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Reactions of dinuclear and polynuclear complexes XIX. Rearrangements of terminal or disubstituted alkyne ligands present in homo- and heterodinuclear complexes of cobalt and molybdenum during reactions with molybdenum and cobalt carbonyl compounds: formation of trinuclear and tetranuclear clusters[1]

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Abstract

The dicobalt alkyne complex $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_6]$ **1a** reacted with $[Mo_2(\eta^5\text{-}C_5H_5)_2CO)_4]$ in refluxing tetrahydrofuran (THF) to give the μ^3-alkylidyne trinuclear cluster $[Co_2Mo(\eta^5\text{-}C_5H_5)(\mu_3\text{-}CCH_2Ph)(CO)_8]$ **3** as the major product. Possible routes to the formation of **3** have been investigated. Among the identified minor products from this reaction were $[CoMo_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CCH_2Ph)(CO)_7]$ **4**, $[Co_2Mo_2(\eta^5\text{-}C_5H_5)_2(\mu_4\text{-}PhC_2H)(\mu\text{-}CO)_4(CO)_4]$ **5** and $[Co_3Mo(\eta^5\text{-}C_5H_5)_2(\mu_4\text{-}PhC_2H)(\mu\text{-}CO)_2(CO)_5]$ **6**. In contrast, when the related dicobalt complexes $[Co_2(\mu\text{-}CF_3C{\equiv}CR)\ (CO)_6]$ ($R = CF_3$ (**1b**), H (**1c**)), which contain alkynes with more strongly electron-withdrawing substituents, were heated with $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ in THF only mixed-dinuclear complexes $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}CF_3C_2R)Co(CO)_3](Mo\text{–}Co)$ ($R = H$ (**7a**), CF_3 (**7b**)) were formed. The reaction of the mixed-dinuclear complex **7b** with $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ led to the mixed-tetranuclear butterfly cluster $[Co_2Mo_2(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)(CO)_3]$ **8**. The thermal reaction of **1b** with the phosphido compound $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}PPh_2)_2]$ gave rise to a single product, $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PPh_2)\{\mu\text{-}PPh_2Co_2(\mu\text{-}CF_3C_2CF_3)(CO)_5\}(CO)_2]$ **9**, in which a phenyl ring of the (μ-phosphido)dimolybdenum moiety is π-bonded to one of the two cobalt atoms. Spectroscopic data for the new complexes are discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Heterotrimetallics; Heterotetrametallics; Cobalt; Molybdenum; Alkylidyne; Alkyne; Phosphido

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1. Introduction

The products of reactions involving alkynes coordinated to polynuclear metal centres are strongly dependent on the nature of the alkyne substituents, as we [1,2] and others [3] have repeatedly shown. The transformations undergone by alkynes in these reactions are usually accompanied by the formation of new M–C, M–H, C–H and C–C bonds and/or by M–C, C–C and C–H bond cleavages [3]. Terminal alkynes undergo rearrangement either into vinylidene ligands by hydrogen migration [4] or into alkylidyne ligands via polynuclear alkenyl intermediates [5]. Multicentered activation of disubstituted alkynes can involve the cleavage of carbon–carbon bonds at a trinuclear ([2]d,[6]), tetranuclear ([2]c,[7]) or higher multi-nuclear [8] metal centre to give alkylidyne ligands. An alternative mode of activation of coordinated disubstituted alkynes leads to expanded metal frameworks through addition reactions ([2]b–d[9]).

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[1] For part XVIII, see [1].

