Metal Atoms in the Synthesis of Metal Clusters. 1.[1] Reaction of Metal Atoms with Organometallics: A New Approach to the Synthesis of Heteronuclear Clusters

Jörg J. Schneider,* Richard Goddard, and Carl Krüger

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim-Ruhr, Germany

Received July 18, 1990

The direct reaction of free cobalt and nickel atoms with organometallic compounds is presented for the first time. These metal atoms react with the organometallic carbonyl compounds $Fe(CO)_5$ and $CpCo(CO)_2$ and the organic ligands mesitylene and 1,2,3,4,5-pentamethylcyclopentadiene (Cp*H) and result in the formation of the new trinuclear cluster compounds (bis-μ_3-carbonyl)bis[(η^6-mesitylene)cobalt]tricarbonyliron (**1**), $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp*})Ni]_2(CO)_3Fe$ (**4**), $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp*})Ni]_2(\eta^5\text{-Cp})Co$ (**5**), and $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp*})(\eta^5\text{-Cp})Ni_2](\eta^5\text{-Cp})Co$ (**6**). Additional products of the reactions are the previously known compounds [(1,2,3-η^3-pentamethyl-2-cyclopenten-1-yl)(η^5-Cp*)]Ni (**2**), as a mixture of its cis and trans isomers, and the dinuclear complex $[(\eta^5\text{-Cp*})Ni]_2(CO)_2$ (**3**). The isomers of the nickel sandwich compound were unambiguously identified through their NMR spectra. A ratio of formation of nearly 1:1 was established by means of ^{1}H and ^{13}C NMR data. Compound **1** has been characterized by an X-ray structure determination (space group $P\bar{1}$, $a = 9.011$ (3) Å, $b = 16.196$ (6) Å, $c = 8.983$ (3) Å, $\alpha = 103.61$ (2)°, $\beta = 119.46$ (2)°, $\gamma = 77.94$ (3)°, $Z = 2$, $R = 0.035$, and $R_w = 0.041$) and reveals a trigonal-pyrimidal structure with triply bridging carbonyl groups. The mesitylene rings cap the cobalt atoms. During the formation of the cluster **6**, a Cp^- transfer from $CpCo(CO)_2$ to a nickel atom is observed. This compound and its Cp* analogue, both formed during the reaction, exist as a mixture that cannot be separated by chromatography. NMR spectroscopy shows that the cluster with the $(\eta^5\text{-Cp*})(\eta^5\text{-Cp})Ni_2$ moiety dominates. A possible mechanism for the formation of both complexes is proposed. Reaction of Ni atoms with $Fe(CO)_2(NO)_2$ and Cp*H results in the formation of Cp*Ni(NO). No cluster formation could be observed in this metal atom reaction.

Ligand-free or naked metal clusters are accessible by means of metal atom routes, but they are very unstable because of their unsaturation and can only be trapped and characterized in noble-gas matrices at low temperature.[2] In the presence of ligands, however, novel stable cluster compounds have been prepared in a few cases.[3] The metal atom cocondensation procedure generally leads to the formation of mononuclear species. This can be attributed to the experimental conditions usually applied in metal vapor chemistry, since an excess of ligand L favors the formation of mononuclear compounds. Similarly, when a high metal to ligand ratio is chosen, metal aggregation is favored and the formation of cluster compounds M_xL_y is also reduced. A reduction in the cluster formation has also been observed to occur when the metal atoms are in excess, since catalytic decomposition of already formed complexes on active metal sites can occur.[4] Clearly, if these effects could be reduced, a promising synthetic route to new metal cluster compounds would be available. Our approach has been to react metal atoms directly with organometallic compounds either (a) on the walls of the cocondensation reactor during the warm-up period (static reactor system) or (b) in solution of an inert solvent at low temperature (rotating reactor system). Here we report some of our results with the new methods. Because metal atoms can be easily generated at low temperature and react well below −100 °C with other substrates, it was hoped that they could offer some new and unpredictable reaction pathways to metal–ligand cluster compounds. The wide range of available organometallic compounds and their as yet unexplored reactions with metal atoms make this approach very promising.

Results and Discussion

The late-transition-metal series (Fe, Co, Ni) exhibits a rich homo- and heteronuclear cluster chemistry.[5] In the laboratory these metals can be used in gram quantities and can therefore offer a new access to metal cluster chemistry.

Cocondensation of Co atoms with mesitylene and $Fe(CO)_5$ at −196 °C affords after workup and recrystallization from THF at −30 °C black-brown crystals of the new trinuclear cluster bis(μ_3-carbonyl)bis[η^6-mesitylene)cobalt]tricarbonyliron (**1**) in moderate yield. An improved yield can be obtained by vaporizing the cobalt atoms directly into a solution of $Fe(CO)_5$ and mesitylene in methylcyclohexane (Scheme I). In both cases the formation of a bis(arene) complex of cobalt is a reasonable intermediate in the first step of the reaction.[6] **1** catalyzes the cyclotrimerization of 2-butene (70 °C/THF) to hexamethylbenzene. With acetonitrile or 2-butene/acetonitrile mixtures, no cyclotrimerization to triazines or pyridines could be observed.

The structure of **1** has been confirmed by a single-crystal X-ray structure analysis and is shown in Figure 1. Two cobalt atoms and one iron atom form a triangle that is capped by the two carbonyl groups to form a trigonal-bipyramidal cluster frame. The two η^6-mesitylene ligands are bonded to the cobalt atoms (the angle between the least-squares planes of the mesitylene rings is 62°), and

---

[1] Part 2: Schneider, J. J.; Goddard, R.; Krüger, C.; Werner, S.; Metz, B. *Chem. Ber.*, in press.

[2] (a) Hanlan, L. A.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 2848. (b) Moskovits, M.; Hulse, J. E. *J. Chem. Soc., Faraday Trans. 2* **1977**. (c) Hanlan, L. A.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 2857. (d) Moskovits, M.; Hulse, J. E. *J. Chem. Phys.* **1977**, *66*, 3988.

