$
mol wt	695.9	709.8	709.8
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
cell dimens (20 °C)			
a, pm	1509.4 (4)	1595.9 (2)	1587.1 (3)
b, pm	849.7 (2)	956.7 (1)	983.6 (4)
c, pm	1817.7 (3)	1585.0 (2)	1545.1 (2)
β, deg	115.64 (3)	109.68 (1)	110.99 (1)
V, nm³	2.1017 (4)	2.2786 (2)	2.2520 (3)
Z	4	4	4
$F(000)$	1344	1376	1376
d_{obsd}, g cm⁻³	2.22	2.10	2.11
d_{calcd}, g cm⁻³	2.20	2.07	2.09
radiation	Ag Kα	Mo Kα	Ag Kα
monochromator	graphite	graphite	graphite
cryst dimens, mm	0.43 × 0.24 × 0.06	0.55 × 0.35 × 0.05	0.43 × 0.39 × 0.04
μ, cm⁻¹	42.9	43.5	39.7
no. of reflcns measd	2804	3420	2687
no. of obsd data ($I \geq 3\sigma(I)$)	1625	2971	1143
no. of variables	221	249	153
R (unit weights)	0.072	0.064	0.076
residual e density, 10⁶ e pm⁻³	+1.3/−1.0	+1.7/−1.8	+1.0/−0.8

Table II. Atomic Parameters for Brown $FeCo_2MoCp(CO)_8(\mu_3\text{-}S)(\mu\text{-}AsMe_2)$ (**1b**)

atom	x	y	z	U_{eq},^{a} 10⁴ pm²
Mo	0.7973 (1)	0.3636 (2)	0.3753 (1)	0.0312 (9)
Fe	0.7980 (2)	0.6054 (4)	0.2945 (2)	0.033 (2)
Co1	0.7173 (2)	0.3644 (4)	0.2022 (2)	0.038 (2)
Co2	0.6248 (2)	0.5172 (4)	0.2702 (2)	0.045 (2)
As	0.7704 (2)	0.5894 (3)	0.1638 (2)	0.038 (1)
S	0.6498 (4)	0.2631 (8)	0.2757 (4)	0.042 (3)
C1	0.620 (3)	0.327 (4)	0.103 (2)	0.08 (2)
O1	0.564 (2)	0.307 (4)	0.038 (1)	0.10 (1)
C2	0.800 (2)	0.220 (3)	0.199 (1)	0.05 (1)
O2	0.853 (2)	0.126 (3)	0.194 (1)	0.10 (1)
C3	0.897 (2)	0.433 (3)	0.334 (1)	0.05 (1)
O3	0.976 (1)	0.423 (3)	0.334 (1)	0.07 (1)
C4	0.779 (2)	0.580 (3)	0.408 (1)	0.04 (1)
O4	0.784 (2)	0.684 (3)	0.449 (1)	0.08 (1)
C5	0.876 (2)	0.772 (4)	0.315 (2)	0.05 (1)
O5	0.928 (2)	0.874 (3)	0.326 (1)	0.09 (1)
C6	0.655 (2)	0.725 (3)	0.260 (2)	0.06 (2)
O6	0.639 (2)	0.859 (3)	0.249 (2)	0.09 (1)
C7	0.517 (2)	0.518 (4)	0.178 (2)	0.06 (2)
O7	0.445 (2)	0.515 (3)	0.120 (1)	0.09 (1)
C8	0.570 (2)	0.538 (3)	0.342 (2)	0.05 (1)
O8	0.538 (2)	0.560 (4)	0.385 (1)	0.10 (2)
C9	0.677 (2)	0.737 (4)	0.081 (2)	0.064 (8)
C10	0.883 (2)	0.591 (3)	0.141 (2)	0.054 (7)
C11	0.932 (1)	0.303 (3)	0.494 (2)	0.037 (4)
C12	0.910 (1)	0.168 (3)	0.443 (2)	0.037 (4)
C13	0.817 (1)	0.110 (3)	0.432 (2)	0.037 (4)
C14	0.781 (1)	0.210 (3)	0.476 (2)	0.037 (4)
C15	0.852 (1)	0.329 (3)	0.514 (2)	0.037 (4)
C11′	0.875 (4)	0.110 (6)	0.436 (3)	0.037 (4)
C12′	0.786 (4)	0.138 (6)	0.444 (3)	0.037 (4)
C13′	0.798 (4)	0.278 (6)	0.490 (3)	0.037 (4)
C14′	0.894 (4)	0.338 (6)	0.510 (3)	0.037 (4)
C15′	0.941 (4)	0.234 (6)	0.477 (3)	0.037 (4)

^{a} All atoms except C9, C10, and C11–C15′ refined anisotropically. Fe corresponds to M1 and Co1 to M2 in Figure 2.

Table III. Atomic Parameters for Purple $FeCo_2MoCp(CO)_8(\mu_3\text{-PMe})(\mu\text{-}AsMe_2)$ (**3a**)

