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METAL CARBIDE CLUSTERS SYNTHESIS SYSTEMATICS FOR HETERONUCLEAR SPECIES *

MAMORU TACHIKAWA, ROLF L. GEERTS, and E.L. MUETTERTIES *

Department of Chemistry, University of California, Berkeley, California 94720 (U.S.A.)

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Summary

The strategies in the synthesis of metal carbide clusters are examined and the full synthesis procedures for a number of heteronuclear metal carbide clusters are presented. Specific classes of carbide clusters prepared are octahedral $Fe_5MC(CO)_x{}^{y-}$ and $Fe_4M_2C(CO)_x{}^{y-}$ clusters and square pyramidal $Fe_4MC(CO)_x{}^{y-}$ clusters. One synthesis strategy was polyhedral expansion based on [$Fe_4C(CO)_{12}{}^{2-}$] or [$Fe_5C(CO)_{14}{}^{2-}$] reactions with coordinately unsaturated metal complexes or labile complexes that readily yield coordinately unsaturated complexes. Selective oxidative degradations of these octahedral carbide clusters provided a synthesis step comprising elision of an iron center to yield square pyramidal $Fe_4MC(CO)_x{}^{y-}$ clusters.

Introduction

Paolo Chini was a fine scientist of great innovative capability — and a very kind and warm personality. The loss to science from Paolo's untimely death is immeasurable. His contributions to the development of metal cluster chemistry were seminal and possessed an artistic elegance indelibly imprinted in cluster and in structural chemistry. The artistry was largely evident in the designed synthesis of structurally unusual and interesting metal carbonyl clusters. For this reason, in contributing to this Paolo Chini memorial issue, we have elected to describe our efforts in the synthesis of metal carbide clusters and to attempt some generalizations about synthesis procedures.

Experimental section

Reagents and general procedures

Because of potential air reactivity of reactants, intermediates and products, all procedures described below were effected under nitrogen or argon atmo-

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* Dedicated to the memory of Professor Paolo Chini.

sphere using Schlenk procedures or in a Vacuum Atmosphere Dri-Lab, Model HE 493. The hydrated chlorides of iridium, ruthenium and rhodium were obtained from Johnson Matthey, Inc., and the transition metal carbonyls or halides from Alfa Ventron. All organometallic intermediates were prepared by standard procedures. Purification and drying of organic solvents [1] and the synthesis of $HFe_4(CH)(CO)_{12}$ [2] and of salts of $[Fe_4C(CO)_{12}{}^{2-}]$ [2] have been described elsewhere.

^1H and ^{13}C NMR spectra were recorded on a modified Bruker 42kG multinuclear, pulse-FT NMR spectrometer equipped with Nicolet Technology Corporation software, and the chemical shifts in ppm were referenced to tetramethylsilane. Infrared spectra were recorded with a Perkin Elmer 283 spectrophotometer (cm^{-1}). Elemental analyses were performed by Mr. V. Tashinian of the UCB Chemistry Department Microanalytical Laboratory.

Preparation of $Fe_5C(CO)_{15}$

In a one liter three-necked flask equipped with a serum cap, a stopper and a stopcock adaptor were placed 10.0 g of $Na_2Fe(CO)_4 \cdot 3/2$ dioxane and a magnetic stir-bar. First, diglyme (100 ml) was introduced by means of a cannula and then $Fe(CO)_5$ (20 ml) by means of a syringe (note that $Fe(CO)_5$ is extremely toxic, and the reaction $Fe(CO)_5 + Na_2Fe(CO)_4$ produces a large amount of CO gas). The septum was replaced by a condenser and the solution was heated, with good stirring, in an oil bath at 150—155°C for 5 hours, then for 1 hour at 160°C. The solution was cooled to room temperature. Addition of 0.7 l of hexane resulted in formation of an oily precipitate and a purple supernatant. The supernatant was discarded, and the residue was washed with 0.3 l of hexane; then the hexane layer was again decanted. The residual hexane was removed by evacuation. The oily precipitate was extracted with 500 ml of degassed water in several portions. This aqueous solution was placed in a two liter flask equipped with a dropping funnel, a stopcock adaptor and a bubbler. A concentrated ferric chloride aqueous solution was added to the extract from the dropping funnel with rapid stirring. This caused formation of a black precipitate and a rapid evolution of carbon monoxide. After addition of excess ferric ion and stirring for 1 hour (the aqueous layer should be yellow due to Fe^{3+} ion), the black powder was collected on a Schlenk frit, washed with 50 ml of water, then dried overnight under vacuum. The solid thus obtained was crystallized from 0.3 l of warm (60°C) toluene giving black needles of $Fe_5C(CO)_{15}$ in 30—60% yield. ^{13}C NMR (ppm, dichloromethane, 20°C) 209.1 (s, 12 CO), 212.8 (s, 3 CO). IR ν(CO) (hexane) 2099 vw, 2050vs, 2031s, 2012w, 1992w. MS (*m/e*, Fe^{56}) 712 ($M+$) and fragments due to successive loss of 15 CO's.

Preparation of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$

This salt was prepared by reaction of a mixture of $Fe_5C(CO)_{15}$ (4.35 g, 6.12 mmol) and $Na_2Fe(CO)_4 \cdot 3/2\ (C_4H_8O_2)$ (2.12 g, 6.12 mmol) to which was added 30 ml of diglyme. After 1 hour of stirring, an aqueous solution of $(C_2H_5)_4NCl \cdot H_2O$ (2.48 g in 100 ml of H_2O) was added over a 3 hour period. Crystals formed and were collected and then washed with ether until washings were colorless. Yield, 5.45 g, 96%. ^{13}C NMR (ppm, tetrahydrofuran, 20°C) 223.4 (s, 3 CO, apical), 227.2 (s, 11 CO, basal). IR ν(CO) (nitromethane)

2028vw, 1965vs, 1953(sh), 1923(sh), 1902(sh), 1948w. Anal. Found: C, 39.71; H, 4.39; N, 3.14; Fe, 28.5. Calcd. for $Fe_5C_{31}H_{40}N_2O_{14}$: C, 39.45; H, 4.27; N, 2.97; Fe, 29.58%.