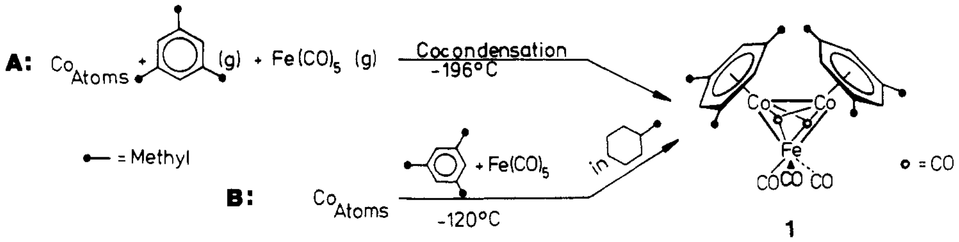
[3] (a) Freeman, M. B.; Hall, L. W.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 1132. (b) Vasquez, L.; Pritzkow, H.; Zenneck, U. *Angew. Chem.* **1988**, *100*, 705; *Angew. Chem., Int. Ed. Engl.* **1988**, *100*, 706. (c) Ozin, G. A.; Coleson, K. M.; Huber, H. X. *Organometallics* **1983**, *2*, 415. (d) Sneddon, L. G.; Carrol, P. J.; Kang, S. O. *Inorg. Chem.* **1989**, *28*, 961. (e) Kang, S. O.; Carrol, P. J.; Sneddon, L. G. *Organometallics* **1988**, *7*, 772.

[4] Ozin, G. A.; Moskovits, M. *Cryochemistry*; Wiley-Interscience: London, 1976.

[5] See e.g.: Wilkinson, G. F., Stone, F. G. A., Abel, E. W., Eds.; *Comprehensive Organometallic Chemistry*; Pergamon Press: London, 1982; Vols. IV (Fe), V (Co), VI (Ni).

[6] Efner, H. F.; Fox, W. B.; Smardzewski, R. R.; Tevault, D. E. *Inorg. Chim. Acta* **1977**, *24*, L93.

Scheme I. Formation of 1 by the Metal Vapor Route



1

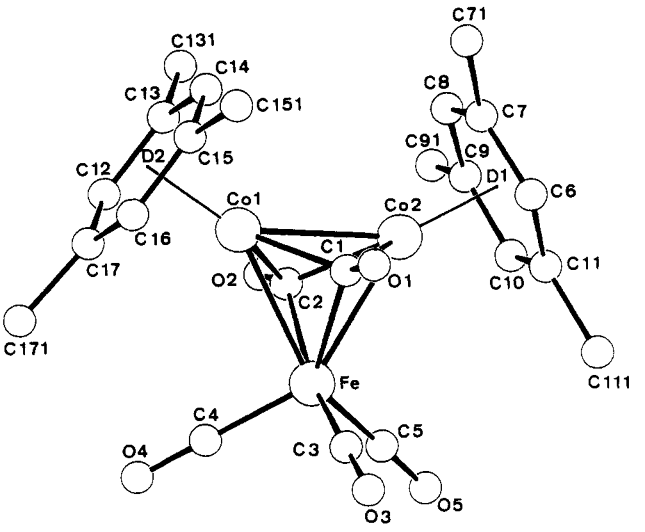


Figure 1. Crystal structure of 1.

Table I. Experimental X-ray Diffraction Data for 1[a]

mol formula	$C_{23}H_{24}O_5Co_2Fe$
mol wt	554.2
cryst color	black
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.011 (3)
b, Å	16.196 (6)
c, Å	8.983 (3)
α, deg	103.61 (2)
β, deg	119.46 (2)
γ, deg	77.94 (3)
V, Å^3	1102 (1)
Z	2
D_{calcd}, g cm^{-3}	1.67
μ, cm^{-1}	21.66
spherical abs cor (min–max)	0.47–0.48
Mo Kα radiation, λ, Å	0.71069
F(000), e	564
diffractometer	Enraf-Nonius CAD4
scan mode	ω–2θ
$[(\sin \theta)/\lambda]_{max}$, Å^{-1}	0.65
T, °C	20
mo. of measd reflns ($\pm h,\pm k,+l$)	5026
no. of indep rflns	5026
no. of obsd rflns ($I > 2R(I)$)	4015
no. of refined params	280
R	0.035
R_w ($w = 1/\sigma^2(F_o)$)	0.041
error of fit	2.06
resid electron dens, e Å^{-3}	0.48
structure soln	heavy-atom method

[a] H atom positions were calculated and kept fixed in the final refinement stages.

the terminal carbonyl groups are attached to the iron atom. Table I contains the crystal data. Bond lengths and angles are given in Table II and atomic coordinates in Table III. The Co–arene distances are distributed in the typical range for η^6 aromatic groups bonded to cobalt.[7] The Co–Co bond length (2.433 (1) Å) is in good agreement with values reported for other homonuclear Co_3 clusters.[8] The Co(1)–Fe and Co(2)–Fe distances are significantly longer than the Co(1)–Co(2) distance (2.501 (1) and 2.471 (1) Å, respectively), which is at first sight in contrast to the nearly identical metal atom radii of Co (1.24 Å) and Fe (1.25 Å).[9] One reason might be the electron deficiency created by the very effective dπ → pπ back-bonding into π^* orbitals of the three terminal CO groups bonded to the Fe atom.

