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Syntheses, Crystal Structures, and DNMR Studies on the Mixed Clusters $CpNiFe(CO)_3(RC\equiv CR')M$ (M = CpNi, $Co(CO)_3$, $Mo(CO)_2Cp$): Some Comments on the Acetylene Rotation Process

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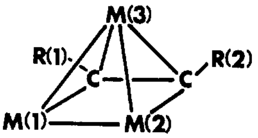
Chiral organotransition-metal tetrahedral clusters of the type ($PhC\equiv CCO_2$-*i*-Pr)MM′, where M = $(C_5H_5)Ni$ and M′ = $(C_5H_5)Mo(CO)_2$, $Co(CO)_3$, or $(C_5H_5)Ni$ react with $Fe_2(CO)_9$ to give square-pyramidal chiral clusters of general formula $(RC\equiv CR')MM'Fe(CO)_3$. When M′ = $(C_5H_5)Ni$, **4** or $Co(CO)_3$, **5**, the $Fe(CO)_3$ moiety caps the basal plane whereas when M′ = $(C_5H_5)Mo(CO)_2$, **6**, the latter moiety caps the basal plane comprised of C–C–Ni–Fe atoms. These molecules are fluxional on the NMR time scale; **4** undergoes racemization while **5** and **6** merely exhibit interconversion of diastereomers demonstrating the intramolecularity of the process. The mechanism of isomerization of these M_3C_2 systems is shown to be related to that of the closely analogous $C_5H_5^+$ cation.

Introduction

With the long-range goal of combining the reactivity of metal surfaces with the control achievable in homogeneous systems, much effort has recently been devoted to improving our understanding of organotransition-metal clusters.[1] In particular, mixed-metal clusters have been prepared in the hope that chiral clusters may find a use in asymmetric synthesis.[2] Clearly, such an undertaking would presuppose that the chirality of the cluster not be lost during the reaction sequence. However, a number of systems are now extant in which not only can the peripheral ligands (carbonyls, hydrides, etc.) migrate across the cluster surface[3] but also the polyhedral vertices can themselves interchange positions, thus causing loss of stereochemical integrity.[4] Typically, $Cp_2Co_2C_4H_4$ has a cobaltacyclopentadiene ring capped by a CpCo moiety; the nonequivalent CpCo fragments have been shown to interchange on the NMR time scale.[5] Similarly, chiral ferro–ferradiene systems are known to racemize, presumably via interchange of the two $Fe(CO)_3$ units.[6]

There are numerous systems in which five fragments together make up what is essentially a square-based pyramid (I); commonly, three of these vertices are comprised of organometallic fragments while the other two are derived from an acetylene (or occasionally from the juxtaposition of two carbyne moieties).[7–9] Such molecules are chiral if M(1) ≠ M(2) or R(1) ≠ R(2) or if there is an asymmetrical arrangement of ligands such as a semibridging carbonyl; of course, an intrinsically chiral substituent, such as (+)-menthyl, would obviously make the cluster nonsuperimposable on its mirror image. It is now clear that molecules of the type wherein cluster chirality is dependent upon the different identities of M(1) and M(2) or R(1) and R(2) undergo rapid racemization and it is such processes that we now discuss.[10]



I

Experimental Section

NMR spectra were obtained on Bruker WP80 and WM 250 instruments. Simulated spectra were obtained by using the computer program DNMR3.[11]

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Table I

	$C_{25}H_{22}FeNi_2O_5$, **4**	$C_{23}H_{17}CoFeNiO_8$, **5**	$C_{27}H_{22}FeMoNiO_7$, **6**
mol wt	575.7	594.9	669.0
temp. °C	18	18	18
space group	triclinic $P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.312 (2)	8.179 (1)	8.634 (3)
b, Å	9.648 (3)	11.910 (2)	9.879 (2)
c, Å	16.149 (3)	12.512 (4)	15.471 (5)
α, deg	104.97 (2)	94.02 (2)	90.71 (2)
β, deg	102.84 (1)	106.73 (2)	100.32 (3)
γ, deg	93.94 (2)	90.33 (2)	99.16 (2)
V, Å^3	1208.9	1163.9	1280.5
Z	2	2	2
ρ (calcd), g/cm^3	1.58	1.70	1.73
crystal dimens, mm	0.20 × 0.25 × 0.30	0.45 × 0.20 × 0.15	0.50 × 0.25 × 0.15
radiatn	Mo Kα	Mo Kα	Ag Kα
linear abs coeff, cm^{-1}	21.8	21.7	14.0
scan type	ω–2θ	ω–2θ	ω–2θ
scan range, deg	1.15 + 0.35 tan θ	1.40 + 1.0 tan θ	2.4 + 1.0 tan θ
θ limits, deg	2–25	1–30	1–21
data collected	5231	5455	4603
unique data used	3122 [$I > 3\sigma(I)$]	3312 [$F > 3\sigma(F)$]	2608 [$I > 3\sigma(I)$]
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.041	0.046	0.053
$R_w = (\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2)^{1/2}$	0.047	0.059	0.055

Preparation of $(C_5H_5)_2Ni_2(PhC_2CO_2$-*i*-Pr), 1. Nickelocene (1 g, 5.3 mmol) and isopropyl phenylpropiolate (0.50 g, 2.7 mmol) were heated in toluene (30 mL) at 105 °C during 10 h under an atmosphere of nitrogen. After removal of solvent, the products were separated by thin-layer chromatography on silica gel using as eluent a 9:1 mixture of petroleum ether/ether. The product was a green oil showing ν_{CO} at 1712 cm^{-1} in heptane solution: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.62, 7.32 (m, C_6H_5), 5.31 (s, C_5H_5), 5.02 (septet, CH), 1.34 (d, CH_3, J = 6.9 Hz); ^{13}C NMR in ($CDCl_3$, 20.1 MHz) δ 130.52, 129.20, 128.04 (C_6H_5), 87.97 (C_5H_5), 68.60 (CH), 21.80 (CH_3).

Preparation of $(C_5H_5)NiCo(CO)_3(PhC_2CO_2$-*i*-Pr), 2. $Co_2(CO)_8$ (1 g, 2.9 mmol), $(C_5H_5)_2Ni$ (1 g, 5.3 mmol), and $C_6H_5C_2CO$-*i*-Pr (1 g, 5.3 mmol) were heated at 100 °C in heptane under N_2 for 6 h and gave rise to the heterobimetallic acetylene complex **2** [25% yield; oil, m/z 453.9756 m/z (calcd) 453.9761; ^{1}H NMR (80 MHz) δ 7.66, 7.35 (m, C_6H_5), 5.31 (s, C_5H_5), 1.29 (d, CH_3, J = 6.6 Hz) in CD_2Cl_2 at 22 °C, δ (in C_6D_6 at 22 °C) 1.13 (d, CH_3, J = 6.4 Hz), IR (neat liquid) ν_{CO} 2055 (s), 2000 (vs), 1700 (s) cm^{-1}] as the main product together with, inter alia, $Ni_2Cp_2(CO)_2$, $Co_2(CO)_6(PhC_2CO_2$-*i*-Pr), and $Ni_2Cp_2(PhC_2CO_2$-*i*-Pr), separated on silica gel using petroleum ether/ether (9:1).

