geometrical distorsions about the metal from tetrahedral values are often very large (e.g., bond angles of 90–95° or 118–120°)[13,14]; (b) a trend toward lower frequences has been considered absolutely unexceptional for the stretching band of any double bond in position with respect to metals of group IV[34] (14[38]); (c) the above reported geometrical parameters of the amide groups probably indicate that strong electron withdrawal takes place due to the metal atom. The normal ν(CO) values observed in similar cases [$H_2C(CONMe_2)_2$ (1670 cm^{-1}) or $BrHC(CONMe_2)_2$ (1665 cm^{-1})[23]] seem to prove that the central carbon atom plays no role in such effect, which, in our opinion, is due to the metals, with increasing effect in the predictable order Ge < Sn.

Such phenomenon gives an alternative and more reliable explanation of the observed ν(CO) values shifted toward lower frequences in the reverse order. A similar effect for tin has already been observed and widely discussed.[35,36] The ^{1}H NMR spectrum of A and the ^{1}H and ^{13}C NMR spectra of B substantiate these arguments. The ^{1}H NMR spectra show the equivalence of the hydrogen atoms of methyl groups bonded to the metals. This equivalence is also confirmed by the signal (−4.7 ppm) assigned to the methyl carbon atoms bonded to Sn (^{13}C NMR spectrum of B). Moreover, this spectrum shows $J(^{119}Sn-^{13}C)$ of 352 Hz, which has been assumed as a proper value for a tetracoordinated tin atom.[37] The relatively low coalescence temperatures of ^{1}H NMR NMe_2 doublet of A and B (~50 and ~20 °C, respectively), compared with $H_2C(CONMe_2)_2$ (>70 °C), are in agreement with a marked σ character of the bonds C(1)–N(1) and C(5)–N(2).

These data are consistent with tetrahedral, four coordination about the metal in both these compounds. They exclude, or at least severely question, the possibility of pentacoordination. The same coordination is retained also in solution. Thus the many structural examples showing only slightly distorted tetrahedral geometry,[9,10,13] and with M···O distances from 2.8 Å to higher values, assumed as bonding distances, should be reexamined.

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Registry No. A, 110698-77-6; B, 108202-42-2; C, 110698-78-7; D, 108202-43-3; E, 7313-22-6; Me_3GeNMe_2, 13361-67-6; Me_3SnNMe_2, 993-50-0; C_3O_2, 504-64-3.

Supplementary Material Available: Tables of hydrogen positional parameters and thermal parameters (4 pages); lists of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page. Supplementary material is also available from the authors upon request.

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Transition-Metal Trihalomethyl Complexes as Cluster-Building Reagents: Preparation and X-ray Crystal Structure of [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$]

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A new mixed-metal ketenylidene complex, [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$] (1) ($PPN^+$ = bis(triphenylphosphine)nitrogen(1+)), has been prepared from trihalomethyl manganese complexes, $Mn(CO)_5(CX_3)$ (X = Cl or Br), in combination with [PPN][$Co(CO)_4$]. Attempts to extend this technique to other trihalomethyl complexes and metal carbonyl anions did not yield any new cluster products. Instead, these reactions were characterized by electron-transfer chemistry, which resulted in oxidation of the anions. Crystal data for 1: triclinic space group $P\bar{1}$; a = 14.859 (4) Å, b = 9.209 (1) Å, c = 16.701 (3) Å, α = 90.08 (2)°, β = 102.79 (2)°, γ = 89.99 (2)°; Z = 2. Protonation of 1 leads to the new mixed-metal methylidyne $MnCo_2(CO)_{10}(\mu_3\text{-}CH)$ (2).

Introduction

Transition-metal trihalomethyl complexes (X = Cl, Br) were rare until recently when a novel route to their preparation was discovered.[1] The facile halogen-exchange reaction between trifluoromethyl transition-metal complexes and boron trihalides affords the corresponding trihalomethyl complexes (X = Cl, Br) conveniently and in high yield (eq 1). The carbon atom in these complexes

$$M-CF_3 + BX_3 \rightarrow M-CX_3 + BF_3 \qquad (1)$$

acts as an electrophile, reacting with nucleophiles (H–NU) to give C–X bond cleavage and C–Nu bond formation (eq 2). The iron complex $CpFe(CO)_2(CCl_3)$, for example, reacts better with water, ammonia, primary amines, and thiols, transforming the CX_3 ligand to –CO, –CN, –CNR,