Table II. Selected Bond Distances (Å) and Angles (deg) for 1[a]

Co(1)–Co(2)	2.433 (1)	Co(1)–Fe	2.501 (1)
Co(1)–D(2)	1.645 (4)	Co(1)–C(1)	1.900 (4)
Co(1)–C(2)	2.000 (3)	Co(2)–Fe	2.471 (1)
Co(2)–D(1)	1.635 (4)	Co(2)–C(1)	1.932 (3)
Co(2)–C(2)	1.982 (4)	Fe–C(1)	2.161 (3)
Fe–C(2)	1.977 (4)	Fe–C(3)	1.801 (4)
Fe–C(4)	1.766 (5)	Fe–C(5)	1.766 (4)
O(1)–C(1)	1.193 (4)	O(2)–C(2)	1.200 (4)
O(3)–C(3)	1.143 (5)	O(4)–C(4)	1.151 (6)
O(5)–C(5)	1.146 (5)		
C(2)–Co(1)–C(1)	91.0 (1)	C(2)–Co(1)–D(2)	132.8 (1)
C(2)–Co(1)–Fe	50.6 (1)	C(2)–Co(1)–Co(2)	52.0 (1)
C(1)–Co(1)–D(2)	135.8 (1)	C(1)–Co(1)–Fe	56.9 (1)
C(1)–Co(1)–Co(2)	51.2 (1)	D(2)–Co(1)–Fe	151.7 (1)
D(2)–Co(1)–Cp(2)	147.9 (1)	Fe–Co(1)–Co(2)	60.1 (1)
C(2)–Co(2)–C(1)	90.6 (1)	C(2)–Co(2)–D(1)	135.1 (1)
C(2)–Co(2)–Fe	51.3 (1)	C(2)–Co(2)–Co(1)	52.7 (1)
C(1)–Co(2)–D(1)	134.3 (1)	C(1)–Co(2)–Fe	57.2 (1)
C(1)–Co(2)–Co(1)	50.5 (1)	D(1)–Co(2)–Fe	147.6 (1)
D(1)–Co(2)–Co(1)	151.1 (1)	Fe–Co(2)–Co(1)	61.3 (1)
C(2)–Fe–C(1)	84.4 (1)	C(2)–Fe–Co(2)	51.5 (1)
C(2)–Fe–Co(1)	51.4 (1)	C(1)–Fe–Co(2)	48.7 (1)
C(1)–Fe–Co(1)	47.4 (1)	Co(2)–Fe–Co(1)	58.6 (1)
O(1)–C(1)–Fe	135.1 (3)	O(1)–C(1)–Co(2)	133.0 (2)
O(1)–C(1)–Co(1)	135.5 (3)	Fe–C(1)–Co(2)	74.1 (1)
Fe–C(1)–Co(1)	75.7 (1)	Co(2)–C(1)–Co(1)	78.8 (1)
O(2)–C(2)–Fe	139.7 (3)	O(2)–C(2)–Co(2)	131.3 (2)
O(2)–C(2)–Co(1)	130.8 (3)	Fe–C(2)–Co(2)	77.2 (1)
Fe–C(2)–Co(1)	77.9 (1)	Co(2)–C(2)–Co(1)	75.3 (1)

[a] D(1) = midpoint C(6)–C(11); D(2) = midpoint C(12)–C(17).

Complex 1 is formally a closed-shell 48-VE (VE = valence electron) M_3 cluster compound. In order to investigate whether exchanging the two $C_6H_3Me_3$–Co fragments with isolobal Cp*–Ni fragments would result in an isostructural cluster with a Ni_2–Fe framework, we evaporated Ni atoms into a cooled solution of 1,2,3,4,5-pentamethylcyclopentadiene (Cp*H) and $Fe(CO)_5$ in methylcyclohexane (−120 °C). As in the previous case, this reaction can be followed visually and is characterized by an almost immediate darkening of the reaction mixture when metal vaporization starts. We were able to isolate three different types of metal complexes from the crude reaction mixture

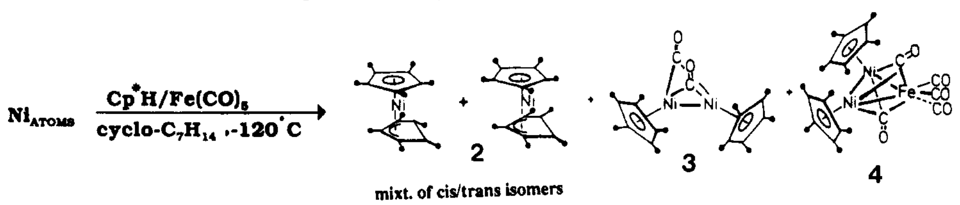
---

(7) (a) Klabunde, K. J.; Behrens, C. B.; Radonovich, L. J.; Collan, D. R.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1014. (b) Bird, P. H.; Frazer, A. R. *J. Organomet. Chem.* **1974**, *73*, 103.

(8) Olson, W. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7657.

(9) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; p 528.

Scheme II. Preparation of 2, 3, and 4 by Metal Vapor Synthesis



Scheme III. Plausible Formation of 2 via a Short-Lived Nickel Hydride Intermediate

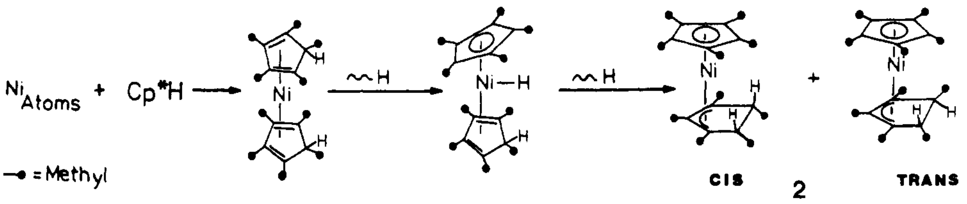


Table III. Fractional Atomic Coordinates with Standard Deviations in Parentheses and Equivalent Isotropic Thermal Parameters (Å²)[a]