Preparation of $(C_5H_5)_2NiMo(CO)_2(PhC_2CO_2$-*i*-Pr), 3. $(C_5H_5)_2Ni$ (1 g, 5.3 mmol), $(C_5H_5)_2Mo_2(CO)_6$ (1.3 g, 2.7 mmol), and PhC_2CO_2-*i*-Pr (1 mL, 5.3 mmol) were heated at 105 °C in 35 mL of toluene for 7 h under N_2. TLC as before afforded 1.19 g (40%) of **3** as a red-brown crystalline solid [mp 90–91 °C; m/z 529.9922, calcd 529.99254; IR (heptane) ν_{CO} 2030 (w), 1978 (sh), 1968 (vs), 1930 (s), 1902 (m), 1857 (s), 1682 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$ at 30 °C at 80 MHz) δ 7.54, 7.25 (m, Ph), 5.24 (s, Cp), 5.14 (s, Cp), 1.35 (d, CH_3, J = 6.4 Hz), (C_6D_6 at 30 °C) δ 1.22, 1.17 (d, d, CH_3, J = 6.1 Hz)] together with $Ni_2Cp_2(CO)$, $Ni_2Cp_2(PhC_2CO_2$-*i*-Pr), and unreacted $Mo_2Cp_2(CO)_6$.

Preparation of $(C_5H_5)NiFeCo(CO)_6(PhC_2CO_2$-*i*-Pr), 5. $Fe_2(CO)_9$ (0.92 g, 2.5 mmol) and **2** (1 g, 2.3 mmol) were heated at 40 °C in heptane for 6 h under an atmosphere of nitrogen. After removal of solvent, the product was chromatographed on silica gel and eluted with petroleum ether/ether (80/20) to give **5** (85%) as a green solid which was recrystallized from heptane/$CHCl_3$. **5**: mp 120 °C ^{1}H NMR δ 7.1–7.6 (m, 5 H, Ph), 6.9 (septet, 1 H, C*H*Me$_2$), 6.58 (s, 5 H, Cp), 0.96 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, Me), 0.83 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, Me); IR ($CHCl_3$) ν_{CO} 2060 (s), 2015 (vs), 2000 (s), 1970 (m), 1960 (m), 1950 (m) cm^{-1}; m/z 593.9001, calcd 593.896.

Preparations of 4 and 6. $Fe_2(CO)_9$ (0.92 g, 2.5 mmol) and **3** (1.2 g, 2.3 mmol) were heated at 40 °C in heptane for 4 h under an atmosphere of nitrogen. Chromatography on silica gel and elution with petroleum ether/ether (90/10) yielded **6** (70%) as a gray solid: mp 145 °C; ^{1}H NMR δ 7.0–7.5 (m, 5 H, Ph), 5.14 (s, 5 H, Cp), 4.85 (m, 1 H, C*H*Me$_2$), 4.70 (s, 5 H, Cp), 1.17 (d, 3 H, $^3J_{HH}$ = 6.2 Hz, Me), 1.02 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, Me); IR (heptane) ν_{CO} 2028 (vs), 1970 (vs), 1876 (w), 1830 (w) cm^{-1}; m/z 585.929 (M − 3CO), calcd 586.9274.

Table II. Positional Parameters for Non-Hydrogen Atoms of $(C_5H_5)_2Ni_2Fe(CO)_3(PhC_2CO_2CMe_2H)$, 4

atom	x/a	y/b	z/c
Ni1	0.17381 (6)	0.33205 (5)	0.25636 (3)
Ni2	0.23613 (6)	0.13777 (5)	0.32507 (3)
Fe	0.02418 (7)	0.28205 (6)	0.35830 (4)
O1	−0.0816 (5)	0.1755 (5)	0.4937 (2)
O2	0.3027 (5)	0.4842 (6)	0.4823 (3)
O3	−0.2170 (5)	0.4853 (4)	0.3494 (3)
O4	−0.3118 (4)	0.2022 (4)	0.1676 (2)
O5	−0.1437 (3)	0.1993 (4)	0.0793 (2)
C1	−0.0435 (6)	0.2143 (6)	0.4393 (3)
C2	0.1946 (6)	0.4036 (7)	0.4322 (3)
C3	−0.1243 (6)	0.4061 (5)	0.3524 (3)
C4	−0.0229 (4)	0.2010 (4)	0.2247 (2)
C5	0.0075 (5)	0.0909 (4)	0.2622 (2)
C6	−0.1760 (5)	0.2028 (4)	0.1563 (2)
C7	−0.2826 (6)	0.1967 (7)	0.0049 (3)
C8	−0.3171 (10)	0.0503 (8)	−0.0541 (4)
C9	−0.2341 (9)	0.3055 (7)	−0.0368 (4)
C10	−0.0922 (5)	−0.0541 (4)	0.2357 (3)
C11	−0.1454 (6)	−0.1296 (5)	0.1476 (3)
C12	−0.2434 (8)	−0.2627 (6)	0.1214 (4)
C13	−0.2908 (7)	−0.3206 (5)	0.1822 (5)
C14	−0.2428 (8)	−0.2462 (6)	0.2675 (4)
C15	−0.1382 (8)	−0.1152 (5)	0.2963 (4)
CP11	0.3761 (6)	0.3877 (5)	0.2094 (3)
CP12	0.2264 (7)	0.3902 (6)	0.1497 (3)
CP13	0.1445 (7)	0.4934 (5)	0.1918 (4)
CP14	0.2371 (8)	0.5552 (6)	0.2745 (5)
CP15	0.3780 (6)	0.4924 (6)	0.2866 (4)
CP21	0.3693 (6)	−0.0412 (5)	0.3069 (3)
CP22	0.3250 (6)	−0.0189 (5)	0.3865 (3)
CP23	0.4021 (7)	0.1177 (7)	0.4399 (3)
CP24	0.4897 (6)	0.1786 (6)	0.3918 (4)
CP25	0.4699 (6)	0.0813 (5)	0.3106 (3)

Similarly, $Fe_2(CO)_9$ and **1** gave **4**: mp 125 °C; m/z 573.9528, calcd 573.9522; IR ν_{CO} 1955 (m), 1915 (s) cm^{-1}; ^{1}H NMR δ 7.0–7.5 (m, 5 H, Ph), 5.28 (s, 5 H, Cp), 4.99 (s, 5 H, Cp), 4.39 (m, 1 H, C*H*Me$_2$), 0.78 (pseudotriplet, 6 H, $^3J_{HH}$ = 6.2 Hz, Me's). **4**, **5** and **6** were all characterized by X-ray crystallography.