Preparation of $[(CH_3)_4N]_2[Fe_5C(CO)_{14}]$

A procedure similar to the tetraethylammonium salt preparation was used. IR ν(CO) (nujol mull) 2030w, 1951vs(br), 1927s, 1890m(sh), 1867m(sh), 1725w, (tetrahydrofuran) 2028w, 1965vs, 1950s(sh), 1923w(sh), 1903w(sh), 1740w, (acetonitrile) 2029w, 1966vs, 1955s(sh), 1751w. Anal. Found: C, 32.99; H, 3.05; N, 3.38. Calcd. for $Fe_5C_{23}H_{24}N_2O_{14}$: C, 33.12; H, 2.91; N, 3.37%.

Reaction of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ with $Fe_2(CO)_9$

$[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ (50 mg) and $Fe_2(CO)_9$ in 1 to 3 molar ratio, were placed in a 50 ml Schlenk flask. The initial deep brown solution resulting from addition of 20 ml of tetrahydrofuran turned to deep purple after stirring at room temperature for 0.5 h as the solid $Fe_2(CO)_9$ disappeared. A small amount of unreacted $Fe_2(CO)_9$ was recovered by filtration. Crystallization of the solid, obtained by removal of the solvent, from methanol gave deep purple needles of $[(C_2H_5)_4N]_2[Fe_6C(CO)_{16}]$. IR ν(CO) (tetrahydrofuran) 2028vw, 1966vs, 1934(sh)m, 1887(sh)w, 1775m(br). Anal. Found: C, 37.69; H, 3.84; N, 2.70. Calcd. for $Fe_6C_{33}H_{40}N_2O_{16}$: C, 37.52; H, 3.82; N, 2.65%.

Preparation of $[(C_2H_5)_4N]_2[Fe_5CrC(CO)_{17}]$

To a Schlenk flask containing 50 mg of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ and 20 mg of $Cr(CO)_3$(pyridine)$_3$ was added 20 ml of tetrahydrofuran. The deep brown solution was stirred at 50° C for 4 hours during which time the solution turned deep purple. The solid obtained from removal of the solvent was crystallized from methanol at —25° C. IR ν(CO) (tetrahydrofuran) 2034w, 1968vs, 1947m(sh), 1932m, 1874w, 1781w. Anal. Found: C, 38.00; H, 3.83; N, 2.69; Cr, 3.00; Fe, 26.4. Calcd. for $Fe_5CrC_{34}H_{40}N_2O_{17}$: C, 37.81; H, 3.73; N, 2.59; Cr, 4.81; Fe, 25.86%.

Oxidation of $[(C_2H_5)_4N]_2[Fe_5CrC(CO)_{17}]$ with ferric ion

A suspension of $[(C_2H_5)_4N]_2[Fe_5CrC(CO)_{17}]$ (50 mg) in a toluene/aqueous ferric chloride system was stirred rapidly for 1 hour during which time nearly all the solids dissolved. A dark brown solid was obtained from the organic layer by removal of the solvent. This solid was dissolved in a minimum amount of dichloromethane from which black crystals of $Fe_4CrC(CO)_{16}$ were isolated after 8 h at —25°C. IR ν(CO) (hexane) 2099vw, 2049vs, 2039s, 2006m, 1961w(br). Mass spec. (m/e, Cr^{52}, Fe^{56}), 736 (M+), 680 (M — 2 CO^+) followed by successive loss of CO's down to 288 ($CrFe_4C$).

Preparation of $[(C_2H_5)_4N]_2[Fe_5MoC(CO)_{17}]$

To a tetrahydrofuran solution of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ (100 mg/20 ml) was added 45 mg of $Mo(CO)_3$(tetrahydrofuran)$_3$. After 0.5 h of stirring, the solvent was removed under vacuum. Crystallization of the resultant black solid from methanol gave black crystalline $[(C_2H_5)_4N]_2[Fe_5MoC(CO)_{17}]$. (63 mg, 51% yield). More product of lower purity was obtained from the supernatant. ^{13}C NMR (ppm, tetrahydrofuran, —90°C) 226.6 (broad singlet, carbonyl). IR ν(CO) (tetrahydrofuran) 2034w, 1968vs, 1942m, 1872w, 1781w. Anal. Found: C, 36.35; H, 3.61; N, 2.50; Mo, 8.55; Fe, 25.2. Calcd. for $Fe_5MoC_{34}H_{40}N_2O_{17}$: C, 36.33; H, 3.59; N, 2;49; Mo, 8.54; Fe, 24.84%.

Preparation of $Fe_4MoC(CO)_{16}$

To a suspension of $[(C_2H_5)_4N]_2[Fe_5MoC(CO)_{17}]$ (200 mg) in toluene (50 ml) was added a 10% aqueous ferric chloride solution. The two layer system was stirred vigorously until all the starting material dissolved. The green-brown toluene layer was collected, and the solvent was removed under reduced pressure. Crystallization of the solid from dichloromethane at —78°C afforded black crystals of $Fe_4MoC(CO)_{16}$ (50% yield). ^{13}C NMR (ppm, dichloromethane, —90°C) 214.1 (s, 3 CO), 210.8 (s, 6 CO), 208.0 (s, 3 CO) and 203.3 (s, 4 CO). IR ν(CO) (hexane) 2099vw, 2055s, 2046vs, 2040s, 2030m(sh), 2025m, 2012m, 1973w, 1953w. Mass spec. (m/e, Mo^{98}, Fe^{56}) 782 (M+) followed by successive loss of 16 carbonyls. Anal. Found: C, 26.44; H, 0.12; Fe, 29.4; Fe, 28;6; Mo, 11.9. Calcd. for $Fe_4MoC_{17}O_{16}$: C, 26.19; H, 0; Fe, 28.66; Mo, 12.31%.

Preparation of $[(C_2H_5)_4N]_2[Fe_5WC(CO)_{17}]$

In a 50 ml Schlenk flask were placed 400 mg of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ and 1.2 equiv. of $W(CO)_3(NCCH_3)_3$. Tetrahydrofuran (30 ml) was added, then the solution was warmed at 60°C for 20 min, which caused color change of the solution from dark brown to deep purple. The solid obtained by removal of the solvent was dissolved in a minimum amount of warm methanol. The solution, after filtration, was cooled to —20°C affording black crystals of $[(C_2H_5)_4N]_2$-$[Fe_5WC(CO)_{17}]$. IR ν(CO) (tetrahydrofuran) 2037vw, 1971vs, 1942m(sh), 1882w(br), 1776w(br). Anal. Found: C, 33.75; H, 3.29; N, 2.39. Calcd. for $Fe_5WC_{34}H_{40}N_2O_{17}$: C, 33.70; H, 3.33; N, 2.31%.