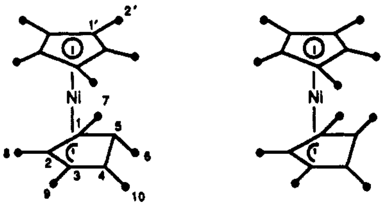
atom	*x*	*y*	*z*	U_{eq}
Co(1)	0.2263 (1)	0.3249 (1)	0.1491 (1)	0.031
Co(2)	0.1181 (1)	0.1875 (1)	0.0005 (1)	0.032
Fe	0.1991 (1)	0.2677 (1)	−0.1461 (1)	0.036
O(1)	−0.1302 (3)	0.3344 (1)	−0.1020 (3)	0.043
O(2)	0.4882 (3)	0.1840 (1)	0.1452 (3)	0.048
O(3)	−0.0897 (4)	0.3460 (2)	−0.4356 (4)	0.076
O(4)	0.4776 (5)	0.3537 (2)	−0.0964 (5)	0.104
O(5)	0.2670 (4)	0.1153 (2)	−0.3607 (4)	0.075
C(1)	0.0140 (4)	0.3013 (2)	−0.0489 (4)	0.035
C(2)	0.3467 (4)	0.2196 (2)	0.0707 (4)	0.038
C(3)	0.0210 (5)	0.3167 (2)	−0.3207 (5)	0.050
C(4)	0.3645 (5)	0.3222 (2)	−0.1164 (5)	0.058
C(5)	0.2390 (5)	0.1748 (2)	−0.1761 (5)	0.049
C(6)	−0.1207 (4)	0.1389 (2)	−0.0922 (5)	0.048
C(7)	−0.0399 (4)	0.1510 (2)	0.0866 (5)	0.050
C(71)	−0.1320 (6)	0.2024 (3)	0.1846 (7)	0.081
C(8)	0.1307 (5)	0.1119 (2)	0.1725 (5)	0.055
C(9)	0.2141 (4)	0.0604 (2)	0.0814 (6)	0.055
C(91)	0.3907 (5)	0.0169 (3)	0.1740 (7)	0.081
C(10)	0.1308 (5)	0.0537 (2)	−0.0974 (5)	0.052
C(11)	−0.0389 (4)	0.0924 (2)	−0.1884 (5)	0.050
C(111)	−0.1285 (6)	0.0820 (3)	−0.3816 (6)	0.075
C(12)	0.4590 (4)	0.3710 (2)	0.3632 (4)	0.047
C(13)	0.3835 (4)	0.3276 (2)	0.4224 (4)	0.045
C(131)	0.4862 (5)	0.2550 (3)	0.5217 (5)	0.065
C(14)	0.2119 (4)	0.3536 (2)	0.3855 (4)	0.045
C(15)	0.1164 (4)	0.4215 (2)	0.2932 (4)	0.042
C(151)	−0.0677 (5)	0.4482 (2)	0.2552 (5)	0.060
C(16)	0.1949 (5)	0.4612 (2)	0.2320 (4)	0.044
C(17)	0.3662 (4)	0.4379 (2)	0.2671 (4)	0.043
C(171)	0.4518 (6)	0.4871 (3)	0.2156 (5)	0.064

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

Table IV. ¹H NMR Chemical Shifts and Coupling Constants of [(1,2,3-η^3-pentamethyl-2-cyclopenten-1-yl)(η^5-Cp*)]Ni (2; Cis/Trans Mixture)

	δ, ppm		J_{CH}, Hz	
position[a]	cis	trans	cis	trans
2′	1.77 (15 H)	1.74 (15 H)		
4	1.76 (2 H)	0.97 (1 H)	J_{45} 7.5 J_{49} n.o.[b] J_{410} 7.4	J_{45} 3.0 J_{49} 0.7 J_{410} 6.9
5		0.53 (1 H)	J_{510} −0.6	J_{56} 6.9
6	0.64 (6 H)	0.99 (3 H)	J_{610} 0.1	J_{610} 1.3
7	1.06 (6 H)	1.01 (3 H)		
8	1.76 (6 H)	1.76 (3 H)		
9		0.99 (3 H)		
10		0.76 (3 H)		

[a] Position numbers are as shown:



[b] no. = not observed.

Table V. ¹³C NMR Chemical Shifts and Coupling Constants of [(1,2,3-η^3-pentamethyl-2-cyclopenten-1-yl)(η^5-Cp*)]Ni (2; Cis/Trans Mixture)

	δ, ppm	
position	cis	trans
1′	95.62	95.98
2′	9.43 (125)[a]	9.87
1	73.82	74.71
2	92.95	93.44
3		74.00
4	44.34	50.71 (126)
5		51.82 (122)
6	14.89 (125)	17.55 (124)
7	14.27 (125)	14.26 (125)
8	11.98 (126)	11.78 (125)
9		13.99 (125)
10		18.51 (125)

[a] Values in parentheses denote ${}^1J_{CH}$ in Hz.

by column chromatography (Scheme II).

The first compound to leave the column was the mononuclear sandwich type complex [(1,2,3-η^3-pentamethyl-2-cyclopenten-1-yl)(η^5-Cp*)]Ni (2; Cp* = 1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl), which is formed as a 1:1 mixture of cis and trans isomers. No further separation of this mixture was possible by column chromatography. An identification of the isomers in the ¹H and ¹³C NMR spectra was possible with the aid of homonuclear decoupling and a COSY experiment (Tables IV and V). ¹H and ¹³C NMR data indicate a 1:1 ratio of both isomers. Formation of the third possible isomer is not observed. Whether the formation of the cis isomer bearing both methyl groups in exo *or* endo positions is favored cannot be decided by NMR experiments, since detection is prevented by the isochronicity of protons 4 and 2′. However, the exo form is most likely, on steric grounds.[10] The formation of this η^3–η^5 type metal sandwich compound is not unexpected, since the presence of

---

[10] A ¹H NMR identification of the cis isomer of 2 with both methyl groups in endo positions has been claimed in: Koelle, U.; Khouzami, F.; Lueken, H. *Chem. Ber.* **1982**, *115*, 1178.

