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The synthesis of heteronuclear transition metal clusters derived from alkylidyne tricobalt cluster precursors

I. The reaction of (μ_3-CCl)Co$_3$(CO)$_9$ with transition metal carbonyl anions. The crystal and molecular structure of (μ_3-CCl)Co$_2$Mo(CO)$_8$(η^5-C$_5$H$_5$)

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Abstract

Metal exchange reactions were used to produce heterometallic clusters derived from alkylidyne tricobalt precursors. Reaction of the cluster (μ_3-CCl)Co$_3$(CO)$_9$ with the potassium salt of (η^5-C$_5$H$_5$)Mo(CO)$_3^-$ produced (μ_3-CH)CoMo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_7$, and (μ_3-CH)Co$_2$Mo(η^5-C$_5$H$_5$)(CO)$_8$ in an overall yield of 35%. The use of the bis(triphenylphosphine)iminium cation as the counterion leads, after work-up, to products with the reactive apical group intact. The structure of (μ_3-CCl)Co$_2$Mo(η^5-C$_5$H$_5$)(CO)$_8$, (1), has been determined. Use of (η^5-C$_5$H$_5$)Cr(CO)$_3^-$ or (η^5-C$_5$H$_5$)W(CO)$_3^-$ also gives substituted products, but in lower yields. The Mn(CO)$_5^-$ anion effects reduction of the starting cluster rather than yielding substituted products.

1. Introduction

In the synthesis of heterometallic transition metal clusters, the alkylidyne tricobalt clusters, RCCo$_3$(CO)$_9$, have proved very versatile. For R = H, alkyl or aryl, substitutions in the cobalt triangle have been effected by:

(i) an addition-elimination sequence using arsenic bridged polynuclear complexes (eqn. (1)) [1]:

$$\mathrm{RCCo_3(CO)_8AsMe_2M(CO)_2Cp} \xrightarrow{-[\mathrm{Co(CO)_3AsMe_2}]_x} \mathrm{RCCo_2M(CO)_8Cp} \quad (1)$$

M = Cr, Mo, W; R = H, CH$_3$, C$_6$H$_5$, p-C$_6$H$_4$CH$_3$, Cp = η^5-C$_5$H$_5$;

(ii) thermolysis of the parent cluster and a suitable binuclear transition metal complex (eqn. (2)) [2];

$$\mathrm{CH_3CCo_3(CO)_9} + \mathrm{L}_n\mathrm{MML}_n \longrightarrow \mathrm{CH_3CCo_2(CO)_5ML}_n \quad (2)$$

ML$_n$ = CpMo(CO)$_3$, CpW(CO)$_3$, CpFe(CO)$_2$ and CpNi;

(iii) electrolytically or chemically induced electron transfer catalysis (eqns. (3) and (4)) [3]:

$$\mathrm{PhCCo_3(CO)_9} + \mathrm{CpMo(CO)_3^-} \xrightarrow{-0.4\mathrm{V}} \mathrm{PhCCo_2MOCp(CO)_8} + \mathrm{Co(CO)_4^-} \quad (3)$$

$$\mathrm{YCCo_3(CO)_9} + \mathrm{CpMo(CO)_3^-} \xrightarrow{\mathrm{BPK}} \mathrm{YCCo_2MCp(CO)_8} + \mathrm{Co(CO)_4^-} \quad (4)$$

BPK = benzophenone ketyl; Y = Me, Ph, H; M = Cr, Mo, W.

At the beginning of our study, very little work had been published on the use of tricobalt clusters containing reactive apical substituents as synthons for mixed metal clusters, despite the range of routes previously used for mixed metal clusters in which the apical substituent was inert, *i.e.* an alkyl or aryl group. The only two reports were those by Chini [4] and Longoni [5].

Chini's synthesis of the carbido clusters Co$_6$(CO)$_{15}$-

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C^{2-} was by the reaction of $(\mu_3\text{-CCl})Co_3(CO)_9$ with $Co(CO)_4^-$ (eqn. (5)) [4].

$$(\mu_3\text{-CCl})Co_3(CO)_9 + Co(CO)_4^- \longrightarrow Co_6(CO)_{15}C^{2-} \tag{5}$$

More recently Longoni obtained condensation products from the reaction of $(\mu_3\text{-CCl})Co_3(CO)_9$ with $Ni_6(CO)_{12}{}^{2-}$ (eqn. (6)) [5].

$$(\mu_3\text{-CCl})Co_3(CO)_9 + Ni_6(CO)_{12}^{2-} \longrightarrow Co_3Ni_9C(CO)_{20}^{3-} + \text{others} \tag{6}$$

The work of Chini and Longoni suggested that a systematic study of the reactivity of halogen-substituted tricobalt clusters with other transition metal carbonyl anions might provide a fruitful area of research. Thus, we initiated a systematic study of the reactions of halogen-substituted alkylidyne tricobalt clusters with various simple transition metal carbonyl anions. Recently, we reported our preliminary findings on the reactivity of the simple transition metal anions, $CpMo(CO)_3^-$, $Mn(CO)_5^-$, with $(\mu_3\text{-CCl})Co_3(CO)_9$ and its phosphine-stabilized derivative $(\mu_3\text{-CCl})Co_3(CO)_7$ dppm [6]. Vahrenkamp recently described the reactions of tricobalt clusters containing reactive apical groups (*i.e.* $SiEt_3$, H, Cl, Br) with $CpM(CO)_3^-$ (M = Mo and W) and Cp_2Ni as well as the new metal exchange reagents $CpMo(CO)_3H$ and $CpMo(CO)_3Cl$ which produce clusters in which one of the cobalts in the triangle has been replaced [7].