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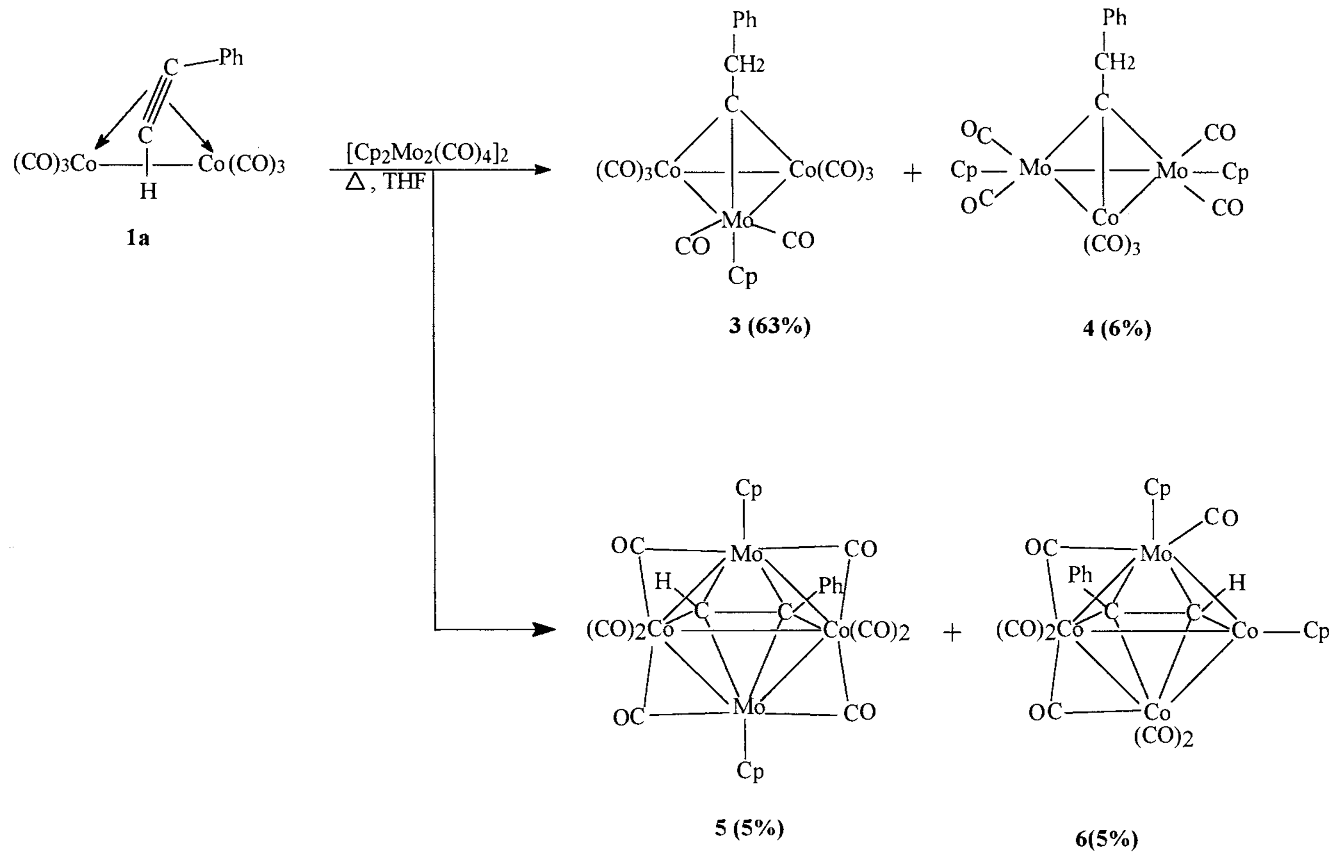


Scheme 1.