Scheme IV. Metal Vapor Synthesis of 5 and 6

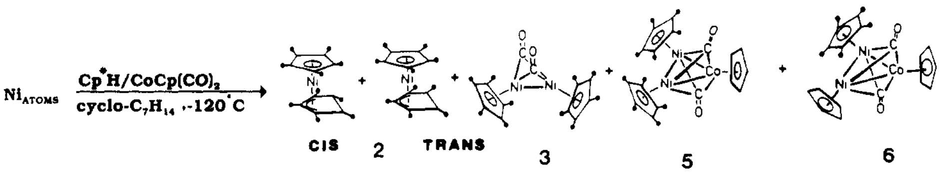


Table VI. ^{1}H (200 MHz) and ^{13}C (75 MHz) NMR Chemical Shifts[a] and Coupling Constants[b] of the Clusters 1, 4, 5, and 6

1	^{1}H (THF-d_8)	5.45 (s, 3 H), 2.24 (2, 9 H)
	^{13}C (THF-d_8)	19.2 (128),[c] 100.7 (169), 111.0, 217.4, 259.5
4	^{1}H	1.43 (s, 30 H)
	^{13}C[d]	8.80, 103.6, 213.2, 244.9
5	^{1}H	1.51 (s, 30 H), 4.59 (s, 5 H)
	^{13}C (THF-d_8)	9.5 (127), 86.0 (176), 101.5, 250.5
6	^{1}H	1.48 (s, 15 H), 4.64 (s, 5 H), 4.59 (s, 5 H)
	^{13}C (THF-d_8)	9.6 (127), 86.4 (177), 93.1 (175), 103.2, 248.9

[a] In toluene-d_8, 30 °C, relative to TMS, unless otherwise stated. [b] $^1J_{CH}$ in Hz. [c] Values in parentheses are $^1J_{CH}$. [d] 50.5 MHz.

a nickel hydride species as an intermediate in metal atom reactions of alkadienes with active hydrogens is quite common[11] (Scheme III). This hydride intermediate is probably subject to a quick hydrogen transfer, leading to the observed mixture of complexes 2.

The second product obtained in the reaction is the previously known dinuclear $Ni_2Cp^*_2(CO)_2$ complex 3, which was identified by its IR, ^{1}H NMR, and mass spectra and elemental analysis. It is possibly formed via CO transfer from $Fe(CO)_5$ to Ni–Cp* fragments, either immediately after the vaporization or during the warm-up process. The third isolated product was the cluster compound $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp}^*)\text{Ni}]_2(\text{CO})_3\text{Fe}$ (4), which is isostructural with 1. It was isolated as deep green diamagnetic, air-stable crystals. Its structure is confirmed by IR and ^{1}H and ^{13}C NMR spectroscopy (Table VI), its mass spectrum, and elemental analysis. An X-ray structure analysis of 4 was hindered by decomposition of the crystals and poor crystal quality. The Cp analogue of 4 has already been prepared by Hsieh and Knight.[12] Its crystal structure was found by Teo[13] to be isostructural with 4.

Since the synthesis of complex 4 supports the hypothesis that the Co–arene fragment can be exchanged with Ni–Cp* in the M_3 cluster frame of 1, we were interested in attempting to exchange the $Fe(CO)_3$ fragment in the cluster core. We therefore reacted $CpCo(CO)_2$, as the organometallic precursor complex, with Ni atoms and Cp*H in methylcyclohexane at −120 °C (Scheme IV). Formally the fragment Cp–Co is isolobal with $Fe(CO)_3$ and is a possible candidate for replacement in the cluster core of 4.

Purification and separation of the crude reaction mixture was again achieved by column chromatography. As in the synthesis of 4, we observed the formation of complexes 2 and 3 as side products of this reaction. The yields of both complexes were, however, much lower in this case. The main product of the reaction was a mixture of the cluster compounds 5 and 6. Mass spectroscopic results (Experimental Section) as well as NMR results are in good agreement with the presence of a mixture of the complexes 5 and 6 (Table VI). Figure 2 shows the ^{1}H NMR spectrum of a sample of 5 and 6 obtained by chromatography, following recrystallization from hexane. A ratio of 30% of 5 and 70% of 6 can be estimated. We were not able to separate 5 and 6 by column chromatography. Even repeated chromatography resulted only in a single band. The mixture of both complexes is obtained as an air-stable brown solid, which decomposes only slowly in solution on exposure to air. The solid is soluble in all common organic solvents. The formation of complex 6 was surprising to us, since a ligand transfer from the organometallic precursor $CpCo(CO)_2$ to a metal atom must have taken place to account for the formation of 6 (Scheme V).

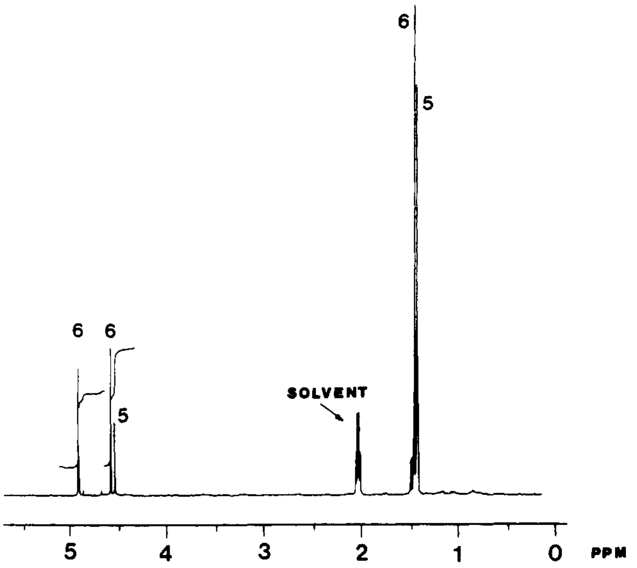
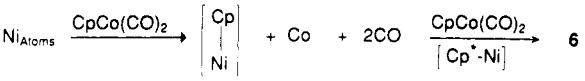


Figure 2. ^{1}H NMR spectrum of a mixture of complexes 5 and 6.

Scheme V. Generation of a Reactive Cp–Ni Intermediate and Its Subsequent Reaction To Form Cluster 6



$$\mathrm{Ni_{Atoms}} \xrightarrow{\mathrm{CpCo(CO)_2}} \left[\begin{array}{c}\mathrm{Cp}\\ |\\ \mathrm{Ni}\end{array}\right] + \mathrm{Co} + 2\mathrm{CO} \xrightarrow[\left[\mathrm{Cp^*\text{-}Ni}\right]]{\mathrm{CpCo(CO)_2}} 6$$

It is possible that in the first step a Cp^- group derived from the excess organometallic source present is transferred to a nickel atom. The Cp–Ni fragment so formed could then react with more $CpCo(CO)_2$ and a Cp*–Ni fragment to form cluster 6. We have recently observed such a Cp^- ligand transfer from an organometallic complex to a metal atom in our studies on reactions with Fe atoms.[14]

An X-ray analysis of the crystals obtained from solutions purified as described above reveals a structure with a metal triangle similar to 1, with two triply bridging μ_3-CO groups, but the structure is heavily disordered in the region of the cyclopentadienyl rings, perhaps due to the presence of both compounds in the structure. The synthesis and structural analysis of the cluster $(\mu_3\text{-CO})_2[(\eta^5\text{-Cp})\text{Ni}]_2(\eta^5\text{-Cp}^*)\text{Co}$, an analogue of 5 and 6 having differently Cp-complexed metal atoms in the M_3 metal core, has been reported by Dahl[15]

---

[11] Blackborrow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Berlin, 1979; p 108.