atom	x	y	z	U_{eq},^{a} 10⁴ pm²
Mo	0.7011 (0)	0.6594 (1)	0.1566 (0)	0.0381 (3)
Fe	0.7613 (1)	0.3706 (1)	0.1792 (1)	0.0416 (5)
Co2	0.8585 (1)	0.5612 (1)	0.2896 (1)	0.0449 (5)
As	0.7127 (1)	0.2742 (1)	0.2871 (1)	0.0504 (5)
Co1	0.7072 (1)	0.5096 (1)	0.2947 (1)	0.0392 (5)
P	0.8275 (1)	0.5461 (2)	0.1467 (1)	0.0434 (8)
C11	0.6077 (5)	0.5223 (8)	0.1659 (5)	0.049 (1)
O11	0.5363 (4)	0.4710 (7)	0.1405 (4)	0.065 (1)
C12	0.7214 (5)	0.7384 (8)	0.2780 (5)	0.047 (1)
O12	0.7304 (5)	0.8222 (6)	0.3337 (4)	0.066 (1)
C13	0.5985 (5)	0.7218 (7)	0.0213 (4)	0.065 (1)
C14	0.5913 (5)	0.8159 (7)	0.0878 (4)	0.065 (1)
C15	0.6721 (5)	0.8925 (7)	0.1207 (4)	0.072 (1)
C16	0.7292 (5)	0.8456 (7)	0.0745 (4)	0.067 (1)
C17	0.6837 (5)	0.7401 (7)	0.0131 (4)	0.065 (1)
C13′	0.6401 (7)	0.705 (1)	0.0028 (7)	0.030 (2)
C14′	0.5782 (7)	0.744 (1)	0.0453 (7)	0.044 (2)
C15′	0.6159 (7)	0.855 (1)	0.1054 (7)	0.032 (2)
C16′	0.7011 (7)	0.885 (1)	0.1001 (7)	0.048 (2)
C17′	0.7161 (7)	0.792 (1)	0.0367 (7)	0.030 (2)
C21	0.9487 (6)	0.4479 (9)	0.3254 (6)	0.064 (1)
O21	1.0113 (5)	0.3764 (8)	0.3504 (6)	0.104 (1)
C22	0.8160 (5)	0.5202 (9)	0.3908 (6)	0.058 (1)
O22	0.8467 (5)	0.5058 (8)	0.4687 (4)	0.084 (1)
C23	0.9125 (6)	0.7225 (9)	0.3276 (7)	0.071 (1)
O23	0.9483 (6)	0.8215 (9)	0.3524 (8)	0.136 (1)
C31	0.8392 (6)	0.2402 (9)	0.1823 (7)	0.072 (1)
O31	0.8900 (5)	0.1517 (8)	0.1856 (7)	0.112 (1)
C32	0.6832 (6)	0.3068 (9)	0.0788 (6)	0.064 (1)
O32	0.6361 (5)	0.2690 (8)	0.0124 (5)	0.097 (1)
C41	0.5992 (7)	0.1716 (9)	0.2629 (8)	0.084 (1)
C42	0.7954 (8)	0.1743 (9)	0.3896 (7)	0.085 (1)
C51	0.6293 (5)	0.5085 (9)	0.3499 (5)	0.047 (1)
O51	0.5774 (4)	0.5028 (7)	0.3836 (4)	0.069 (1)
C6	0.8927 (6)	0.5755 (9)	0.0729 (6)	0.063 (1)

^{a} All atoms except C13–C17′ refined anisotropically. Co1 corresponds to M1 and Fe to M2 in Figure 3.

an excess pressure of 0.5–1.0 bar over commercial silica gel columns (Merck Lobar-Fertigsäulen, LiChroPrep, Si 60, 40–63 µm, Grösse B, 2.5 × 31 cm). In each case the major isomer (**a**) was eluted in the first, purple, fraction and the minor isomer (**b**) in the second, brown, fraction. For **1a,b** and **3a,b** the identity in the composition of the isomeric mixture and the single isomers was confirmed, after recrystallization from pentane/dichloromethane (20:1), by elemental analyses and EI-MS.

Structure Determinations. The crystal structure of **1a** has been reported.[14a] Black crystals of **1b** and **3a,b** were obtained from benzene/pentane. The notoriously bad quality of the crystals of the minor isomers **1b** and **3b** prevented high-quality data sets and low R values. Crystal quality and space group were checked by Weissenberg techniques. Re-

flection data were obtained by standard diffractometer methods at room temperature: 2θ range 1–40°, ω–2θ measurement, scan width (in ω) 0.80 + 0.45 tan θ, scan speed 0.7–7 deg/min, takeoff angle 6°. The minimum number of octants was measured in each case. Due to the irregular shapes of the crystals no absorption corrections were attempted for **3a,b**, but for **1a** the correction was applied. The structures were solved by using direct methods[15b-d] and refined by full-matrix refinement using unit weights until the shift/esd ratios were less than 0.2. The number of atoms to be refined anisotropically was limited by the condition that the reflection/parameter ratio did not fall below 7. The C_5H_5 ligands were treated as rigid bodies with C–C distances of 142 pm; for **1c** their C

Table IV. Atomic Parameters for Brown
$FeCo_2MoCp(CO)_8(\mu_3\text{-}PMe)(\mu\text{-}AsMe_2)$ (3b)

atom	x	y	z	U_{eq},[a] 10^4 pm^2
Mo	0.7076 (2)	0.6414 (4)	0.1659 (2)	0.040 (2)
Co1	0.7647 (3)	0.3606 (6)	0.1835 (4)	0.047 (3)
Co2	0.8628 (4)	0.5340 (6)	0.3104 (4)	0.056 (3)
As	0.7048 (3)	0.2630 (4)	0.2837 (4)	0.057 (3)
Fe	0.7039 (4)	0.4889 (5)	0.3003 (4)	0.040 (3)
P	0.8382 (7)	0.534 (1)	0.1647 (8)	0.045 (6)
C11	0.604 (3)	0.521 (4)	0.173 (3)	0.05 (1)
O11	0.534 (2)	0.474 (3)	0.147 (2)	0.072 (9)
C12	0.734 (2)	0.715 (4)	0.286 (3)	0.05 (1)
O12	0.745 (2)	0.792 (3)	0.352 (2)	0.076 (9)
C13	0.728 (2)	0.788 (5)	0.052 (3)	0.04 (2)
C14	0.659 (2)	0.694 (5)	0.006 (3)	0.05 (1)
C15	0.586 (2)	0.715 (5)	0.037 (3)	0.04 (2)
C16	0.610 (2)	0.822 (5)	0.103 (3)	0.14 (5)
C17	0.698 (2)	0.867 (5)	0.112 (3)	0.05 (1)
C13'	0.620 (6)	0.72 (1)	0.033 (6)	0.04 (4)
C14'	0.602 (6)	0.80 (1)	0.101 (6)	0.00 (2)
C15'	0.680 (6)	0.88 (1)	0.147 (6)	0.05 (4)
C16'	0.746 (6)	0.85 (1)	0.108 (6)	0.03 (3)
C17'	0.709 (6)	0.75 (1)	0.037 (6)	0.14 (8)
C21	0.953 (3)	0.439 (4)	0.347 (3)	0.06 (1)
O21	1.023 (3)	0.368 (4)	0.361 (2)	0.12 (1)
C22	0.824 (3)	0.471 (4)	0.410 (3)	0.05 (1)
O22	0.846 (2)	0.451 (4)	0.488 (2)	0.10 (1)
C23	0.925 (3)	0.674 (6)	0.367 (3)	0.09 (2)
O23	0.964 (3)	0.770 (5)	0.392 (3)	0.12 (1)
C31	0.843 (3)	0.234 (5)	0.199 (3)	0.07 (1)
O31	0.895 (2)	0.148 (4)	0.204 (2)	0.09 (1)
C32	0.692 (3)	0.324 (5)	0.084 (3)	0.07 (1)
O32	0.634 (2)	0.295 (3)	0.003 (2)	0.09 (1)
C41	0.592 (3)	0.161 (5)	0.250 (3)	0.08 (1)
C42	0.781 (3)	0.146 (5)	0.382 (3)	0.07 (1)
C51	0.639 (3)	0.494 (4)	0.361 (3)	0.05 (1)
O51	0.586 (2)	0.490 (3)	0.400 (2)	0.065 (8)
C6	0.907 (3)	0.552 (5)	0.091 (3)	0.08 (1)

[a] Only Fe, Co, Mo, As, and P refined anisotropically. Fe corresponds to M1 and Co1 to M2 in Figure 3.

atoms were assigned a common temperature factor. In all three cases two orientations of the C_5H_5 ligands had to be taken into account with 70% weighting for the unprimed and 30% weighting for the primed atoms. Table I gives the crystallographic details; Tables II–IV list the atomic parameters.

