9.4 mg (2.6×10^{-2} mmol) of $NiCl_2(PEt_3)_2$, and 4.3 mg (3.2×10^{-2} mmol) of pentamethyldisilane was heated for 20 h at 180°C in a sealed glass tube. The mixture was chromatographed on silica gel using hexane to give 0.2034 g (78% yield) of **18**.

Reaction of 19 with Phenyl(trimethylsilyl)acetylene. A mixture of 0.4827 g (1.64 mmol) of **19**, 0.3345 g (1.92 mmol) of phenyl(trimethylsilyl)acetylene, 11.7 mg (3.2×10^{-2} mmol) of $NiCl_2(PEt_3)_2$, and 0.1628 g (0.52 mmol) of docosane as an interanal standard was heated in a sealed glass tube for 20 h at 200 °C. The mixture was analyzed by VPC as being **20** (52%) and **21** (10%). Pure **20** was obtained from recrystallization of the mixture from ethanol. Compound **21** in the filtrate was isolated by preparative VPC. For **20**: mp 157.0–157.5 °C; MS, *m/e* 468 (M^+); ^1H NMR δ −0.23 (s, 15 H, Me_2Si and Me_3Si), 0.01 (s, 6 H, Me_2Si), 6.72–7.31 (m, 15 H, phenyl ring protons); ^{13}C NMR δ −0.7 (Me_2Si), 1.5 (Me_2Si), 1.6 (Me_3Si), 125.3, 126.3, 126.8, 127.4, 127.5, 127.8, 146.2, 146.5, 146.9 (phenyl ring carbons), 142.6, 163.5, 166.9, 181.2 (olefinic carbons). Anal. Calcd for $C_{29}H_{36}Si_3$: C, 74.29; H, 7.74. Found: C, 74.49; H, 7.83. All spectral data obtained for **21** were identical with those of an authentic sample.[10]

Reaction of 20 with Hydrogen Chloride. In a 25-mL two-necked flask fitted with a condenser and an inlet tube for hydrogen chloride was placed a solution of 64.0 mg (0.14 mmol) of **20** and 17.7 mg (0.078 mmol) of cetane in 8 mL of dry benzene. Hydrogen chloride gas was passed into the solution for 15 min at room temperature. The solvent was evaporated under reduced pressure, and then 2 mL of methyllithium (4 mmol) was added to the residue. The mixture was stirred for 2 h at room temperature and hydrolyzed with water. The mixture was analyzed by VPC as being 1,1-diphenylethene[22] (74%) and phenyltris(trimethylsilyl)ethene[15] (49%). All spectral data obtained for both products were identical with those of authentic samples.

Reaction of 13 with a Catalytic Amount of $NiCl_2(PEt_3)_2$. A mixture of 98.0 mg (0.42 mmol) of **13**, 3.2 mg (9×10^{-3} mmol) of $NiCl_2(PEt_3)_2$, and 45.8 mg (0.28 mmol) of tridecane was placed in a glass tube. The tube was sealed under reduced pressure and heated for 15 h at 135 °C. VPC analysis of the mixture showed the presence of dimer **11** in 45% yield. Recrystallization of the mixture from ethanol gave 26.6 mg of **11**, mp 182–183 °C. All spectral data for **11** were identical with those of an authentic sample.[20]

Acknowledgment. We are indebted to the Crystallographic Research Center, Intstitute of Protein Research, Osaka University, for computer calculations. We also express our appreciation to Toshiba Silicon Co., Ltd., Shin-etsu Chemical Co., Ltd., and Toray Silicon Co., Ltd., for a gift of organochlorosilanes.

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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(22) An authentic sample was obtained from Aldrich Chemical Co., Inc.

A Rationalized Synthesis and X-ray Crystal Structure of $Cp_3Co_2MoFe(CO)_5CCO_2$-*i*-Pr: A Heterometallic M_4C Closo Cluster

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A series of synthetic manipulations carried out on the cluster system $Co_3(CO)_9CR$, where R = CO_2-*i*-Pr, yields a variety of mixed-metal clusters. Treatment with Cp_2Ni, $[CpNi(CO)]_2$, or $[CpMo(CO)_3]_2$ leads to replacement or modification of one, two, or all three of the original $Co(CO)_3$ vertices. Upon treatment with $Fe_2(CO)_9$, these tetrahedral M_3CR molecules can be expanded to the analogous $M_3Fe(CO)_3CR$ square-based pyramidal systems. However, $CpMo(CO)_2(CpCo)_2(\mu\text{-}CO)CR$ yields the closo trigonal bipyramidal molecule $Cp_3Co_2MoFe(CO)_5CR$ which has been fully characterized by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.309$ (5) Å, $b = 14.731$ (6) Å, $c = 17.298$ (7) Å, $\beta = 124.63$ (6)°, and $Z = 4$. The structure has been solved by direct and Fourier methods and refined by full-matrix least squares to R_1 and R_2 values of 0.0522 and 0.0571 for 3133 observed reflections. The cluster adopts a butterfly arrangement of metal atoms with the CpCo moieties at the wingtips. The concept of isolobality is used to compare this latter molecule, which is one of the few examples of a heterometallic closo trigonal-bipyramidal M_4CR cluster, with previously known homometallic Fe_4CR clusters.

Introduction

Early organotransition-metal cluster syntheses were, to some extent, serendipitous,[1] but recent publications from several laboratories[2] have laid a solid basis for devising logical routes to selected systems. Typically, Stone and his co-workers[3] have pioneered the use of the metal–carbyne synthon ($L_nM{\equiv}CR$) as a method for obtaining a plethora of clusters (Scheme I). In contrast, Vahrenkamp has noted that it is possible to treat the $RCCo_3(CO)_9$ system with radicals ML_n so as to displace a $Co(CO)_3$ unit

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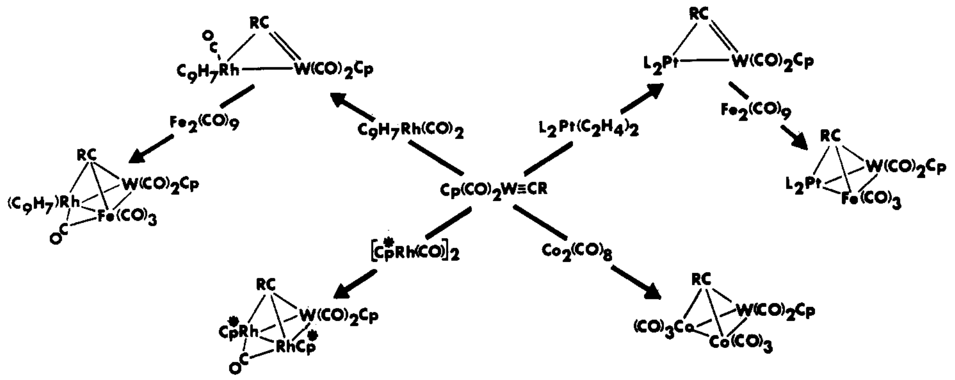
Scheme I. Use of the Metal-Carbyne Unit as a Building Block in Clusters



and hence incorporate the new moiety into the cluster.[4] In a similar vein Robinson[5] has synthesized the mixed-metal clusters $PhCCo_2M(CO)_8Cp$ (M = Cr, Mo, W) and $PhCCo_2Fe(CO)_7Cp$ employing electron transfer catalysis techniques. The reactions involve attack of a metal carbonylate nucleophile on a cluster radical anion, the latter being generated by addition of a catalytic amount of benzophenone ketyl.

Concomitant with these synthetic achievements, the theoretical underpinnings on which these reactions are based have been described in terms of the isolobality principle.[6] This concept, recently reviewed by Hoffmann[7] and by Albright,[8] is used to classify molecular fragments according to the number, symmetry, energy, spatial extension, and electron occupancy of their frontier orbitals. Some typical isolobal relationships are shown.

$$\mathrm{Pt(CO)_2} \xleftrightarrow[\circ]{} \mathrm{Fe(CO)_4} \xleftrightarrow[\circ]{} \mathrm{CH_2}$$

$$\mathrm{Co(CO)_3} \xleftrightarrow[\circ]{} \mathrm{CpMo(CO)_2} \xleftrightarrow[\circ]{} \mathrm{CpNi} \xleftrightarrow[\circ]{} \mathrm{CH}$$

$$\mathrm{CpCo} \xleftrightarrow[\circ]{} \mathrm{Fe(CO)_3} \xleftrightarrow[\circ]{} \mathrm{BH}$$

Thus, in their simplest isolobal terms, the previously mentioned molecules synthesized by Stone and by Vahrenkamp correspond to tetrahedrane, C_4H_4.