The thermal or photochemical activation of such carbonyl compounds as $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[NiCp(CO)]_2$, $[M_2Cp_2(CO)_6]$ and $[M_2Cp_2(CO)_4]$ (M = Mo, W), is an efficient procedure for adding $M(CO)_x$ building blocks to alkyne-bridged clusters, thereby giving product clusters of higher nuclearity. We have examined the reactions of the dicobalt alkyne complexes $[Co_2(\mu\text{-}R^1\text{–}C{\equiv}C\text{–}R^2)(CO)_6]$ **1** with $[Fe_2Cp_2(CO)_4]$ [2c], $[CoCp(CO)_2]$ [2](d) and $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ [2](b), and have noted that the reactivity of **1** depends markedly on the nature of the substituents, R^1 and R^2, of the alkyne, as well as on which carbonyl reagent is used. When disubstituted alkynes are present in **1** the integrity of the alkyne ligand is maintained in the product which is a *closo*-octahedral '$M_2Co_2C_2$' cluster stabilised by a $\mu_4\text{–}\eta^2$ bound alkyne ([2]c,d). In contrast, if **1** contains a terminal alkyne, the reactions give mainly μ_4-vinylidene mixed-metal compounds, together with complexes showing a spiked-triangular metal atom frame ([2]c). However, when the molybdenum bis-thiolato reagent $[Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2]$ is used, only tetranuclear mixed-metal '$M_2Co_2C_2$' butterfly clusters are formed ([2]b). A general conclusion from our previous results is that, irrespective of the reagent and the alkyne, the reaction of $[Co_2(\mu\text{-}R^1\text{–}C{\equiv}C\text{–}R^2)(CO)_6]$ with a carbonyl compound yields a tetranuclear cluster. This accords with the very recent report of Morris et al. ([9]a) on the reaction of the dinuclear μ-alkyne-dimolybdenum compound $[Mo_2Cp_2(\mu\text{-}R^1\text{–}C{\equiv}C\text{–}R^2)(CO)_4]$ with $[Co_2(CO)_8]$. In contrast, by reacting **1** with $[Fe_3(CO)_{12}]$ Vahrenkamp et al. ([4]a) have shown that the expansion of the dinuclear μ-alkyne complex is restricted to the formation of a trimetallic species which is stabilised by a μ_3-vinylidene ligand.

Our long-term aim is to develop versatile and rational methods for the synthesis of heteropolymetallic alkyne clusters. Accordingly, we have extended our study to include the reactions of the dinuclear μ-alkyne complexes $[Co_2(\mu\text{-}R^1\text{–}C{\equiv}C\text{–}R^2)(CO)_6]$ **1** and $[MoCoCp(\mu\text{-}R^1\text{–}C{\equiv}C\text{–}R^2)(CO)_5]$ **2** with a different group of metal carbonyl compounds. The results of this extension we now describe.

2. Results and discussion

2.1. Reaction of $[Co_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_6]$ with $[Mo_2Cp_2(CO)_n]$ ($n = 4, 6$)

Treatment of $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_6]$ **1a** in refluxing tetrahydrofuran with $[Mo_2Cp_2(CO)_4]$ in a 1:1 molar

Table 1
Spectroscopic data for **3**–**8** complexes

Complex	IR (cm^{-1}) υ(CO)[a]	NMR (δ) ^{1}H[b]	^{13}C[b,d]
3	2070; 2028; 2006; 1943	7.35 (m, 5H, Ph); 5.33 (s, 5H, Cp); 5.05 (s, 2H, CH_2)	288.1 (s, $\mathbf{C}CH_2$); 207.3 (br., $\mathbf{C}$O); 143.9, 130.0, 128.4, 126.95 (s, $\mathbf{C}_6H_5$); 90.35 (s, $\mathbf{C}$5H5), 63.25 (s, $\mathbf{C}H_2$) 223.05 (s, Mo($\mathbf{C}$O)$_2$)[c]; 203.5 (s, Co($\mathbf{C}$O)6)[c]; 63.25 (t, $J = 128$[f], $\mathbf{C}H_2$)[e]
4	2035; 1998; 1966; 1912; 1850	7.25 (m, 5H, Ph); 5.20 (s, 10H, Cp); 5.10 (s, 2H, CH_2)	279,4 (s, $\mathbf{C}CH_2$); 228.5 (s br, Mo($\mathbf{C}$O)$_2$); 226.9 (s, Mo($\mathbf{C}$O)$_2$); 206.2 (s br, Co($\mathbf{C}$O)$_3$); 144.15, 130.0, 128.1, 126.9 (s, $\mathbf{C}_6H_5$); 92.5 (s, $\mathbf{C}_5H_5$); 66.35 (s, $\mathbf{C}H_2$) [c]227.6 (s, $\mathbf{C}$O); 225.2 (s, $\mathbf{C}$O); 225.3 (s, $\mathbf{C}$O); 224.45 (s, $\mathbf{C}$O); 222.4 (s, $\mathbf{C}$O); 206.05 (s br, Co($\mathbf{C}$O)$_3$); 93.4 (s, $\mathbf{C}_5H_5$); 91.3 (s, $\mathbf{C}_5H_5$)
6	2038; 2004; 1984; 1837; 1780	8.60 (s, 1H, CH); 7.7–7.3 (m, 5H, Ph); 4.74 (s, 5H, Cp); 4.52 (s, 5H, Cp)	
8[g]	2013; 1971; 1840; 1775	5.43 (s, 5H, Cp); 5.11 (s, 5H, Cp); 4.59 (s, 5H, Cp)	255.6 (s br., $\mathbf{C}$O); 247.4 (s, $\mathbf{C}$O); 200.5 (br,$\mathbf{C}$O); 194.8 (br, $\mathbf{C}$O); 133.5 (q, $J_{CF} = 40$, $\mathbf{C}CF_3$); 133.4 (q, $J_{CF} = 40$, $\mathbf{C}CF_3$); 127.8 (q, $J_{CF} = 276$, $\mathbf{C}F_3$); 127.5 (q, $J_{CF} = 276$, $\mathbf{C}F_3$); 94.15 (s, $\mathbf{C}_5H_5$); 91.5 (s, $\mathbf{C}_5H_5$); 85.8 (s, $\mathbf{C}_5H_5$)