We report below our findings on the reaction between $(\mu_3\text{-CCl})Co_3(CO)_9$ and $CpM(CO)_3^-$ (M = Cr, Mo, W) in some detail. Also presented are results of our observations on the reaction of $(\mu_3\text{-ClC})Co_3(CO)_9$ with the transition metal carbonyl anions $Mn(CO)_5^-$, $CpFe(CO)_2^-$, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, and $Fe_3(CO)_{11}^{2-}$.

2. Results and discussion

2.1. Reaction of $(\mu_3\text{-CCl})Co_3(CO)_9$ with $CpM(CO)_3^-$ (M = Cr, Mo, W)

Reaction of the cluster $(\mu_3\text{-CCl})Co_3(CO)_9$ with $CpMo(CO)_3^-$ (1:1 stoichiometry, potassium salt, THF, room temperature) yielded $(\mu_3\text{-CH})Co_2MoCp(CO)_8$ (20%) and $(\mu_3\text{-CH})CoMo_2Cp_2(CO)_7$ (15%) as the two main products. The reaction using the PPN^+ ($PPN^+ = (Ph_3P)_2N^+$) salt of $CpMo(CO)_3^-$, is cleaner, with less minor product formation. The major product isolated was the mono-metal-substituted product with the apical group intact, namely $(\mu_3\text{-CCl})Co_2MoCp(CO)_8$ (40%). It is unclear why the mono- and di-substituted products are obtained from the K^+ salt and only one product from the PPN^+ salt, and also why this result is only observed with molybdenum. In the light of the relatively low yields obtained for the chromium and tungsten reactions, it seems probable that the K^+ plays a role in the reaction and that the mono-substituted product becomes susceptible to attack by a second $CpMo(CO)_3^-$ group. The lower yields in the chromium and tungsten reaction reduces the chance of formation of the more highly substituted products. For the $CpMo(CO)_3^-$ reaction, one of the minor products observed appears to be an ionic cluster, but it is unstable with respect to decomposition to $[CpMo(CO)_3]_2$ and $Co(CO)_4^-$, and has not been fully characterized. An alternative route to substituted metal complexes involves use of trimethyamine oxide (TMAO) to generate a coordinatively unsaturated species by carbonyl abstraction [8]. This route was successfully employed in the present work to give $HCCo_2MoCp(CO)_8$ in very high yield (*ca.* 80%). This yield is comparable to the best yields obtained previously by Vahrenkamp when employing dimethylarsine transfer reagents [1]. The order of reagent addition in the TMAO-assisted reactions affects the product distribution. High yields of the hydrogen-substituted product was obtained when the TMAO was treated with the $(\mu_3\text{-CCl})Co_3(CO)_9$ prior to the addition of $CpMo(CO)_3^-$ (as the PPN^+ salt). When $(\mu_3\text{-CCl})Co_3(CO)_9$ was added to a mixture of TMAO/$CpMo(CO)_3^-$ (these reagents do not react with one another), a mixture of H- and Cl-containing products was obtained in approx. 5:2 ratio (overall yield 72%).

It is also possible, as shown by Vahrenkamp [2], to substitute a second, different metal into the triangle. Thus reaction of $(\mu_3\text{-CCl})Co_2MoCp(CO)_8$ with $NaCpW(CO)_3$ gave $(\mu_3\text{-CH})CoMoWCp_2(CO)_7$ in yields of 20%.

The use of either PPN^+ or Na^+ salts of $CpCr(CO)_3^-$ resulted in low yields (*ca.* 20%) of mono-substituted products. The PPN^+ salt gave $(\mu_3\text{-CCl})Co_2CrCp(CO)_8$, while the Na^+ salt gave $(\mu_3\text{-CH})Co_2CrCp(CO)_8$.

Reaction of solutions of $NaCpW(CO)_3$ with $(\mu_3\text{-CCl})Co_3(CO)_9$ gave $[CpW(CO)_3]_2$ and $Co(CO)_4^-$ as the major products, and $(\mu_3\text{-CH})Co_2WCp(CO)_8$ was isolated in trace amounts. The use of the PPN^+ salt improved the yield of metal-substituted product to 12%, the compound isolated being $(\mu_3\text{-CCl})Co_2WCp(CO)_8$.

In one experiment $(\mu_3\text{-CBr})Co_3(CO)_9$ was treated with $PPNCpMo(CO)_3$. The reaction was sluggish at room temperature and heating (35–40°C, 3 h) was required to drive it to completion. Only moderate yields of $HCCo_2MoCp(CO)_8$ were obtained (27%). The isolation of the H-substituted product in this case probably reflects the more forcing conditions required for reaction since all the PPN^+ reactions with $(\mu_3$-

$CCl)Co_3(CO)_9$ proceed at room temperature, generally with retention of the Cl in the products.

We assume at this stage that the H is derived from adventitious water. A radical species, such as would be associated with an electron transfer catalysed (ETC) mechanism, should yield the same products for both K/Na^+ reactions and the PPN^+ reaction. That this was not the case suggests nucleophilic attack with assisted abstraction of the halide, which is more favourable for KCl and NaCl formation than for PPNCl formation.