Isomerizations. (a) **1a** and **3a** (15 mg each) were placed in an NMR tube, which was then attached to a vacuum line. Prepurified benzene (1 mL) was condensed onto the sample and the tube sealed in vacuum. NMR spectroscopy showed that no equilibration occurred at room temperature. Above 40 °C decomposition started, which was faster for **1a** than for **3a**. At 70 °C, about 10% of **3a** was decomposed after 24 h; at 40 °C, about 20% of **1a** was decomposed after 24 h. Only after decomposition was noticeable did isomerization set in, which reached equilibrium when 20–30% of the starting material was decomposed.

(b) **1a**, **1b**, and **3a,b** (10 mg each) were dissolved in 0.5 mL of degassed and distilled benzene or deuteriochloroform in NMR tubes and kept under nitrogen at room temperature. Equilibration occurred in 1–2 days for **1** and in 2–4 days for **3**. During this time decomposition occurred, but to an extent of less than 10%.

(c) Solutions of **1a** and **3a** as prepared in isomerization a were subjected to an atmosphere of 95% N_2 and 5% CO before the NMR tubes were sealed. At room temperature and after ca. 10 h for **1a** and ca. 20 h for **3a** there was about 20% decomposition, and the isomer equilibrium was reached.

(d) Experiments like a–c were performed with 1–2-mg samples of **2a** and **4a** and experiments like a and c were performed with 1–2 mg samples of **1b** and **3b**, in cyclohexane solutions with IR monitoring. Except for the less precise determination of quantities, the observations were analogous to those in a–c.

(e) Under the conditions of fastest equilibration, i.e. those in b, solutions of the isomeric mixtures of **1** and **3** in C_6H_6 or $CDCl_3$ were kept in sealed NMR tubes at 5, 20, 30, 50 and 70 °C. Except for decomposition, which was negligible at 5 °C and complete at 70 °C within about 4 days for **3** and within about 2 days for **1**, no change of the sample compositions occurred.

CO Reactions. In addition to the reported[14b] CO reactions of the isomer mixtures of **1–3** the following reactions were performed.

Table V. Summary of Reactions with CO

starting complex	products and yield	recovered material
3 (isomer mixture, 47 mg, 0.066 mmol)	**7** (9 mg, 30%), **5** (15 mg, 29%)	**3** (8 mg, 16%)
4 (isomer mixture, 42 mg, 0.053 mmol)	**7** (3 mg, 11%), **6** (13 mg, 31%)	**4** (9 mg, 21%)
3a (42 mg, 0.059 mmol)	**7** (8 mg, 28%), **5** (14 mg, 29%)	**3** (isomer mixture, 6 mg, 15%)
3b (16 mg, 0.022 mmol)	**7** (5 mg, 50%), **5** (6 mg, 35%)	**3** (isomer mixture, traces)
4a (42 mg, 0.053 mol)	**7** (2 mg, 9%), **6** (13 mg, 32%)	**4** (isomer mixture, 9 mg, 21%)
4b (15 mg, 0.019 mmol)	**7** (3 mg, 35%), **6** (5 mg, 33%)	

(a) **MeP-Capped Clusters.** In each case a slow stream of CO was bubbled through a solution of the MeP-capped cluster in 3 mL of benzene for 2 h at room temperature. Subsequent chromatography with benzene/hexane (1:3) over a 30 × 2.5 cm silica gel column allowed us to isolate the reaction products (for formulas, see text). Table V summarizes the results for the pure isomers and the isomer mixtures of **3** and **4**.

(b) **Sulfur-Capped Clusters.** These were known[14a] to undergo fast reactions with CO to yield the open clusters **8** and **9** (see text). Their pure isomers yielded identical products: 2 mg each of **1a,b**, and **2a,b** in 3 mL of cyclohexane were vigorously stirred in a CO atmosphere. IR control indicated that it took no longer than 10 min to use up all the starting material. Then the only product in solution was **8** for **1a,b** and **9** for **2a,b**. By keeping the solutions of **8** and **9** under vacuum with stirring for 12 to 15 h, quantitative reconversion to **1** and **2** occurred, which then consisted of the isomer mixtures.

Donor Ligand Reactions. The clusters **1** and **2** were very labile toward donor reagents. Reactions with RNC, $P(OMe)_3$, and PR_3 led to mixtures of products, which also changed on the chromatography column. The clusters **3** and **4** were somewhat more stable, but only for the reactions with equimolar amounts of PPh_3 could pure products be isolated in reasonable yields. More basic phosphine ligands also led to degradation of **3** and **4**, and among the reaction products monosubstituted derivatives of the trinuclear parent clusters $FeCoM(\mu_3\text{-}PMe)Cp(CO)_8$ could be detected, e.g. in the reaction of **4** (67 mg, 0.084 mmol) with PMe_2Ph (12 mg, 0.085 mmol) in benzene (4 mL). After 12 h the solvent was removed in vacuum, the residue extracted with three 3-mL portions of pentane, and the extract chromatographed with benzene/hexane (1:1) over a 2 × 14 cm silica gel column. After the first fraction, an unidentified greenish oil, from the second, green, fraction 4 mg (7%) of $FeCoW(\mu_3\text{-}PMe)Cp(CO)_7PMe_2Ph$ (**13b**)[12b] was crystallized. Three more fractions (brown, green, purple) each contained milligram quantities of unidentified products.