We here report synthetic and spectroscopic data on a series of complexes derived from the $RCCo_3(CO)_9$ system whereby one, two, or even all three tricarbonylcobalt verticles have been replaced by isolobal organometallic fragments. We also present X-ray crystallographic data on the closo five-vertex molecule $(CpCo)_2[Mo(CO)_2Cp][Fe(CO)_3]CR$ in which all three organometallic vertices of the original tetrahedron have been modified or replaced and then the molecule expanded via reaction with a tricarbonyliron fragment.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl, and toluene was distilled from P_2O_5. ^1H and ^{13}C NMR spectra were recorded in C_6D_6 solutions on Bruker WP 80, WM 250, and WM 400 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using KBr solution cells and cyclohexane as solvent. Mass spectrometry was performed on a VG micromass 7070 spectrometer equipped with a VG 2035 data system.

$Co_3(CO)_9CCO_2R$, 1 [R = $CH(CH_3)_2$]. Following the general procedure of Seyferth,[9] $Co_2(CO)_8$ and $CCl_3CO_2CH(CH_3)_2$ reacted to give the product in 40% yield. Spectroscopic data matched those previously reported.[10]

$CpNiCo_2(CO)_6CCO_2R$, 2. 1 (0.68 g, 1.29 mmol) and Cp_2Ni (0.55 g, 2.91 mmol) were dissolved in THF (50 cm^3), and the solution was stirred at room temperature for 1 week. The product was purified chromatographically, as previously described[11] and was obtained in 96% yield.

$CpMo(CO)_2Co_2(CO)_6CCO_2R$, 3. To a solution containing 1 (1.23 g, 2.33 mmol) in THF (50 cm^3) was added $[CpMo(CO)_3]_2$ (0.59 g, 1.21 mmol). The reaction mixture was heated under reflux to completion (~10 h). The progress of the reaction was monitored by TLC (eluent, ether/petroleum ether, 15:85; grayish purple spot, 1, R_f 0.80, and dark green spot, 3, R_f 0.69). The solution was allowed to cool to room temperature, the solvent removed in vacuo, and the residue chromatographed on silica gel. Elution first with petroleum ether and then a mixture of ether/petroleum ether, (10:90), allowed separation of the two bands. Recrystallization of the dark green band from ether/petroleum ether gave black crystals of 3 (0.46 g, 0.76 mmol; 33%): mp 89–91 °C; ^1H NMR δ 1.31 (d, 6 H), 4.75 (s, 5 H), 5.19 (septet, 1 H, J = 6.2 Hz); ^{13}C NMR δ 92.4 (C_5H_5), 67.9 (CH), 22.1 (CH_3); IR ν_{CO} 2080 (m), 2075 (sh), 2050 (s), 2030 (s), 2000 (s), 1945 (w), 1900 (w), 1670 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z (%): 576, $C_{17}H_{12}O_9Co_2Mo^+$ (1); 548, $C_{16}H_{12}O_8Co_2Mo^+$ (2); 520, $C_{15}H_{12}O_7Co_2Mo^+$ (1); 492, $C_{14}H_{12}O_6Co_2Mo^+$ (2); 464, $C_{13}H_{12}O_5Co_2Mo^+$ (2); 436, $C_{12}H_{12}O_4Co_2Mo^+$ (7); 408, $C_{11}H_{12}O_3Co_2Mo^+$ (2); 380, $C_{10}H_{12}O_2Co_2Mo^+$ (2); 322, $C_7H_6OCo_2Mo^+$ (1); 294, $C_6H_6Co_2Mo^+$ (3); 229, $CHCo_2Mo^+$ (2); 219, $C_7H_5O_2Mo^+$ (2); 180, $C_7H_5O_2Co^+$ (43); 152, $C_6H_5OCo^+$ (42); 124, $C_5H_5Co^+$ (100). Molybdenum-containing ions exhibited the correct isotope abundance patterns, but the only ones listed are for the ^{98}Mo contributors. Anal. Calcd for $C_{18}H_{12}Co_2MoO_{10}$: C, 35.91; H, 2.01. Found: C, 35.98; H, 2.16.

Reactions of 3 with Cp_2Ni. To a solution of 3 (0.60 g, 1.00 mmol) in THF (30 cm^3) was added Cp_2Ni (0.80 g, 4.23 mmol). The reaction mixture was stirred overnight at room temperature. The reaction was monitored by TLC (eluent, ether/petroleum ether, 10:90) and indicated the formation of a major and a minor component. Removal of solvent left a brownish black solid which was chromatographed on silica gel. Separation was effected by using ether/petroleum ether/benzene, 5:75:20, to give the major component (subsequently shown to be a mixture of 4, 5, and 6) and the minor component which could not be identified due to extensive decomposition. Spectroscopic data indicated that the

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major component was a mixture of 4, 5, and 6, and this material was together treated with $Fe_2(CO)_9$.

Reaction of 4, 5, and 6 with $Fe_2(CO)_9$. To a solution containing 0.20 g of the mixture of 4, 5, and 6 in toluene (10 cm^3) was added $Fe_2(CO)_9$ (0.22 g, 0.60 mmol). The suspension was stirred at 50 °C for 2 h; the progress of the reaction was monitored by TLC (eluent, ether/petroleum ether, 25:75) and indicated three products. The solution was allowed to cool to room temperature, the solvent removed in vacuo, and the residue chromatographed on silica gel. The first band was eluted with ether/petroleum ether to give dark brown crystals of 4 (0.046 g, 0.08 mmol): mp 114–116 °C. ^1H NMR δ 1.29 (d, 3 H), 1.33 (d, 3 H), 4.99 (s, 5 H), 5.17 (s, 5 H), 5.25 (septet, ^1H, J = 6.2 Hz); ^{13}C NMR δ 93.7 (C_5H_5), 92.0 (C_5H_5), 67.9 (CH), 22.1 (CH_3); IR ν_{CO} 2060 (s), 2040 (m), 2005 (s), 1990 (sh), 1925 (m), 1665 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z (%): 569, $C_{19}H_{14}O_7CoMoNi^+$ (1); 500, $C_{17}H_{17}O_4CoMoNi^+$ (3); 472, $C_{16}H_{17}O_3CoMoNi^+$ (3); 444, $C_{15}H_{17}O_2CoMoNi^+$ (3); 386, $C_{12}H_{11}OCoMoNi^+$ (5); 358, $C_{11}H_{11}CoMoNi^+$ (5); 293, $C_6H_6CoMoNi^+$ (5); 228, $CHCoMoNi^+$ (5); 219, $C_7H_5O_2Mo^+$ (5); 189, $C_{10}H_{10}Co^+$ (50); 180, $C_7H_5O_2Co^+$ (30); 163, $C_5H_5Mo^+$ (5); 152, $C_6H_5OCo^+$ (30); 124, $C_5H_5Co^+$ (100); 123, $C_5H_5Ni^+$ (15). Anal. Calcd for $C_{20}H_{17}CoNiMoO_7$: C, 41.21; H, 2.94. Found: C, 40.95; H, 3.27.

The second band gave black crystals of 8 (0.15 g, 0.22 mmol): mp 178 °C; ^1H NMR δ 1.42 (d, 6 H), 4.80 (s, 10 H), 5.04 (s, 5 H), 5.57 (septet, 1 H, J = 6.3 Hz); ^{13}C NMR δ 89.9 (CoC_5H_5), 92.3 (MoC_5H_5), 22.5 (CH_3); IR ν_{CO} 2180 (s), 2160 (sh), 2080 (s), 1955 (w), 1910 (m), 1840 (w), 1795 (w), 1660 (ester) cm^{-1}. Anal. Calcd for $C_{25}H_{22}Co_2FeMoO_7$: C, 42.65; H, 3.15. Found: C, 42.71; H, 3.01. This compound was also characterized by an X-ray crystallographic structure determination.