Preparation of $Fe_4WC(CO)_{16}$

A toluene suspension of $[(C_2H_5)_4N]_2[Fe_5WC(CO)_{17}]$ was stirred rapidly with an aqueous ferric chloride solution for 0.5 h. The green-brown organic layer was collected and filtered through a layer of Celite; then the solid obtained by removal of toluene was crystallized from dichloromethane at —25°C. IR ν(CO) (hexane) 2099vw, 2052s, 2047vs, 2037s, 2025m(sh), 2003m, 1964vw, 1950vw. Mass spec. (m/e, Fe^{56}, W^{184}) 868 ($Fe_4WC(CO)_{16}^+$) followed by successive loss of 16 carbonyls.

Preparation of $[(C_2H_5)_4N][Fe_5RhC(CO)_{14}(1,5\text{-}C_8H_{12})]$

A deep brown methanolic solution (15 ml) which contained 50 mg of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ and 13 mg of $[RhCl(C_8H_{12})]_2$ turned to deep purple after it was heated at 60°C for 10 min. The solution was stirred at room temperature for 2 more hours before it was concentrated under reduced pressure. Purple plates of $[(C_2H_5)_4N][Fe_5RhC(CO)_{14}(C_8H_{12})]$ were obtained from the solution at —25°C. ^1H NMR (δ, acetone-d_6) 1.40 (tt, 12 H), 2.16 (m, 4 H), 2.48 (m, 4 H), 3.50 (q, 8 H), 5.01 (m, 4 H). ^{13}C NMR (ppm, dichloromethane) 223.1 (s, carbonyl), 87.6 (d, $J = 9.2$ Hz, olefinic carbon of C_8H_{12}), and 31.2 (s, aliphatic carbon of C_8H_{12}). Tetraethylammonium ion ^{13}C resonances were not identified. IR ν(CO) (tetrahydrofuran) 2038m, 1993m(sh), 1981s, 1968m(sh), 1931w, 1800w. Anal. Found: C, 36.30; H, 3.22; N, 1.41; Fe, 27.0; Rh, 8.0. Calcd. for $Fe_5RhC_{31}H_{32}NO_{14}$: C, 36.51; H, 3.07; N, 1.33; Fe, 26.53; Rh, 9.78%.

Preparation of $[(C_2H_5)_4N][Fe_5RhC(CO)_{16}]$

To a solid mixture of 50 mg of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ and 11 mg of $[RhCl(CO)_2]_2$ was added 5 ml of methanol. The deep purple solution thus formed was stirred for 1 h at room temperature. Then, the volume of the solution was reduced to 2 ml and the solution was cooled to —25° C to give deep purple crystals of $[(C_2H_5)_4N][Fe_5RhC(CO)_{16}]$. This compound was also obtained from the reaction of CO (1 atm) with $[(C_2H_5)_4N][Fe_5RhC(CO)_{14}(C_8H_{12})]$ in tetrahydrofuran at 20° C. ^{13}C NMR (ppm, dichloromethane) 218.0 (d, J = 9.8 Hz, carbonyl resonance, 20° C). IR ν(CO) (tetrahydrofuran) 2062vw, 2003vs, 1983m, 1843w. Anal. Found: C, 30.69; H, 2.16; N, 1.45; Rh, 7.76; Fe, 28.8; C, 31.06; H, 2.11; N, 1.47; Rh, 9.50; Fe, 24.1. Calcd. for $Fe_5RhC_{25}H_{20}NO_{16}$: C, 30.87, H, 2.07; N, 1.44; Rh, 10.58; Fe, 28.71%.

Oxidation of $[(C_2H_5)_4N][Fe_5RhC(CO)_{16}]$

A dichloromethane solution of $[(C_2H_5)_4N][Fe_5RhC(CO)_{16}]$ and an aqueous ferric chloride solution was stirred vigorously for 4 hours. The organic layer gave a black solid after removal of the solvent under vacuum. The solid was washed with water and then dissolved in a minimum amount of dichloromethane. The solution, upon cooling, afforded microcrystalline solids of $[(C_2H_5)_4N]$-$[Fe_4RhC(CO)_{14}]$. IR ν(CO) (tetrahydrofuran) 2066vw, 2025s, 2002vs, 1980m, 1957w, 1925vw, 1887vw. Anal. Found: C, 31.33, H, 2.35; N, 1.58; (on a separate sample) Rh, 12.0; Fe, 25.7. Calcd. for $Fe_4RhC_{23}H_{20}NO_{14}$: C, 32.09; H, 2.34; N, 1.63; Rh, 11.96; Fe, 25.96%.

Preparation of $[(C_2H_5)_4N][Fe_5IrC(CO)_{14}(1,5\text{-}C_8H_{12})]$

$[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ (300 mg) and 0.6 equiv. of $[ClIr(1,5\text{-}C_8H_{12})]_2$ were dissolved in 20 ml of methanol; the solution was allowed to stand for 12 hours. The resultant purple solution was concentrated under reduced pressure to a volume of ~5 ml. This solution was filtered. The solution was cooled to —20° C to give black crystals which were collected by filtration. Anal. Found: C, 33.42; H, 3.03; N, 1.32. Calcd. for $Fe_5IrC_{31}H_{32}NO_{14}$: C, 33.42; H, 2.90; N, 1.26%. ^1H NMR (δ, acetone-d_6): 1.39 (tt, 12 H), 2.28 (m, 4 H), 2.47 (m, 4 H); 3.41 (q, 8 H) and 4.36 (m, 4 H). IR ν(CO) (dichloromethane): 2036m, 1984vs, 1968m, 1932w, 1802w.