[a] In CH_2Cl_2.

[b] Chemical shifts (δ) in ppm measured in $CDCl_3$ at room temperature unless otherwise stated by c.

[c] In CD_2Cl_2 at 198 K.

[d] Hydrogen^{-1} decoupled unless otherwise stated by e.

[f] J in Hz.

[g] ^{19}F-NMR ($CDCl_3$) : δ-44.45 (q, $J_{FF} = 9$, CF_3), -41.26 (q, $J_{FF} = 9$, CF_3).

ratio afforded the trinuclear metal complex [$Co_2Mo(\mu_3$-$CCH_2Ph)(\eta$-$C_5H_5)(CO)_8$] **3** as the major product (Scheme 1). Careful separation by column chromatography yielded three additional by-products of this reaction: the trinuclear cluster [$CoMo_2(\mu_3$-$CCH_2Ph)(\eta$-$C_5H_5)_2(CO)_7$] **4**, and the tetranuclear compounds [$Co_2Mo_2(\mu$-$PhC_2H)(\eta$-$C_5H_5)_2(\mu$-$CO)_4(CO)_4$] **5** and [$Co_3Mo(\mu$-$PhC_2H)(\eta$-$C_5H_5)_2(\mu$-$CO)_2(CO)_5$] **6**. If **1a** was made to react with [$Mo_2Cp_2(CO)_6$] instead of [$Mo_2Cp_2(CO)_4$], the yields of **3**, **4** and **6** all improved, suggesting that a common path leads to these compounds.

The clusters **3**–**6** were fully characterized by microanalysis, IR, and ^{1}H- and ^{13}C-NMR spectroscopy. The presence of the μ_3-C atom in **3** is clearly indicated by the appearance in the ^{13}C-NMR spectrum (Table 1) of a signal at δ 288.1 ppm [10]. The CO region of the low-temperature (190 K) ^{13}C-NMR spectrum revealed two resonances at δ 223.05 and 212.6 ppm (intensity ratio 1:3). The former signal is in the region typical for a $Mo(CO)_2$ group, the latter is assigned to two $Co(CO)_3$ groups. As the temperature increased the two signals first broadened and then collapsed at about 293 K ($\Delta G^{\neq} = 12.4 \pm 0.3$ kcal mol^{-1}). At room temperature a fluxional process renders the eight exchanging carbonyls groups equivalent on the ^{13}C-NMR time scale. Confirmation of the presence of a benzyl group in **3** was obtained from its ^{1}H- and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum consists of one peak for the Cp ligand, together with appropriate signals for the CH_2Ph group.

