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The synthesis of heteronuclear transition-metal clusters derived from methylidyne tricobalt cluster precursors: the reaction of $Mn(CO)_5^-$ with (μ_3-CCl)$Co_3(CO)_7$(μ-dppm). The crystal and molecular structure of (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm), a methylidyne cluster containing a seven-coordinate manganese atom*

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The reaction of manganese pentacarbonyl anion with chloromethylidyne tricobaltnonacarbonyl, (μ_3-CCl)$Co_3(CO)_9$, leads to reduction of the cluster with formation of $Mn_2(CO)_{10}$ and $Co(CO)_4^-$, whilst reaction of $Mn(CO)_5^-$ with the bis(diphenylphosphino)methane (dppm)-stabilised cluster (μ_3-CCl)$Co_3(CO)_7$(μ-dppm) leads to the formation of (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm), 1. The unique feature of the structure of 1 is the incorporation of a seven-coordinate manganese atom into the metal triangle.

Keywords: Transition metal, cluster, methylidyne, heteronuclear, cobalt, manganese, carbonyl

INTRODUCTION

Reaction of the metal exchange reagents $Cp_2Mo_2(CO)_6$, $Cp_2W_2(CO)_6$ and $[CpNi(CO)]_2$ (Cp is cyclopentadienyl) with the cluster complexes $RCCo_3(CO)_9$ (R = H, Me, Ph) and $R'GeCo_3(CO)_9$ {R' = t-Bu, Me, Ph and L_nM [L_nM = $CpMo(CO)_3$, $CpW(CO)_3$ $CpFe(CO)_2$ CpNi(CO) and $Co(CO)_4$]} leads to the formation of mixed metal clusters containing the ECo_2M core unit, and by further reaction $ECoMo_2$, ECoMoW, ECoMoNi and ECoMoFe (E = C or Ge) core units[1–4] can be prepared. The transition-metal anions derived from these metal transfer reagents also react with methylidyne tricobalt clusters, to produce heterometallic clusters.[1–4] The facile elimination of $Co(CO)_4^-$ is one of the driving forces for these substitution reactions. These results are in accord with the order of the relative nucleophilicities of these anions,[5] and thus any transition-metal carbonyl anion that is more nucleophilic than $Co(CO)_4^-$ should replace it in the metal triangle.

Recently we have initiated a systematic study of the reactivity of simple transition-metal anions with (μ_3-ClC)$Co_3(CO)_9$, where the presence of the chlorine atom provides a second site for possible substitution, and its phosphine derivatives (μ_3-ClC)$Co_3(CO)_{9-n}L_n$, where the leaving group nucleophilicity is increased by phosphine substitution thus leading to a more stable cluster, and reducing the tendency for the elimination of a $Co(CO)L_3^-$ unit from the metal triangle.

This preliminary report describes the results of our investigation of the reaction of $Mn(CO)_5^-$ (an anion that is more nucleophilic than $Co(CO)_4^-$ but not noted for its cluster-forming reactions) with (μ_3-ClC)$Co_3(CO)_9$ and (μ_3-CCl)$Co_3(CO)_7$-(μ-dppm) [dppm = bis(diphenylphosphino)methane].

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* Supplementary material is deposited with the Cambridge Crystallographic Data Centre, UK.

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Table 1 Selected bond lengths and standard deviations (Å) for $(\mu_3\text{-CH})Co_2Mn(CO)_8(\mu\text{-dppm})$

Co2–Co1	2.527(1)	Mn–Co1	2.616(2)	Mn–Co2	2.561(2)
P1–Co1	2.198(2)	P2–Co2	2.181(2)	C1–Co1	1.793(10)
C1–O1	1.131(10)	C2–Co1	1.772(10)	C2–O2	1.137(9)
C3–Co2	1.739(10)	C3–O3	1.159(10)	C4–Co2	1.802(10)
C4–O4	1.125(10)	C5–Mn	1.818(10)	C5–O5	1.142(10)
C6–Mn	1.821(10)	C6–O6	1.104(10)	C7–Mn	1.814(11)
C7–O7	1.151(11)	C8–Mn	1.833(11)	C8–O8	1.154(10)
CB–Co1	1.842(8)	CB–Co2	1.858(8)	CB–Mn	2.028(8)

RESULTS AND DISCUSSION

Addition of $PPNMn(Co)_5$ (PPN^+ = bis(triphenylphosphine)iminium cation), in tetrahydrofuran, to a solution of $(\mu_3\text{-ClC})Co_3(CO)_9$ in THF leads, over 3 h, to the reduction of the cluster, with the formation of $Mn_2(CO)_{10}$ and $Co(CO)_4^-$ as the only carbonyl-containing products. However, if the cluster is stabilized towards reduction by the replacement of two of the equatorial carbonyls by the bidentate phosphine ligand dppm, then reaction with $Mn(CO)_5^-$ followed by chromatographic work-up [Chromatotron: silica gel, CH_2Cl_2/hexane (20 : 80) eluent] affords the title cluster in good yield.