PPh$_3$ Reactions of 3. **3** (isomer mixture; 37 mg, 0.052 mmol) and triphenylphosphine (13.5 mg, 0.051 mmol) in benzene (4 mL) were stirred for 20 h. The solvent was removed in vacuum and the residue chromatographed with benzene/hexane (1:1) over a 2 × 10 cm silica gel column. The first, green, fraction, after crystallization from benzene/hexane (1:6), yielded 5 mg (12%) of dark green $FeCoMo(\mu_3\text{-}PMe)Cp(CO)_7PPh_3$ (**12**), mp 188 °C. Anal. Calcd for $C_{31}H_{23}CoFeMoO_7P_2$: C, 47.72; H, 2.97; Co, 7.55. Found: C, 47.60; H, 2.63; Co, 6.98. The second, brown-green, fraction contained traces of an unidentified product. From the third, purple, fraction, after recrystallization from dichloromethane/n-pentane (1:20), 38 mg (76%) of black $FeCo_2Mo(\mu_3\text{-}PMe)Cp(CO)_7(\mu\text{-}AsMe_2)PPh_3$ (**10**), mp 158°, was obtained. Anal. Calcd for $C_{33}H_{29}AsCo_2FeMoO_7P_2$: C, 41.98; H, 3.10; Co 12.48. Found: C, 41.71; H, 3.09; Co 11.99.

The pure isomers of **3** were subjected to the same reaction with equimolar amouts of PPh_3 and the same workup procedure. The products were identical with those from the reaction with the isomer mixture of **3**: **3a** (32 mg, 0.046 mmol) yielded **12** (3.6 mg, 10%) and **10** (24 mg, 55%); **3b** (25 mg, 0.035 mmol) yielded **12** (1.8 mg, 7%) and **10** (14 mg, 43%).

PPh$_3$ Reactions of 4. **4** (isomer mixture, 107 mg, 0.134 mmol) and triphenylphosphine (35 mg, 0.134 mmol) in benzene (8 mL) were treated and worked up as before. Chromatography yielded in the first, green, fraction 16 mg (14%) of dark green $FeCoW(\mu_3\text{-}PMe)Cp(CO)_7PPh_3$ (**13a**), mp 192 °C. Anal. Calcd for $C_{31}H_{23}CoFeO_7P_2W$: C, 42.85; H, 2.67; Co, 6.79. Found: C, 42.94; H, 2.88; Co, 6.69. The second and third fractions (brown-green, red) contained traces of unidentified material; the fourth, red, fraction contained traces of remaining **4**. The fifth, purple, fraction, eluted with benzene/hexane (2:1) yielded, after crystallization from dichloromethane/pentane, 102 mg (73%) of black

Table VI. Spectra of the Isomers

no.	IR (C_6H_{12}), cm^{-1}	^{1}H NMR (C_6H_6),[a] δ or $\delta/(J, Hz)$	Mössbauer,[b] mm/s
1a	2045 m, 2008 vs, 1995 vs, 1978 s, 1946 m, 1854 w, 1821 w, 1775 w	Cp 4.83 AsMe$_2$ 1.54, 1.70	$\delta = 0.110$ (3) $\Delta E_Q = 0.545$ (2)
1b	2046 m, 2017 vs, 1997 vs, 1987 s, 1964 w, 1822 w, 1774 m	Cp 4.85 AsMe$_2$ 1.42, 1.48	$\delta = 0.093$ (2) $\Delta E_Q = 0.545$ (2)
2a	2045 m, 2001 vs, 1994 vs, 1986 s, 1948 m, 1853 w, 1816 w, 1765 w	Cp 4.70 AsMe$_2$ 1.49, 1.64	
2b	2043 m, 2011 vs, 1991 vs, 1984 s, 1965 w, 1815 w, 1765 w	Cp 4.74 AsMe$_2$ 1.36, 1.44	
3a	2034 m, 1985 vs, 1966 s, 1932 w, 1857 w, 1823 w, 1771 w	Cp 4.69; PMe 2.55/13.6 AsMe$_2$ 1.60, 1.82	$\delta = 0.082$ (1) $\Delta E_Q = 0.835$ (3)
3b	2038 w, 1992 vw, 1982 vs, 1979 m, 1947 w, 1772 w	Cp 4.75; PMe 2.48/13.5 AsMe$_2$ 1.43, 1.57	$\delta = 0.052$ (1) $\Delta E_Q = 1.052$ (2)
4a	2035 m, 1986 vw, 1966 s, 1936 w, 1857 w, 1827 w, 1763 w	Cp 4.62; PMe 2.33/13.2 AsMe$_2$ 1.51, 1.77	
4b	2039 w, 1991 vs, 1983 vs, 1972 m, 1946 w, 1761 w	Cp 4.68; PMe 2.28/13.2 AsMe$_2$ 1.40, 1.55	

[a] Internal Me$_4$Si as reference. [b] Referenced to Fe.

FeCo$_2$W(μ_3-PMe)Cp(CO)$_7$(μ-AsMe$_2$)PPh$_3$ (**11**), mp 169 °C. Anal. Calcd for C$_{33}$H$_{29}$AsCo$_2$FeO$_7$P$_2$W: C, 38.41; H, 2.83; Co, 11.40. Found: C, 38.44; H, 2.85; Co, 11.08.
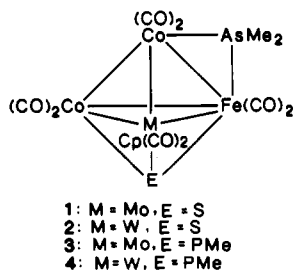
The pure isomers of **4** were subjected to the same reaction with equimolar amounts of PPh$_3$ and the same workup procedure. The product distribution was identical with that from the reaction of the isomer mixture of **4**: **4a** (35 mg, 0.044 mmol) yielded **13a** (3.9 mg, 10%) and **11** (23 mg, 50%); **4b** (21 mg, 0.027 mmol) yielded **13a** (2.1 mg, 9%) and **11** (15 mg, 55%).

CO Reaction of 11. CO was bubbled through a solution of **11** (23 mg, 0.022 mmol) in toluene (15 mL). After 4–5 min, TLC indicated that no more **11** was present and **4** (isomeric mixture) and a small amount of its CO degradation product **6** had formed. The solvent was removed in vacuum and the residue crystallized from benzene/pentane (1:4) to yield 15 mg (84%) of **4**.

PPh$_3$ Reaction of FeCoMo(μ_3-PMe)Cp(CO)$_8$ (14). **14** (53 mg, 0.096 mmol) and PPh$_3$ (27 mg, 0.102 mmol) in benzene (10 mL) did not react at room temperature. After the mixture was stirred for 3 h at 50 °C, the solvent was removed in vacuum and the residue crystallized from benzene/hexane (1:5) to yield 60 mg (80%) of **12**.