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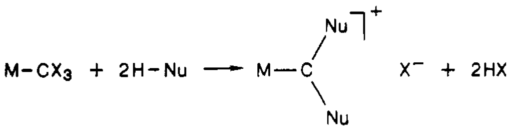

$$\mathrm{M{-}CX_3 + 2H{-}Nu \longrightarrow [M{-}C(Nu)_2]^+ X^- + 2HX} \quad (2)$$

and sulfur-substituted carbenes, respectively.[2] Similar reactivity has been observed for transition-metal dihalocarbene complexes.[3]

The electrophilic character of trihalomethyl complexes prompted us to investigate their reactivity with organometallic nucleophiles. We hoped to displace one or more halides with transition-metal carbonyl anions, building new dimer or cluster complexes via formation of new metal-carbon bonds (eq 3). Previous workers have shown that

$$\mathrm{M{-}CX_3 + M'L_n^- \rightarrow M{-}CX_2{-}M'L_n + X^-} \xrightarrow{+M'L_n^-} \ldots \quad (3)$$

the organic analogues of M–CX_3 complexes, $CHCl_3$ and CCl_4, react with metal carbonyl anions of Co, Rh, and Ni to yield cluster products, in which the carbon atom from the polyhalomethane has been incorporated into the cluster.[4] Herein we describe our efforts to build new clusters from trihalomethyl transition-metal complexes. A portion of this work has been communicated.[5]

Experimental Section

General Procedures. All manipulations were performed under an atmosphere of purified N_2 by using standard Schlenk techniques. Hexane, tetrahydrofuran (THF), and Et_2O were distilled from sodium benzophenone ketyl before use, CH_2Cl_2 was distilled from P_2O_5, and pentane was distilled from 4A molecular sieves. The following complexes were prepared by literature methods: $Mn(CO)_5(CX_3)$ (X = Cl, Br),[1] $CpFe(CO)_2(CCl_3)$,[1] $[PPN][Co(CO)_4]$,[6] $NaCo(CO)_4$,[7] $[PPN]_2[Fe_3(CO)_{11}]$,[8] $[PPN][Mn(CO)_5]$,[6] $CpMo(CO)_3H$,[9] $Co_3(CO)_9(\mu_3\text{-CBr})$[10] ($PPN^+$ = bis(triphenylphosphine)nitrogen(1+)).

$Mn_2(CO)_{10}$ (Aldrich) and $Re_2(CO)_{10}$ (Strem) were used without further purification. $Cp_2Fe_2(CO)_4$ (Aldrich) was recrystallized from CH_2Cl_2/hexane. The anions $NaMn(CO)_5$, $NaRe(CO)_5$, and $NaCpFe(CO)_2$ were generated from the corresponding dimers by Na/Hg reduction in THF and used without isolation. Trifluoromethanesulfonic acid (Aldrich) was distilled under vacuum prior to use.

Infrared spectra were recorded on either a Perkin-Elmer 283 or 399 spectrometer. The solution cells had CaF_2 windows and a 0.1 mm path length. ^{13}C and ^1H NMR spectra were obtained on a JEOL FX-270 spectrometer at 67.80 and 269.65 MHz, respectively.

Preparation of $[PPN][MnCo_2(CO)_9(\mu_3\text{-CCO})]$ (1) from $Mn(CO)_5(CBr_3)$. Freshly prepared $Mn(CO)_5(CBr_3)$ (0.892 g, 1.20 mmol) and $[PPN][Co(CO)_4]$ (2.447 g, 3.45 mmol) were dissolved in 25 mL of dichloromethane at −78 °C. The reaction mixture was warmed to room temperature over 30 min until the solution was dark brown and CO evolution ceased. The solvent was removed in vacuo, and the resulting solid was extracted with four 20-mL portions of hexane to remove the $Mn(CO)_5Br$, which was identified by IR and MS. The remaining solid was extracted into 100 mL of $i\text{-}Pr_2O$, filtered, and layered with 150 mL of pentane. The Et_2O-insoluble residue turned bright blue in an EtOH solution of NH_4SCN, indicating the presence of Co^{2+}.[11] A dark brown crystalline solid formed from the $i\text{-}Pr_2O$/pentane solution. This solid was collected by filtration, washed with 20 mL of pentane, and dried in vacuo; yield 0.537 g (31%) based on Co. The product can also be prepared by an analogous procedure using $Mn(CO)_5(CCl_3)$ instead of $Mn(CO)_5(CBr_3)$ and a reaction time of 3 h at room temperature. IR (Nujol mull): ν_{CO} 2049 (sh), 1996 (s), 1974 (s), 1925 (m), 1885 (sh), 1829 (sh), 1780 (w) cm^{-1}. $^{13}C\{^1H\}$ NMR: δ 214.4 (s, br), terminal CO's; δ 169.3 (s), CCO; δ 73.3 (s, br), CCO; at −90 °C in CD_2Cl_2. Anal. Calcd for $C_{47}H_{30}O_{10}NP_2MnCo_2$: C, 56.25; H, 3.01; N, 1.40; Mn, 5.84; Co, 11.75. Found: C, 55.90; H, 3.29; N, 1.37; Mn, 5.52; Co, 11.55.