Structural Determinations of 4, 5 and 6. The structural data from the X-ray diffraction studies of **4**, **5**, and **6** are summarized in Tables I–VII. All the crystallographic data were obtained on small single crystals at room temperature using

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Table III. Positional Parameters for Non-Hydrogen Atoms of $C_5H_5NiCo(CO)_3Fe(CO)_3(PhC_2CO_2CMe_2H)$, 5

atom	x/a	y/b	z/c
Ni	0.14418 (9)	0.18392 (6)	0.32095 (6)
Co	0.09269 (10)	0.27127 (6)	0.14377 (6)
Fe	0.30206 (10)	0.11899 (6)	0.19270 (6)
C1	0.3361 (7)	0.2879 (4)	0.2204 (4)
C2	0.3605 (7)	0.2405 (4)	0.3208 (4)
C3	0.4600 (8)	0.3642 (4)	0.1924 (4)
O1	0.5922 (6)	0.3374 (4)	0.1780 (4)
O2	0.3995 (5)	0.4683 (3)	0.1845 (4)
C4	0.5081 (9)	0.5563 (5)	0.1596 (5)
C5	0.626 (1)	0.6070 (7)	0.2689 (7)
C6	0.381 (1)	0.6401 (6)	0.0969 (7)
C30	0.0229 (8)	0.3960 (5)	0.2050 (6)
O30	−0.0190 (7)	0.4740 (4)	0.2438 (5)
C31	−0.1024 (9)	0.1869 (5)	0.0932 (5)
O31	−0.2241 (6)	0.1330 (4)	0.0595 (5)
C32	0.1040 (9)	0.3181 (6)	0.0121 (6)
O32	0.1134 (9)	0.3465 (6)	−0.0699 (5)
C40	0.1444 (8)	0.0085 (5)	0.1585 (5)
O40	0.0463 (6)	−0.0650 (4)	0.1355 (4)
C41	0.3514 (8)	0.1170 (5)	0.0623 (5)
O41	0.3790 (7)	0.1180 (5)	−0.0218 (4)
C42	0.4695 (8)	0.0286 (5)	0.2557 (5)
O42	0.5723 (7)	−0.0332 (4)	0.2926 (5)
C21	0.5042 (7)	0.2620 (4)	0.4246 (4)
C22	0.5636 (8)	0.1774 (5)	0.4959 (5)
C23	0.6974 (9)	0.2006 (6)	0.5938 (6)
C24	0.7727 (9)	0.3068 (6)	0.6198 (6)
C25	0.7116 (9)	0.3914 (6)	0.5500 (6)
C26	0.5769 (8)	0.3688 (5)	0.4537 (5)
CP1	−0.039 (1)	0.0752 (7)	0.3560 (7)
CP2	0.113 (1)	0.0788 (7)	0.4433 (7)
CP3	0.147 (1)	0.1857 (7)	0.4908 (7)
CP4	0.023 (1)	0.2560 (8)	0.4349 (7)
CP5	−0.099 (1)	0.1859 (7)	0.3481 (7)

Table IV. Positional Parameters for Non-Hydrogen Atoms of $C_5H_5Mo(CO)_2C_5H_5NiFe(CO)_3(PhC_2CO_2Me_2H)$, 6

atom	x/a	y/b	z/c
Mo	0.1267 (1)	0.2237 (1)	0.15065 (8)
Ni	0.1225 (2)	0.1424 (1)	0.3106 (1)
Fe	0.3461 (2)	0.0832 (2)	0.2421 (1)
C1	0.363 (1)	0.282 (1)	0.2415 (9)
C2	0.242 (1)	0.312 (1)	0.2822 (9)
C3	0.502 (1)	0.381 (1)	0.224 (1)
O1	0.639 (1)	0.364 (1)	0.2492 (9)
O2	0.463 (1)	0.4894 (8)	0.1845 (7)
C4	0.590 (2)	0.595 (2)	0.167 (1)
C5	0.517 (2)	0.674 (2)	0.094 (1)
C6	0.657 (3)	0.684 (2)	0.254 (2)
C20	0.243 (1)	0.123 (1)	0.0803 (9)
O20	0.292 (1)	0.068 (1)	0.0289 (8)
C21	0.001 (1)	0.044 (1)	0.167 (1)
O21	−0.081 (1)	−0.062 (1)	0.1563 (7)
C30	0.456 (2)	0.082 (1)	0.3473 (9)
O30	0.534 (2)	0.085 (1)	0.4161 (9)
C31	0.263 (2)	−0.097 (1)	0.227 (1)
O31	0.213 (1)	−0.211 (1)	0.2188 (7)
C32	0.510 (2)	0.072 (1)	0.189 (1)
O32	0.617 (1)	0.064 (1)	0.1582 (8)
CP1	0.128 (2)	0.395 (1)	0.050 (1)
CP2	0.016 (2)	0.279 (2)	0.009 (1)
CP3	−0.109 (2)	0.257 (2)	0.060 (1)
CP4	−0.081 (2)	0.354 (2)	0.125 (1)
CP5	0.067 (2)	0.440 (1)	0.119 (1)
C11	0.240 (1)	0.438 (1)	0.3352 (9)
C12	0.094 (2)	0.482 (1)	0.3415 (9)
C13	0.092 (2)	0.595 (2)	0.395 (1)
C14	0.233 (2)	0.664 (2)	0.439 (1)
C15	0.378 (2)	0.624 (2)	0.436 (1)
C16	0.378 (2)	0.510 (1)	0.380 (1)
CP6	0.034 (2)	−0.033 (2)	0.377 (1)
CP7	−0.093 (2)	0.036 (2)	0.345 (1)
CP8	−0.055 (2)	0.169 (2)	0.389 (1)
CP9	0.089 (2)	0.182 (2)	0.439 (1)
CP10	0.150 (2)	0.054 (2)	0.432 (1)

Table V. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_5)_2Ni_2Fe(CO)_3(PhC_2CO_2CHMe_2)$, 4

	Bond Distances		
Ni1–Ni2	2.442 (1)	Fe–C4	2.032 (3)
Ni1–Fe	2.393 (1)	Fe–C5	2.054 (3)
Ni2–Fe	2.388 (1)	C4–C5	1.363 (4)
Ni1–C4	1.883 (3)	C4–C6	1.493 (4)
Ni2–C5	1.906 (3)	C5–C10	1.484 (5)
	Bond Angles		
Ni1–Fe–Ni1	61.4 (2)	Ni2–C5–C4	104.3 (2)
Ni1–Ni2–Fe	59.4 (2)	C5–C4–C6	125.3 (3)
Ni2–Ni1–Fe	59.2 (2)	C4–C5–C10	127.0 (3)
Ni1–C4–C5	108.8 (2)		

Table VI. Selected Bond Distances (Å) and Angles (deg) for Compound 5

	Bond Distances		
Co–Ni	2.442 (1)	Fe–C1	2.021 (5)
Co–Fe	2.481 (1)	Fe–C2	2.029 (5)
Ni–Fe	2.423 (1)	C1–C2	1.376 (8)
Co–C1	1.947 (6)	C1–C3	1.488 (9)
Ni–C2	1.890 (5)	C2–C21	1.485 (7)
	Bond Angles		
Co–Fe–Ni	59.64 (3)	Ni–C2–C1	106.2 (4)
Co–Ni–Fe	61.48 (3)	C2–C1–C3	125.5 (5)
Ni–Co–Fe	58.88 (3)	C1–C2–C21	127.8 (5)
Co–C1–C2	106.1 (4)		