The final band gave a trace amount of 7 which was characterized mass spectrometrically. Major mass spectral peaks occurred at m/z (%): 564, $C_{22}H_{22}O_4MoNi_2^+$ or $C_{20}H_{22}O_2FeMoNi_2^+$ (4); 508, $C_{20}H_{22}O_2MoNi_2^+$ (1); 450, $C_{17}H_{16}OMoNi_2^+$ (1); 422, $C_{16}H_{16}MoNi_2^+$ (14); 357, $C_{11}H_{11}MoNi_2^+$ (2); 292, $C_6H_6MoNi_2^+$ (1); 226, $CMoNi_2^+$ (1); 186, $C_{10}H_{10}Fe^+$ (100); 121, $C_5H_5Fe^+$ (38).

$CpMo(CO)_2Cp_2Co_2(CO)CCO_2R$, 6. To a solution containing 3 (0.24 g, 0.41 mmol) in THF (40 cm^3) was added 2 mL of C_5H_6. The reaction mixture was heated under reflux overnight. The progress of the reaction was monitored by TLC (eluent, benzene/petroleum ether, 90:10; yellow-orange spot, C_5H_6, R_f 0.85, dark green spot, 3, R_f 0.56, and yellow-brown spot, 6, R_f 0.37). The solution was cooled to room temperature the solvent removed in vacuo, and the residue chromatographed on silica gel. Elution with petroleum ether/benzene, 10:90, allowed for separation of the three bands. Recrystallization of the yellow-brown band from the eluent mixture gave brown crystals of 6 (0.055 g, 0.092 mmol, 22%): mp 120 °C dec; ^1H NMR δ 1.44 (d, 6 H), 4.79 (s, 10 H), 5.04 (s, 5 H), 5.36 (septet, 1 H, J = 6.3 Hz); ^{13}C NMR δ 92.9 (MoC_5H_5), 90.5 (CoC_5H_5), 68.4 (CH), 23.2 (CH_3); IR ν_{CO} 1990 (w), 1910 (s), 1845 (m), 1795 (w), 1655 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z (%): 594, $C_{23}H_{22}O_5Co_2Mo^+$ (1); 566, $C_{22}H_{22}O_4Co_2Mo^+$ (2); 538, $C_{21}H_{22}O_3Co_2Mo^+$ (2); 452, $C_{17}H_{16}OCo_2Mo^+$ (5); 424, $C_{16}H_{16}Co_2Mo^+$ (9); 359, $C_{11}H_{11}Co_2Mo^+$ (5), 294, $C_6H_6Co_2Mo^+$ (3); 228, CCo_2Mo^+ (3); 219, $C_7H_5O_2Mo^+$ (2); 191, $C_6H_5OMo^+$ (2); 189, $C_{10}H_{10}Co^+$ (100); 180, $C_7H_5O_2Co^+$ (100); 180, $C_7H_5O_2Co^+$ (2); 163, $C_5H_5Mo^+$ (1); 152, $C_6H_5OCo^+$ (2); 124, $C_5H_5Co^+$ (50). Anal. Calcd for $C_{23}H_{22}Co_2MoO_5$: C, 46.65; H, 3.74. Found: C, 46.88; H, 3.99.

$CpMo(CO)_2CpNiCo(CO)_3CCO_2R$, 4. To a solution containing 3 (0.61 g, 1.00 mmol) in benzene (40 cm^3) was added $[CpNi(CO)]_2$ (0.31 g, 1.00 mmol). The reaction mixture was heated at 60 °C for 5 days. The progress of the reaction was monitored by TLC (eluent, benzene/petroleum ether, 90:10); red spot, $[CpNi(CO)]_2$, R_f 0.91, green spot, 3, R_f 0.56, and brown spot, 4, R_f 0.37). The solution was allowed to cool to room temperature, the solvent removed in vacuo, and the residue chromatographed on silica gel. Elution with benzene/petroleum ether, 90:10, allowed separation of the three bands. Recrystallization of the brown band gave dark brown crystals of 4 (0.095 g, 0.16) mmol, 16%). Spectroscopic data for the compound matched these obtained when the product was isolated from the reaction of 3 and Cp_2Ni.

Table I. Crystal Data

compound	$C_{25}H_{22}Co_2FeMoO_7$
fw (daltons)	704.0
cryst size, mm	0.075 × 0.10 × 0.35
systematic absences	O_kO, $k = 2n + 1$, hOl, $l = 2n + 1$
space group	$P2_1/c$ (No. 14)
unit cell	
a, Å	12.309 (5)
b, Å	14.731 (6)
c, Å	17.298 (7)
β, deg	124.63 (6)
vol, $Å^3$	2581 (1)
Z	4
ρ_{calcd}, g/cm^3	1.812
temp, °C	22
linear abs coeff μ, cm^{-1}	23.9
abs limits	1.647–1.354
std reflctns (esd, %)	2,3,–1 (1.48), 1,4,–2 (1.44)
max 2θ reflctns measd	45°, $h,k,\pm l$
no. of independent reflctns	3376
no. with $I > 0$ (used)	3133
final R_1, R_2[a]	0.0522, 0.0571
final shift/error, max (av)	0.181 (0.049)
χ (secondary extinction)	0.00014
final diff map max peak (valley), e $Å^{-3}$	0.67, –0.47
weighting scheme	$(\sigma_F^2 + 0.000921F_o^2)^{-1}$
error in an observn of unit wt	1.18

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

Reaction of 2 with $Fe_2(CO)_9$. When 2 was treated with $Fe_2(CO)_9$, the product 9 was obtained in 9% yield: mp 150 °C dec; ^1H NMR δ 1.45 (d, 6 H), 5.09 (septet, 1 H, J = 6.3 Hz), 5.63 (s, 5 H); ^{13}C NMR δ 91.7 (C_5H_5), 70.7 (CH), 22.3 (CH_3); IR ν_{CO} 2040 (m), 1995 (w), 1985 (s), 1965 (s), 1680 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z: 592, $C_{17}H_{12}O_9Co_2FeNi^+$; 536, $C_{15}H_{12}O_7Co_2FeNi_+$; 480, $C_{13}H_{12}O_5Co_2FeNi^+$; 452, $C_{12}H_{12}O_4Co_2FeNi^+$; 424, $C_{11}H_{12}O_3Co_2FeNi^+$; 331, $C_5H_7O_2FeCo_2Ni^+$; 273, $C_2HOCo_2FeNi^+$; 254, $C_6H_6Co_2Ni^+$; 188, CCo_2Ni^+; 140, $C_3O_3Fe^+$; 123, $C_5H_5Ni^+$; 66, $C_5H_6^+$; 59, Co^+; 58, Ni^+; 56, Fe^+. Anal. Calcd for $C_{19}H_{12}Co_2FeNiO_{11}$: C, 35.18; H, 1.86. Found: C, 35.40; H, 1.60.

Reaction of 3 with $Fe_2(CO)_9$. Similarly, 3 and $Fe_2(CO)_9$ gave 10 in 6% yield: mp 181–183 °C; ^1H NMR δ 1.34 (d, 6 H), 5.09 (septet, 1 H, J = 6.3 Hz), 5.21 (s, 5 H); ^{13}C NMR δ 91.4 (C_5H_5), 67.9 (CH), 21.4 (CH_3); IR ν_{CO} 2015 (s), 1985 (s), 1975 (s), 1920 (m), 1890 (w), 1655 (ester) cm^{-1}. Major mass spectral peaks occurred at m/z: 744, $C_{21}H_{12}O_{13}Co_2FeMo^+$; 688, $C_{19}H_{12}O_{11}Co_2FeMo^+$; 576, $C_{15}H_{12}O_7Co_2FeMo^+$; 520, $C_{13}H_{12}O_5Co_2FeMo^+$; 511, $C_{10}H_7O_7Co_2FeMo^+$; 483, $C_9H_7O_6Co_2FeMo^+$; 455, $C_8H_7O_5Co_2FeMo^+$; 436, $C_{10}H_{12}O_2Co_2FeMo^+$; 371, $C_5H_7O_2Co_2FeMo^+$; 322, $C_7H_6OCo_2Mo^+$; 315, $C_5H_7O_2Co_2Mo^+$; 292, $C_6H_6Co_2Mo^+$; 257, $C_2HOCo_2Mo^+$; 219, $C_7H_5O_2Mo^+$; 163, $C_5H_5Mo^+$; 98, Mo^+; 59, Co^+; 56, Fe^+. Anal. Calcd for $C_{21}H_{12}Co_2FeMoO_{13}$: C, 33.99; H, 1.63. Found: C, 34.31; H, 1.80.