Preparation of $[(C_2H_5)_4N][Fe_5IrC(CO)_{16}]$

A purple tetrahydrofuran solution of $[(C_2H_5)_4N][Fe_5IrC(CO)_{14}(C_8H_{12})]$ turned to red-purple when the solution, under 1 atm of carbon monoxide, was heated at 50° C for 3 hours. Removal of the solvent under vacuum was followed by crystallization of the resultant solid from dichloromethane at —25° C to give black needles. IR ν(CO) (tetrahydrofuran) 2068vw, 2024s, 2008vs, 1978m, 1936w, 1815w. Anal. Found: 28.45; H, 2.05; Ni, 1.33. Calcd. for $Fe_5IrC_{25}H_{20}NO_{16}$: C, 28.28; H, 1.90; N, 1.32%.

Preparation of $Fe_5NiC(CO)_{16}$

To a 30 ml Schlenk flask which contained 200 mg of $[(C_2H_5)_4N]_2$-$[Fe_5C(CO)_{14}]$ and 1.2 equiv. of $Ni(1,5\text{-}C_8H_{12})_2$ was added 10 ml of dry tetrahydrofuran and 5 ml of methanol. After 0.5 h of stirring, carbon monoxide was bubbled through the purple solution for 5 minutes; then the solution was stirred for 1 hour. A black solid was obtained by removal of the solvent under vacuum. A slurry of the solid in a toluene/aqueous ferric chloride two layer system was rapidly stirred until the solid disappeared. The organic layer was decanted and filtered through a layer of Celite and then the toluene was removed under vacuum. Recrystallization of the resultant solid from dichloromethane at —25°C afforded black plates. IR $\nu(CO)$ (hexane) 2099vw, 2065m, 2041vs, 2014m, 1990vw, 1983vw, 1886vw(br). Mass spec. (m/e, Fe^{56}, Ni^{58}) 798 (M^+) and envelopes corresponding to loss of up to 16 carbon monoxides, 294 (Fe_4NiC) and 238 (Fe_3NiC). Anal. Found: C, 25.57; H, 0.15; N, 0.05. Calcd. for $Fe_5NiC_{17}O_{16}$: C, 25.58; H, 0; N, 0%.

Preparation of $[(C_2H_5)_4N]_2[Fe_5NiC(CO)_{15}]$

Upon standing at room temperature, a tetrahydrofuran/toluene solution of $[(C_2H_5)_4N]_2[Fe_5NiC(CO)_{14}(C_8H_{12})]$, prepared from $Fe_5C(CO)_{14}{}^{2-}$ and $Ni(C_8H_{12})_2$ (IR $\nu(CO)$ (C_4H_8O): 2006m, 1948vs, 1928m(sh), 1898w(br), 1798w(br), 1745w(br)), deposited deep violet crystals accompanied by formation of a non-crystalline residue. The supernatant and the residue were removed by decantation, and the crystals were washed with ether. The same compound was obtained when a methanolic solution of $[(C_2H_5)_4N]_2[Fe_5NiC(CO)_{14}(C_8H_{12})]$ was exposed to carbon monoxide. IR $\nu(CO)$ (nitromethane) 2036vw, 1988m, 1961vs, 1938m(sh), 1891w, 1761w. Anal. Found: C, 38.92; H, 4.34; N, 2.57; Fe, 26;1; Ni, 5.31. Calcd. for $Fe_5NiC_{32}H_{40}N_2O_{15} \cdot C_4H_8O$: C, 39.21; H, 4.39; N, 2.54; Fe, 25.32; Ni, 5.32%.

Preparation of $Fe_5PdC(CO)_{16}$

A solution of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ and 0.5 equiv. of $[(C_3H_5)PdCl]_2$ in methanol was stirred for 1 hour. Then the solvent was removed by evacuation. Toluene and an aqueous ferric chloride solution were added to the resultant solid, and the two layer system was stirred rapidly for 0.5 h. The organic layer was collected and filtered through a layer of Celite. Removal of the toluene solvent gave a black solid which was then crystallized from chloroform. IR $\nu(CO)$ (dichloromethane) 2104w, 2074m, 2041s, 2013m, 1993m(sh), 1924vw(sh). Anal. Found: C, 23.66; H, 0.17; N, 0.01. Calcd. for $Fe_5PdC_{17}O_{16}$: C, 24.14; H, 0; N, 0%.

Preparation of $[(C_2H_5)_4N]$ $[Fe_5CuC(CO)_{14}(NCCH_3)]$

To a 100 ml Schlenk flask which contained 150 mg of $[(C_2H_5)_4N]_2$-$[Fe_5C(CO)_{14}]$ and 1.1 equiv. of $[Cu(NCCH_3)_4]PF_6$ (65 mg) were added 30 ml of tetrahydrofuran, and the resultant solution was stirred at room temperature for 2 days. The solvent was removed, and the brown solid thus obtained was crystallized from dichloromethane at —20°C. ^1H NMR (δ, acetone-d_6), 1.43 (tt, 12 H), 2.47 (s, 3 H), and 3.47 (q, $J = 7.2$ Hz, 8 H). IR $\nu(CO)$ (tetrahydrofuran) 2040w, 1982s, 1962m, 1928w, 1918(sh). Anal. Found: C, 32.80; H, 2.70; N, 3.01. Calcd. for $Fe_5CuC_{25}H_{23}N_2O_{14}$: C, 32.70; H, 2.52; N, 3.05%. The acetonitrile ligand in this complex, presumably coordinated to copper, was not displaced by carbon monoxide (60° C under 1 atm of CO for a tetrahydrofuran solution of the complex).

Oxidation of $[(C_2H_5)_4N][Fe_5CuC(CO)_{14}(NCCH_3)]$ with ferric ion

A dichloromethane solution of $[(C_2H_5)_4N][Fe_5CuC(CO)_{14}(NCCH_3)]$ was stirred rapidly with an aqueous solution of ferric chloride for 2 hours. The dichloromethane layer was separated and was evaporated to give a black solid that was extracted with toluene. After concentrating the toluene extract, it was cooled to —20° C to give deep purple needles identified as $Fe_5C(CO)_{15}$ by its IR ν(CO) spectrum.