Table VII. Selected Bond Disatnces (Å) and Angles (deg) for Compound 6

	Bond Distances		
Fe–Ni	2.504 (2)	Mo–C1	2.25 (1)
Fe–Mo	2.728 (2)	Mo–C2	2.20 (1)
Ni–Mo	2.616 (2)	C1–C2	1.38 (2)
Fe–C1	1.95 (1)	C1–C3	1.48 (3)
Ni–C2	1.92 (1)	C2–C11	1.49 (2)
	Bond Angles		
Ni–Mo–Fe	55.83 (6)	Fe–C1–C2	105.3 (9)
Ni–Fe–Mo	59.82 (6)	Ni–C2–C1	108.3 (9)
Fe–Ni–Mo	64.36 (6)	C2–C1–C3	126 (1)
		C1–C2–C11	128 (1)

Enraf-Nonius CAD 4 diffractometers equipped with a graphite monochromator. The unit-cell dimensions were determined by least-squares refinement of the best angular positions for 25 independent reflections. During the collection of intensity data, the intensities of three standard reflections were monitored periodically; only statistical fluctuations were noted in each case. Data were corrected for Lorentz and polarization effects and anomalous scattering corrections were included in all structure factor calculations. Atomic scattering factors were taken from ref 12.

The three structures were solved by the heavy atom method and refined by full-matrix least-squares treatment. For **4** and **5** the hydrogen atoms were located at the end of the refinement. Their positional parameters were kept constant for **4** but refined for **5**. All the non-hydrogen atoms were refined anisotropically except for 11 peripheral atoms in **5** and for 24 peripheral atoms in **6**. In each case the residual electron density peaks after the last Fourier synthesis were less than 0.5 electron/Å^2 near the heavy atoms.

Results and Discussion

Syntheses and Crystallographic Characterizations. The five-vertex trimetallic dicarbon clusters M_3C_2 adopt either a trigonal-bipyramidal or a square-based pyramidal geometry depending on whether the skeletal electron count is 12 or 14, respectively. These systems have been compared to the *closo*-boranes or -carboranes $R_2C_2B_3H_3$ and the *nido*-boranes, e.g., B_5H_9, respectively.[13] In the former

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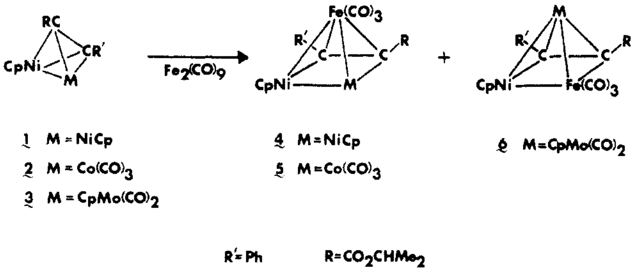
(12) Cromer, D. T.; Waber, J. T. In "International Tables for X-Ray Crystallography"; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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

Scheme I. The Expansion of $M_2C_2R_2$ Tetrahedral Molecules to Square-Based Pyramidal Clusters



case, the cluster carbons may be contiguous as in $Ph_2C_2Fe_3(CO)_9$[14] or diaxial as in $R_2C_2Co_3Cp_3$.[15] In the nido case, the two carbons are always found adjacent in the basal plane.[7] Although some of these molecules were originally found among the mixtures of products arising from the thermolyses of mononuclear metal carbonyl derivatives and acetylenes, several rational synthetic routes have now been developed to this type of cluster. With hindsight, the most obvious is, of course, addition of an alkyne to a metal triangle with concomitant elimination of carbon monoxide, hydrogen, or some weakly bonded ligand (eq 1).[16] A second method involves the coupling of two metal–carbyne fragments in the presence of another metal carbonyl (eq 2),[8] while our own approach[10b] involves the expansion of a preformed M_2C_2 tetrahedral cluster (eq 3).

$$(CH_3CN)_2Os_3(CO)_{10} \xrightarrow[C_6H_6,\ 25\ ^\circ C]{R_2C_2} (RC{\equiv}CR)Os_3(CO)_{10} \quad (1)$$

$$2Cp(CO)_2W{\equiv}CR \xrightarrow[\text{toluene, } 80\ ^\circ C]{Ru_3(CO)_{12}} (RC{\equiv}CR)Cp_2W_2Ru(CO)_7 \quad (2)$$

$$(R_2C_2)M_2 \xrightarrow[\text{heptane, } 40\ ^\circ C]{Fe_2(CO)_9} (RC{\equiv}CR)M_2Fe(CO)_3 \quad (3)$$

The third approach to cluster syntheses has some attractiveness in that not only are the conditions mild and easily controllable but also numerous excellent routes exist to the tetrahedral precursors whether they be of the M_2C_2, M_3C, or M_4 type.[1b,9,17] Indeed, we have recently shown that the cluster expansion route is applicable also to the M_3C tetrahedral molecules.[4,18] Furthermore, one is not restricted simply to the addition of $Fe(CO)_3$ units but one can introduce other fragments bearing two skeletal electrons in their three frontier orbitals.[19] In essence, one is progressing from a tetrahedron (nido trigonal bipyramid) to a square-based pyramid (nido octahedron) and even to the nido pentagonal bipyramid by the addition of a two-electron vertex to the precursor polyhedral cluster.[4] Thus, as shown in Scheme I, one can expand a variety of tetrahedral molecules to their square-based pyramidal homologues, by adding an $Fe(CO)_3$ fragment to the previously reported[10a] precursors.

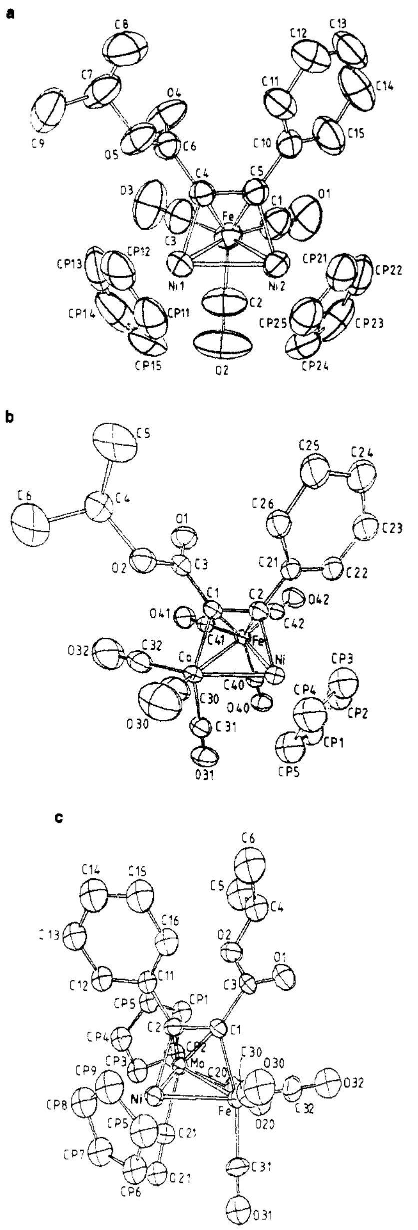


Figure 1. (a) ORTEP diagram of $(CpNi)_2Fe(CO)_3(PhC_2CO_2\text{-}i\text{-}Pr)$, 4. (b) ORTEP diagram of $CpNiCo(CO)_3Fe(CO)_3(PhC_2CO_2\text{-}i\text{-}Pr)$, 5. (c) ORTEP diagram of $CpNiCpMo(CO)_2Fe(CO)_3(PhC_2CO_2\text{-}i\text{-}Pr)$, 6.