Collection of the X-ray Data. An acicular crystal, sealed in a Lindemann capillary, was used for X-ray studies. Precession photographs showed the crystal was monoclinic, and unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range 19.4° < 2θ < 29.7°. All measurements were made on a Syntex $P2_1$ diffractometer with use of Mo Kα radiation (λ = 0.71069 Å). Crystal data and other numbers related to data collection are summarized in Table I.

Intensities were measured with use of a coupled θ(crystal)–2θ counter scan. The methods of selection of scan rates and initial data treatment have been described.[12,13] Corrections were made for Lorentz–polarization effects and absorption.

Solution of the Structure. The phases were determined by direct methods; 50 reflections were used with $|E| > 1.6$ and 12 sets of starting phases. The metal atoms were easily located in the E map, and subsequent refinement and electron density difference syntheses revealed all the non-hydrogen atoms. Further refinement with anisotropic temperature factors for all atoms

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(12) Hughes, R. P.; Krishnamachari, N.; Lock, C. J. L.; Powell, J.; Turner, G. *Inorg. Chem.* **1977**, *16*, 314.

(13) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525.

Table II. Atomic Positional Coordinates and Temperature Factors (Å^2)

	x	y	z	U_{eq}[a]
Co(1)	2127 (1)	706 (1)	7546 (1)	32.5 (5)
Co(2)	1904 (1)	3000 (1)	6522 (1)	37.4 (6)
Mo	3307 (1)	1515.1 (4)	6864.3 (4)	24.6 (4)
Fe	2651 (1)	2282 (1)	8012 (1)	28.4 (6)
C(1)	4551 (8)	967 (6)	8105 (6)	38 (5)
O(1)	5411 (6)	606 (5)	8789 (4)	58 (5)
C(2)	4348 (9)	2652 (6)	7346 (6)	43 (5)
O(2)	5104 (7)	3244 (5)	7608 (5)	63 (5)
C(3)	3645 (8)	1752 (6)	9117 (6)	38 (5)
O(3)	4295 (7)	1459 (4)	9866 (4)	57 (4)
C(4)	1298 (8)	2476 (6)	8093 (5)	47 (6)
O(4)	456 (6)	2578 (5)	8180 (4)	70 (6)
C(5)	4551 (8)	967 (6)	8105 (6)	39 (5)
O(5)	5411 (6)	606 (5)	8789 (4)	60 (5)
C(6)	1514 (7)	1757 (5)	6702 (5)	24 (4)
C(7)	78 (7)	1598 (5)	5958 (5)	27 (4)
O(6)	−348 (5)	1271 (4)	5202 (4)	44 (3)
O(7)	−674 (5)	1868 (4)	6245 (3)	38 (3)
C(8)	−2116 (8)	1689 (7)	5599 (7)	54 (6)
C(9)	−2767 (10)	2504 (9)	4948 (9)	86 (7)
C(10)	−2565 (12)	1589 (13)	6247 (11)	128 (11)
C(11)	2600 (13)	−693 (7)	7856 (11)	64 (6)
C(12)	2525 (13)	−295 (8)	8550 (7)	65 (6)
C(13)	1238 (14)	68 (7)	8140 (9)	61 (6)
C(14)	514 (9)	−169 (7)	7187 (8)	54 (6)
C(15)	1319 (13)	−599 (6)	6996 (7)	54 (6)
C(21)	449 (13)	3511 (7)	5128 (7)	64 (7)
C(22)	1746 (17)	3769 (9)	5442 (11)	81 (10)
C(23)	2275 (12)	4337 (7)	6277 (11)	72 (8)
C(24)	1328 (12)	4376 (6)	6478 (8)	56 (7)
C(25)	227 (10)	3876 (7)	5770 (9)	93 (8)
C(31)	3597 (11)	220 (6)	6238 (6)	46 (6)
C(32)	2283 (9)	494 (6)	5586 (6)	45 (6)
C(33)	2324 (11)	1354 (7)	5250 (6)	51 (6)
C(34)	3655 (14)	1615 (7)	5681 (8)	58 (7)
C(35)	4473 (10)	896 (8)	6310 (7)	57 (7)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$.

minimized $\sum w(|F_o| - |F_c|)^2$ and was terminated when the maximum shift/error fell below 0.2. No attempt was made to locate the hydrogen atoms. Corrections were made for secondary extinction by the method in SHELX.[14] Scattering curves were from Cramer and Waber,[15] and anomalous dispersion corrections[16] were applied to the curves for Mo, Fe, and Co. The atom parameters are listed in Table II.

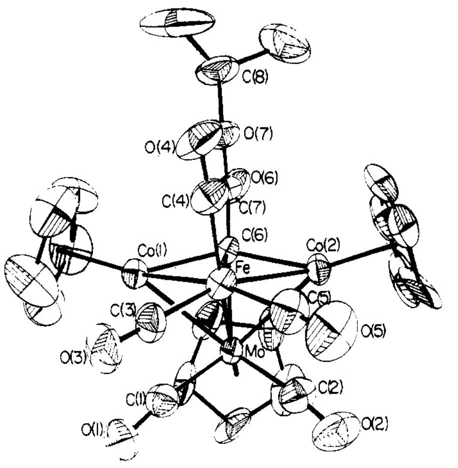

Figure 1. Structure of $Cp_3Co_2MoFe(CO)_5CCO_2CH(CH_3)_2$.

Results

The ready availability of molecules of the type $RCCo_3(CO)_9$, together with their known propensity to undergo substitution reactions in which a $Co(CO)_3$ vertex is replaced by another organometallic group, makes them ideal starting materials for mixed-cluster syntheses. Since the consecutive substitution of tricarbonylcobalt moieties by different isolobal fragments might ultimately produce a tetrahedral molecule in which the identity of each of the vertices was different, it was recognized that a probe for chirality was essential. Thus, all syntheses commenced with $RCCo_3(CO)_9$, in which R = CO_2CHMe_2, so that the potentially diastereotopic methyl groups could be exploited. As shown in Scheme II, replacement of a $Co(CO)_3$ vertex in **1** by either a CpNi unit or a $CpMo(CO)_2$ fragment, as in **2** or **3**, respectively, proceeds satisfactorily. Indeed, Vahrenkamp has reported similar results but with different substituents on the carbynyl carbon atom. Now, further reaction of the Co_2Mo system **3** with excess Cp_2Ni gave not only the expected chiral compound **4** possessing cobalt, nickel, molybdenum, and carbon atoms at the polyhedral vertices but also yielded two other compounds, **5** and **6**, from which **4** could not easily be separated chromatographically. Consequently, this mixture was treated with $Fe_2(CO)_9$—a reagent which is known[17,18] to deliver an $Fe(CO)_3$ moiety to tetrahedral clusters and bring about expansion to the square-based pyramidal geometry. Fortuitously, under our reaction conditions, only two of the products reacted with $Fe_2(CO)_9$ to yield the five-vertex clusters **7** and **8** and leave the chiral molecule **4** unchanged. The identity of **4** was readily established mass spectroscopically; subsequently, **4** was synthesized independently via the reaction of **3** with $[CpNi(CO)]_2$. The molecule exhibited two cyclopentadienyl resonances in both the ^1H and ^{13}C NMR spectra. Gratifyingly, the isopropyl methyls are now diastereotopic and each appears as a doublet coupled to the unique proton of the isopropyl group. In order to see whether this molecule exhibited similar dynamic behavior to the related $Cp_2NiMoFe(CO)_5(PhC{\equiv}CCO_2$-*i*-Pr) system,[17] a variable-temperature NMR study was carried out on **4**. It was not possible to coalesce the methyl peaks at 110 °C so, if the molecule is fluxional, the barrier is too high for it to be measured by NMR line-broadening techniques.