Table I. Crystallographic Data for $[PPN][MnCo_2(CO)_9(\mu_3\text{-CCO})]$

formula	$C_{47}H_{30}O_{10}NP_2MnCo_2$
mol wt	1003.51
space group	$P\bar{1}$
a, Å	14.859 (4)
b, Å	9.209 (1)
c, Å	16.701 (3)
α, deg	90.08 (2)
β, deg	102.79 (2)
γ, deg	89.99 (2)
vol, Å^3	2228.64
Z	2
d_{calcd}, g cm^{-1}	1.495
abs coeff (μ), cm^{-1}	11.296
scan speed, deg min^{-1}	4.12
scan range, 2θ, deg	5–55
reflecns measd	$\pm h,\pm k,\pm l$
temp, °C	−90
unique data	10736
data, $I > 3\sigma(I)$	7960
final no. of parameters refined	568

Preparation of 1 from $Co_3(CO)_9CBr$ and $[PPN][Mn(CO)_5]$. A solution of $[PPN][Mn(CO)_5]$ (0.565 g, 0.770 mmol) in 10 mL of dichloromethane was added via syringe to a stirred solution of $Co_3(CO)_9CBr$ (0.135 g, 0.259 mmol) at room temperature. The reaction mixture turned from deep purple to brown within the time of mixing. Dichloromethane was removed in vacuo and the residue extracted with two 20-mL portions of pentane to remove $Mn_2(CO)_{10}$. The remaining residue was extracted with 20 mL of ethyl acetate and filtered to remove insoluble PPNBr and $PPNCo(CO)_4$. After the solvent was removed in vacuo, the residue was extracted with a mixture of 6 mL of diethyl ether and 60 mL of diisopropyl ether and filtered. The solution was reduced to ca. 30 mL in volume and layered with 50 mL of pentane. The brown crystalline 1 that formed by slow diffusion was filtered and dried in vacuo; yield 0.172 g (66%).

Preparation of $MnCo_2(CO)_{10}(\mu_3\text{-CH})$ (2). Trifluoromethanesulfonic acid (25 μL, 0.283 mmol) was added dropwise to a stirring solution of 1 (0.257 g, 0.256 mmol) in 20 mL of CH_2Cl_2 at room temperature. The dark brown solution turned dark green. The solvent was removed in vacuo, and the solid was extracted with two 20-mL portions of hexane. The product was crystallized by slow cooling from hexane as dark green crystals and dried in vacuo; yield 0.034 g (28%). IR (hexane): ν_{CO} 2061 (s), 2050 (vs), 2002 (w), 1978 (m), 1920 (w) cm^{-1}. ^1H NMR: δ 9.39 (s) in CD_2Cl_2. MS: m/e 466 (parent peak), loss of 10 CO's. Anal. Calcd for $C_{11}HO_{10}MnCo_2$: C, 28.35; H, 0.21; Mn, 11.79; Co, 25.30. Found: C, 28.13; H, 0.49; Mn, 11.82; Co, 25.16.

Example of Other Reactions: $CpFe(CO)_2CCl_3$ + $NaCpFe(CO)_2$. A 0.10 M solution of $NaCpFe(CO)_2$ in THF (4.2 mL, 0.42 mmol) was added via syringe to solid, freshly prepared $CpFe(CO)_2(CCl_3)$ (0.125 g, 4.2 mmol). The solution immediately turned deep red, and the infrared spectrum showed the disappearance of the starting materials and the appearance of peaks

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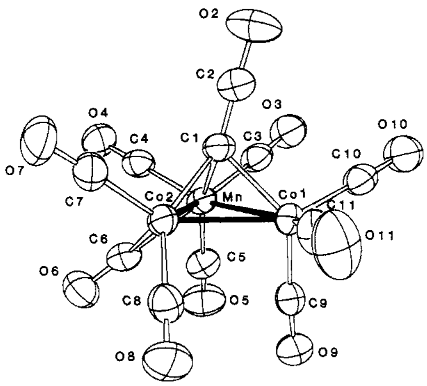

Figure 1. An ORTEP drawing of $MnCo_2(CO)_9(\mu_3\text{-}CCO)^-$ showing the numbering scheme.

consistent with $Cp_2Fe_2(CO)_4$ and $CpFe(CO)_2Cl$. The volatile components were distilled from the reaction mixture in vacuo. GC–MS analysis of the volatile sample showed the presence of CH_2Cl_2. The solid reaction products were extracted with CH_2Cl_2, yielding a red-brown solution and a white solid, which was determined to be NaCl. After removal of the solvent in vacuo, the CH_2Cl_2 extract was analyzed by MS, which confirmed the presence of $Cp_2Fe_2(CO)_4$ and $CpFe(CO)_2Cl$.