An interesting feature of the infrared spectra of the Co_2Mo clusters is the large number of carbonyl bands (Table 1). We have noted that there is a variation between some of the spectra reported here and those reported in the literature for analogous compounds with different R groups in the apical position. The main variation is in the relative intensities of the bands, particularly the two highest bands. We attribute this variation to the presence of isomers in solution. For the Co_2Mo clusters, the cyclopentadienyl group can be on the upper (*i.e.* on the same side of the metal triangle as the apical carbon) or on the lower face. If both isomers exist in solution, a doubling of the number of infrared bands would be expected, as is seen. Consistent with this view of isomers in solution, the solid state spectrum of $(\mu_3\text{-CCl})Co_2MoCp(CO)_8$ shows a much simpler spectrum, only one of the higher bands being observed (2089 s cm^{-1}). The solid state structure $(\mu_3\text{-CCl})Co_2MoCp(CO)_8$ shows the Cp ring on the upper face. The structure of the phenyl derivative shows the Cp ring on the lower face; unfortunately the solid state spectrum of this compound was not reported [1a].

For the Cr analogues, only one band above 2070 cm^{-1} is observed. Presumably the smaller Cr atom introduces enough steric interaction to prevent isomerization in solution. Consistent with this, the larger W analogues also show two high frequency bands in solution whose intensities vary depending on the apical substituent.

2.2. *Reaction of $(\mu_3\text{-}CCl)Co_3(CO)_9$ with other transition metal carbonyl anions; $Mn(CO)_5^-$, $CpFe(CO)_2^-$, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, $Fe_3(CO)_{11}^{2-}$*

When $Mn(CO)_5^-$ (as the PPN^+ salt) was treated with $(\mu_3\text{-CCl})Co_3(CO)_9$, the only carbonyl-containing products obtained were $Mn_2(CO)_{10}$ and $Co(CO)_4^-$. A similar result was obtained when the $CpFe(CO)_2^-$ anion was used. Attempts to correlate the behaviour of the various anions used in this work with yields of substituted products is difficult. The absence of substituted products with $Mn(CO)_5^-$ and $CpFe(CO)_2^-$ presumably relates to the relative tendencies of the anions to reform the parent dimers via electron transfer reactions. For the series $CpM(CO)_3^-$ (M = Cr, Mo, W), chromium complexes are well known to react less cleanly and give lower yields. Molybdenum and tungsten might be expected to give comparable yields. Vahrenkamp found this to be the case when using the dimethylarsine route to these substituted clusters [1]. Presumably the low yields of tungsten products obtained in this work relate to the greater tendency of the $CpW(CO)_3^-$ anion to be oxidized back to the parent dimer. The fact that moderate yields are obtained when the essentially non-ion pairing PPN $^+$ cation is used suggests that the alkali metal cations must be "non-innocent" in those reactions involving the Na^+ or

TABLE 1. Collected spectroscopic and analytical data

$\nu(CO)$ (cm^{-1})	^1H chemical shifts ($CDCl_3$) (ppm)
$(\mu_3\text{-CH})CCo_2Mo(CO)_8(\eta^5C_5H_5)$	
2088m, 2074m, 2062vw, 2050m, 2044s, 2034vs, 2022s, 2002s, 1990m,sh, 1960w, 1940m, 1898m	5.3 (Cp), 11.5 (μ_3-CH)
$(\mu_3\text{-CH})CCoMo_2(CO)_7(\eta^5C_5H_5)_2$	
2042m, 1996s, 1989m, 1920w, 1850w,	5.5, 5.4 (Cp), 11.3 (μ_3-CH)
$(\mu_3\text{-CCl})CCo_2Mo(CO)_8(\eta^5C_5H_5)$	
2092s, 2080m, 2054s, 2042s,sh, 2038vs, 2022s,sh, 2004s, 1962w, 1945m, 1922w, 2089s, 2044vs, 2020m-s,sh, 1997s, 1946s, 1900s	5.5 (Cp)
$(\mu_3\text{-CH})CCo_2Cr(CO)_8(\eta^5C_5H_5)$	
2090m, 2058s,sh, 2046vs, 2038vs, 200s,sh, 200m,sh, 1960m, 1945w, 1915w, 1890w	5.0 (Cp), 13.0 (μ_3-CH)
$(\mu_3\text{-CCl})CCo_2Cr(CO)_8(\eta^5C_5H_5)$	
2092m, 2054s,sh, 2046vs, 2032s, 202m,sh, 1915w, 1860vw, 1780vw	5.0 (Cp)
$(\mu_3\text{-CCl})CCo_2W(CO)_8(\eta^5C_5H_5)$	
2090m, 2080m, 2050s, 2035s, 200s,sh, 2010vs, 1955m, 1945w-m, 1890m-s	5.5 (Cp)
$(\mu_3\text{-CH})CCoMoW(CO)_7(\eta^5C_5H_5)_2$	
2082w, 2078w, 2039s, 200vs, 1984s, 1958s, 1943s, 1898s, 1843s, 1828m	5.4, 5.3 (Cp), 11.9 (μ_3-CH)