Results

Product Identification. The four clusters **1–4** with FeCo$_2$M cores (M = Mo, W) and μ_3-E bridging (E = S, PMe), which had resulted from cluster buildup sequences, were previously assigned the constitution given here.[14] The assignment rested on the spectral similarity between **1** and the corresponding RuCo$_2$Mo cluster, both of which had been subjected to crystal structure analysis. However, since iron and cobalt positions cannot be distinguished by means of X-ray data, the assignment is unambiguous only for the RuCo$_2$Mo cluster. (For the sake of clarity, the CO bridges present in **1–4** (cf. Figure 2 and 3) are not drawn here.) Additional uncertainty about the location of the iron and two cobalt atoms arose from the observation[14] that **1** and **3** consisted of isomer mixtures. The finding that **2** and **4** also exist as isomer mixtures and the isomer separations for all four cases have now provided material for detailed studies but not completely clarified the bonding situation in **1–4**.

(CO)$_2$Co——AsMe$_2$
(CO)$_2$Co————Fe(CO)$_2$
M
Cp(CO)$_2$
E

1: M = Mo, E = S
2: M = W, E = S
3: M = Mo, E = PMe
4: M = W, E = PMe

Standard medium-pressure chromatography using commercial 31-cm silica gel columns provided an easy means of separating the isomers. In all four cases the major isomer (**a**, red-purple for **1** and **2**, purple for **3** and **4**) was eluted first, followed by the minor isomer (**b**, brown for **1** and **2**, greenish brown for **3** and **4**). The
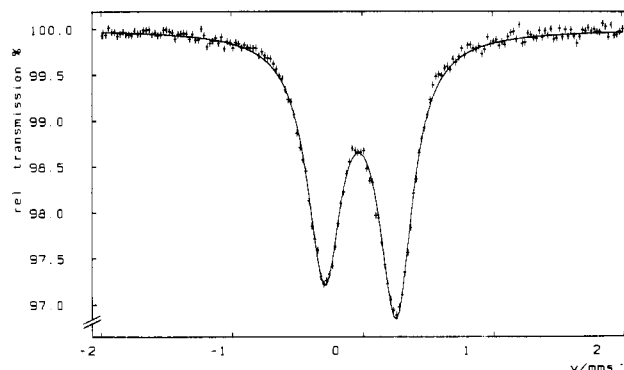

Figure 1. Mössbauer spectrum of FeCo$_2$MoCp(CO)$_8$(μ_3-S)(μ-AsMe$_2$), brown isomer **1b**.
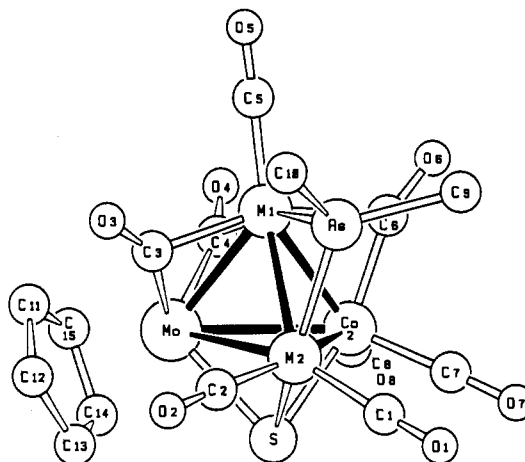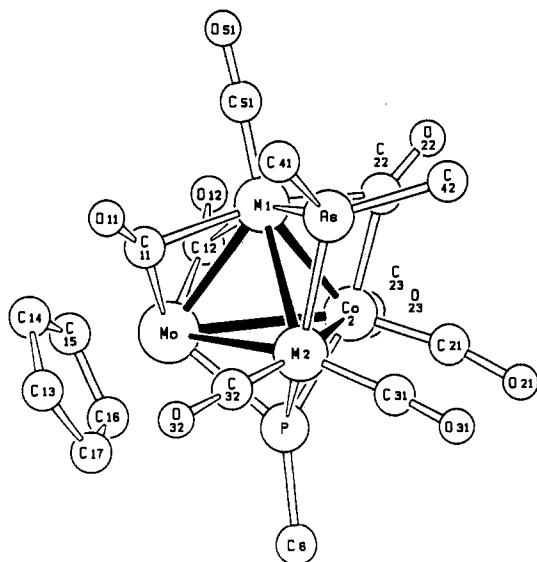

Figure 2. Molecular structure of both isomers of **1**. The atom numberings of **1a**[14a] and **1b** are identical. In the final refinement of **1a**, M1 was Co and M2 was Fe, and in the final refinement of **1b**, M1 was Fe and M2 was Co. H atoms were not included in the refinement.

mass ratios of the two isomers **a** and **b** were 80:20 for **1**, 90:10 for **2**, 70:30 for **3**, and 90:10 for **4**. Elemental analyses and EI mass spectra confirmed for **1** and **3** that the two isomers **a** and **b** have identical compositions.

Table VI lists the spectroscopic data of the eight complexes. The two isomers are quite similar, but significantly different in all respects. The simplest indication is the color in solution (see above). In the NMR spectra, of the three or four resonances, those assigned to the AsMe$_2$ units show the largest difference and were used to determine the amounts of compounds present in solution. In each case there is an upfield shift in the AsMe$_2$ resonances and a downfield shift in the Cp resonances in going

Figure 3. Molecular structure of both isomers of **3**. The atom numberings are identical for both isomers. In the final refinement of **3a**, M1 was Co and M2 was Fe, and in the final refinement of **3b**, M1 was Fe and M2 was Co. H atoms were not included in the refinement.

Table VII. Framework Atomic Distances (pm) for **1a,b** (E = S) and **3a,b** (E = P)

dist	1a[14a]	1b	3a	3b
Mo–Co2	280.5 (2)	279.7 (4)	284.0 (1)	286.9 (6)
Mo–M1	257.1 (2)	252.8 (4)	259.1 (1)	258.0 (6)
Mo–M2	282.1 (3)	284.0 (4)	290.7 (1)	288.9 (6)
Co2–M1	249.9 (3)	256.7 (5)	249.2 (2)	251.1 (8)
Co2–M2	255.8 (3)	257.9 (5)	263.8 (2)	264.4 (8)
M1–M2	260.8 (2)	259.2 (4)	263.3 (2)	265.2 (7)
M1–As	225.7 (3)	223.1 (4)	225.9 (1)	223.7 (7)
M2–As	228.5 (3)	229.5 (4)	229.5 (2)	229.6 (7)
Mo–E	233.6 (4)	233.9 (6)	234.2 (2)	233.2 (10)
Co2–E	219.5 (4)	218.7 (8)	215.4 (2)	214.3 (13)
M2–E	217.5 (5)	217.7 (7)	213.7 (3)	214.5 (11)

from isomer a to isomer b. The most noticeable difference in the IR spectra is the presence of three bands attributable to CO bridges in isomer a while only one or two such bands appear for isomer b. Otherwise the striking similarity of the IR spectra among the isomers a and b is noticeable.