Spectroscopic data: ν_{co} (CH_2Cl_2), cm^{-1}: 2068 (w–m), 2050 (s), 1998 (vs), 1970 (sh), 1925 (w, br), ^1H NMR ($CDCl_3$), ppm: 12.1 (br), $\underline{H}C$; 7.25 (m) $C_6\underline{H}_5$; 3.71 (br), 2.75 (br) $C\underline{H}_2$. Analysis: manganese, cobalt and phosphorus analyses are satisfactory.

The substitution of the manganese atom into the metal triangle is in contrast to a similar reaction[6] in which reaction of $PPNMn(CO)_5$ with $Co(CO)_4GeCo_3(CO)_9$ leads to the production of $Mn(CO)_5GeCo_3(CO)_9$, i.e. substitution is at the apical group rather than in the metal triangle. No product with manganese incorporated into the triangle was noted in this earlier work.

The methylidyne proton is evidenced by a broad resonance at 12.1 ppm ($CDCl_3$) in the proton NMR. The position of the resonance is identical to that in the related cluster $(\mu_3\text{-HC})Co_2MoCp(CO)_6(\mu\text{-dppm})$ (12.0 ppm). Since the hydrogen-substituted cluster, rather than the chlorine-substituted cluster, is the one that is finally isolated, it is assumed that the substitution takes place during chromatographic work-up. We have noted this exchange previously and are repeating these reactions with non-chromatographic work-up to verify the source of the hydrogen.

Crystals of **1** suitable for X-ray crystallography were obtained from petroleum spirit (60–80°C fraction). The structure of the molecule is shown in Fig. 1. Selected bond lengths (Å), bond angles (°) and fractional coordinates are listed in Tables 1, 2 and 3.

The structure of **1** consists of an unsymmetrical triangle of metal atoms capped by a methylidyne unit; the Co–Co edge of the metal triangle is bridged by the bidentate dppm unit. The most striking feature of the structure is the apparent seven-coordination of the manganese atom. The coordinaton sphere of the manganese atom consists of the two cobalt atoms, four carbonyl ligands and a long interaction to the methylidyne carbon [2.028(8) Å]. The two Mn–Co distances are significantly different at 2.616(2) Å [Mn–Co1] and 2.561(2) Å [Mn–Co2]. This appears to arise as a mechanism to reduce the interaction between the methylidyne unit and the axial carbonyl on manganese on that face of the triangle.

The $Mn(CO)_4$ unit is twisted slightly to take the carbonyl group, C5O5, away from the methylidyne carbon—the distance (CB–C5) is moderately short at 2.269 Å. As a result of this twist the other axial carbonyl, C8O8, is moved into closer proximity to Co1 and its axial carbonyl, C1O1 [C8–Co1 2.725 Å; C8–C1 2.757 Å]. This increased interaction is manifest in the lengthening of the Mn–Co1 distance and a deviation in the Mn–C8–O8 angle from 180° to 167.5°. This is the only carbonyl group to show any marked deviation from linearity.

The Co–Co distance of 2.528(1) Å is longer than the equivalent bond of the related compounds $(\mu_3\text{-CCl})Co_3(CO)_7(\mu\text{-dppm})$[7] and $(\mu_3\text{-CCH}_3)Co_3(CO)_7(\mu\text{-dppm})$[8, 9]—2.492(1) Å and 2.488 Å (averaged over both determinations), respectively—but similar to that in the related cluster $(\mu_3\text{-HC})Co_2MoCp(CO)_6(\mu\text{-dppm})$

Table 2 Selected bond angles and standard deviations (°) for μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm)