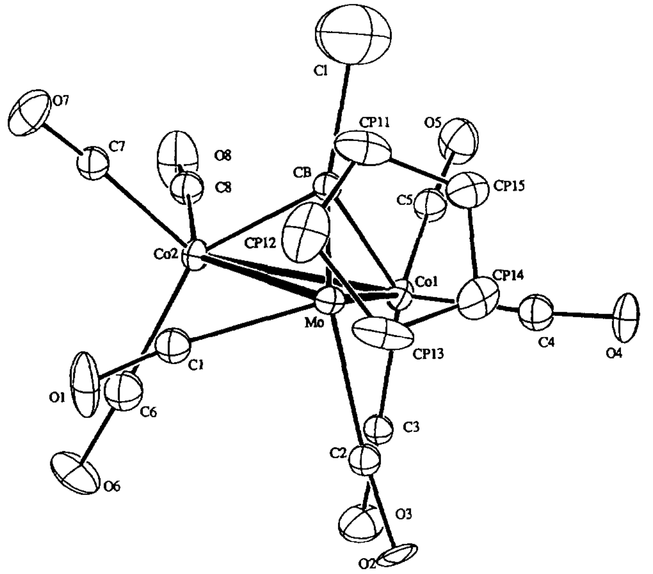

Fig. 1. The molecular structure of (μ_3-CCl)$Co_2Mo(CO)_8Cp$ and the numbering scheme employed.

TABLE 2. Selected bond lengths (Å) and bond angles (°) and e.s.d.s for the non-hydrogen atoms of (μ_3-CCl)$Co_2Mo(CO)_8(\eta^5$-$C_5H_5)$

Bond distances			
Mo1–Co1	2.730(1)	Co1–CB	1.907(6)
Mo1–Co2	2.740(3)	Co2–CB	1.867(6)
Mo1–CB	2.052(7)	Cl–CB	1.755(6)
Co1–Co2	2.503(1)		
Mo1–C_{CO}	1.976 ave	$(C{-}O)_{Co,ax}$	1.127 ave
$(C{-}O)_{Mo}$	1.153 ave	Co–C_{ax}	1.837 ave
$(C{-}O)_{Co,ax}$	1.121 ave	Co–C_{eq}	1.793 ave
C_{CP}–C_{CP}	1.406(14)–1.382(13)		
Mo–C_{CP}	2.346(7)–2.301(7)		
Bond angles			
Co1–CB–Mo1	87.2(2)		
Co_2–CB–Mo1	88.3(2)		
Co1–Mo1–Co2	54.4(1)		
Co1–Co2–Mo1	62.4(1)		
Mo1–Co1–Co2	63.2(1)		
Co2–CB–Co1	82.4(2)		
Cl–CB–Mo1	131.7(3)		
Cl–CB–Co1	126.2(3)		
Cl–CB–Co_2	125.7(3)		
O1–C1–Mo1	171.6(6)		
O2–C2–Mo1	171.0(7)		
O–C–Co	177.4(7)–179.6(7)		
C_{CP}–C_{CP}–C_{CP}	107.3(8)–108.6(8)		

TABLE 3. Fractional coordinates and thermal parameters with e.s.d.s for the non-hydrogen atoms of (μ_3-CCl)$Co_2Mo(CO)_8(\eta^5$-$C_5H_5)$

Atom	x	y	z	$(U_{11}+U_{22}+U_{33})/3$
Mo1	0.2706(1)	0.2763(1)	0.3364(1)	0.035(1)
Co1	0.3331(1)	0.1585(1)	0.1186(1)	0.036(1)
Co2	0.0660(1)	0.2352(1)	0.1798(1)	0.037(1)
Cl	0.2869(2)	0.5059(2)	0.0500(2)	0.101(1)
CB	0.2501(6)	0.3404(6)	0.1498(6)	0.036(3)
CP11	0.2697(12)	0.4481(12)	0.4706(10)	0.095(7)
CP12	0.3675(13)	0.3359(10)	0.5068(8)	0.084(7)
CP13	0.4887(10)	0.3350(9)	0.4085(9)	0.075(6)
CP14	0.4650(10)	0.4450(8)	0.3120(8)	0.066(5)
CP15	0.3310(12)	0.5146(8)	0.3509(9)	0.080(6)
O1	0.3493(8)	−0.0436(6)	0.4303(6)	0.081(4)
O2	−0.0492(7)	0.2236(9)	0.4981(6)	0.094(4)
O3	0.2638(7)	−0.1524(6)	0.1774(6)	0.081(4)
O4	0.6551(6)	0.1673(7)	0.1484(6)	0.068(4)
O5	0.3760(7)	0.2218(7)	−0.1597(5)	0.083(4)
O6	−0.1024(7)	−0.0322(7)	0.3027(6)	0.087(5)
O7	−0.1419(7)	0.4678(7)	0.2385(6)	0.086(4)
O8	0.0110(7)	0.2300(9)	−0.0787(6)	0.102(5)
C1	0.3142(8)	0.0704(7)	0.3892(7)	0.051(4)
C2	0.0648(9)	0.2375(9)	0.4308(7)	0.060(5)
C3	0.2905(8)	−0.0337(8)	0.1562(7)	0.053(4)
C4	0.5255(8)	0.1649(7)	0.1377(7)	0.050(4)
C5	0.3576(8)	0.1961(8)	−0.0527(7)	0.053(4)
C6	−0.0367(8)	0.0678(8)	0.2584(7)	0.056(5)
C7	−0.0639(8)	0.3770(8)	0.2163(6)	0.052(4)
C8	0.0319(8)	0.2622(8)	0.2137(7)	0.058(5)

K^+ salts of the anions, and they facilitate electron transfer reactions which lead to dimer formation and reduction of the parent cluster.