The molecules **4**, **5**, and **6** have been characterized crystallographically and ORTEP views are shown in Figure 1. The molecular structures of these three cluster compounds show the acetylenic bond almost perfectly parallel to a metal–metal vector. These two parallel "bonds" define a pseudosquare (actually a trapezium) which is capped by the remaining metal unit, thus conferring on **4**, **5**, and **6** the nido-type structure previously alluded to. The most striking observation is that while in **4** and **5** the $Fe(CO)_3$ unit caps the basal plane containing the four original vertices, in **6** it is the $CpMo(CO)_2$ moiety which occupies the apical position. This nido structure with CC‖MM is observed for all trimetallic alkyne M_3C_2 complexes possessing 14 skeletal electrons.[7] It is noteworthy that even

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[14] Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.

[15] (a) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559. (a) A mixed-metal diaxial system is also known: Freeland, B. H.; Payne, N. C.; Stalteri, M. A.; Van Leeuven, H. *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* **1983**, *C39*, 1533.

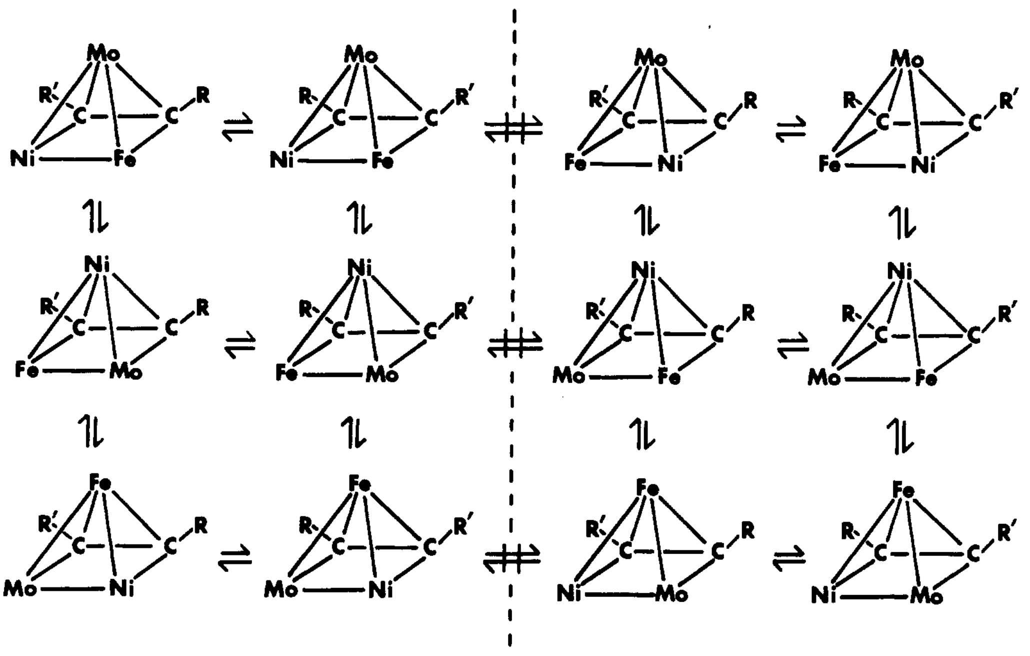
[16] (a) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172. (b) Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19. (c) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.

[17] (a) Bruce, M. I.; Rodgers, J. R.; Snow, M. R.; Wong, F. S. *J. Organomet. Chem.* **1982**, *240*, 299. (b) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457. (c) Ginley, D. S.; Brock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85. (d) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (e) Tilney-Basset, J. F. *J. Chem. Soc.* **1961**, 577. (f) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

[18] Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Faggiani, R.; Lock, C. J. L.; Jaouen, G., submitted for publication.

[19] Typically, use of (indenyl)$Rh(C_2H_4)_2$ allows the incorporation of the (indenyl)Rh fragment which is isolobal with $Fe(CO)_3$: unpublished results from these laboratories.

Scheme II. Acetylene Rotation on One Face of a Cluster Showing Interconversion of Diastereomers but Not of Enantiomers



for the rather unsymmetrical compound 6, this regular geometry is preserved. As is customary for such compounds, the acetylenic ligand is bent and lies in a plane not perpendicular to the trimetallic plane; the dihedral angles between these planes are 74.0°, 74.5°, and 80.2° in 4, 5, and 6, respectively. The bond lengths and bond angles in Tables V–VII are of the same order of magnitude as those observed in similar M_3C_2 systems.[7] In particular, the M–C distances in the basal pseudosquare plane are shorter than those involving the capping metallic unit. Finally, a weak semibridging interaction should be noted in 6 between a carbonyl bonded to the molybdenum atom and the iron atom [Mo–C(20) = 1.74 (2) Å; Fe···C(20) = 2.56 (2) Å].

Conventional electron counting would assign each of the metals in 4 and 5 an 18-electron configuration; in contrast, the EAN formalism is not appropriate in 6 since the Fe, Ni, and Mo atoms would possess 17-, 18-, and 19-electron counts, respectively.[20] Nevertheless, within the framework of the Wade–Williams–Rudolph–Mingos[13] approach to the bonding in supposedly "electron-deficient" clusters, each of the molecules 4, 5, and 6 possesses 14 skeletal electrons which occupy seven globally delocalized[21] molecular orbitals. Indeed, there are now several known examples of M_3C_2 clusters in which the capping vertex is not the one anticipated on the basis of the 18-electron rule.[22] Even more fascinating is the discovery that the delicate balance existing between these isomers is reflected in the occurrence of both isomers of $(PhC_2Ph)Cp_2W_2Os(CO)_7$ in the same crystal.[23] The orientation of the alkyne moiety relative to the metal triangle has been the subject of a recent extended Hückel molecular orbital investigation.[24]

NMR Fluxionality. To our knowledge, the first reports of NMR fluxionality in molecules of the M_3C_2 type were the almost simultaneous publications from the laboratories of Rausch[25] and of Deeming.[26] In the former publication, it was shown that equivalencing of the Cp resonances of $Cp_3Rh_3(CO)RC_2R$ occurred at high temperature suggesting that not only the carbonyl group but also the alkyne ligand was mobile.[25] In the Deeming paper,[26] not only was benzyne trapped on an osmium triangle but also the molecular dynamics of molecules of the type $(C_6H_4)Os_3(CO)_7(PMe_2)_2$ or $HOs_3(C_6H_4)(PMe_2)(CO)_9$ were unravelled. The problem is complicated by hydride and carbonyl migrations but, ignoring these interesting side issues, it was suggested that there might be a rotation of the benzyne moiety relative to the metal triangle. Subsequent studies with indyne and with isopropylbenzyne complexes supported this proposal.[27] Previous studies on this phenomenon have involved homometallic triangles with either alkyne or vinylidene ligands.[28] We now report the use of heterometallic clusters which allows a more precise understanding of the factors involved.