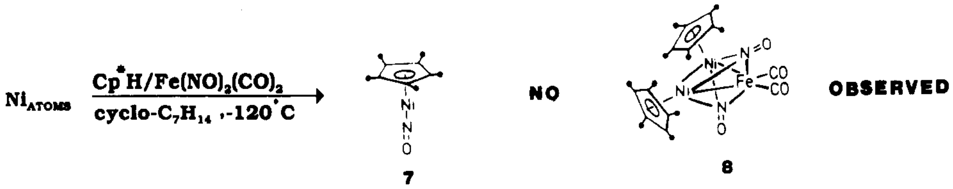
[12] Hsieh, A. T. T.; Knight, J. *J. Organomet. Chem.* **1971**, *26*, 125.

[13] Teo, B. K. Ph.D. Dissertation, University of Wisconsin, 1973; *Diss. Abstr.* **1973**, *34B*, 3193B.

[14] See ref 1.

[15] Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942.

Scheme VI. Reaction of Ni Atoms, Cp*H, and $Fe(CO)_2(NO)_2$ To Form 7



and shown to have an identical cluster framework with triply bridging CO groups.

In an extension of the same theme we decided to investigate whether the triply bridging CO groups could be replaced by other ligands. The NO group appeared to be a suitable candidate, since it has already shown its capability to function as a triply bridging ligand in metal cluster bonding.[16] Attempts at reaction with the organometallic $Fe(NO)_2(CO)_2$ molecule were unsuccessful. In the reaction of Co atoms, mesitylene, and $Fe(NO)_2(CO)_2$ in methylcyclohexane we could isolate nothing but the educt. When reacting Ni atoms with a solution of $Fe(NO)_2(CO)_2$ and Cp*H, we isolated the compound Cp*Ni(NO) (7) in moderate yield but there was no formation of the cluster $(Cp^*)_2Ni_2(NO)_2(CO)_2Fe$ (8) (Scheme VI). Formally $Fe(NO)_2(CO)_2$ transfers a NO group to a Ni–Cp* fragment. Such an NO transfer is already known with $BF_3{\cdot}xNO$ as a reagent in metal atom chemistry.[17]

Conclusion

As described above, the reaction of metal atoms with metalloorganic carbonyl compounds and organic ligands can lead to novel metal cluster compounds. The resulting geometry of the cluster compounds is determined by a combination of the accessible ligands available to electronically saturate the particular metal atom ensemble involved. In the three cases where cluster formation was observed, the complexes attain electronically saturated, closed-shell configurations. The clusters thus adopt a geometry that is in agreement with the 18-VE rule. It appears that the formation of reactive intermediates M–L (L = mesitylene, Cp*, Cp) plays a crucial role in the buildup of clusters 1, 4, 5, and 6. The organometallic complexes can therefore be considered as trapping agents for reactive Ni–Cp* and Co–arene 15-VE fragments. Furthermore, the results obtained in this study show that M–L fragments generated by reacting metal atoms with an appropriate ligand are exchangeable with other M–L fragments which can also be formed by the metal vapor route. The reaction of metal atoms with organometallic compounds, here specifically metal carbonyls, offers a novel route to new metal cluster compounds. We are presently engaged in extending this approach to the reaction of metal atoms with other inorganic and organometallic compounds.

Experimental Section

General Information. Unless otherwise stated, all experiments were carried out in Schlenk type glassware under argon and with solvents that were thoroughly dried and deoxygenated. $Fe(CO)_5$ was a gift from BASF, Ludwigshafen, FRG. $Fe(NO)_2(CO)_2$,[18] $CpCo(CO)_2$,[19] and 1,2,3,4,5-pentamethylcyclopentadiene[20] were prepared by following published procedures. Al_2O_3 was deactivated by adding 5% H_2O and homogenizing the mixture for several hours. NMR spectra were recorded on a Bruker AM-200 and WH-400 (^1H, ^{13}C) and Bruker AM-300 (^{13}C) spectrometers; the samples were sealed in NMR tubes, and the signal of the solvent was used as internal reference. Chemical shifts are reported on the δ scale. IR spectra were recorded as KBr pellets on a Nicolet 7199 FT-IR spectrometer. MS spectra were recorded on a Varian MAT-5 instrument with the fractional sublimation technique. Metal vapor reactions were conducted in 6-L glass vessels which were connected to a metal vapor reactor system based on that described by Timms.[21] Metal vaporization was from alumina-coated tungsten crucibles (GTE-Sylvania) that were heated resistively. Nickel (Merck) was 99.5% pure, and cobalt (Aldrich) was 99.6% pure. Microanalyses were performed by Dornis & Kolbe Microanalytical Laboratory, Mülheim/Ruhr, Höhenweg, Germany.

Bis(μ_3-carbonyl)bis[(η^6-mesitylene)cobalt]tricarbonyliron (1). Method A. Over 1 h 30 g (0.25 mol) of mesitylene and 20 g (0.10 mol) of $Fe(CO)_5$ were cocondensed with 1.2 g (20 mmol) of Co atoms at −196 °C/10^{-4} Torr on the walls of the metal atom reactor. After warmup and an argon flush 300 mL of THF was introduced into the reactor and the brown reaction mixture was siphoned out. After filtraton over Celite excess arene, $Fe(CO)_5$, and solvent were removed under reduced pressure. The brown-black residue was redissolved in 80 mL of THF, and the solution was filtered and cooled to −30 °C overnight, which afforded 1.1 g (20%, based on metal vaporized) of black crystals of 1. IR (ν, cm^{-1}): 1985, 1920, 1905, 1645, 1560, 1370, 905, 860. Anal. Calcd for $C_{23}H_{24}O_5Co_2Fe$: C, 49.85; H, 4.37; Co, 21.27; Fe, 10.08. Found: C, 48.90; H, 4.32; Co, 21.89; Fe,. 10.26.