Reaction of (μ_3-CCl)$Co_3(CO)_9$, with the iron containing anions, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, $Fe_3(CO)_{11}^{2-}$, which might be anticipated as the most likely to provide higher nuclearity clusters, proved to be very difficult. There is no doubt that reaction took place in each case; however, the products were unstable and could not be isolated in pure form. This was despite the presence of the bulky PPN^+ cation in most reactions. The formation of $Co(CO)_4^-$ in each case suggests that displacement from the cobalt triangle had occurred; however, the nature of the products is still unknown.

3. Discussion of the structure of (μ_3-CCl)$Co_2Mo(CO)_8Cp$

Crystals of **1** suitable for X-ray crystallography were obtained from CH_2Cl_2/Et_2O. The structure of the molecule is shown in Fig. 1. Selected bond lengths (Å), bond angles (°) and fractional coordinates are listed in Tables 2 and 3.

The structure consists of a molybdenum dicobalt triangle capped by a chloroalkylidyne unit. The structure shows no major variations when compared to that of the phenyl analogue, (μ_3-CPh)$Co_2Mo(CO)_8Cp$ [1a] or the methyl analogue, (μ_3-CH)$CCoMo_2(CO)_7(\eta^5C_5H_5)_2$ [11]. The two molybdenum–cobalt bond lengths are 2.740(3) Å and 2.730(1) Å, in the expected range. The bond lengths and bond angles between the alkylidyne carbon and Mo, Co1 and Co2 are also in the expected range. The Co1–Co2 bond distance, 2.503(1) Å, differs slightly from Co–Co bond lengths in complexes such as $(\mu_3\text{-CH})CCo_2(CO)_9$ and $(\mu_3\text{-CH}_3)CCo_3(CO)_9$ (2.477(6) Å and 2.466(7) Å respectively) [12,13]. This lengthening is due to the capping effect of the bulky cyclopentadienyl molybdenum group. The decrease in the bond angle between Co1–Mo–Co2 to 54.4(1)° and the increase in the Co1–Co2–Mo angles to > 60° also reflects this distortion.

The carbonyls on the cobalt atoms are all as expected, with the $Co\text{–}C_{axial}$ lengths (1.837 Å ave) longer than the $Co\text{–}C_{eq}$ lengths (1.793 Å ave) and a concomitant decrease in the $C\text{–}O_{axial}$ distance (1.121 Å ave) and increase in the $C\text{–}O_{eq}$ distance (1.127 Å ave). The Co–C–O angles are all close to the expected 180° (range 177.4–179.6°). The carbonyls on the molybdenum show the expected distances, but the Mo–C–O angles are slightly reduced, to 171.6° and 171.0°, respectively. This distortion may reflect a slight degree of donor semi-bridging character [14]. The cyclopentadienyl geometry is as expected.

Supplementary data including hydrogen atomic and thermal parameters, all non-hydrogen bond distances and bond angles, non-hydrogen thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. Observed and calculated structure factors are available from the authors.

4. Conclusion

In our hands, the reaction of the alkylidyne tricobalt carbonyl cluster $(\mu_3\text{-CCl})Co_3(CO)_9$ with the metal transfer reagents gives substituted clusters in moderate to good yield. The use of TMAO promotes the reaction, giving yields of 70–80%, which are comparable to the best yields obtained for clusters with inert apical substituents. The nature of the products depends on the counterion used with the metal anion. The alkali metal cations (Na^+ or K^+) give products in which the Cl group ligand has been replaced by an H ligand, possibly from adventitious water. The PPN^+ cation gives products with the chloro group intact. The presence of the H derivative in the PPN^+/TMAO reactions must be attributed to the water co-crystallized in the TMAO reagent.

Use of metal anions with particularly high reduction potentials (*ca.* > 1.7 V) results in oxidation to dimers and reduction of the parent cluster.

Infrared spectroscopy indicates that isomers of the Co_2Mo exist in solution, the isomerism arising from the position of the cyclopentadienyl group with respect to the apical group.

There is evidence for the formation of unstable derivatives (probably ionic) in the $CpMo(CO)_3^-$ reactions. Unstable Fe containing derivatives were also obtained. These unstable products are the subject of further study.

5. Experimental details

All reactions were carried out under dry nitrogen by use of standard Schlenk techniques. Solvents were purified and dried by standard procedures prior to use. ^1H NMR spectra were recorded on a Bruker CXP300 spectrometer. Routine infrared spectra were recorded on a Hitachi 260-10 instrument using NaCl solution cells. Chromatographic separations were carried out on a Harrison Research Model 7924T Chromatatron. The adsorbent was silica gel (PF-254) with $CaSO_4 \cdot 1/2H_2O$. Bands were eluted with the solvent(s) indicated in the text. A modification of the literature method (THF was used as the solvent for the reaction) was used to prepare $(\mu_3\text{-CCl})Co_3(CO)_9$ [15]. $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were used as received from STREM Chemicals. $[CpMo(CO)_3]_2$ was prepared by reaction of CpH with $Mo(CO)_3(CH_3CN)_3$. The metal carbonyl anions were prepared by reduction of the appropriate dimer with sodium/potassium alloy by Ellis's method [16] or by reaction of NaCp with $M(CO)_6$ in the case of Cr and W [17]. The bis(triphenylphosphine)iminium salts were prepared by metathesis reactions with PPNCl (STREM chemicals).