Co2-Co1-Mn	59.7(0)	Co2-Co1-P1	95.2(1)	Co2-Co1-C1	102.0(3)
Co2-Co1-C2	149.5(3)	Co2-Co1-CB	47.2(2)	Mn-Co1-P1	144.4(1)
Mn-Co1-C1	112.7(3)	Mn-Co1-C2	93.7(3)	Mn-Co1-CB	50.5(3)
P1-Co1-C1	96.2(3)	P1-Co1-C2	100.4(3)	P1-Co1-CB	94.0(3)
C1-Co1-C2	102.1(4)	C1-Co1-CB	148.4(4)	C2-Co1-CB	105.3(3)
Co1-Co2-Mn	61.9(0)	Co1-Co2-P2	97.2(1)	Co1-Co2-C3	146.8(3)
Co1-Co2-C4	99.9(3)	Co1-Co2-CB	46.6(2)	Mn-Co2-P2	142.3(1)
Mn-Co2-C3	87.2(3)	Mn-Co2-C4	114.1(3)	Mn-Co2-CB	51.7(3)
P2-Co2-C3	101.2(3)	P2-Co2-C4	99.6(3)	P2-Co2-CB	90.8(3)
C3-Co2-C4	104.0(5)	C3-Co2-CB	105.4(4)	C4-Co2-CB	146.2(4)
Co1-Mn-Co2	58.4(0)	Co1-Mn-C5	111.6(3)	Co1-Mn-C6	154.4(3)
Co1-Mn-C7	97.8(3)	Co1-Mn-C8	73.5(3)	Co1-Mn-CB	44.5(2)
Co2-Mn-C5	99.3(3)	Co2-Mn-C6	102.9(3)	Co2-Mn-C7	156.2(3)
Co2-Mn-C8	76.9(3)	Co2-Mn-CB	46.0(2)	C5-Mn-C6	87.2(4)
C5-Mn-C7	90.6(4)	C5-Mn-C8	171.0(4)	C5-MC-CB	72.5(4)
C6-Mn-C7	99.1(5)	C6-Mn-C8	85.7(4)	C6-Mn-CB	136.1(4)
C7-Mn-C8	96.0(4)	C7-Mn-CB	119.1(4)	C8-Mn-CB	109.1(4)
Co1-C1-O1	177.2(9)	Co1-C2-O2	179.7(7)	Co2-C3-O3	179.0(9)
Co2-C4-O4	179.0(10)	Mn-C5-O5	175.7(10)	Mn-C6-O6	179.3(11)
Mn-C7-O7	178.4(9)	Mn-C8-O8	167.3(8)	Co1-CB-Co2	86.2(3)
Co1-CB-Mn	84.9(3)	Co2-CB-Mn	82.3(3)		

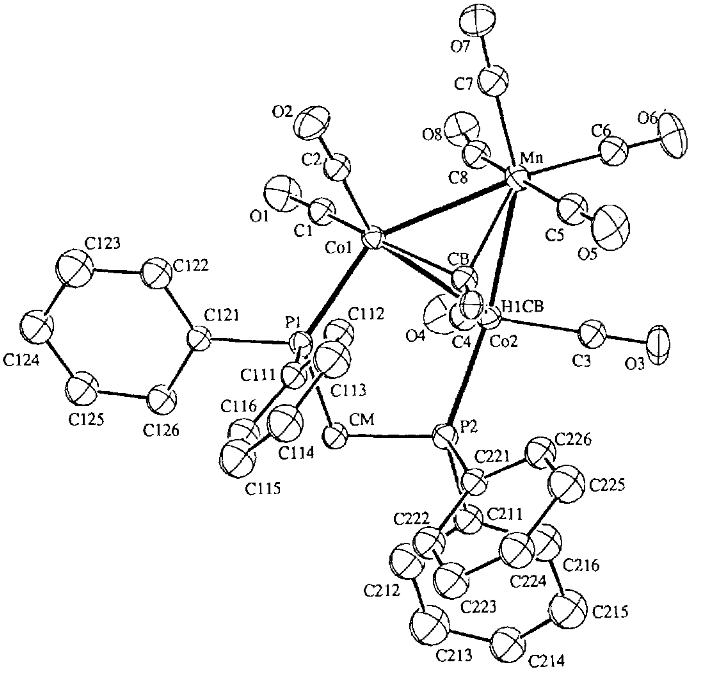

Figure 1 Structure of (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm) showing the numbering scheme employed. Crystal data: $C_{35}H_{23}Co_2MnO_8P_2.C_6H_{12}$, mol.wt 890.43; orthorhombic space group, $P_{2_12_12_1}$; $a = 14.344(3)$ Å, $b = 16.020(3)$ Å, $c = 17.288(3)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 3972(1)$ Å^3 and $Z = 4$; $D_{calc.} = 1.49$ g cm^{-1}; $F(000) = 1816$; λ(Mo-K$_\alpha$) = 0.7107 Å; μ(Mo-K$_\alpha$) = 12.52 cm^{-1}. The structure was solved by direct methods (MULTAN) and refined by least-squares (BLOCKLS and RAELS) with non-hydrogens anisotropic, equivalent phenyl ring bonds constrained to be equal, each hydrogen atom (in a calculated position) with the same thermal parameter as the atom to which it is attached. $R = 3.60\%$ and $R_w = 4.27\%$ for 327 parameters and 2217 observed data [$I > 3\sigma(I)$] from 2922 measured (at 22°C).