X-ray Crystallography of [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$]. An irregularly shaped crystal of dimension 0.57 × 0.33 × 0.33 mm was grown by slow diffusion of hexane into diisopropyl ether and was mounted on a glass fiber. The final unit cell parameters were produced by least-squares refinement of 25 centered reflections. A lack of the appropriate symmetry elements in the axial photographs precluded the assignment of a monoclinic space group. Data were collected on an Enraf-Nonius CAD-4 diffractometer while using Mo Kα radiation with a graphite monochromator. The intensities of six standard reflections were monitored throughout the data collection and showed a 22.1% loss of intensity. Crystallographic data and data collection parameters are summarized in Table I.

All calculations were performed on a Digital Equipment Corp. VAX 11/730 computer by using the Enraf-Nonius SDP-Plus crystallographic computing package and the Molecular Structure Corp. TEXLS full-matrix least-squares program. The structure was solved by direct methods with MULTAN, and subsequent non-hydrogen atoms were located by difference Fourier techniques. No absorption correction was applied to the data. The structure was refined by using full-matrix least-squares techniques. Scattering factors were taken from ref 12. All non-hydrogen atoms were refined anisotropically (Table II). Hydrogen atoms on the phenyl rings were added in calculated positions and were included in the structure factor calculation but were not refined. Least-squares refinement converged with residuals of $R = 0.047$, $R_w = 0.056$. The next highest peak in the difference Fourier map ($\rho = 0.753$ e Å^{-3}) was within 0.978 Å of Co2.

Results and Discussion

Structure of [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$]. The ketenylidene complex **1** consists of discrete anions and cations with no unusually close interion distances. The numbering scheme is shown on the ORTEP diagram in Figure 1. Bond distances and angles are given in Table III.

The metal–metal bond distances in **1** agree closely with those found in the literature for related molecules.[13] The assignments of the metals as Mn or Co were based on the bond lengths between the metals and coordination numbers. The Mn atom has the highest coordination number, due to the single bridging CO. The Co1–Co2 distance represents the shortest metal–metal bond in the cluster (2.480 (1) Å), in agreement with the relative covalent radii of Co and Mn (Co, 1.26 Å; Mn, 1.39 Å).[14] The μ_3-CCO

Table II. Fractional Coordinates of Non-Hydrogen Atoms for [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$][a]