Attempted preparation of $[Fe_5MC(CO)_{17}^-]$; M = Mn, Re

In these reactions $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ was allowed to react with $M(CO)_3(pyridine)_2Br$; M = Mn or Re, or $Mn(CO)_3(2\text{-picoline})_2Br$ in tetrahydrofuran with or without addition of 2 equivalents of $BF_3{\cdot}O(C_2H_5)_2$, or in methanol. However, no mixed-metal carbide cluster was obtained from any of the above reactions. When BF_3-etherate was used to enhance the dissociation of pyridine from the manganese or rhenium compounds, the formation of the mono-protonated carbide cluster, $[HFe_5C(CO)_{14}^-]$ was observed, presumably due to the reaction between BF_3 and adventitious water acting as an H^+ source.

Reaction of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ with $Fe_2(CO)_9$

$Fe_2(CO)_9$ (33 mg) was suspended in a tetrahydrofuran solution of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (50 mg/2 ml) and the slurry was stirred rapidly for 1 hour. The solution turned purple as $Fe_2(CO)_9$ reacted. The solid obtained by removal of the solvent yielded dark violet crystals which were spectroscopically identified as $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_6C(CO)_{16}]$ (IR ν(CO) (dichloromethane) 2028 vw, 1967vs, 1944(sh), 1770m(br)), as well as by chemical oxidation by aqueous ferrich chloride to give $FeC(CO)_{15}$.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4Mo_2C(CO)_{18}]$

A tetrahydrofuran solution of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (100 mg) and $Mo(CO)_3$(*m*-xylene) (17 mg) was allowed to stand for 2 days before the solvent was removed under reduced pressure. The solid was dissolved in dichloromethane (2 ml), the solution was filtered, and 4 ml of ethyl acetate was added to the filtrate. The filtrate was then cooled to —78° C; crystals formed; these were collected and vacuum dried. IR ν(CO) (dichloromethane) 2040vw, 1979s(sh), 1967vs, 1942m(sh), 1892m(br), 1782w(br). Anal. Found: C, 54.76; H, 3.47; N, 1.36; Fe, 10.8; Mo, 9.01. Calcd. for $Fe_4Mo_2C_{91}H_{60}N_2P_4O_{18}$: C, 54.41; H, 3.01; N, 1.39; Fe, 11.12; Mo, 9.55%.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[CrFe_4C(CO)_{15}]$

To a Schlenk flask containing $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (200 mg, 0.121 mmol) and 1.2 equiv. $Cr(CO)_3(pyridine)_3$ (55 mg), was added 30 ml of tetrahydrofuran. The brown-red solution was stirred at 60° C for 8 hours during which time the solution turned brown. The tetrahydrofuran was removed under vacuum; and the resulting solid was redissolved in 5 ml dichloromethane. This solution was filtered and then 5 ml ethyl acetate was slowly added. Crystals formed at —25° C; these were collected by filtration and vacuum dried. Anal. Found: C, 59.92; H, 4.07; N, 1.52. Calcd. for $CrFe_4C_{52}H_{30}NP_2O_{15}$: C, 59.22; H, 3.39; N, 1.57%. IR ν(CO) (tetrahydrofuran) 1978s, 1938m. The tungsten analog was prepared in a similar fashion from $W(CO)_3(NCCH_3)_3$.

Preparation of $(C_6H_5)_3PNP(C_6H_5)_3[RhFe_4C(CO)_{12}(1,5\text{-}C_8H_{12})]$

A solution of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (200 mg, 0.121 mmol) and 1.2 equivalents $[Rh(C_8H_{12})Cl]_2$ (36 mg) in 20 ml tetrahydrofuran was stirred for 2 hours whereupon it turned from brown to black. The tetrahydrofuran was removed under vacuum, the resulting solid redissolved in diethyl ether, and this solution filtered. The diethyl ether was then removed under vacuum, and the product $[(C_6H_5)_3PNP(C_6H_5)_3][RhFe_4C(CO)_{12}(C_8H_{12})]$ was crystallized at —20° C from a warm ethanol solution. Anal. Found: C, 50.08; H, 3.44; N, 0.94. Calcd. for $RhFe_4C_{57}H_{42}NP_2O_{12}$: C, 51.81; H, 3.20; N, 1.06%. ^{13}C CO NMR (ppm, tetrahydrofuran, —90° C): 232.83 (2 CO), 219.58 (3 CO), 218.64 (3 CO), 216.95 (2 CO), 211.5 (2 CO). IR ν(CO) (tetrahydrofuran): 2034m, 1996s, 1973s, 1840vw.

Preparation of $(C_6H_5)_3PNP(C_6H_5)_3[IrFe_4C(CO)_{12}(1,5\text{-}C_8H_{12})]$

This compound was prepared in a similar fashion to the rhodium analog from $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ and $[Ir(C_8H_{12})Cl]_2$. ^{13}C CO NMR (ppm, dichloromethane, —65° C); 226.3 (2 CO), 222.7 (3 CO), 220.0 (3 CO), 215.5 (2 CO), 211.6 (2 CO). IR ν(CO) (tetrahydrofuran): 2038m, 1994s, 1970s, 1888w, 1809m. Anal. Found: C, 48.37; H, 3.13; N, 0.97; Fe, 15.2. Calcd. for $IrFe_4C_{57}H_{42}P_2NO_{12}$: C, 48.54; H, 3.0; N, 0.99; Fe, 15.9%.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[NiFe_4C(CO)_{12}(1,5\text{-}C_8H_{12})]$

A solution of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (200 mg, 0.121 mmol) and 1.2 equiv. $Ni(C_8H_{12})$ (40 mg) in 20 ml tetrahydrofuran was stirred for 3 hours, whereupon the solution changed from red-brown to brown. The tetrahydrofuran was removed under vacuum, the resulting solid redissolved in 3 ml dichloromethane, and this solution was filtered. To this solution was added 5 ml ethyl acetate and the product crystallized at —20° C. IR ν(CO) (tetrahydrofuran): 1965s, 1930w, 1890w.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)_3]_2[Ni_2Fe_4C(CO)_{14}]$

A solution of $[(C_6H_5)_2PNP(C_6H_5)_3]_2[Fe_4C(CO)_{12}]$ (200 mg, 0.121 mmol) and 2.2 equivalents of $Ni(1,5\text{-}C_8H_{12})_2$ (74 mg) in 20 ml tetrahydrofuran was stirred for 2 hours whereupon the solution turned from brown to black. Carbon monoxide was then passed through the solution for 5 min, and the solution was stirred for an additional hour. The solvent was then removed by evacuation, the solid residue was washed with hexane and was dried. The resulting solid was dissolved in 5 ml CH_2Cl_2, the solution was filtered, and 5 ml of ethyl acetate was added. Upon cooling to —25° C, the product crystallized as black platelets. IR ν(CO) (tetrahydrofuran) 1975vs, 1960s, 1935m, 1895w(br), 1810w(br). Anal. Found: C, 56.38; H, 3.45; N, 1.55. Fe, 12.9; Ni, 6.47. Calcd. for $Ni_2Fe_4C_{87}H_{60}O_{14}P_4N_2$: C, 57.35; H, 3.32; N, 1.54; Fe, 12.26; Ni, 6.44%.