5.1. Reaction of $(\mu_3\text{-CCl})Co_3(CO)_9$ with $KCpMo(CO)_3$

A solution of $(\mu_3\text{-CCl})Co_3(CO)_9$ (1.81 g, 3.80 mmol) in THF (20 ml) was added to one of $KCpMo(CO)_3$ (1.08 g; 3.80 mmol) in THF (10 ml) at room temperature. After 3 h stirring the green/brown solution was filtered and the solvent was removed *in vacuo*. The solid was extracted with hexane (3 × 10 ml). The combined extracts were light green in colour. Chromatographic workup (100% hexane) yielded two products, $(\mu_3\text{-CH})Co_2MoCp(CO)_8$ (0.4 g, 20%) and $(\mu_3\text{-CH})CoMo_2Cp_2(CO)_7$ (0.34 g, 15%) and a portion of unreacted starting cluster. Extraction of the hexane insoluble residue with CH_2Cl_2 yielded $[CpMo(CO)_3]_2$. The remaining residue was extracted with THF to yield a brown solution (ν(CO), THF, 2008s, 1980vs, 1955s, 1910m, 1828m). Slow decomposition of this product prevented further analysis. Elemental anal. Found: C, 32.9; H, 1.3. $(\mu_3\text{-CH})Co_2MoCp(CO)_8$ calc.: C, 32.6; H, 1.2%.

5.2. Reaction of $(\mu_3\text{-CCl})Co_3(CO)_9$ with $PPNCpMo(CO)_3$

A solution of $PPNCpMo(CO)_3$ (1.0 g, 1.3 mmol) in CH_2Cl_2 (15 ml) was added to one of $(\mu_3\text{-CCl})Co_3(CO)_9$ (0.65 g, 1.36 mmol) in THF (10 ml). After 4 h stirring at ambient temperature, the anion had been consumed. Removal of the reaction solvent gave a dark brown solid. Extraction with hexane (2 × 10 ml) gave a green solution which contained two compounds (TLC). This fraction was chromatographed (hexane eluent) to give unreacted (μ_3-CCl)$Co_3(CO)_9$ and (μ_3-CCl)Co_2MoCp-$(CO)_8$ (0.25 g, 40%). The resulting cluster was crystallized from a reduced volume of the hexane solution which was left to stand at −25°C overnight. The remaining solid contained $[CpMo(CO)_3]_2$ and PPN-$Co(CO)_4$ as the major products. Elemental anal. Found: C, 31.2; H, 0.8. (μ_3-CCl)$Co_2MoCp(CO)_8$ calc.: C 30.5; H, 0.9%.

5.3. Reaction of (μ_3-CCl)$Co_3(CO)_9$/$(CH_3)_3NO \cdot 2H_2O$ with PPNCpMo$(CO)_3$

A solution of $(CH_3)_3NO \cdot 2H_2O$ (0.12 g, 1.08 mmol) in freshly distilled CH_3CN (10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.50 g, 1.05 mmol) in CH_3CN (10 ml) and the mixture was stirred at room temperature for 1 h. The completion of the reaction was indicated by the infrared spectrum of the resulting product which was different from the starting material (ν(CO), Nujol, 2058s, 2038m, sh, 1990vs, 1980vs, 1820w). PPNCpMo-$(CO)_3$ (0.50 g, 0.64 mmol) in CH_3CN (20 ml) was added and the resulting mixture left to stir for 10 min. An immediate change in the colour of the solution from a purple/brown to green was observed. The end of the reaction was indicated by the complete consumption of the anion and the solvent was then removed *in vacuo*. The resulting residue was extracted into CH_2Cl_2 (10 ml) and layered with Et_2O (5 ml) to remove the PPN$Co(CO)_4$ formed. After filtration, the remaining solution was layered with hexane (8 ml). This removed $[CpMo(CO)_3]_2$ from the solution. Concentration of the solution gave green crystals of (μ_3-CH)$Co_2MoCp(CO)_8$ (0.27 g, 82%).

5.4. Reaction of (μ_3-CCl)$Co_2MoCp(CO)_8$ with NaCpW$(CO)_3$

A solution of (μ_3-CCl)CoMoCp$(CO)_8$ (0.30 g, 0.55 mmol) in THF (10 ml) was added to one of NaCpW$(CO)_3$ (0.20 g, 0.55 mmol) in THF (10 ml) and the mixture stirred at room temperature for 48 h, after which the anion had been consumed. The resulting mixture was layered with Et_2O (10 ml). This gave a mixture of a pale brown solid and dark red crystals. These were identified as Na$Co(CO)_4$ and $[CpW(CO)_3]_2$. The mixture was filtered and the filtrate was vacuum dried. Extraction with hexane (2 × 5 ml) yielded a dark green solution consisting of two fractions (TLC). Chromatographic workup (CH_2Cl_2 eluent) yielded two green fractions which were identified as the starting cluster, (μ_3-CCl)$Co_2MoCp(CO)_8$ and the disubstituted complex, (μ_3-CCl)CoMoW$Cp_2(CO)_7$. The latter fraction was reduced in volume and allowed to stand at −25°C overnight. This yielded (μ_3-CH)CoMoW$Cp_2(CO)_7$ as a dark green crystalline complex (0.07 g, 19%). Elemental anal. Found: C, 30.6; H, 1.8. (μ_3-CH)CoMo-W$Cp_2(CO)_7$ calc.: C, 30.3; H, 1.4%.