atom	*x*	*y*	*z*
Co1	0.21821 (3)	0.30302 (5)	0.69347 (3)
Co2	0.22062 (3)	0.45233 (6)	0.81764 (3)
Mn	0.30867 (3)	0.55219 (6)	0.71348 (3)
O2	0.4488 (2)	0.1970 (4)	0.8254 (2)
O3	0.4380 (2)	0.4530 (4)	0.6139 (2)
O4	0.4439 (2)	0.7576 (3)	0.8051 (2)
O5	0.2223 (2)	0.7699 (4)	0.5908 (2)
O6	0.1940 (2)	0.7593 (3)	0.7994 (2)
O7	0.2813 (2)	0.4545 (4)	0.9949 (2)
O8	0.0227 (2)	0.4296 (4)	0.8016 (2)
O9	0.0821 (2)	0.4719 (3)	0.5789 (2)
O10	0.3104 (2)	0.1374 (4)	0.5866 (2)
O11	0.1079 (3)	0.0786 (4)	0.7518 (2)
C1	0.3222 (2)	0.3698 (4)	0.7802 (2)
C2	0.3881 (2)	0.2797 (4)	0.8052 (2)
C3	0.3869 (3)	0.4911 (5)	0.6515 (2)
C4	0.3909 (2)	0.6769 (4)	0.7687 (2)
C5	0.2551 (2)	0.6832 (5)	0.6389 (2)
C6	0.2209 (2)	0.6443 (4)	0.7867 (2)
C7	0.2593 (3)	0.4523 (4)	0.9253 (2)
C8	0.1000 (3)	0.4376 (4)	0.8080 (2)
C9	0.1383 (3)	0.4118 (4)	0.6251 (2)
C10	0.2731 (3)	0.2024 (5)	0.6275 (2)
C11	0.1524 (3)	0.1655 (5)	0.7309 (3)
P1	−0.20199 (5)	0.16716 (9)	0.86227 (5)
P2	−0.22896 (5)	0.06694 (9)	0.68915 (5)
N	−0.1948 (2)	0.0704 (3)	0.7859 (2)
C21	−0.2689 (2)	0.0740 (4)	0.9236 (2)
C22	−0.3077 (2)	−0.0601 (4)	0.8964 (2)
C23	−0.3634 (3)	−0.1311 (4)	0.9405 (2)
C24	−0.3802 (3)	−0.0705 (5)	1.0106 (2)
C25	−0.3411 (3)	0.0595 (6)	1.0380 (2)
C26	−0.2854 (3)	0.1328 (5)	0.9952 (2)
C31	−0.2552 (2)	0.3407 (3)	0.8365 (2)
C32	−0.3496 (2)	0.3583 (4)	0.8326 (2)
C33	−0.3933 (2)	0.4860 (4)	0.8023 (2)
C34	−0.3446 (3)	0.5968 (4)	0.7766 (2)
C35	−0.2507 (3)	0.5805 (4)	0.7809 (2)
C36	−0.2060 (2)	0.4534 (4)	0.8106 (2)
C41	−0.0873 (2)	0.1986 (4)	0.9234 (2)
C42	−0.0134 (2)	0.1258 (4)	0.9055 (2)
C43	0.0744 (2)	0.1478 (4)	0.9538 (2)
C44	0.0882 (2)	0.2415 (5)	1.0197 (2)
C45	0.0148 (3)	0.3142 (5)	1.0373 (3)
C46	−0.0732 (3)	0.2940 (5)	0.9893 (3)
C51	−0.3409 (2)	−0.0162 (3)	0.6561 (2)
C52	−0.3594 (2)	−0.1139 (4)	0.5910 (2)
C53	−0.4478 (2)	−0.1711 (4)	0.5643 (2)
C54	−0.5176 (2)	−0.1304 (4)	0.6027 (2)
C55	−0.4995 (2)	−0.0357 (4)	0.6675 (2)
C56	−0.4123 (2)	0.0224 (4)	0.6947 (2)
C61	−0.2348 (2)	0.2414 (3)	0.6405 (2)
C62	−0.1520 (2)	0.3092 (4)	0.6358 (2)
C63	−0.1532 (3)	0.4448 (4)	0.5995 (2)
C64	−0.2354 (3)	0.5124 (4)	0.5686 (2)
C65	−0.3176 (3)	0.4482 (4)	0.5739 (2)
C66	−0.3178 (2)	0.3118 (4)	0.6092 (2)
C71	−0.1478 (2)	−0.0385 (3)	0.6483 (2)
C72	−0.1451 (2)	−0.0249 (4)	0.5654 (2)
C73	−0.0824 (2)	−0.1076 (4)	0.5344 (2)
C74	−0.0231 (2)	−0.2008 (4)	0.5846 (3)
C75	−0.0254 (2)	−0.2146 (4)	0.6655 (3)
C76	−0.0880 (2)	−0.1331 (4)	0.6986 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. See Figure 1 for numbering scheme.

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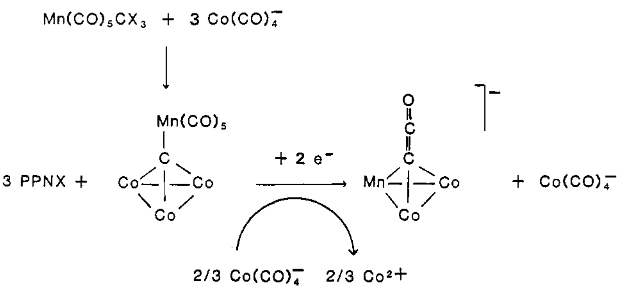
Table III. Selected Bond Distances (Å) and Angles (deg) for $[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)]^a$

Bond Distances			
Co1–Co2	2.480 (1)	Mn–C5	1.791 (3)
Co1–Mn	2.643 (1)	Mn–C6	2.148 (3)
Co2–Mn	2.568 (1)	O2–C2	1.173 (3)
Co1–C1	1.968 (3)	O3–C3	1.144 (4)
Co2–C1	1.914 (3)	O4–C4	1.153 (4)
Mn–C1	2.002 (3)	O5–C5	1.161 (4)
Co1–C9	1.767 (3)	O6–C6	1.168 (4)
Co1–C10	1.770 (3)	O7–C7	1.137 (3)
Co1–C11	1.796 (4)	O8–C8	1.131 (3)
Co2–C6	1.843 (3)	O9–C9	1.146 (3)
Co2–C7	1.762 (3)	O10–C10	1.140 (4)
Co2–C8	1.769 (3)	O11–C11	1.141 (4)
Mn–C3	1.808 (3)	C1–C2	1.281 (4)
Mn–C4	1.778 (3)		