To investigate the mechanism of this fascinating rearrangement, we have synthesized molecules with several independent probes. Thus in $(C_5H_5)_2Ni_2Fe(CO)_3(PhC_2CO_2CHMe_2)$, 4, the molecule is rendered chiral by the use of an unsymmetrical alkyne and this has the secondary effect of making the nickel atoms (and their atta-

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[20] The weakly semibridging interaction between a carbonyl on molybdenum and the iron atom may perhaps be viewed as an attempt by the molecule to alleviate the situation.

[21] McGlinchey, M. J.; Tal, Y. *Stud. Phys. Theor. Chem.* **1983**, *28*, 124 and references therein.

[22] (a) Einstein, F. W. B.; Freeland, B. H.; Tyers, K. G.; Sutton, D.; Waterous, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 371. (b) Braunstein, P.; Rosé, J.; Bars, O. *J. Organomet. Chem.* **1983**, *252*, C101. (c) Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1981**, *213*, 175.

[23] (a) Churchill, M. R.; Bueno, C.; Wasserman, J. J. *Inorg. Chem.* **1982**, *21*, 640. (b) Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519.

[24] Halet, J.-F.; Saillard, J.-Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218.

[25] Yamamoto, T.; Garber, A. R.; Bodner, G. M.; Todd, L. J.; Rausch, M. D.; Gardner, S. A. *J. Organomet. Chem.* **1973**, *56*, C23.

[26] Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2859.

[27] (a) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123. (b) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1879.

[28] For these and related phenomena see: (a) Todd, L. J.; Wilkinson, J. R.; Rausch, M. D.; Dickson, R. S. *J. Organomet. Chem.* **1975**, *101*, 133. (b) Evans, J. *Adv. Organomet. Chem.* **1977**, *16*, 319. (c) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1975**, *97*, C16. (d) Jackson, W. G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1975**, *90*, C13. (e) Clauss, R. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528. (f) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43.

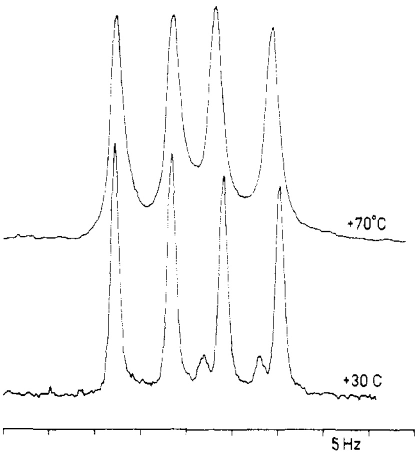


Figure 2. 80-MHz ^1H NMR spectrum of 6.

ched cyclopentadienyl ligands) nonequivalent. In principle, one could use ^{61}Ni NMR as we have done previously[29] to probe the different environments in which nickel atoms can find themselves; however, it is a reasonably safe assumption that the C_5H_5 ligands do not become detached from their respective nickel atoms and so we chose instead to monitor the ^1H and ^{13}C NMR signals of the rings. The chirality of the molecule as a whole is reflected in the diastereotopic nature of the methyl groups in the isopropyl substituent.

One can now test for two different processes. One could visualize, for example, the rotation of the nickel–nickel vector relative to the iron–carbon–carbon triangle. This may be improbable but cannot be dismissed out of hand since the $(C_5H_5)Ni$ fragment is isolobal with a CH unit,[30] thus making CpNi–NiCp a pseudoalkyne. If such a rotation were to occur, this would, of course, interconvert the two different C_5H_5 environments but would not racemize the molecule; i.e., the diastereotopic character of the Me_2CH group would be unaffected. In contrast, a formal rotation of the alkyne moiety relative to the Fe–Ni–Ni triangle would not only racemize the molecular cluster but would also interconvert the two $(C_5H_5)Ni$ environments. Furthermore, if the acetylene rotation were the only mechanism at work, the activation energy barriers for the $(C_5H_5)Ni$ interconversion and for the methyl coalescence must be identical. Gratifyingly, the experimental $\Delta G^{\ddagger}$ in each case is 63 ± 3 kJ/mol.

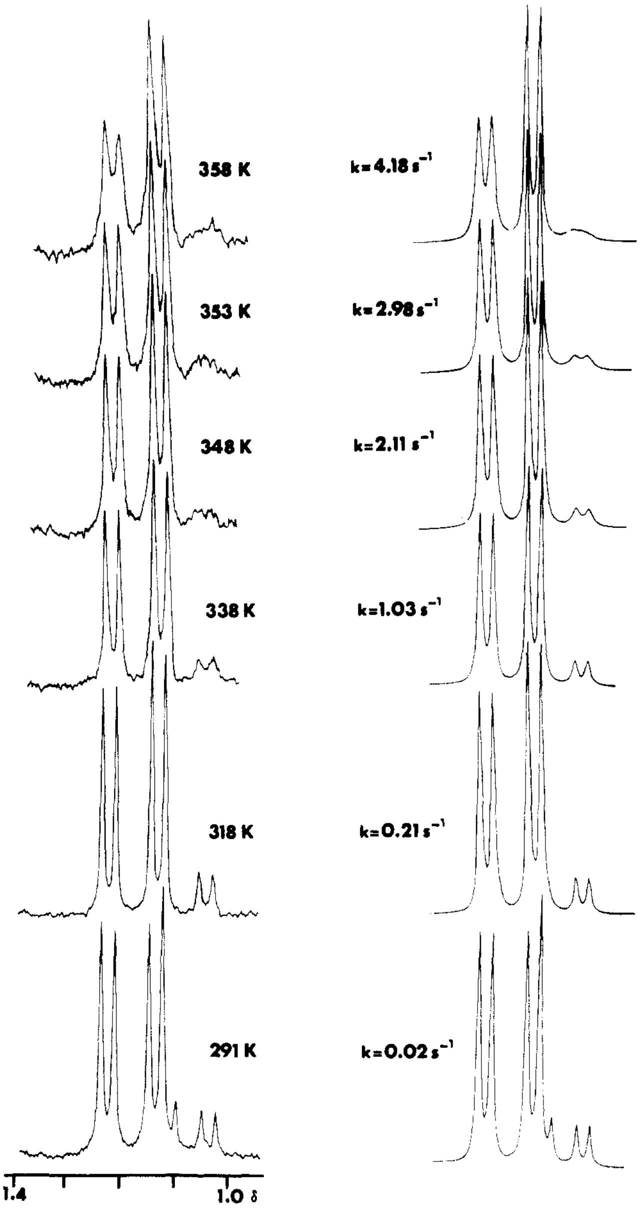
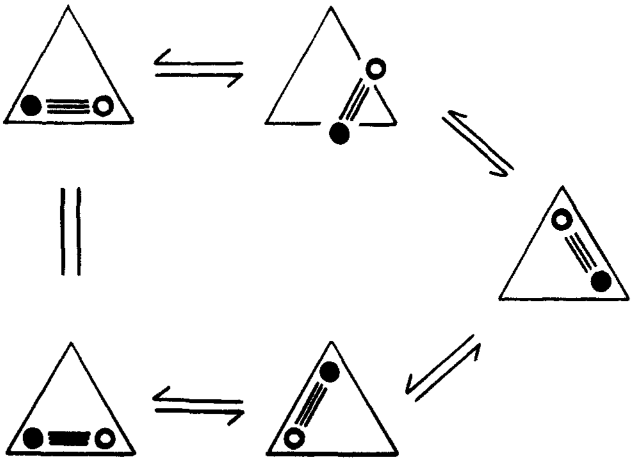


Figure 3. Experimental and simulated 250-MHz variable-temperature ^1H NMR spectra of 6.