The Mössbauer data for **1a,b** and **3a,b** again are quite similar, but their difference is well outside the standard deviation. To give an indication of the reliability of the data, Figure 1 shows a characteristic Mössbauer spectrum. For both pairs of isomers, isomer b has the smaller isomer shift and an equal or greater nuclear quadrupole coupling than isomer a. Finally, X-ray powder data were obtained for **1a,b** and **3a,b**. The patterns, showing only few prominent maxima, look similar but the 2θ values are different. The powder reflection maxima can be reproduced by using the single-crystal reflection intensities (see below), the most prominent lines occurring for Cu Kα radiation at $2\theta = 10.41°$ for **1a** (100, 110, 001), 12.16° for **1b** (−1,1,1, 110, 011), 11.50° for **3a** (−1,0,2, −1,1,1), and 11.29° for **3b** (−1,0,2, −1,1,1). The main purpose of the powder data was to ensure that the single crystals used for the structure determinations and the bulk material were identical.

Molecular Structures. Whereas structure determinations normally resolve problems of isomerism, in this case they have created them. In fact, the structure determination of **1b** which completes the pair **1a,b** was only done after the structures of **3a,b** had turned out so similar that it was feared that a crystal of **3a** had been used in the X-ray analysis of **3b**. Subsequently (see above) the identities of the single crystals of **1a,b** and **3a,b** were established with certainty, and the molecular shapes of these compounds actually are nearly the same.

Figures 2 and 3 show the molecular geometry for **1a,b** and **3a,b**. For the pair **3** all crystallographic details including unit cells and atomic positions are very similar whereas **1a** crystallizes triclinic and **1b** monoclinic. However, the RuCo$_2$Mo analogue[14a] of **1a** again has a unit cell very similar to that of **1b**. In all four structure solutions (for this purpose the data set of **1a**[14a] was reprocessed) the positions called M1 and M2 were alternatively used for cobalt and iron. Thereby the R value changed by less than 0.1% and the only significant parameter changes concerned the temperature factors of these atoms. No preference for one alternative could be deduced from these findings, and the mediocre quality of the data of **1b** and **3b** has prevented more precise statements. Arbitrary assignments had therefore to be made for the location of iron in isomers a and b. The spectral similarity between **1a** and the corresponding RuCo$_2$Mo cluster[14a] makes us assign the ruthenium position for iron, i.e. M2, in the major isomers a whereas the iron position in the minor isomers b, which we assign to M1

here, is a matter open to discussion since the position assigned to Co2 in Figures 2 and 3 must also be considered as a possible one for the iron atom. As shown by computations for **3a**, again no preference can be found, but further permutations of the assignments of atomic positions were not performed. See the Discussion for our preference for M1 and M2 as possible iron positions.

The positional uncertainties do not affect the statement that the molecular shapes are nearly identical. Table VII demonstrates this for the heavy-atom frameworks. Whereas all heavy atom bond distances are within the normal range for mixed-metal clusters,[3] some details are noteworthy. Thus the CO-bridged metal–metal bonds are considerably shorter than the corresponding nonbridged ones, cf. Mo–M1 vs. Mo–M2 or Mo–Co2 and M1–Co2 vs. M2–Co2. This even makes the Mo–M1 bond shorter than the light-metal bonds M1–M2 or Co2–M2. On the other hand the consistency in the As–M and E–M bonds is obvious despite the fact that E changes form S to P and that the two metal atoms bound to As have quite different surroundings. The asymmetry of the molecules makes the two methyl groups on arsenic nonequivalent as reflected in the NMR spectra. The occurrence of bridging CO IR absorptions corresponds to the presence of three bridging CO ligands in the molecules. The structures in the solid state cannot explain, however, that the isomers b show only one or two ν(CO-bridge) bands in solution in contrast to three for the isomers a. This may be related to the semibridging nature (and hence greater mobility) of C3O3 and C4O4 in **1** and C11O11 and C12O12 in **3**, respectively, consistently these CO groups have long M1–C distances (199–212 pm for the former and 222–230 pm for the latter) and wide Mo–C–O angles (151–156° for the former and 159–164° for the latter). Altogether the electronic difference between a and b, which is most obvious from the colors and IR spectra of the isomers, finds no correspondence even in the details of their molecular geometries.

Isomerization. Detailed equilibration and isomerization studies for **1** and **3** and small-scale experiments with **2** and **4** lead to the conclusion that under rigorously clean conditions the isomers do not interconvert at room temperature in solution. It is only when impurities are present or when partial decomposition has occurred that the isomer equilibrium is reached within 10–100 h. The condition "impurity" is fulfilled in solvents that have not been purified beyond degasification and distillation or under an atmosphere of prepurified nitrogen. Partial decomposition can occur thermally (for **1** and **2** easier than for **3** and **4**) or by the presence of small amounts of CO in the atmosphere which leads to cluster breakdown (see below). The equilibrium mixture is reached under the same conditions from both sides a or b. Within the range of accessible temperatures (5 to 70°C) the equilibrium composition shows no significant change indicating that the thermal effects in the isomer interconversions are small. The similar equilibrium isomer ratios for all four clusters (3:7 to 1:9) indicate similar energetic relations among them.