Bond Angles			
Co2–Co1–Mn	60.07 (2)	Co2–C6–O6	142.8 (3)
Co1–Co2–Mn	63.10 (2)	Co2–C7–O7	177.5 (3)
Co1–Mn–Co2	56.82 (1)	Co2–C8–O8	179.3 (3)
O2–C2–C1	177.7 (3)	Mn–C3–O3	178.4 (3)
Co1–C9–O9	174.2 (3)	Mn–C4–O4	179.4 (3)
Co1–C10–O10	178.3 (3)	Mn–C5–O5	178.3 (3)
Co1–C11–O11	177.3 (4)	Mn–C6–O6	137.4 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. See Figure 1 for numbering scheme.

Scheme I



moiety is nearly linear (O2–C2–C1) = 177.7 (3)°) and tilts 14° away from the perpendicular to the plane defined by the metal atoms, in the direction of Co1.

Mechanism of Cluster Building Reaction. The ketenylidene complex 1 forms as the only cluster product in the reaction between $Mn(CO)_5(CX_3)$ and $[PPN][Co(CO)_4]$ (eq 4). Ketenylidene complexes appear to form by

$$\underset{\substack{\textbf{3a}:\ X = Cl\\ \textbf{3b}:\ X = Br}}{Mn(CO)_5(CX_3)} + [PPN][Co(CO)_4] \rightarrow \underset{\textbf{1}}{[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)]} \quad (4)$$

migration of a CO ligand onto an exposed, three-coordinate carbide atom.[15] Assuming the trihalomethyl ligand on Mn is the source of the capping carbon atom in 1, the three halides must be removed from carbon in the course of the reaction. The proposed reaction mechanism appears in Scheme I. The intermediate $Co_3(CO)_9(\mu_3\text{-}C\text{–}Mn(CO)_5)$ is proposed in analogy to the reaction between RCX_3 and $Co(CO)_4^-$, which yields $Co_3(CO)_9(\mu_3\text{-}CR)$.[16] Vahrenkamp and co-workers have demonstrated numerous metal exchange reactions between these $Co_3(\mu_3\text{-}CR)$ clusters and metal fragments so the intramolecular metal exchange reaction proposed in the next step has considerable precedence.[17] Cleavage of the Mn–C bond generates an unsaturated three-coordinate carbide atom, and CO migration onto the carbide produces the ketenylidene complex. The metal-exchange step requires a two-electron reduction to balance the charge. Electron transfer has also been shown to occur in exchange reactions between $ECo_3(CO)_9$-type clusters and $Fe(CO)_4^{2-}$.[17d] The reducing agent is assumed to be $Co(CO)_4^-$, since Co^{2+} is found in the reaction mixture. The provenance of the $Mn(CO)_5X$ that forms in this reaction is uncertain, but it probably forms independently of the main reaction pathway. Homolytic reactions of 3 with organic compounds are known to yield $Mn(CO)_5X$.[2a]

An alternate synthesis of the ketenylidene 1 lends support to the mechanism outlined in Scheme I. The tricobalt cluster $Co_3(CO)_9(\mu_3\text{-}CBr)$ reacts with 3 equiv of $[PPN][Mn(CO)_5]$ to yield the ketneylidene 1 as well as $Mn_2(CO)_{10}$ and $[PPN][Co(CO)_4]$ (eq 5). Displacement of bromide

$$Co_3(CO)_9CBr + 3[PPN][Mn(CO)_5] \rightarrow [PPN][MnCo_2(CO)_9CCO] + Mn_2(CO)_{10} + [PPN][Co(CO)_4] + PPNBr \quad (5)$$

by $Mn(CO)_5^-$ might yield the same intermediate postulated in Scheme I. Again, this intermediate was not observed. Even the addition of 1 equiv of $[PPN][Mn(CO)_5]$ at −78 °C produced the final products and leftover $Co_3(CO)_9(\mu_3\text{-}CBr)$. An in situ ^{13}C NMR experiment in which 1 equiv of $[PPN][Mn(CO)_5]$ was combined with $Co_3(CO)_9(\mu_3\text{-}CBr)$ at −80 °C detected no signals that could be assigned to $Co_3(CO)_9(\mu\text{-}CMn(CO)_5)$. The anion $Mn(CO)_5^-$ acts as the reducing agent in this reaction, as evidenced by the formation of $Mn_2(CO)_{10}$. Since $Mn(CO)_5^-$ is a much stronger reducing agent than $Co(CO)_4^-$, the latter anion does not compete effectively as a reductant.[18]