Scheme III. Migration of an Alkyne about the Molecular Periphery Does Not Racemize the Cluster



One must, however, consider yet another possible occurrence. It is conceivable that there is a dissociation of the cluster into noncomplexed alkyne and an unsaturated metal triangle (perhaps weakly stabilized by solvent). Such an event would simultaneously equilibrate not only the methyls but also the cyclopentadienyl environments. One must, therefore, ensure that the process is indeed intramolecular. Such an experiment is readily accomplished by making all three of the metal atoms different as in 5 or 6. As shown in Scheme II, *acetylene rotation does not* interconvert enantiomers but merely diastereomers. Thus when alkyne rotation is slow on the NMR time scale, each diastereomer will show in the methyl region four peaks—two magnetically nonequivalent methyls, each split into a doublet by the unique isopropyl hydrogen. Now rapid alkyne rotation will equilibrate the diastereomers but cannot interconvert enantiomers without migration of the alkyne from one face of the triangle to the opposite face - a process which surely would require cluster dissociation. In the event, the low temperature 80 MHz ^1H NMR spectrum of 6 (see Figure 2) shows two sets of four lines

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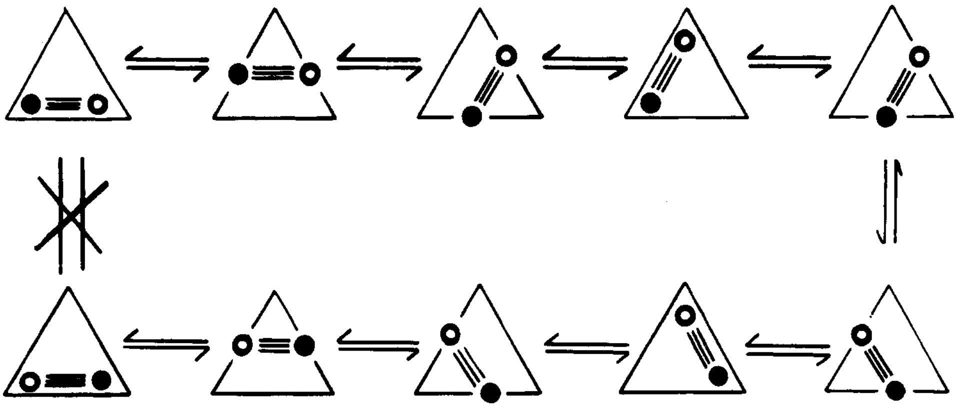
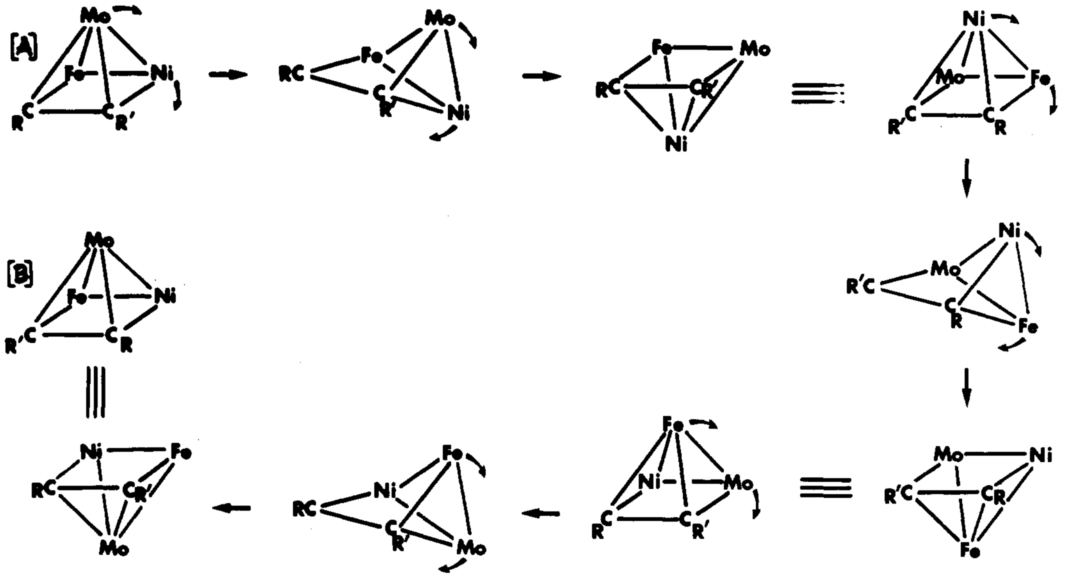
[29] Nguyen Hao; McGlinchey, M. J.; Sayer, B. G.; Schrobilgen, G. J. *J. Magn. Reson.* **1982**, *46*, 158.

[30] (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339.

Scheme IV. "Windshield Wiper" Motion of an Unsymmetrical Alkyne Leading to Racemization of the Cluster



Scheme V. A Rearrangement Mechanism for the MM'M''(RC≡CR') Cluster Analogous to That of the $C_5H_5^+$ System



(in the ratio ~6:1) presumably corresponding to the ratio of the two major diastereomers) but shows just four lines at high temperature indicating that the stereochemical integrity of the chiral cluster is conserved.[31] Figure 3 shows the variable-temperature 250-MHz proton NMR spectra in the isopropyl methyl region for **6** and the corresponding simulated spectra obtained from the program DNMR3.[11] Interestingly, the only way to get a good fit between the experimental and calculated spectra is to invoke exchange between the high-field doublet of the minor diastereomer and the low-field doublet of the major diastereomer. The experimental $\Delta G^{\ddagger}$ of 69 ± 4 kJ/mol is similar to that obtained for **4**, indicating that the same mechanistic pathway is involved.

Mechanistic Implications. At this point we should mention that Hoffmann and Schilling[32] have reported a preliminary theoretical analysis of the acetylene rotation process taking $(C_2H_2)Fe_3(CO)_9{}^{2-}$ as a model compound. Making the assumption of a rigid metal triangle they calculated the different barriers that a migrating alkyne would have to overcome as it traversed various paths around the metal triangle. Scheme III shows the first of these routes in which the acetylene essentially circumambulates the periphery of the triangle; the calculated barrier to such a process is 42 kJ/mol. However, such a mechanism would not interconvert the termini of the alkyne, and so if the molecule were chiral because of the asymmetry of the acetylene, it would not be racemized. The results we have presented here, as well as Deeming's data[27a] on the indyne–Os_3 complex, militate against such a mechanism.