Preparation of $[(C_6H_5)_3PNP(C_6H_5)][CuFe_4C(CO)_{12}(CH_3CN)]$

This compound was prepared from $Cu(NCCH_3)_4PF_6$ in a fashion analogous to the foregoing as black crystals. IR ν(CO) (tetrahydrofuran): 2040m, 2012s, 2005m, 1981s.

Results and discussion

Synthesis strategy

All synthetic procedures described in this paper were directed towards heteronuclear metal carbide clusters. The term carbide is used in the context of definitions set out in an earlier review [3] of metal carbide clusters: A carbide carbon atom is one within bonding distance of metal atoms only. Structural classes and subclasses were also defined in that review.

Major synthetic procedures [3] employed to date for metal carbide cluster synthesis include:

(a) Pyrolysis of a metal carbonyl complex with either carbon monoxide or the solvent serving as the source of the carbide carbon atom (generally a low yield, nonselective synthesis);

(b) Reduction of a neutral metal carbonyl, especially with an anionic metal carbonylate with the carbide atom probably derived from carbon monoxide in most syntheses of this type (moderately selective syntheses).

(c) Reaction of polyhalomethanes and neutral or anionic metal carbonyl complexes with the carbide carbon atom derived from the halomethane;

(d) Conversion of a metal carbide carbonyl cluster to a larger or smaller carbide cluster by polyhedral expansion or degradation reactions (often selective, high yield synthetic procedures).

In this article we elaborate on the polyhedral expansion and contraction procedures for the specific and selective synthesis of metal carbide clusters with two or more different metal atoms in the framework structure [4]. All polyhedral expansion syntheses were based on the two peripheral or exposed metal carbides $[Fe_5C(CO)_{14}{}^{2-}]$ and $[Fe_4C(CO)_{12}{}^{2-}]$ [2,5], and all polyhedral contraction syntheses were based on $[Fe_5M(CO)_x{}^{y-}]$ clusters. Accordingly, all the heteronuclear metal carbide clusters contained a majority of iron cluster atoms although the synthetic strategies are applicable to any peripheral metal carbide cluster as the initial reagent.

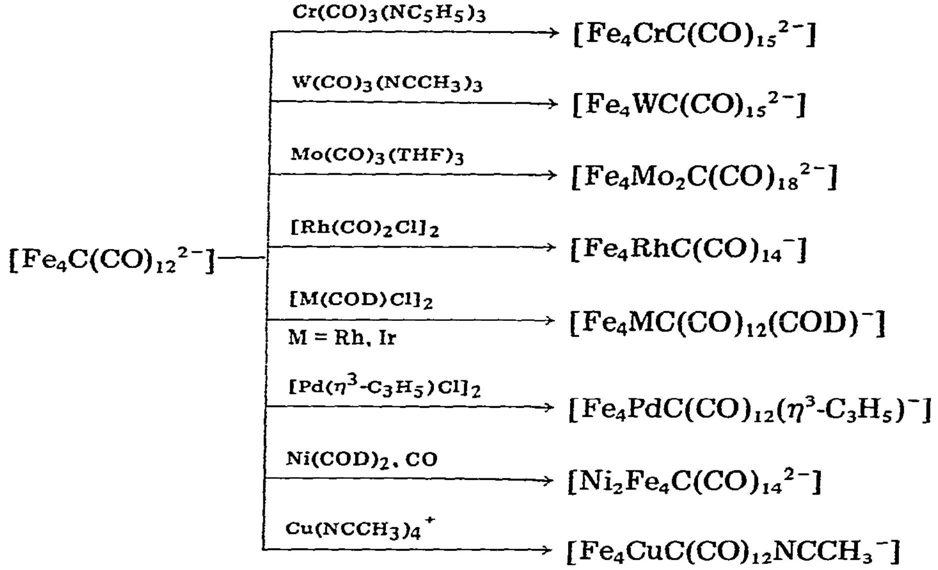
The two key starting reagents for the syntheses reported in this paper were prepared in several steps from the reaction of iron pentacarbonyl with iron tetracarbonyl dianion, general synthesis procedure (b). The initial carbide formed, $Fe_6C(CO)_{16}{}^{2-}$, was not isolated but was oxidatively degraded to $Fe_5C(CO)_{15}$ with aqueous ferric ion — a new modified two-step, one reaction flask

SCHEME 1

$$Fe(CO)_5 \xrightarrow{Fe(CO)_4{}^{2-}} [Fe_6C(CO)_{16}{}^{2-}] \xrightarrow{Fe^{3+}} Fe_5C(CO)_{15} \xrightarrow{Fe(CO)_4{}^{2-}} [Fe_5C(CO)_{14}{}^{2-}]$$

$$[Fe_5C(CO)_{14}{}^{2-}] \xrightarrow{H^+} HFe_4(\eta^2\text{-}CH)(CO)_{12} \xrightarrow{R_3N} [Fe_4C(CO)_{12}{}^{2-}]$$

SCHEME 2



synthesis that provided the five-atom cluster in up to 60% overall yield (Scheme 1). Reduction of $Fe_5C(CO)_{15}$ with $Fe(CO)_4{}^{2-}$ gave the key five-atom $[Fe_5C(CO)_4{}^{2-}]$ cluster carbide anion. Protonation of this anion yielded $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ in high yield and the other key reagent, the four-atom $[Fe_4C(CO)_{12}{}^{2-}]$ carbide cluster ion, was generated by deprotonation (Scheme 1).