Method B. The reaction vessel was charged with 30 g (0.25 mol) of mesitylene 20 g (0.10 mol) of $Fe(CO)_5$ dissolved in 300 mL of methylcyclohexane. At a temperature of approximately −90 °C the reactor was evacuated to a pressure of 10^{-3} Torr and tuned to operation conditions. Metal vaporization was conducted at −120 °C. Over 1 h at a rotation speed of 80 rpm 1.5 g of Co metal (25 mmol) was vaporized into a steadily renewed film of methylcyclohexane/$Fe(CO)_5$ and mesitylene. Workup as above yielded 3.5 g (50.5%) of black crystals of 1.

(μ_3-CO)$_2$[(η^5-Cp*)Ni]$_2$(CO)$_3$Fe (4). Nickel vaporization (2 g, 34 mmol) at 10^{-4} Torr into a −120 °C solution of Cp*H (8 g, 58 mmol) and $Fe(CO)_5$ (15 g, 76 mmol) in 250 mL of methylcyclohexane over 1.5 h produced first a deep red and then, in later stages of the reaction, a bright green solution, which after filtration and removal of all volatiles left a deep brown-green oily residue. The material was absorbed on ca. 8 g of Al_2O_3 (5% H_2O) and chromatographed. First zone (pentane): 1.0 g (3 mmol), 9%; *cis*/*trans*-2 (red crystals, ethanol, −30 °C); MS (EI, 25 °C) *m/e* 330 (75%), 315 (95), 300 (92), 194 (35), 192 (60), 178 (100), 133 (20), 119 (28). Anal. Calcd for $C_{20}H_{32}Ni$: C, 72.73; H, 9.70; Ni, 17.79. Found: C, 72.57; H, 9.99; Ni, 17.84. Second zone (pentane): 0.6 g (1.4 mmol), 8%; 3 (red crystals, pentane, −78 °C); MS (EI, 82 °C) *m/e* 442 (20), 384 (100), 328 (38); IR (ν, cm^{-1}) 2980, 2900, 2922, 1799, 1775, 1450, 1372, 1350, 1150, 1020, 790, 640, 610, 590, 480; ^1H NMR (toluene-d_8, 200 MHz) 1.8 ppm (30 H). Anal. Calcd for $C_{22}H_{30}O_2Ni_2$: C, 59.53; H, 6.76. Found: C, 59.16; H, 6.81. Third zone (pentane/toluene): 1.3 g (2.2 mmol), 7%; 4 (green crystals, pentane, −30 °C); MS (EI, 108 °C) *m/e* 582 (6), 554 (3), 526 (8), 496 (15), 466 (27), 438 (33), 384 (35), 326 (21), 119 (8), 41 (13), 28 (100); IR (ν, cm^{-1}) 2972, 2910, 2005, 1970, 1940, 1712, 1440, 1370, 1355, 1145, 1050, 930, 790, 610, 580. Anal. Calcd for $C_{25}H_{30}O_5Ni_2Fe$: C, 51.38; H, 5.13; Ni, 20.11; Fe, 9.68. Found: C,

---

[16] (a) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5933. (b) Müller, J.; Schmitt, S. *J. Organomet. Chem.* **1977**, *C54*, 97. Müller, J.; Sonn, I.; Akhnoukh, T. *J. Organomet. Chem.* **1988**, *367*, 133.

[17] Middelton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120.

[18] Eisch, J. J.; King, R. B. *Organometallic Synthesis*; Academic Press: New York, 1966; Vol. 1, p 167.

[19] Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

[20] Manriquez, J. M.; Fagan, P. J.; Schertz, L. D.; Marks, T. J. *Inorg. Synth.* **1982**, *21*, 181.

[21] Timms, P. L. *Angew. Chem.* **1975**, *87*, 295; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273.

51.39; H, 5.31; Ni, 20.12; Fe, 9.43.

(μ_3-CO)$_2$[(η^5-Cp*)Ni]$_2$(η^5-Cp)Co (5) and (μ_3-CO)$_2$[(η^5-Cp*)(η^5-Cp)Ni$_2$](η^5-Cp)Co (6). The vessel of the metal vapor reactor was charged with 10 g (74 mmol) of Cp*H and 8 g (44 mmol) of CpCo(CO)$_2$ dissolved in 300 mL of methylcyclohexane. Nickel vaporization was started at −120 °C/10^{-4} Torr and continued for 90 min (ca. 1 g of Ni vaporized). The initial red color of the solution turned to a dark brown toward the end of the reaction. Filtration and removal of all volatiles and then chromatography (Al$_2$O$_3$, 5% H$_2$O) afford three different zones. First zone (pentane): traces of *cis/trans*-**2**. Second zone: trace amounts of **3**. Third zone (pentane/diethyl ether): 0.9 g, ≃20% as a mixture of complexes **5** and **6** (black-brown crystals, hexane, −30 °C); even repeated rechromatographing of this single zone did not result in a splitting of this fraction; MS (EI, 120 °C) *m/e* 566 (3, M$^+$, **5**), 496 (10, M$^+$, **6**), 259 (73), 189 (100); IR (ν, cm^{-1}) 2970, 2905, 2835, 1705, 1410, 1370, 1350, 1150, 1105, 1045, 1000, 830, 810, 785, 560, 550. Anal. Calcd for C$_{27}$H$_{35}$O$_2$Ni$_2$Co: C, 57.10; H, 6.17; Ni, 20.70; Co, 10.39. Calcd for C$_{22}$H$_{25}$O$_2$Ni$_2$Co: C, 53.10; H, 5.02; Ni, 23.60; Co, 11.86. Found: C, 56.12; H, 6.19; Ni, 20.08; Co, 10.21.