Hoffmann and Schilling also present the results of calculations on two other pathways both of which do allow racemization but require that the alkyne perform more intricate manoeuvres, one of which is shown in Scheme IV. These pathways have barriers of 38 and 42 kJ/mol, respectively. Naively, one might visualize the alkyne executing a windshield wiper motion across a triangular face, but things are not so simple. As pointed out by Stone,[23b] we are viewing the molecule in projection. If we assume the metal triangle to be all in one plane, the acetylene must also rotate with respect to its own triple-bond axis since the substituents are not colinear with the alkyne carbons. This must be particularly important for small cycloalkynes[27a] where the ring geometry is rather rigid.

It is perhaps useful to reduce the problem to its simplest organic analogue, the $C_5H_5^+$ system, which has been exhaustively discussed by Stohrer and Hoffmann.[33] They

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(31) We show both the 80- and 250-MHz ^{1}H NMR spectra of **6** since only in the former case is the rate sufficiently rapid at an accessible temperature to see complete interconversion of diastereomers. The 250-MHz spectrum exhibits nicely resolved signals, but the frequency difference between them is too large to permit coalescence of the peaks. Simulation of the 250-MHz spectrum shows two equal intensity doublets only when the rate constant exceeds 1000 s^{-1}.

(32) Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 231.

(33) Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661.

have pointed out that in the interconversion of the various C_{4v} isomers (which we now recognize as belonging in the *nido*-B_5H_9 category) the intermediacy of a D_{3h} closo structure is strongly disfavored. Indeed, they propose the sequence $C_{4v} \rightarrow C_s \rightarrow C_{2v} \rightarrow C_s \rightarrow C_{4v}$ and we show below (Scheme V) how this can be applied to the M_3C_2 system.[34] It is clear from Scheme V that the overall effect of this rearrangement has the same result as does alkyne rotation; furthermore the molecules [A] and [B] are seen to be diastereomers rather than enantiomers. In conclusion, we have observed that tetrahedral M_2C_2 organotransition-metal clusters react with the two-electron donor $Fe(CO)_3$ and expand to give the square-based pyramidal (nido-octahedral) geometry. These M_3C_2 clusters are fluxional, and this phenomenon can be rationalized in terms of a formal rotation of the alkyne moiety relative to the metal triangle. The process is shown to be intramolecular and has an activation energy barrier in the range 60–70 kJ/mol. The data are consistent with a "modified windshield wiper" motion as in the second Schilling–Hoffmann proposal and unequivocally eliminate the mechanism involving circumambulation about the periphery of the metal triangle.

Studies in progress will further elaborate the mechanisms of alkyne rotation and vertex interchanges as well as the orientation of alkynes in *closo*-M_3C_2 systems.

Acknowledgment. It is a particular pleasure to thank Professors T. A. Albright (University of Houston) and R. Hoffmann (Cornell University) for valuable discussions on the mechanism of alkyne rotation. Financial support from the CNRS (France) and NSERC (Canada) is gratefully acknowledged. M.M. is the recipient of an NSERC post-graduate scholarship.

Registry No. **1**, 81141-83-5; **2**, 79816-41-4; **3**, 79839-04-6; **4**, 81141-86-8; **5**, 81141-85-7; **5** (R′ = CO_2CHMe_2, R = Ph), 81146-26-1; **6**, 81141-84-6; **6** (R = CO_2CHMe_2, R = Ph), 96109-50-1; $(C_5H_5)_2Ni$, 1271-28-9; $Co_2(CO)_8$, 10210-68-1; $Ni_2Cp_2(CO)_2$, 12170-92-2; $Co_2(CO)_6(PhC_2CO_2$-*i*-Pr), 96095-83-9; $Ni_2Cp_2(PhC_2CO_2$-*i*-Pr), 81141-83-5; $(C_5H_5)_2Mo_2(CO)_6$, 60974-85-8; $Fe_2(CO)_9$, 15321-51-4; isopropyl phenylpropiolate, 22767-95-9.

Supplementary Material Available: Tables of structure factors, thermal parameters, and bond lengths and angles for **4**, **5**, and **6** (39 pages). Ordering information is given on any current masthead page.

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(34) A reviewer has pointed out that an edge-bridged tetrahedron (such as $Os_5H_2(CO)_{16}$, 74 electrons) represents an alternative and isoelectronic possibility for the square pyramid (such as $Os_5C(CO)_{15}$, 74 electrons); we note that the C_s structures in Scheme IV could be viewed as edge-bridged tetrahedral molecules.

Reductive Elimination of Aryl Carboxylates from Acyl(aryloxy)nickel(II) and -palladium(II) Complexes

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Received November 14, 1984

Acyl(*p*-cyanophenoxy)nickel(II) and -palladium(II) complexes, $M(COR)(OC_6H_4$-*p*-$CN)L_2$ (M = Ni, Pd; L_2 = bpy, $(PEt_3)_2$), have been prepared by insertion reactions of CO into the metal–carbon bonds of the corresponding methylnickel(II) and -palladium(II) complexes. Addition of π-acids such as CO, maleic anhydride, and acrylonitrile selectively induces reductive elimination of *p*-cyanophenyl acetate from acylnickel(II) complexes, whereas thermolysis of the complexes mainly results in decarbonylation. In contrast, reductive elimination from the palladium analogue proceeds smoothly on thermolysis, and no apparent accelerating effect of added π-acids is observed. Kinetic studies of both reductive eliminations reveal that the former proceeds via an associative mechanism involving a five-coordinate intermediate, whereas the latter proceeds via two mechanisms, one being a dissociative pathway involving a three-coordinate species and the other being a direct reductive elimination from a four-coordinate species.

Introduction

Attack of external nucleophiles such as OH^- and RO^- on carbonyl, olefinic, and allylic ligands coordinated to transition metals constitutes one of the most important synthetic means for producing oxygen-containing organic compounds as catalyzed by transition-metal complexes.[1] In contrast, another conceptually possible approach for inducing C–O bond formation by a process involving reductive elimination (A) has received very little attention. In contrast, studies of reductive eliminations involving C–C bond formation from diorganotransition-metal complexes (B), have been the subject of considerable mechanistic[2] and theoretical[2a,5] studies. Syntheses utilizing the reductive elimination process (B) catalyzed by nickel and palladium complexes have been well developed.[1] Only a few attempts have been reported for utilizing the reductive elimination

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(1) For example: (a) Collman, J. P.; Hegedas, L. S. "Principle and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980;. (b) Davies, S. G. "Organotransition Metal Chemistry; Application to Organic Synthesis"; Pergamon Press: New York, 1982. (c) Falbe, J. "New Syntheses with Carbon Monoxide"; Springer-Verlag: Berlin, 1980. (d) Wender, I.; Pino, P. "Organic Syntheses via Metal Carbonyls"; Wiley: New York, 1977.

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