It is to be emphasized that the proposed mechanism is quite speculative. A reviewer has pointed out that the reactions of $Co(CO)_4^{2-}$ with bromoform and chloroform yields products $(OC)_9Co_3CX$ (X = Cl, Br), that are not expected from a simple nucleophilic displacement. The same reviewer proposes a mechanism based on single electron transfer.

Reaction with H⁺. The ketenylidene complex 1 reacts rapidly with 1 equiv of HSO_3CF_3. Proton attack at the α-carbon atom yields the capping methylidene complex, $MnCo_2(CO)_{10}(\mu_3\text{-}CH)$ (2) (eq 6). This mode of reaction is typical of negatively charged ketenylidene complexes of the first-row transition metals.[19]

$$\underset{\textbf{1}}{[PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)]} + HSO_3CF_3 \rightarrow \underset{\textbf{2}}{MnCo_2(CO)_{10}(\mu_3\text{-}CH)} + PPNSO_3CF_3 \quad (6)$$

NMR Spectroscopy. The ^{13}C NMR spectrum of 1 at −90 °C displays the typical resonances of a ketenylidene complex. The α-carbon and β-carbon peaks occur at +73.3 and +169.3 ppm, respectively, well within the observed range for ketenylidenes.[19,20] The carbonyl ligands on the metal framework are equivalent on the NMR time scale and result in a single peak at +214.4 ppm. The framework CO ligand and the α-carbon atom resonances both appear

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broadened, since these atoms are bonded to quadrupole Mn and Co.

Other Reactions. The cluster-building reaction to form **1** (eq 4) appears to be specific to the cation $\mathrm{PPN^+}$. When $\mathrm{[Et_4N][Co(CO)_4]}$ or $\mathrm{[Ph_4P][Co(CO)_4]}$ are substituted for $\mathrm{[PPN][Co(CO)_4]}$, **1** forms but in extremely low yield. The salt $\mathrm{NaCo(CO)_4}$ reacts with **3** to form $\mathrm{Co_4(CO)_{12}}$ and $\mathrm{Mn(CO)_5X}$, with no yield of **1**. In contrast, the reaction with $\mathrm{Co_3(CO)_9(\mu_3\text{-}CBr)}$ (eq 5) works equally well with $\mathrm{NaMn(CO)_5}$ in tetrahydrofuran. The reaction is also specific to the Mn trihalomethyl reagent. The reaction between $\mathrm{[PPN][Co(CO)_4]}$ and $\mathrm{CpFe(CO)_2(CBr_3)}$ yields $\mathrm{CpFe(CO)_2Br}$ and $\mathrm{Co_3(CO)_9(\mu_3\text{-}CH)}$. The source of the hydrogen atom on the capping CH moiety is unknown.

Other reactions between $\mathrm{M{-}CX_3}$ complexes and mononuclear transition-metal anions met with disappointing results. In every case, the complexes $\mathrm{Mn(CO)_5(CCl_3)}$ (**3a**) and $\mathrm{CpFe(CO)_2(CCl_3)}$ reacted immediately with the sodium salts of the organometallic anions to give oxidation of the anion to the corresponding dimer (eq 7). The

$$\mathrm{M{-}CCl_3 + NaM' \rightarrow M'_2 + \ldots} \qquad (7)$$

$$\mathrm{M' = Mn(CO)_5,\ Re(CO)_5,\ CpFe(CO)_2}$$

remainder of the reaction products were not always identified. However, in the reaction between $\mathrm{CpFe(CO)_2(CCl_3)}$ and $\mathrm{NaCpFe(CO)_2}$ in THF, the reaction mixture contained $\mathrm{Cp_2Fe_2(CO)_4}$, $\mathrm{CpFe(CO)_2Cl}$, NaCl, and $\mathrm{CH_2Cl_2}$. The reactions appear sensitive to cation effects. Although **3a** rapidly oxidizes $\mathrm{NaMn(CO)_5}$ to $\mathrm{Mn_2(CO)_{10}}$, it does not react at all with $\mathrm{[PPN][Mn(CO)_5]}$.