Reactions. We have described the CO reactions of the isomer mixtures of **1–3**.[14b] The results obtained have now been confirmed for **4** and for the pure isomers of all four clusters. The most important observation is that in each case both isomers produce the same cluster degradation products. For the phosphorus-bridged systems the first observable and isolable CO reaction

Table VIII. Spectra of the PPh₃ Derivatives

no.	IR (C₆H₁₂), cm⁻¹							¹H NMR (CDCl₃),[a] δ or δ/(J, Hz)			
								PMe	Cp	PPh	AsMe
10	1985 m	1968 vs	1945 s	1916 w	1834 w	1787 w	1753 w	3.22/11.4	5.03	7.3 m	1.87, 2.07
11	1984 m	1967 vs	1945 s	1915 w	1830 w	1792 w	1760 w	3.07/10.8	5.00	7.2 m	1.73, 1.94
12	2030 m	1981 s	1965 vs	1945 m	1932 m	1905 m		2.18/13.0	5.31	7.3 m	
13a	2028 m	1980 m	1964 vs	1949 m	1930 w	1903 m		2.27/13.0	5.35	7.4 m	

[a] Internal Me₄Si as reference.

product is **5** or **6** respectively, resulting from the addition of 3 equiv of CO. Addition of another CO ligand then produces the trinuclear cluster **7** and the stable organometallic Lewis base Cp-

5: M = Mo
6: M = W

7
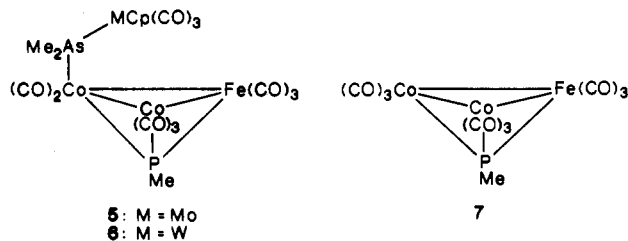
(CO)₃M–AsMe₂ (M = Mo, W). This reaction sequence is the retrosynthesis of **3** and **4**[14a] and it involves movement of the μ-AsMe₂ ligand from a FeCo (or CoCo) unit to a MCo unit (M = Mo, W) and movement of the μ₃-PMe ligand from a MFeCo or MCoCo triangle (M = Mo, W) to a FeCo₂ triangle. It is noticeable that unchanged **3** and **4** recovered after CO reactions of the pure isomers consist of the isomer mixtures.

The pure isomers of **1** and **2** just like the isomer mixtures react with CO in solution within minutes to form the open clusters **8** and **9** corresponding to the addition of 2 mol of CO. This reaction

8: M = Mo
9: M = W
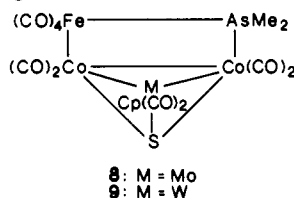
differs from the previous one in that the AsMe₂ bridge stays attached to two light transition metals and the capping sulfur unit stays attached to the heavy metal. But the fact that both isomers generate the same products also requires severe rearrangements in the cluster framework in at least one of the isomers. It is known that the subsequent CO degradiation products of **8** and **9** are sulfur-bridged FeCoM clusters (M = Mo, W)[14b] showing that this step is also different from the one for **3** and **4**. The known reconversion in vacuum[14b] of **8** and **9** to **1** and **2** produces the standard isomer mixtures and thus provides another way of isomer equilibration for **1** and **2**.

Knowing the CO lability of clusters **1–4**, it was to be predicted that they would also be degraded by more basic ligands. This was the case for most reactions attempted. No pure products could be isolated from any of the reactions tried between **1** and **2** and RNC, P(OR)₃, or PR₃ units. For **3** and **4** the situation was somewhat better, but only with triphenylphosphine could derivatives of tetranuclear clusters be obtained. At room temperature, using a 1:1 ratio, monosubstituted **10** and **11** resulted in good

10: M = Mo
11: M = W

12: M = Mo, L = PPh₃
13a: M = W, L = PPh₃
b: M = W, L = PMe₂Ph
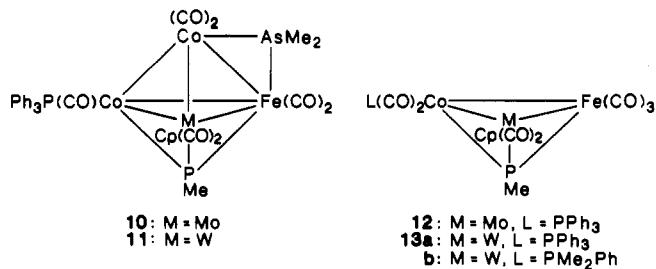
yields. Again the pure isomers of **3** and **4** produced the same

derivatives **10** and **11**, indicating very facile equilibration during chemical reactions. In each case the cluster substitution product (**10, 11**) was accompanied by a cluster degradation product: from **3** and PPh₃ resulted **12**; from **4** and PPh₃ resulted **13a**. A similar trinuclear derivative **13b**[12b] was also the only isolable product of the reaction of **4** with PMe₂Ph. These degradations differ from those with CO in that in **12** and **13** a FeCoM (M = Mo, W) triangle remains while **7** has a FeCo₂ triangle.

The spectra that were used for the identification of **10–13** are summarized in Table VIII. The IR spectra of **10** and **11**, except for a shift to low wavenumbers, are quite similar to those of the major isomers **3a** and **4a**. This leads us to assign the metal framework as discussed above. The PPh₃ ligand is likely to be on Co2 since Co2 is the most exposed metal and together with M1 it is the only metal in **3** and **4** that does not bear two strong donor ligands already. This assignment is supported by the purple color of **10** and **11**. The structures for the new clusters **12** and **13a** can be referred to the known one of **13b**[12b] due to the similarity in the IR spectra.

A chemical consequence of the high number of strong donor ligands in **10** and **11** is the ease of replacement of PPh₃ by CO. Thus **11** reacted with CO in solution within minutes, re-forming **4**. TLC control indicated that from the beginning **4** was present in this reaction as the isomer mixture. This way yet another isomerization reaction is established. In order to test whether the compounds **12** and **13** result from degradation of **10** and **11** or whether degradation produces FeCoM(μ₃-PMe)Cp(CO)₈[12b] first, which then undergoes substitution, a sample of FeCoMo(μ₃-PMe)Cp(CO)₈ was treated with PPh₃ under the same conditions as **3**. No reaction occurred, and only heating produced the substitution derivative **12**. This supports the idea that the formation of **10** and **12** from **3** (or **11** and **13** from **4**) occurs via an addition–elimination sequence.

Discussion

The main puzzle resulting from the above findings concerns the location of the iron and two cobalt atoms in the two isomers a and b. No positive information could be obtained either from the four structure determinations or from spectra and chemical reactions. By their extreme geometrical similarity the two isomers prove how easily electronic imbalances can be accommodated in polynuclear metal frameworks.

For the heavy-atom frameworks of clusters **1–4**, principally the three alternatives A, B, and C must be taken into consideration, where M is Mo or W and the two bridging ligands are symbolized by dotted lines. Although there cannot be geometric isomerism

A   **B**   **C**
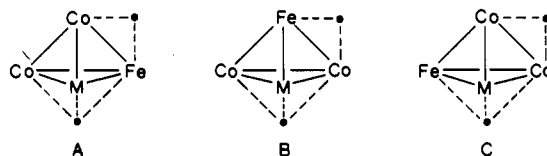
in a tetrahedron with three different metal atoms alone, the FeCo₂MAsE heavy-atom framework allows just these three isomers, provided the μ₃-E ligand is attached to Mo or W and the μ-AsMe₂ ligand bridges two light transition-metal atoms as observed. And although, as noted above, no definitive proof exists for any one of them, to our opinion A and B can be preferred as outlined below.