5.5. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with PPNMn$(CO)_5$

A solution of (μ_3-CCl)$Co_3(CO)_9$ (0.12 g, 0.25 mmol) in THF (10 ml) was added to one of PPNMn$(CO)_5$ (0.185 g, 0.25 mmol) in THF/CH_2Cl_2 (10:5 ml). The resulting solution was stirred at room temperature for 30 min, during which the colour changed from purple/brown to red/brown. The solvent was removed *in vacuo*. The resulting residue was extracted with hexane (15 ml) to yield a yellow fraction, identified as $Mn_2(CO)_{10}$. The remaining hexane insoluble solid was extracted with CH_2Cl_2 (10 ml) giving a brown fraction with PPN$Co(CO)_4$ as the only carbonyl containing product.

5.6. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with PPNCpCr$(CO)_3$

A solution of PPNCpCr$(CO)_3$ (0.50 g, 0.68 mmol) in CH_2Cl_2 (10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.32 g, 0.67 mmol) in THF (15 ml). After 2 days stirring at room temperature, the solvent was removed *in vacuo*. The resulting brown/green residue was extracted with hexane (2 × 10 ml) to give a purple solution, mainly consisting of unreacted (μ_3-CCl)$Co_3(CO)_9$. Extraction of the hexane-insoluble solid with CH_2Cl_2 gave a greenish solution from which fine green crystals of (μ_3-CCl)$Co_2CrCp(CO)_9$ (0.07 g, 20%) were isolated. This green fraction also consisted of a trace of (μ_3-CH)$Co_2CrCp(CO)_8$ as indicated by proton NMR. Elemental anal. Found: C, 30.7; H, 1.5. (μ_3-CCl)Co_2 CrCp$(CO)_8$ calc: C, 30.4; H, 1.2%.

5.7. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with NaCpCr$(CO)_3$

A solution of NaCpCr$(CO)_3$ (0.30 g, 1.3 mmol) in THF (5 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.64 g, 1.3 mmol) in THF (15 ml) and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure. Extraction of the residue with hexane (2 × 10 ml) gave a green solution which was reduced in volume and kept at −25°C overnight. (μ_3-CH)$Co_2CrCp(CO)_8$ was obtained as a dark green crystalline solid (0.13 g, 20%). The remaining hexane-insoluble residue was extracted with CH_2Cl_2 (10 ml) to yield a brown solution containing $Co(CO)_4^-$ and a dark brown CH_2Cl_2 insoluble solid (ν(CO), THF, 1990vs, 1890m, 1855w). Elemental anal. Found: C, 35.8; H, 1.8. (μ_3-CH)$Co_2CrCp(CO)_8$ calc.: C, 35.6; H, 1.3%.

5.8. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with NaCpW$(CO)_3$

A solution of NaCpW$(CO)_3$ (0.40 g, 1.1 mmol) in THF (10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.50 g, 1.1 mmol) in THF (10 ml) and the mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum and the resulting brown solid was extracted with hexane (2 × 10 ml). This extract contained (μ_3-CCl)$Co_3(CO)_9$ and a trace of (μ_3-CH)Co_2WCp$(CO)_8$. The hexane-insoluble residue was extracted with CH_2Cl_2 (10 ml). Three products were contained in this extract. Layering with hexane (5 ml) gave a pale brown solid (NaCo$(CO)_4$) and red crystals ($[CpW(CO)_3]_2$). The remaining product decomposed before full characterization could be effected (ν(CO) 1995, 1975, 1855 and 1820 cm^{-1}).

5.9. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with PPNCpW$(CO)_3$

A solution of PPNCpW$(CO)_3$ (0.50 g, 0.57 mmol) in THF/CH_2Cl_2 (10:5 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.30 g, 0.63 mmol) and the mixture was stirred at room temperature for 5 min. The solvent was removed under vacuum and the residue extracted with hexane (15 ml). The resulting solution consisted of unchanged (μ_3-CCl)$Co_3(CO)_9$ and a green product (TLC). Reduction of the volume of the solution and storage at -25°C for several days yielded (μ_3-CCl)Co_2WCp$(CO)_8$ as dark green needles (0.04 g, 12%). The remaining hexane-insoluble solid was extracted with CH_2Cl_2 (20 ml) to give a reddish solution containing $Co(CO)_4^-$ and $[CpW(CO)_3]_2$.

5.10. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with $Na_2Fe(CO)_4$

A solution of $Na_2Fe(CO)_4$ (0.45 g, 2.1 mmol) in THF (10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (1.0 g, 2.1 mmol) in THF (15 ml) and the mixture stirred at room temperature overnight. No change was observed. The temperature was raised to 50°C and stirring continued for a further 4 h. Completion of the reaction was indicated by the absence of $Fe(CO)_4^{2-}$ and formation of $Co(CO)_4^-$. The mixture was layered with Et_2O (10 ml) to remove the NaCo$(CO)_4$ formed. This procedure was repeated several times. Final filtration gave a dark red solution which was shown to be of an anionic nature (ν(CO), THF, 2060w, 2020m, sh, 2004s, 1990vs, 1970s, 1950m, 1810w, 1770w). The solvent was removed *in vacuo*, and the residue redissolved in the minimum amount of CH_2Cl_2 (4 ml) and allowed to stand at -25°C for several days. During this time total decomposition occurred.

5.11. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with $PPN_2Fe_2(CO)_8$

A solution of (μ_3-CCl)$Co_3(CO)_9$ (0.80 g, 1.7 mmol) in THF (10 ml) was added to a slurry of $PPN_2FE_2(CO)_8$ (2.4 g, 1.7 mmol) in THF (20 ml) and the mixture stirred at room temperature for 3 h. The solution turned brown/red. Filtration followed by layering with Et_2O (10 ml) removed the PPNCo$(CO)_4$ formed. The remaining solution was reduced in volume and layered with hexane (10 ml). This yielded a dark brown crystalline product. Analysis proved difficult due to the unstable nature of the complex. (ν(CO), CH_2Cl_2, 2064w, 2052m, sh, 2022m, sh, 2000s, 1990m, sh, 1970w).