The reaction between $\mathrm{M{-}CCl_3}$ complexes and the cluster dianion $\mathrm{[PPN]_2[Fe_3(CO)_{11}]}$ results in oxidation and degradation of the cluster (eq 8 and 9). A control experiment with $\mathrm{Mn(CO)_5(CF_3)}$ gave no reaction. The hydride complex $\mathrm{CpMo(CO)_3H}$ reacts with $\mathrm{Mn(CO)_5(CCl_3)}$, yielding $\mathrm{CpMo(CO)_3Cl}$.

$$\mathrm{Mn(CO)_5(CCl_3) + [PPN]_2[Fe_3(CO)_{11}] \rightarrow Fe(CO)_5 + Mn_2(CO)_{10} + FeMn(CO)_9^-} \qquad (8)$$

$$\mathrm{CpFe(CO)_2(CCl_3) + [PPN]_2[Fe_3(CO)_{11}] \rightarrow Fe(CO)_5 + Cp_2Fe_2(CO)_4} \qquad (9)$$

The reactions between $\mathrm{M{-}CX_3}$ complexes and mononuclear anions appear to be dominated by electron-transfer processes, which result in oxidation of the anion to the corresponding dimer (eq 10). The potentials for oxidation

$$\mathrm{M^-} \xrightarrow{-2e^-} \mathrm{M_2} \qquad (10)$$

of the anions ($-E_{1/2}$) follow the series $\mathrm{CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_5^- > Co(CO)_4^-}$.[18] The anion that is the most stable toward oxidation, $\mathrm{Co(CO)_4^-}$, was also the only one to successfully cluster-build with $\mathrm{Mn(CO)_5CX_3}$. The reactions of **3a** with $\mathrm{NaMn(CO)_5}$ (oxidation to $\mathrm{Mn_2(CO)_{10}}$) and $\mathrm{[PPN][Mn(CO)_5]}$ (no reaction) demonstrate the influence of $\mathrm{PPN^+}$. Similar electron-transfer processes occur in the reaction of $\mathrm{Co_3(CO)_9(\mu_3\text{-}CBr)}$ with $\mathrm{NaCpFe(CO)_2}$ or $\mathrm{NaRe(CO)_5}$. The anions were oxidized to the corresponding dimers with production of $\mathrm{Co(CO)_4^-}$, but no new cluster products were formed.

Conclusions

A novel route to the formation of a mixed-metal ketenylidene complex **1** has been discovered through use of the trihalomethyl complexes $\mathrm{Mn(CO)_5CX_3}$ (X = Cl, Br) as cluster-building reagents. However, attempts to generalize this method have been unsuccessful, due to the tendency of $\mathrm{M{-}CX_3}$ complexes to oxidize transition-metal carbonyl anions.

Listings of observed and calculated structure factors, positional and anisotropic thermal parameters, and bond distances and angles (106 pages) have been submitted previously and are available through ref 5.

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Registry No. **1**, 103619-62-1; **2**, 103619-63-2; **3a**, 86392-59-8; **3b**, 86392-60-1; $\mathrm{[PPN][Co(CO)_4]}$, 53433-12-8; $\mathrm{[PPN][Mn(CO)_5]}$, 52542-59-3; $\mathrm{Co_3(CO)_9CBr}$, 19439-14-6; $\mathrm{NaCpFe(CO)_2}$, 12152-20-4; $\mathrm{CpFe(CO)_2(CCl_3)}$, 86392-66-7; $\mathrm{Cp_2Fe_2(CO)_4}$, 12154-95-9; $\mathrm{CpFe(CO)_2Cl}$, 12107-04-9; $\mathrm{Re(CO)_5CCl_3}$, 110935-93-8; $\mathrm{NaRe(CO)_5}$, 33634-75-2; $\mathrm{Re_2(CO)_{10}}$, 14285-68-8; $\mathrm{NaMn(CO)_5}$, 13859-41-1; $\mathrm{Mn_2(CO)_{10}}$, 10170-69-1; $\mathrm{[PPN]_2[Fe_3(CO)_{11}]}$, 66039-65-4; $\mathrm{Fe(CO)_5}$, 13463-40-6; $\mathrm{FeMn(CO)_9^-}$, 84143-94-2; $\mathrm{CpMe(CO)_3H}$, 12176-06-6; $\mathrm{CpMo(CO)_3Cl}$, 12128-23-3; $\mathrm{CpFe(CO)_2(CBr_3)}$, 88180-69-2; $\mathrm{CpFe(CO)_2Br}$, 12078-20-5; $\mathrm{Co_3(CO)_9(\mu_3\text{-}CH)}$, 15664-75-2; Mn, 7439-96-5; Co, 7440-48-4.