The separation of the products resulting from the treatment of the mixture of **4**, **5**, and **6** with $Fe_2(CO)_9$ not only allowed the recovery of the chiral molecule **4** but also yielded two new five-vertex clusters, viz., **7** and **8**. The former was isolated in very low yield and was identified mass spectroscopically as $(CpNi)_2[Mo(CO)_2Cp][Fe(CO)_3]CR$ via its characteristic $FeMoNi_2$ isotope pattern. This product was clearly derived from an $RCMoNi_2$ tetrahedral cluster, and the incorporation of an $Fe(CO)_3$

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(14) Initial data used programs from the XRAY 76 package. (Stewart, J. M. The XRAY 76 system, Technical Report TR-446, Computer Science Center, University of Maryland, Maryland, 1976) and the structure was solved with use of SHELX (Sheldrick, G. M. SHELX—Programme for Crystal Structure Determination, Cambridge University, England, 1976). The least-squares planes program NRC-22 (Pippy, M. E.; Ahmed, F. R. Mean Plane and Torsion Angles, National Research Council of Canada, Ottawa, Canada, 1978) and ORTEP-II (Johnson, C. K. ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976) were also used. All calculations were carried out on CYBER 170/730 and 815 computers. We note that the 110 reflection was too strong to count accurately and was not used.

(15) Cromer, D. T.; Waber, J. T. "International Tables for Crystallography", Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B, pp 99–101.

(16) Cromer, D. T. ref 15, Table 2.3.1, pp 149–150.

(17) (a) Jaouen, G.; Marinetti, A.; Mentzen, B.; Mutin, R.; Saillard, J.-Y.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* 1982, *1*, 753. (b) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.-Y.; Ben Naceur, J.; Mentzen, B.; Jaouen, G. *Organometallics* 1985, *4*, 1123.

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Table III. Selected Interatomic Distances (Å) and Angles (deg)

		Bond Distances			
Mo–Co(1)	2.620 (1)	Mo–Co(2)	2.637 (1)	Mo–Fe	2.773 (1)
Mo–C(6)	2.091 (7)	Co(1)–Fe	2.422 (1)	Co(1)–C(6)	1.951 (7)
Co(2)–Fe	2.431 (1)	Co(2)–C(6)	1.962 (7)	Fe–C(6)	2.021 (6)
Mo–C(1)	1.967 (9)	Mo–C(2)	1.982 (9)	Fe–C(3)	1.762 (9)
C(1)–O(1)	1.175 (9)	C(2)–O(2)	1.16 (1)	C(3)–O(3)	1.152 (9)
Fe–C(4)	1.787 (9)	Fe–C(5)	1.771 (9)	C(6)–C(7)	1.500 (9)
C(4)–O(4)	1.15 (1)	C(5)–O(5)	1.140 (9)	C(7)–O(6)	1.198 (8)
C(7)–O(7)	1.335 (8)	O(7)–C(8)	1.489 (9)	C(8)–C(9)	1.53 (2)
C(8)–C(10)	1.51 (2)	Co(1)–C(11)	2.13 (1)	Co(1)–C(12)	2.113 (9)
Co(1)–C(13)	2.102 (9)	Co(1)–C(14)	2.142 (8)	Co(1)–C(15)	2.126 (9)
Co(2)–C(21)	2.163 (9)	Co(2)–C(22)	2.10 (1)	Co(2)–C(23)	2.12 (2)
Co(2)–C(24)	2.135 (9)	Co(2)–C(25)	2.138 (9)	Mo–C(31)	2.320 (8)
Mo–C(32)	2.360 (7)	Mo–C(33)	2.341 (8)	Mo–C(34)	2.322 (8)
Mo–C(35)	2.319 (8)				
		Bond Angles			
Mo–Co(1)–C(6)	51.9 (2)	Fe–Co(1)–C(6)	53.7 (2)	Mo–Co(1)–Fe	66.6 (1)
Mo–Co(2)–C(6)	51.6 (2)	Fe–Co(2)–C(6)	53.5 (2)	Mo–Co(2)–Fe	66.2 (1)
Co(1)–Mo–Fe	53.3 (1)	Co(1)–Mo–C(6)	47.6 (2)	Co(1)–Fe–Mo	60.1 (1)
Co(2)–Mo–Fe	53.3 (1)	Co(2)–Mo–C(6)	47.3 (2)	Co(2)–Fe–Mo	60.5 (1)
Co(1)–Fe–C(6)	51.4 (2)	Co(1)–C(6)–Fe	74.9 (2)	Co(1)–C(6)–Mo	84.8 (2)
Co(2)–Fe–C(6)	51.3 (2)	Co(2)–C(6)–Fe	75.2 (2)	Co(2)–C(6)–Mo	81.1 (3)
Fe–Mo–C(6)	46.5 (2)	Mo–C(6)–Fe	84.8 (2)	C(6)–Fe–Mo	48.7 (2)
Co(1)–Mo–C(1)	67.0 (2)	Co(1)–Mo–C(2)	125.9 (3)	Fe–Mo–C(1)	75.5 (2)
Co(2)–Mo–C(1)	126.2 (3)	Co(2)–Mo–C(2)	65.0 (2)	Fe–Mo–C(2)	74.7 (3)
C(6)–Mo–C(1)	108.9 (3)	Mo–C(1)–O(1)	169.2 (7)	C(1)–Mo–C(2)	88.4 (3)
C(6)–Mo–C(2)	107.1 (3)	Mo–C(2)–O(2)	168.7 (8)	Co(1)–C(6)–Co(2)	146.1 (4)
Co(1)–Fe–C(3)	79.9 (3)	Co(1)–Fe–C(4)	167.7 (3)	C(1)–Fe–C(5)	56.3 (2)
Co(2)–Fe–C(3)	162.6 (3)	Co(2)–Fe–C(4)	95.5 (3)	Co(2)–Fe–C(5)	102.0 (3)
C(6)–Fe–C(3)	131.1 (3)	C(6)–Fe–C(4)	96.2 (4)	C(6)–Fe–C(5)	93.8 (3)
Mo–Fe–C(3)	106.9 (3)	Mo–Fe–C(4)	110.6 (3)	Mo–Fe–C(5)	142.3 (2)
C(3)–Fe–C(4)	96.2 (4)	C(3)–Fe–C(5)	95.1 (4)	C(4)–Fe–C(5)	96.5 (4)
Fe–C(3)–O(3)	175.4 (7)	Fe–C(4)–O(4)	175.0 (9)	Fe–C(5)–O(5)	177.0 (8)
Co(1)–C(6)–C(7)	80.9 (3)	Co(2)–C(6)–C(7)	86.3 (3)	Mo–C(6)–C(7)	124.2 (3)
C(6)–C(7)–O(6)	124.8 (6)	C(6)–C(7)–O(7)	111.2 (6)	O(6)–C(7)–O(7)	124.0 (6)
C(7)–O(7)–C(8)	116.8 (6)	O(7)–C(8)–C(9)	108.4 (8)	O(7)–C(8)–C(10)	104.1 (8)
C(9)–C(8)–C(10)	111 (1)	Fe–C(6)–C(7)	138.6 (5)	Co(1)–Fe–Co(2)	101.3 (1)
Co(1)–Mo–Co(2)	91.1 (1)				

fragment parallels the reaction of $R_2C_2Ni_2Cp_2$ with $Fe_2(CO)_9$ which likewise led to a 14-skeletal electron square-based pyramidal (nido octahedral) system.[17] It is noteworthy that the presumed intermediate **5** and isolated product **7** result from replacement of all three of the original tricarbonylcobalt vertices in the starting material.