The main argument in favor of structure A for the major isomers is the similarity of the IR spectra of all four isomers a with that of the ruthenium analogue of **1a**, whose structure is

known.[14a] If this assignment is accepted, then only structures B and C have to be considered for isomers b. We prefer B, and our line of reasoning is as follows: (i) An 18-electron configuration for all metal atoms without making donor–acceptor metal–metal bonds can only be achieved for A and B, making the reasonable assumption that the bridging AsMe$_2$ ligand donates two electrons to iron and one electron to cobalt. (ii) The Mössbauer data for isomers a and b are so similar that the iron atoms must be in similar environments. This condition seems to be better realized for the positions of M1 and M2 than for the positions of M2 and Co2 in Figures 2 and 3. (iii) There exist clusters of composition FeCoM$_2$Cp$_2$(CO)$_7$(μ_3-S)(μ-AsMe$_2$) (M = Mo, W) with structures similar to those of **1** and **2**[14a]. In these, a MCp(CO)$_2$ unit occupies the location of the Co2(CO)$_3$ unit in **1**. Together with the experience[11] that a Co(CO)$_3$ position is the most likely one to be occupied by another organometallic fragment, this eliminates the Co2 position in **1** from being available for the iron atom. Although these three arguments provide just circumstantial evidence for B, similar arguments in favor of C are less easily found.

The chemical behavior of the two isomers cannot be used to argue about their structures. Thus one might conclude that the simplest heavy-ligand fluctuation, i.e. moving the AsMe$_2$ bridge from the M1–M2 bond to the M1–Co2 bond with an opposite shift of one CO ligand, favors structure C. This argument would assign a greater inertness to the metal–metal bonds than to the metal–arsenic or metal–E bonds (E = S, PMe), which is not the case: cf. the CO reactions of **1** to **4**. In fact, a rotation of the FeCo$_2$As unit together with its ligands around the axis of the FeCo$_2$ triangle would interconvert A and B without breaking any metal–arsenic bond.

An even greater number of possibilities than those for the structures exist for the mechanisms of isomer interconversions. The reactions of the clusters with donor ligands show that any metal–metal or metal–heavy-atom ligand (P, S, As) bond is easily broken, thereby providing an open cluster framework that should be more prone to reorganization than the cluster itself. However, two observations argue against donor ligand induced opening as an intermediate step in cluster isomerization: (i) in the presence of the donor ligand (CO, PR$_3$) the addition or substitution product is always preferred, and (ii) it takes more drastic conditions to re-form clusters **1**–**4** from the donor reaction products than it takes to isomerize the clusters alone. On the other hand the clusters do not isomerize under very pure conditions, which eliminates an intramolecular fluctional process as the isomerization mechanism. In our opinion a homolytic metal–metal bond cleavage or a one-electron-transfer process induces isomerization. The impurities present in solution or those resulting from partial decomposition can initiate such a process by their electrophilic/nucleophilic or redox properties, thereby weakening metal–metal and metal–ligand bonding and facilitating the metal-scrambling process. Support for this comes from the fact that electron-transfer catalysts greatly facilitate metal exchange in cobalt-containing clusters[16] as well as the cluster aggregation process leading to **1**–**4**,[17] in the latter case however at the expense of a higher proportion of undesired products. The general weakness of bonds between light transition metals[18] makes it then understandable that only iron and cobalt but not molybdenum or tungsten are involved in the changes during isomerization.

All chemical reactions of clusters **1**–**4** also involve isomerization processes. In each case—CO additions of **1**–**4** or phosphine reactions of **3** and **4**—both isomers a and b lead to the same products, in each back-reaction the isomer mixture is generated from a single precursor and in each CO reaction the triply bridging ligand changes its location. It is noteworthy that the reaction conditions allow isomerization of unreacted **3** and **4** in the process of CO addition, possibly via partial decomposition. And in one

case—the PPh$_3$ degradation of **3**—it was possible to show clearly that the donor is introduced by an additive pathway. It is not surprising that donor-induced cluster opening results in cluster rearrangement. But, as discussed above, the isomerizations of the cluster alone probably do not occur by such a mechanism.

The fact that two metals of different electron count can alternatively occupy metal sites in the same ligand environment sheds some light on the electronic similarity of transition elements that do not differ greatly in their atomic number. Although the electron distribution must be different in isomers a and b no indication for this can be seen in the structures of the compounds or in their reactivities. Similar conclusions can be drawn from the Mössbauer data. The environments of the iron atoms must be very similar (geometrically and electronically) in both isomers, their charges must be low, and the change in electron count cannot be localized but must be accommodated by the molecule as a whole. The Mössbauer data correlate well with those of other μ_3-bridged iron-containing clusters,[19] indicating coordination numbers of six or higher but low symmetry around the iron atoms. The similar ability of neighboring transition elements to accommodate or delocalize charge has most clearly been demonstrated by ESR experiments,[20] and many structure determinations have shown[21] that atomic radii of transition metals quite often are controlled more by their steric and electronic environment than by their position in the periodic table. It remains a challenge in mixed-metal cluster work to exploit the reciprocity of great similarities and small differences in the chemistry of neighboring transition metals.

Conclusions

The separation and structural characterization of isomers a and b of clusters **1**–**4** have demonstrated the ability of these FeCo$_2$M clusters (M = Mo, W) to exist as stable entities with different arrangements of the iron and cobalt atoms within the same ligand environment. The similarity of the molecular shapes is so high that the iron and cobalt positions cannot be assigned with certainty. The occurrence of isomer equilibration only in the presence of impurities indicates that radical type metal–metal bond cleavages initiate the isomerization processes. The fact that donor ligand (CO, PR$_3$) induced cluster openings generate identical products from the different isomers correlates with the enhanced framework lability of partially opened clusters, as does the re-formation of the isomer mixtures from the open derivatives. Similarly, cluster framework mobility is obvious from the changes in location of the μ-AsMe$_2$ and μ_3-E (E = S, PMe) ligands in the course of the cluster interconversions. As a generalization it might be stated that in reactivity studies a cluster composed of first-row transition metals may well behave like the sum of its individual metal components rather than like a durable molecular entity.

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