5.12. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with $PPN_2Fe_3(CO)_{11}$

A solution of $PPN_2Fe_3(CO)_{11}$ (1.0 g, 0.64 mmol) in CH_2Cl_2/THF (10:10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.30 g, 0.53 mmol) in THF (10 ml). After 3 days stirring at room temperature all the starting cluster had been consumed. The solvent was removed *in vacuo* to give a dark brown residue which was redissolved in CH_2Cl_2 (10 ml). The solution was layered with Et_2O (10 ml) to remove the PPNCo$(CO)_4$. After filtration and removal of the solvent, redissolution in CH_2Cl_2 (10 ml) and layering with hexane (20 ml) gave a dark brown oil which was left to stand at -25°C. Very small crystals were observed but isolation proved to be difficult due to their very air sensitive nature. (ν(CO), CH_2Cl_2, 2080w, 2038vs, 2020s, 1998s, 1990m-s, sh, 1970m, sh, 1855w). Inductively coupled plasma analysis gave a Co/Fe ratio of 1:2.

5.13. Reaction of (μ_3-CCl)$Co_3(CO)_9$ with KCpFe$(CO)_2$

A solution of KCpFe$(CO)_2$ (0.40 g, 1.9 mmol) in THF (10 ml) was added to one of (μ_3-CCl)$Co_3(CO)_9$ (0.88 g, 1.9 mmol) in THF (15 ml) and the mixture was stirred for 10 min. The resulting dark red solution was filtered. Spot TLC (silica gel; CH_2Cl_2/hexane) and infrared spectroscopy indicated three main products; unreacted (μ_2-CCl)$Co_3(CO)_9$, $[CpFe(CO)_2]_2$ and KCo$(CO)_4$.

5.14. Reaction of (μ_3-CBr)$Co_3(CO)_9$ with PPNCpMo$(CO)_3$

A solution of (μ_3-CBr)$Co_3(CO)_9$ (0.30 g, 0.58 mmol) in THF (10 ml) was added to one of PPNCpMo$(CO)_3$ (0.50 g, 0.64 mmol) in THF/CH_2Cl_2 (5:10 ml). After 2 h stirring at room temperature, no significant change had occurred. The mixture was then stirred for 3 h at 35–40°C. The solvent was removed under reduced pressure and the residue extracted with hexane (2 × 10 ml), to give a bright green solution. Volume reduction and storage at -25°C for several days gave (μ_3-CH)Co_2MoCp$(CO)_8$ (0.13 g, 27%). The hexane insoluble solid was extracted with CH_2Cl_2 (15 ml) to yield a brown solution (ν(CO), CH_2Cl_2, 2032s, 2020w, sh, 1938vs, 1890m, 1820m). Layering with Et_2O (10 ml) yielded $[CpMo(CO)_3]_2$, a sandy brown product (non-carbonyl containing) and $Co(CO)_4^-$. Further layering with Et_2O gave mainly $Co(CO)_4^-$ and $[CpMo(CO)_3]_2$. This suggested that the brown solution contained an ionic product which decomposed to $[CpMo(CO)_3]_2$ and $Co(CO)_4^-$.

5.15. *Crystallography*

$(\mu_3\text{-CCl})Co_2Mo(CO)_8(\eta^5\text{-}C_5H_5)$ (**1**) crystallizes as black crystals in the triclinic space group $P\bar{1}$. For **1**, a crystal of maximum dimensions, 0.31 × 0.24 × 0.15 mm^3 was mounted on a quartz fibre and the lattice parameters (at 22°C) were determined and refined with the least squares routine on an Enraf-Nonius CAD4 four circle diffractometer equipped with a graphite monochromator.

Crystal data. **1**, $(\mu_3\text{-CCl})Co_2Mo(CO)_8(\eta^5\text{-}C_5H_5)$; $C_{14}H_5ClCo_2MoO_8$; mol. wt. = 550.43 g mol^{-1}; triclinic space group $P\bar{1}$; $a = 8.949(2)$ Å, $b = 9.393(2)$ Å, $c = 10.813(2)$ Å, $\alpha = 81.14(2)°$, $\beta = 81.01(2)°$, $\gamma = 89.04(2)$, $U = 886.9(4)$ Å^3 and $Z = 2$: $D_{calc} = 1.24$ g cm^{-1}; $F(000) = 532$ electrons; λ (Mo Kα) = 0.7107 Å; μ (Mo Kα) = 27.16.

For **1**, 2856 independent reflections of 3110 unique reflections collected were used. Lorentz, polarization and absorption corrections were applied to all reflections (Gaussian integration method, maximum and minimum transmission factors were 0.69 and 0.54, respectively) using locally written programs. Refinement of **1** utilized BLOCKLS [9]. Scattering factors for neutral atoms were obtained from [10].

The atomic coordinates of the three transition metal atoms were located by Patterson methods. Fourier and difference Fourier methods revealed all non-hydrogen atoms in chemically acceptable positions. All non-hydrogen atoms were refined with anisotropic thermal parameters, with the hydrogen atoms included in calculated positions with hydrogen thermal parameters set to be the same as the atoms to which they are bonded. Refinement converged at $R_1 = 0.044$ and $R_w = 0.044$.

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