Table 3 Fractional coordinates for the non-hydrogen atoms of (μ_3-CH)$Co_2Mn(CO)_8$(μ-dppm)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Co1	0.59682(7)	0.39333(6)	0.01697(6)	C111	0.5900(2)	0.6048(2)	−0.0252(2)
Co2	0.77029(8)	0.36851(7)	0.02834(6)	C112	0.5866(4)	0.5824(3)	−0.1023(2)
Mn	0.67730(9)	0.27675(8)	−0.06526(7)	C113	0.5766(5)	0.6425(4)	−0.1596(3)
P1	0.6031(1)	0.5256(1)	0.0503(1)	C114	0.5701(4)	0.7250(4)	−0.1397(4)
P2	0.8106(2)	0.4977(1)	0.0499(1)	C115	0.5733(5)	0.7485(3)	−0.0637(4)
O1	0.5259(5)	0.3344(5)	0.1658(4)	C116	0.5833(5)	0.6883(2)	−0.0064(3)
O2	0.4278(5)	0.3932(5)	−0.0761(4)	C121	0.5149(3)	0.5589(2)	0.1202(2)
O3	0.9378(5)	0.3052(5)	−0.0446(5)	C122	0.4214(3)	0.5445(4)	0.1067(3)
O4	0.7783(6)	0.3027(6)	0.1862(4)	C123	0.3544(3)	0.5698(4)	0.1597(4)
O5	0.7526(6)	0.3388(5)	−0.2138(4)	C124	0.3810(4)	0.6095(3)	0.2262(3)
O6	0.7997(6)	0.1329(5)	−0.0884(5)	C125	0.4733(4)	0.6244(4)	0.2407(3)
O7	0.5072(6)	0.2143(5)	−0.1436(4)	C126	0.5402(3)	0.5991(3)	0.1876(2)
O8	0.6387(5)	0.1875(4)	0.0818(4)	C211	0.9112(3)	0.5149(2)	0.1132(2)
C1	0.5550(7)	0.3557(6)	0.1083(5)	C212	0.9007(4)	0.5538(4)	0.1839(3)
C2	0.4940(7)	0.3932(6)	−0.0399(5)	C213	0.9770(5)	0.5668(5)	0.2318(3)
C3	0.8705(7)	0.3297(6)	−0.0153(6)	C214	1.0636(5)	0.5409(4)	0.2090(4)
C4	0.7758(7)	0.3285(7)	0.1257(6)	C215	1.0754(3)	0.5022(5)	0.1392(5)
C5	0.7213(8)	0.3174(6)	−0.1564(6)	C216	0.9992(3)	0.4892(4)	0.0912(4)
C6	0.7540(8)	0.1875(6)	−0.0798(6)	C221	0.8421(2)	0.5647(2)	−0.0317(2)
C7	0.5738(7)	0.2374(6)	−0.1133(5)	C222	0.8407(5)	0.6505(2)	−0.0245(3)
C8	0.6518(6)	0.2304(6)	0.0293(6)	C223	0.8646(5)	0.7014(3)	−0.0865(3)
CB	0.6936(5)	0.4017(5)	−0.0526(5)	C224	0.8897(4)	0.6664(4)	−0.1556(3)
CM	0.7128(5)	0.5514(5)	0.0972(5)	C225	0.8914(5)	0.5815(4)	−0.1639(2)
				C226	0.8676(4)	0.5306(3)	−0.1019(2)

[2.523(2) Å] (D. N. Duffy, M. M. Kassis and A. D. Rae, unpublished results).

The Mn–$C_{methylidyne}$ distance of 2.028(8) Å, whilst longer than the Mn–$C_{carbonyl}$ distances, is in the range noted for other Mn–C bonds [2.005(4) Å,[10] 2.131(2)–2.072(2) Å[11]]. The length is very close to that found for the Mo–$C_{methylidyne}$ bond in (μ_3-HC(Co_2MoCp(CO)$_6$(μ-dppm) [2.074(13) Å]. The two Co–$C_{methylidyne}$ distances of 1.839(8) Å [Co1–CB] and 1.857(7) Å [Co2–CB] fall within the range of values found in (μ_3-CCl)$Co_3(CO)_7$(μ-dppm) [1.861(5)–1.856(5) Å] and (μ_3-CCH_3)$Co_3(CO)_7$(μ-dppm) [1.887(5)–1.82(1) Å], but are shorter than the analogous bonds in (μ-HC)Co_2MoCp(CO)$_6$-(μ-dppm) (1.900 Å and 1.923 Å).

The dppm ligand and the carbonyls (except C8O8) show no marked deviations from the expected values and so will not be discussed further here.

The disordered solvent molecule (a cyclohexane—from the petroleum spirit solvent used in recrystallization) was located within the cavity resulting from the packing of the dppm ligands.

Supplementary material includes a full list of interatomic bond lengths and bond angles, the thermal parameters for the non-hydrogen atoms, the atomic and thermal parameters used for the hydrogen atoms, the atomic parameters of the solvent molecule and tables of observed and calculated structure factors.

This work is being extended to other transition-metal carbonyl anions and other phosphine-substituted clusters, the results on which will be published shortly.

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