The major product of the reaction of **4**, **5**, and **6** with diiron enneacarbonyl, viz., **8**, showed only a single type of methyl signal in the NMR spectrum, suggesting that the molecule possessed a plane of symmetry rendering it achiral. Furthermore, it was clear that three cyclopentadienyl groups were present and the chemical shifts indicated that one was bonded to molybdenum while the remaining two were attached to cobalt. The molecular structure was determined by X-ray crystallography; Figure 1 shows an ORTEP diagram of **8**, and the crystallographic data as well as the relevant bond lengths and bond angles are collected in Tables I through III.

The structure is perhaps best described as a trigonal-bipyramidal M_4C cluster in which the metals adopt a butterfly arrangement and the carbynyl carbon is equatorial. The CpCo units are found at the wingtips of the butterfly while the $CpMo(CO)_2$ and $Fe(CO)_3$ moieties comprise the hinge. The molecule has approximate C_s symmetry. A formal electron count would assign each of the cobalt atoms 17 electrons while the molybdenum would possess 19. From the structure it appears that an attempt is made to alleviate the situation via a weak semibridging interaction of each carbonyl on molybdenum with a cobalt atom. Thus, the Mo–C–O angles are 169°, and the Co(1)–C(1) and Co(2)–C(2) distances are 2.590 (7) and 2.544 (7) Å, respectively, much shorter than the sum of the van der Waals radii (3.25 Å)[19] and 0.2 Å shorter than the Co(1)–C(3) distance of 2.735 (7) Å. Further, the Fe–C–O angles are all almost 180°. Other bond lengths and angles agree well with values found for fragments in similar environments.

Discussion

In our continuing investigations into the NMR fluxionality of organotransition-metal clusters, we had need of tetrahedral molecules of the type M_3CR so as to augment our previous studies on $M_2C_2R_2$[10] and $M_3C_2R_2$[17] systems. As we have pointed out elsewhere,[20] the readily synthesized $RCCo_3(CO)_9$ clusters possess 12 skeletal electrons and can be viewed either as having six localized bonds along the edges of the tetrahedron or as being nido trigonal-bipyramidal molecules using six globally delocalized[21] orbitals. This latter view invokes the Wade–Mingos[22] model which has been used to rationalize the structures of a variety of boranes or metalloboranes as well as main-group and transition-metal clusters. This is not merely a semantic point since the ^{59}Co NQR data as well as photoelectron spectroscopic results on the $RCCo_3(CO)_9$ systems can be nicely accounted for in terms of the delocalized model.[23]

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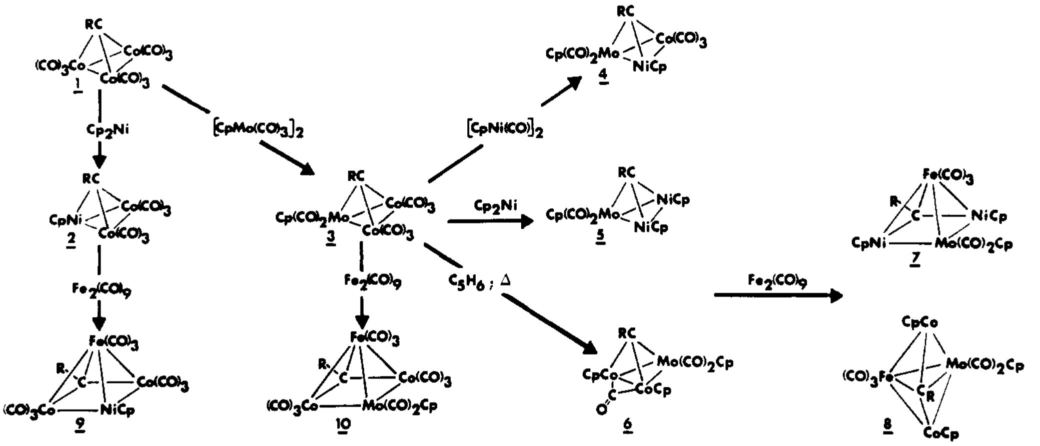
Scheme II. Synthetic Scheme Relating Molecules 1 through 10



So, taking the point of view that the $RCCo_3(CO)_9$ and $R_2C_2Co_2(CO)_6$ systems may be thought of as having globally delocalized rather than edge-localized bonding, these molecules can be considered to be coordinatively unsaturated (even though a conventional electron count would assign each cobalt 18 electrons). This perspective allows one to rationalize the apparently high reactivity of these species toward electrophiles and may also suggest the possibility of fluxionality of the polyhedral vertices.[24]

The synthetic sequence described above represents a rational route to mixed-metal M_4CR closo clusters. Previous syntheses of closo Fe_4C systems resulted from either the oxidation of an octahedral Fe_6C carbido cluster or synthetic manipulations of $[Fe_4(CO)_{13}]^{2-}$,[25,26] while the present route is based on the expansion of a tetrahedral molecule. In retrospect, the stepwise sequence leading to the final product is now apparent (Scheme II). The role of Cp_2Ni is twofold; not only can it result in substitution of $Co(CO)_3$ by an isolobal CpNi fragment but also, upon prolonged thermolysis, it shows a propensity to release cyclopentadienyl groups which are capable of displacing the labile carbonyl ligands on cobalt. We have noted previously that treatment of $RCCo_3(CO)_9$ clusters with Cp_2Ni led to cyclopentadienylation at cobalt competitive with replacement of a Co vertex by a CpNi moiety.[11] To bring about clean substitution without cyclopentadienylation, it is necessary to use $[CpNi(CO)]_2$.[4] As shown in Scheme II, it is possible to prepare the chiral molecule 4 without the byproducts 5 and 6. Furthermore, treatment of 3 with cyclopentadiene yields 6 in which two Cp rings have displaced five carbonyl groups, thus leaving only a single bridging carbonyl functionality; subsequent reaction with $Fe_2(CO)_9$ gave the closo molecule 8. This independent synthesis of 8 is reminiscent of the approach adopted by Aime and Osella,[27] who found that when they treated *nido*-$HRu_3(CO)_9C_5H_7$ with $[CpNi(CO)]_2$, the net result was the incorporation of CpNi (a three-electron unit) while CO and H were eliminated to yield *closo*-$CpNiRu_3(CO)_8C_5H_7$.

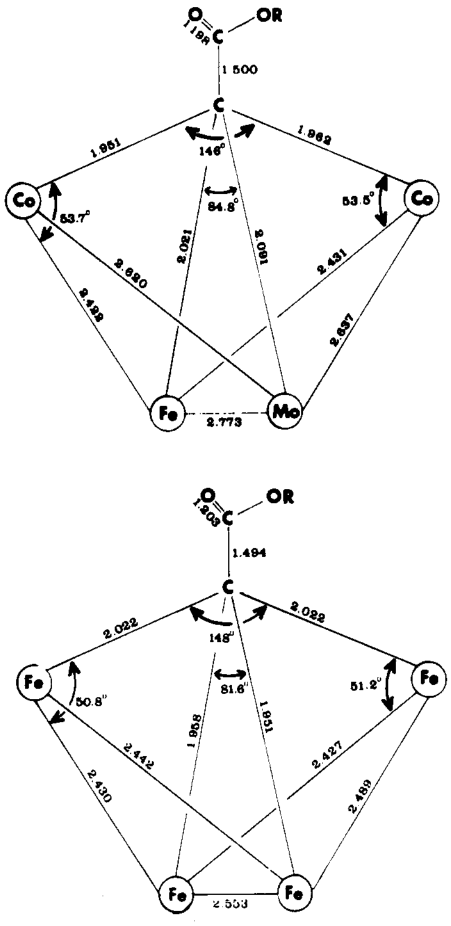
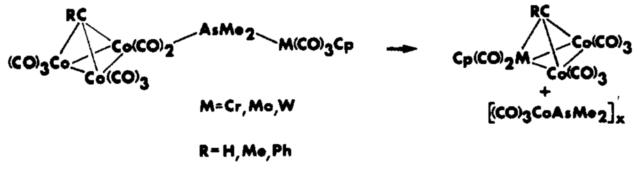


Figure 2. Comparison of core geometries of $Cp_3Co_2MoFe(CO)_5CCO_2CH(CH_3)_2$ and $[Fe_4(CO)_{12}CCO_2CH_3]^-$.