Both the $[Fe_5C(CO)_{14}{}^{2-}]$ and $[Fe_4C(CO)_{12}{}^{2-}]$ carbide clusters fulfil two important criteria for polyhedral expansion reactions. Both are peripheral or exposed carbides or more specifically, and significantly, the metal polyhedra are not closed polyhedra with all faces triangular but have "open" faces susceptible to attack by mononuclear metal complex fragments whereby larger (up to six metal atoms) metal carbides can be generated. Secondly, the relatively high electron density on these two cluster anions facilitates attack by coordinately unsaturated mononuclear metal complexes *. A partial illustration of polyhedral expansion reactions based on these two "open" metal carbides is depicted in Schemes 2 and 3; all the reactions illustrated in these schemes or described in the experimental section employ coreactants that readily generate coordinately unsatured mononuclear metal complexes. Both reactions appear to have a large scope. With the butterfly carbide reactant, $[Fe_4C(CO)_{12}{}^{2-}]$, there are two possible products in the polyhedral expansion reaction: (i) a peripheral Fe_4MC carbide cluster of 74-electron count and square pyramidal form with an iron atom always residing in the unique apical position or (ii) a cage Fe_4M_2C carbide cluster with an octahedral Fe_4M_2 polyhedron. The former is an

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* The reactants employed were either coordinately unsaturated or were coordinately saturated species that readily form coordinately unsaturated fragments in solution by ligand dissociation or by fragmentation.

SCHEME 3

$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{M(CO)_3L_3}} [\mathrm{Fe_5MC(CO)_{17}}^{2-}]\ (\mathrm{M = Cr, Mo, W})$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Fe_2(CO)_9}} [\mathrm{Fe_6C(CO)_{16}}^{2-}]$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Rh_2(CO)_4Cl_2}} [\mathrm{Fe_5RhC(CO)_{16}}^{-}]$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{M_2(COD)_2Cl_2}} [\mathrm{Fe_5MC(CO)_{14}(COD)}^{-}]\ (\mathrm{M = Rh, Ir})$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Ni(COD)_2}} [\mathrm{Fe_5NiC(CO)_{14}(COD)}^{2-}]$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Ni(COD)_2 + CO}} [\mathrm{Fe_5NiC(CO)_{15}}^{2-}]$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Pd_2(C_3H_5)_2Cl_2}} \mathrm{Fe_5PdC(CO)_{16}}$$
$$[\mathrm{Fe_5C(CO)_{14}}^{2-}] \xrightarrow{\mathrm{Cu(NCCH_3)_4}^{+}} [\mathrm{Fe_5CuC(CO)_{14}(NCCH_3)}^{-}]$$

intermediate to the latter and presumably control of reaction conditions (high dilution techniques for example) could allow selective synthesis of five-metal-atom carbides in reaction systems like $[\mathrm{Fe_4C(CO)_{12}}^{2-}]$ and $\mathrm{Mo(CO)_3(THF)_3}$ where the octahedral $[\mathrm{Fe_4Mo_2C(CO)_{18}}^{2-}]$ product prevailed under normal reaction conditions (why the reaction with the chromium and tungsten analogs ceased at the $\mathrm{Fe_4MC}$ stage presently is not understood). For reaction systems like $[\mathrm{Fe_4C(CO)_{12}}^{2-}]$ and $\mathrm{Rh_2(CO)_4Cl_2}$, the reaction ceased with the formation of the five-atom product $[\mathrm{Fe_4RhC(CO)_{14}}^{-}]$ because this mono anion species apparently lacks sufficient electron density to exhibit reactivity towards the reactants. No reaction of any monovalent anionic $\mathrm{M_5C}$ cluster to give an $\mathrm{M_6C}$ cluster has been observed to date in our studies. With $[\mathrm{Fe_5C(CO)_{14}}^{2-}]$ as the carbide reactant, the sole reaction products naturally were the six-atom $\mathrm{Fe_5MC}$ clusters all of which were normal 86-electron, octahedral clusters.

These two types of polyhedral expansion reactions should be generally applicable to open * polyhedral four-atom or five-atom cluster reactants be they simple clusters, carbide clusters, or nitride clusters. The merits of this type of synthesis is that reactants can be logically selected and that they are relatively selective, high yield reactions. As other new open polyhedral cluster species are prepared, this basic synthesis reaction gains substantially in scope.

There is an apparent limitation to the reaction scope in polyhedral expansion reactions. The qualifier "apparent" is applied because the limitation is based

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* That is polyhedra which are fragments of polyhedra with all triangular faces. Typically, the electron counts for these open four- and six-atom polyhedra are 62 and 74, respectively; using the polyhedral borane jargon, they are *arachno* and *nido* clusters, respectively.

SCHEME 4

$$\begin{aligned}
&[Fe_5CrC(CO)_{17}{}^{2-}] && && Fe_4CrC(CO)_{16}\\
&[Fe_5MoC(CO)_{17}{}^{2-}] && \xrightarrow{Fe^{3+}} && Fe_4MoC(CO)_{16}\\
&[Fe_5WC(CO)_{17}{}^{2-}] && && Fe_4WC(CO)_{16}\\
&[Fe_5RhC(CO)_{16}{}^{-}] && && [Fe_4RhC(CO)_{14}{}^{-}]
\end{aligned}$$

purely upon experimental observations and is not predicated on an understanding of reaction mechanism. The polynuclear metal carbide reactant in these expansion reactions has always been a polyhedral fragment of an octahedral M_6C structure and has been a di-negative anion. A number of reactions have been attempted, but with no success, with fragments of octahedral M_6C clusters which only have a single negative charge. Reversal of charge relationships — i.e., a di-negative mononuclear metal carbonyl and a neutral metal carbide carbonyl cluster that is a fragment of an octahedral M_6C structure — led not to a polyhedral expansion reaction but to a reduction of the carbide cluster. An example of this reaction sequence was the conversion of $Fe_5C(CO)_{15}$ to $[Fe_5C(CO)_{14}{}^{2-}]$ by reaction with $[Fe(CO)_4{}^{2-}]$.