Reaction of Cp*H with Ni Atoms and Fe(CO)$_2$(NO)$_2$ in Methylcyclohexane. Into a solution of 7 g (47 mmol) of Fe(CO)$_2$(NO)$_2$ and 6 g (44 mmol) of Cp*H in 250 mL of methylcyclohexane was vaporized 1 g (17 mmol) of Ni atoms over 1 h. After vaporization of all volatiles and filtration a large amount of unreacted metal was left on the filter frit. Column chromatography of the residue yielded three different zones. First zone: trace amounts of **2**. Second zone: trace amounts of Fe(NO)$_2$(CO)$_2$. Third zone (pentane): 0.5 g (2.3 mmol), 14% of **7** (shiny red crystals, pentane, −30 °C); MS (EI, 30 °C) *m/e* 225 (38), 223 (98), 195 (32), 193 (100), 191 (68), 177 (14), 119 (18); IR (ν, cm^{-1}) 3550 (overtone), 3500 (overtone), 2985, 2910, 2930, 1795, 1760, 1465, 1382, 1065, 1025, 645; ^{1}H NMR (toluene-d_8) 1.83 ppm (s, 15 H); ^{13}C NMR (toluene-d_8) 94.5 ppm (s). Anal. Calcd for C$_{10}$H$_{15}$NONi: C, 53.64; H, 6.71; N, 6.25; Ni, 26.24. Found: C, 53.57; H, 6.74; N, 6.19; Ni, 26.28.

Acknowledgment. J.J.S. wishes to thank Prof. Dr. G. Wilke for financial support and continued interest in this work.

Supplementary Material Available: Detailed information on the crystal structure determination of **1**, including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles (7 pages); a list of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Synthesis and Structural Characterization of Mononuclear Iron(II) Ferracarboranes

Sharon S. Lee, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, University of California, Los Angeles,
Los Angeles, California 90024

Received June 22, 1990

Neutral iron(II) ferracarboranes of the type [*closo*-3-CO-3-L-3-L′-3,1,2-FeC$_2$B$_9$H$_{11}$] (**3**, L = CO, L′ = PPh$_3$; **4**, L = PPh$_3$, L′ = CH$_3$CN; **5**, L = CO, L′ = CH$_3$CN; **6**, L = CO, L′ = P(OCH$_3$)$_3$; **7**, L = L′ = P(OCH$_3$)$_3$; **8**, L = L′ = CO) have been prepared by the Cu(I) oxidation of the dimeric iron dicarbollide complex [*closo*-3-CO-3,3′-(μ-CO)-3,1,2-FeC$_2$B$_9$H$_{11}$]$_2^{2-}$ (**2**) in the presence of the designated monodentate ligands. Complexes **3**, **4**, **7**, and **8** have been structurally characterized by single-crystal X-ray diffraction. Crystallographic parameters are as follows (compound: crystal system; space group; crystal parameters; *Z*; unique data ($I > 3\sigma(I)$); R, R_w). **3**: monoclinic; *A*2/*a*; *a* = 18.384 (3) Å, *b* = 12.762 (2) Å, *c* = 23.059 (3) Å, β = 104.081 (4)°; 8; 1780; 7.4, 8.8. **4**: monoclinic; *C*2/*c*; *a* = 28.050 (2) Å, *b* = 11.5715 (9) Å, *c* = 19.042 (2) Å, β = 116.846 (2)°; 8; 1702; 6.5, 7.7. **7**: orthorhombic; *Pbnm* (standard setting *Pnma*); *a* = 10.397 (2) Å, *b* = 14.419 (3) Å, *c* = 15.092 (3) Å; 4; 1051; 7.1, 8.9. **8**: monoclinic; *P*2$_1$/*n*; *a* = 6.971 (4) Å, *b* = 15.900 (9) Å, *c* = 11.237 (7) Å, β = 91.42 (2)°; 4; 1108; 6.2, 7.4. The closo 12-vertex icosahedral geometry comprising a polyhedral (d^{6}Fe)C$_2$B$_9$ framework and the pseudooctahedral coordination exhibited by the iron atom are common structural features displayed by all four ferracarboranes.

Introduction

Cyclopentadienyliron compounds[1] are among the most widely studied species in transition-metal organometallic chemistry. Although the structural and electronic similarities between the dicarbollide anion and the cyclopentadienide anion were demonstrated long ago[2] in the synthesis of the carborane analogue of ferrocene, [*commo*-3,3′-Fe[3,1,2-FeC$_2$B$_9$H$_{11}$]$_2$]$^{2-}$ (**1**), ferracarboranes remained relatively unexplored. An exception is the recently reported synthesis and structural characterization of (η^6-arene)iron dicarbollide complexes.[3] However, the intensely studied field of mononuclear cyclopentadienyliron compounds containing simple monodentate ligands still lacks counterparts in carborane chemistry.

Although evidence of arene substitution by carbon monoxide and trimethyl phosphite in (η^6-arene)-FeMe$_2$C$_2$B$_9$H$_9$ systems was reported by Stone and coworkers,[3c] neither ^{11}B NMR, ^{1}H NMR, nor X-ray structural characterization data were reported. As part of our ongoing investigation of metallacarborane derivatives, we have prepared a series of novel monodicarbollide complexes that contain iron. In addition, we report herein the

---

[1] *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: New York, 1983–1989; Organoiron Compounds, Series B, Vols. 11–15.

[2] (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (c) Hawthorne, M. F. *Acc. Chem. Res.* **1968**, *1*, 28.

[3] (a) Garcia, M. P.; Green, M.; Stone, F. G. A.; Somerville, R. G.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 871. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77. (c) Garcia, M. P.; Green, M.; Stone, F. G. A.; Somerville, R. G.; Welch, A. G.; Briant, C. E.; Cox, D. N.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1985**, 2343. (d) Kang, H. C.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1987**, *26*, 3409. (e) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *J. Organomet. Chem.* **1990**, *394*, 29.

0276-7333/91/2310-0670$02.50/0