Scheme III. Vahrenkamp's Route to Mixed-Metal Clusters



To our knowledge, there are very few five-vertex closo clusters and molecule 8 is the first such M_4C heterometallic system containing three different transition metals to be structurally characterized.[28] The currently known exam-

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(26) (a) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 781. (b) Whitmire, K. H.; Shriver, D. F.; Holt, E. M. *J. Chem. Soc., Chem. Commun.* **1980**, 778. (c) Whitmire, K. H.; Shriver, D. F.; Holt, E. M. *J. Chem. Soc., Chem. Commun.* **1980**, 780.

(27) Aime, S.; Osella, D. *Inorg. Chim. Acta* **1982**, *57*, 207.

ples possess an Fe_4C framework. The molecule $HFe_4(CO)_{12}CCH_3$ and the related anions $[Fe_4(CO)_{12}CCH_3]^-$ and $[Fe_4(CO)_{12}COCH_3]^-$ exhibit a tetrahedral arrangement of metal atoms with the alkylidyne group capping one of the triangular faces.[26,29] The methoxy Fe_4 anionic cluster is formally derivable by methylation of $[Fe_4(CO)_{13}]^{2-}$ which has a carbonyl triply bridging a triangular face.[26] In the present case, one sees a butterfly arrangement of metal atoms with the alkylidyne in an equatorial position of the trigonal bipyramid. This structure is remarkably similar to that found by Bradley for $[Fe_4(CO)_{12}CCO_2CH_3]^-$;[25] the comparison of the two metal frameworks is shown in Figure 2. Notably, the Co_{ax}–C–Co_{ax} angle in **8** is 146° while the corresponding Fe–C–Fe angle in $[Fe_4(CO)_{12}CO_2CH_3]^-$ is 148°.[25,30]

In terms of the isolobal analogy, the axial $Fe(CO)_3$ fragments have been replaced by CpCo units; one equatorial $Fe(CO)_3$ moiety (which furnishes three frontier orbitals and two electrons to the cluster) has been replaced by a three-electron vertex, viz., $CpMo(CO)_2$. The overall skeletal electron counts for the two clusters are identical (60 cluster valence electrons) since our $MoCo_2FeCR$ system is neutral while Bradley's Fe_4CR molecule is anionic. In terms of Wade's electron-counting rules, the Bradley cluster and also the $Co_2MoFeCR$ molecule **8** would be viewed as closo trigonal bipyramids since they possess six skeletal electron pairs.

Other related systems $HFe_4(CO)_{12}CH$[31] and $HFe_4(CO)_{12}COCH_3$[26] also show the butterfly structure; however, the angle between the axial Fe's and the equatorial C are considerably larger, viz., 170.5° and 160.9°, respectively. These latter molecules are assigned 62 cluster valence electrons and are in accord with the rules developed by Lauher.[32] In $HFe_4(CO)_{12}CH$ the electron pair associated with the C–H bond interacts with the metal skeleton, thus providing an extra pair of skeletal electrons. This is similar to butterfly carbide clusters, such as those very recently reported by Shriver,[33] in which all four electrons associated with the carbon atom participate in cluster bonding and the wingtip–carbon–wingtip angle approaches linearity.

It is particularly interesting to note that in the molecule $HFe_4(CO)_{12}CCH_3$ and the corresponding anions $[Fe_4(CO)_{12}CCH_3]^-$ and $[Fe_4(CO)_{12}COCH_3]^-$, the alkylidyne group is axial while in $[Fe_4(CO)_{12}CO_2CH_3]^-$, $HFe_4(CO)_{12}COCH_3$, $HFe_4(CO)_{12}CH$, and **8** the alkylidyne fragment is sited equatorially. One might speculate that the difference may well be electronic since the axial carbyne bears an electron-donating methyl while with an electron-withdrawing ester substituent the carbyne adopts an equatorial site. However, these effects must be rather subtle since, although the methoxy anion is a capped tetrahedron, the corresponding neutral species adopts the butterfly configuration. Indeed, very recent studies have demonstrated that interconversion between the capped tetrahedral and butterfly isomers of $[HFe_4(CO)_{13}]^-$ occurs in solution.[34]

The series of reactions we have outlined in this report features several interesting aspects of the chemistry of small clusters. It demonstrates a simple and straightforward method of synthesizing heteronuclear clusters via the substitution of one vertex by another. One might speculate that the initial attack produces a transient five-vertex cluster containing at least one electron in an orbital of antibonding character with respect to the cluster skeleton. Subsequent elimination of one of the original vertices could then generate the final product. This proposed addition–elimination mechanism is reminiscent of Vahrenkamp's earlier mixed-cluster syntheses[35] which apparently involved attack upon an open face by a pendant metal center linked to the "leaving group" via a dimethylarsino bridge, as in Scheme III. Of course, the substituting fragments, viz., CpNi or $CpMo(CO)_2$ are isolobal with $Co(CO)_3$ and with CH and bear three electrons in their frontier orbitals. In contrast, the $Fe(CO)_3$ moiety furnishes only two electrons to the total involved in skeletal bonding and so need not populate any antibonding orbitals. Again invoking the analogy between boranes and metal clusters, one could say that the addition of a vertex with an extra pair of electrons brings about the change from a tetrahedron (nido trigonal bipyramid) to the 14-electron square-based pyramid (nido octahedron). The generality of this reaction is shown by the addition of $Fe(CO)_3$ to either **2** or **3** giving **9** and **10**, respectively. In both cases, there is only one methyl environment in the NMR spectrum again suggesting the formation of a molecule of C_s symmetry.

Nevertheless, a number of factors still need to be understood. All of the reactions thus far reported involved replacement of $Co(CO)_3$ verticles. It remains to be seen whether other good "leaving groups" can be found. It is also noteworthy that one can replace two cobalt vertices by CpNi (albeit in low yield) when a molybdenum is already present but cannot yet do so in the absence of the $CpMo(CO)_2$ group. Thus we had shown earlier[11] that attempts to synthesize $(CpNi)_2Co(CO)_3CR$ failed. Indeed, under more forcing conditions we observed instead cyclopentadienylation of the cobalt with concomitant loss of carbonyls. Attempts to establish a hierarchy of replaceable vertices are continuing and will be the subject of future reports.

To conclude, we have shown that multiple replacement of $Co(CO)_3$ vertices in $RCCo_3(CO)_9$ leads to a variety of clusters some of which are chiral. Treatment of these tetrahedral molecules with $Fe(CO)_3$ gives rise to square-pyramidal clusters. However, initial replacement of five of the carbonyls to produce a Cp_2Co_2CO unit, in which the carbonyl is bridging, reacts with $Fe_2(CO)_9$ to provide a rational route to trigonal-bipyramidal M_4CR systems.

Acknowledgment. We thank Dr. R. E. Lenkinski of the Southwest Ontario Regional NMR Centre, Guelph,

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[28] Several $R_2C_2M_3$ closo clusters have been characterized crystallographically: (a) Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292. (b) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559. (c) Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101. (d) Freeland, B. H.; Payne, N. C.; Stalteri, M. A.; Van Leeuven, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1533. (e) Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. In $CpWOs_3(CO)_{11}C{\cdot}C_6H_4CH_3$ the alkylidyne moiety caps a triangular Os_2W face and so would be classifiable as a closo trigonal-bipyramidal cluster. (f) Roland, E.; Vahrenkamp, H. *Organometallics* **1983**, *2*, 1048. The structure of $CpWRuCo_2(CO)_{10}$-c-$C_6H_4CH_3$ could likewise be classified as a closo trigonal bipyramid.

[29] (a) Bogdan, P. L.; Holt, E. M.; Whitmire, K. H.; Kolis, J. W.; Shriver, D. F. *J. Organomet. Chem.* **1984**, *272*, 169. (b) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621.