Polyhedral contraction provides a relatively selective synthetic route to open polyhedral four- and five-atom clusters. Specifically illustrated in this article are the conversions of octahedral Fe_5MC clusters to square pyramidal Fe_4MC clusters but the synthetic strategy should be generally applicable to large clusters, carbide clusters, nitride clusters, or any cage cluster (P, As, O, or metal atom as the interstitial atom). The degradation reaction of most general applicability is oxidation, with ferric ion, of the iron carbide system as shown in Scheme 4; however, other degradation reactions, for example with acidic reagents (as is effective in the degradation of $[Fe_5C(CO)_{14}{}^{2-}]$ to the $[Fe_4C(CO)_{12}{}^{2-}]$ precursor, namely $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ should be possible. This type of synthetic strategy has not been intensively investigated by us as yet.

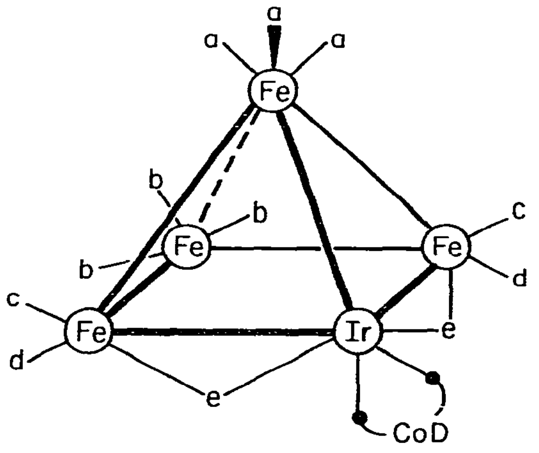
The combination of polyhedral expansion and contraction reactions also provides a rational route to metal carbide clusters with three or more different metal atoms but none has been reported yet.

Structure and stereochemistry

The structures of four heteronuclear metal carbide clusters have been established rigorously from X-ray crystallographic investigations. Two five-atom clusters have been so defined, namely $[Fe_4RhC(CO)_{14}{}^{-}]$ and $Fe_4MoC(CO)_{16}$ [4]. Both have square pyramidal form with the unique metal atom at a basal site and the carbide carbon atom in the tetragonal Fe_3M face slightly displaced out of the Fe_3M plane away from the apical iron atom. Two six-atom clusters have been crystallographically defined, specifically $[Fe_5MoC(CO)_{17}{}^{2-}]$ [4] and $Fe_5NiC(CO)_{16}$ [6]. Both have an octahedral Fe_5M array with a more or less centered carbide carbon atom, i.e., both are octahedral cage M_6C carbide clusters.

Stereochemistry in the context of ligand arrangement about the Fe_4MC and Fe_5MC carbide clusters is explicitly established for the four clusters (mentioned above) studied by X-ray crystallography. In addition, most of the carbide clusters described in the Experimental section have been investigated by ^{13}C NMR spectroscopy. Because of facile carbonyl ligand site exchange even at low temperatures, the ^{13}C NMR data provided no information * about ligand stereochemistry with respect to the Fe_6C, Fe_5MC or Fe_4M_2C core structure. Site exchange of CO ligands in all octahedral Fe_5MC and Fe_4M_2C carbide clusters investigated was extremely facile; all exhibited single CO ^{13}C resonances from 20 to ~−90°C. Even for $[Fe_4Mo_2(CO)_{18}{}^{2-}]$, the ^{13}C NMR spectrum consisted of a single resonance. In this case, the molybdenum atoms are believed to be *cis* because the characterized intermediate Fe_4MoC cluster had the molybdenum atom at a basal site; barring a substantial polytopal rearrangement, the Fe_4Mo_2C clusters should have a *cis* Mo_2Fe_4 stereochemistry.

In the square pyramidal Fe_4MC and Fe_5C clusters, the activation energy for CO ligand site exchange was substantially higher than for the octahedral M_6C carbide clusters. Carbonyl ligand exchange was generally a slow (NMR time scale) process for exchange between apical and basal metal atom sites, but in some clusters such as $[Fe_4RhC(CO)_{14}{}^-]$, CO site exchange between apical and basal sites was evident at ambient temperatures. Typically, intermetal and intrametal CO site exchange was fast within the basal set of metal atoms at ambient temperatures. This feature prevailed at low temperatures when all the metal atoms were identical. With different metal atoms in the basal set, as in $Fe_4MoC(CO)_{16}$, intermetal atom CO site exchange became slow on the NMR time scale although intrametal site exchange remained fast. Unique ligands centered at basal metal atom sites were effective in raising the barriers to intermetal CO site exchange. For example, the anionic carbide cluster $[Fe_4IrC(CO)_{12}(1,5\text{-cyclooctadiene})^-]$ had at −65° C a ^{13}C spectrum of five resonances with relative intensities of 2 : 3 : 3 : 2 : 2 consistent with I.



(I)

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* This statement must be qualified for two octahedral Fe_5RhC clusters where a limited definition of ligand stereochemistry was obtained from the ^{13}C NMR data despite rapid CO exchange even at low temperatures. Absence of ^{103}Rh splitting in the ^{13}C NMR spectra of $[Fe_5RhC(CO)_{14}(COD)^-]$ for the single CO resonance and the presence of ^{103}Rh—^{13}C splitting of the olefinic diene ^{13}C resonances establish that only the 1,5-cyclooctadiene ligand is bound to the rhodium atom and the remaining CO ligands are bound to iron atoms. In $[Fe_5RhC(CO)_{16}{}^-]$, the ^{13}C CO DNMR resonance was a doublet and the magnitude of the ^{103}Rh—^{13}C splitting indicated that two carbonyl ligands are bound to the rhodium atom.

Exchange at higher temperatures in this cluster, and in the analogous [$Fe_4RhC(CO)_{12}$(1,5-cyclooctadiene)$^-$] cluster, first involves the carbonyl ligands associated with the basal iron atoms adjacent to the unique iridium (rhodium) atom. The dynamical features of this process are readily explained by a step that comprises breaking of the bridge carbonyl bond to yield an iron atom with three terminal carbonyl groups; then this is followed by intrametal CO site exchange at this iron atom whereby CO environments c, d, and e (see I) are equilibrated.

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