[30] We note that there are two mixed metal clusters $HCpNiRu_3(CO)_9(\mu_4\text{-}C{=}CHR)$ and $CpFeCo_3(\mu\text{-}CO)_2(CO)_7(\mu_4\text{-}C{=}CH_2)$ which possess a somewhat similar butterfly arrangement of metals. These exhibit Ru–C–Ni and Fe–C–Co angles of 153° and 155°, respectively. However, in both of these complexes, the μ_4-carbon is not carbynyl but is part of a vinylidene group: Carty, A. J.; Taylor, N. J.; Sappa, E.; Tiripicchio, A. *Inorg. Chem.* **1983**, *22*, 1871. Brun, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaun, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 1357.

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[34] Horwitz, C. P.; Shriver, D. F. *Organometallics* **1984**, *3*, 756.

[35] Beurich, H.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 863.

Ontario, for the high field spectra, Dr. J. W. Kolis for useful discussions, and the Natural Sciences and Engineering Research Council of Canada for financial support. G.J. thanks the France-Canada Scientific Exchange Program for a visiting professorship; M.M. is the recipient of an NSERC postgraduate Scholarship.

Registry No. **1**, 36834-86-3; **2**, 88008-84-8; **3**, 97950-29-3; **4**, 97919-68-1; **5**, 97950-30-6; **6**, 97950-31-7; **7**, 97919-69-2; **8**, 97950-32-8; **9**, 97950-33-9; **10**, 97919-70-5; C_5H_6, 542-92-7; $[CpNi(CO)]_2$, 12170-92-2; $[CpMo(CO)_3]_2$, 12091-64-4; Cp_2Ni, 1271-28-9; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Lists of calculated and observed structure factors, isotropic and anisotropic thermal parameters, and complete bond angles (19 pages). Ordering information is given on any current masthead page.

Communications

New Nickel *o*-Xylyl Complexes. Crystal and Molecular Structure of $Ni_3(CH_2C_6H_4Me\text{-}o)_4(PMe_3)_2(\mu_3\text{-}OH)_2$

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Summary: The formation of the new nickel *o*-xylyl derivatives $NiCl(\eta^1\text{-}CH_2C_6H_4CH_3)(PMe_3)_2$, **1**, $NiCl(\eta^3\text{-}CH_2C_6H_4CH_3)(PMe_3)$, **2**, and $Ni_3(\eta^1\text{-}CH_2C_6H_4CH_3)_4(PMe_3)_2(\mu_3\text{-}OH)_2$, **3**, is reported. A crystal structure determination on **3** shows the complex crystallizes in the space group $P\bar{1}$ with a = 10.428 (2) Å, b = 12.646 (3) Å, c = 16.551 (3) Å, α = 70.68 (2)°, β = 79.54 (1)°, γ = 69.20 (2)°, V = 1920.4 Å^3, and Z = 2. The molecule possesses a distorted trigonal-bipyramidal $Ni_3(OH)_2$ core with the Ni(II) ions in a distorted square-planar environment. Apart from the hydroxo ions, the coordination sphere of the nickel(II) ions is completed by two *o*-xylyl groups for one of the Ni(II) and by one alkyl group and one PMe_3 ligand for the others.

The chemistry of organonickel compounds continues to attract much attention, both from a synthetic and from a structural point of view.[1] Following previous studies on the formation of nickel alkyl and acyl complexes,[2] we have investigated reactions of the *o*-methylbenzyl ligand, *o*-$CH_3C_6H_4CH_2$, with several nickel complexes. Here we report preliminary results based on reactions with $NiCl_2(PMe_3)_2$ and $Ni(cod)_2$ that lead to the formation[3] of a σ-bonded derivative, $NiCl(\eta^1\text{-}CH_2C_6H_4CH_3)(PMe_3)_2$, **1**, a π-allyl derivative, $NiCl(\eta^3\text{-}CH_2C_6H_4CH_3)(PMe_3)$, **2**, and an unusual trimetallic compound, $Ni_3(\eta^1\text{-}CH_2C_6H_4CH_3)_4(PMe_3)_2(\mu_3\text{-}OH)_2$, **3**, containing two hydroxo groups triply bridging one NiR_2 fragment and two $Ni(R)(PMe_3)$ fragments.

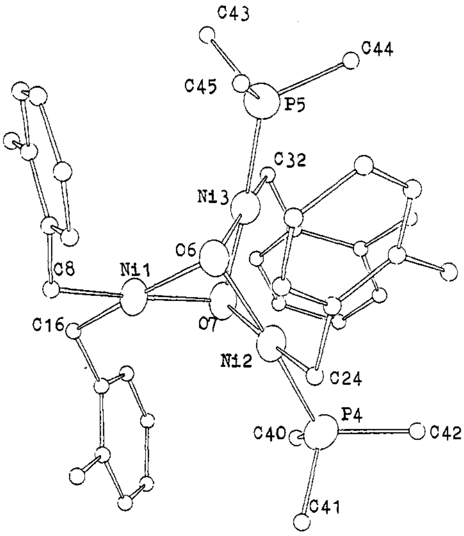

Figure 1. Molecular structure of **3** and atom labeling scheme. The C_6H_4Me labels have been ommitted for clarity. Important bond distances (Å) and angles (deg) include the following: Ni1–O = 2.000 (8) (av); Ni2–O7 and Ni3–O6 = 1.97 (1) (av); Ni2–O6 and Ni3–O7 = 1.92 (1) (av); Ni–C = 1.95 (1) (av); Ni–P = 2.110 (4) (av); O6–Ni–O7 = 72 (1) (av); Ni–O–Ni = 89 (1) (av); C–Ni–L (L = C or P) = 90.1 (5) (av).

Treatment of $NiCl_2(PMe_3)_2$ with $Mg(o\text{-}CH_3C_6H_4CH_2)Cl$ results in the formation of **1** or of a mixture of **1** and **2** depending upon the reaction conditions. From the resulting mother liquor, small amounts of very dark crystals of **3** can be collected after standing at −20 °C for 2–3 days. Although it is not easy to rationalize the formation of **3**, it is evident that adventitious water, possibly introduced at some stage during workup of the reaction, must play an important role. In fact, formation of **3** is not observed when the reaction is carried out with recently prepared Grignard solutions and under very strict anhydrous conditions.[4a] Complex **3** is very air sensitive, and although

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[1] Jolly, P. W. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vol. 6.

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[3] The new compounds described in this paper have been fully characterized by analytical data and IR and multinuclear NMR spectroscopies.

[4] (a) The best yield of **3** is obtained as follows: 0.28 g of $NiCl_2(PMe_3)_2$ (1 mmol) in 30 mL of Et_2O was reacted at −40 °C, for ca. 30 min with 3 equiv of a 0.5 N solution of $Mg(o\text{-}CH_3C_6H_4CH_2)Cl$ in Et_2O. The resulting mixture was stirred at room temperature for 4 h, the solvent removed in vacuo, and the residue extracted with 40 mL of petroleum ether. Complex **3** was obtained in ca. 30%, together with small amounts of **1**, after concentration to ca. 5 mL, addition of a drop of water, and cooling at −30 °C for 48 h. (b) Crystal data: $C_{38}H_{56}Ni_3O_2P_2$; M = 782.5; triclinic; space group $P\bar{1}$; a = 10.428 (2) Å, b = 12.646 (3) Å, c = 16.551 (3) Å, α = 70.68 (2)°, β = 79.54 (1)°, γ = 69.20 (2)°, V = 1920.4 Å^3; ρ_{calcd} = 1.35 g cm^{-3}, Z = 2, $F(000)$ = 828; μ(Mo Kα) = 11.25 cm^{-1}. Intensity data collected on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique; 6817 independent reflections measured in a hemisphere, with $2 < \theta < 25°$; 1983 reflections considered observed, $I \geq 4\sigma(I)$ after data reduction. Structure solved by Patterson and Fourier techniques and refined by least-squares methods. The hydrogens attached to O(6) and O(7) were found by means of a Fourier difference map and included in the refinement with fixed contributions. The final R value was 0.044. All computations were made with the Oxford CRYSTALS package.[5] No absorption and no extinction correction were made.

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