The ^{13}C-NMR spectrum of **4** showed a characteristic resonance for a μ_3-C atom at δ 259 ppm and the presence of a benzyl group attached to this carbon atom (Table 1). Useful structural information was obtained by a variable temperature study. At room temperature the CO ligands gave rise to a sharp resonance at δ 226.9 ppm and to broad signals at δ 228.5 and 206.2 ppm. On cooling to 190 K the bands at 228.5 and 226.9 ppm sharpened into two sets of two distinct peaks, as might be expected for two non-equivalent CO ligands of $Mo(CO)_2$ groups [11]. The resonance at δ 206.2 ppm remained broad and is assigned to a $Co(CO)_3$ group. The $M(CO)_3$ fragment [e.g. $Co(CO)_3$] is known to exhibit dynamic behaviour even at very low temperatures, whilst for $M(CO)_2$ groups the fluxional process can be slowed down. Moreover, the sharp resonances at δ 228.5 and 226.9 ppm are in the region typical for a Mo(CO) group. As the sample was warmed the signals at δ 228.5 and 226.9 ppm coalesced at 240 K ($\Delta G^{\neq} = 10.3 \pm 0.3$ kcal mol^{-1}) and 226 K ($\Delta G^{\neq} = 10.3 \pm 0.3$ kcal mol^{-1}), respectively. It is likely that the CO ligands bonded to the molybdenum atoms undergo rapid tripodal rotation involving the Cp ligand. On warming the sample to 373 K a single carbonyl resonance was observed for the four carbonyl groups attached to molybdenum atoms; this suggests that a higher energy fluxional process ($\Delta G^{\neq} = 18.0 \pm 0.3$ kcal mol^{-1}) is operative. The low-energy $\upsilon(CO)$ stretch at 1850 cm^{-1} is consistent with the involvement of these four carbonyl ligands in site exchange via bridge-terminal CO interconversions.

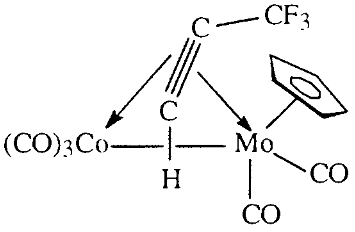
The molecular formula of **5** was tentatively assigned from elemental analysis and by comparison of its spectroscopic data with those for the similar but-2-yne cluster $[Co_2Mo_2Cp_2(\mu_4\text{-}MeC_2Me)(\mu\text{-}CO)_5(CO)_5]$, which we had synthesised a few years ago by reacting $[Mo_2Cp_2(\mu\text{-}MeC_2Me)(CO)_4]$ with $[Co_2(CO)_8]$ and characterised unambiguously by an X-ray diffraction study of the orthorhombic crystals [12]. The but-2-yne complex is a tetrametallic butterfly cluster with a bridging alkyne ligand. The orthorhombic polymorph was first obtained by Schacht and Vahrenkamp [13] as a by-product in the metal-exchange reaction of $[Co_2Mo(\mu^3\text{-}CMe)(CO)_8(\eta\text{-}C_5H_5)]$ with $Na_2[Ru(CO)_4]$. More recently Adams et al. ([9]a) obtained a monoclinic form by heating $[Mo_2Cp_2(\mu\text{-}MeC_2Me)(CO)_4]$ with dicobalt octacarbonyl. The molecules present in the two polymorphic forms do not differ significantly in structure ([9]a[13]). Our results for the orthorhombic form agree with those already published [12,13] and we therefore do not comment further upon them. The close similarity of the ^{13}C-NMR spectra of **5** and $[Mo_2Co_2Cp_2(\mu_4\text{-}MeC_2Me)(\mu\text{-}CO)_4(CO)_4]$ (see Section 3) suggests that the two compounds have identical geometries, with four bridging carbonyl ligands which are indicated by low-field resonances at about δ 246 ppm, and two μ_4-C_2 atoms at about δ 170 and 140 ppm. An alternative synthesis of complex **5** has been described ([9]a), but there is no previous report on its ^{13}C-NMR spectrum.

The ^{1}H-NMR and IR data for **6** are in accord with the butterfly cluster structure shown in Scheme 1. The frequencies of the five absorptions observed in the $\upsilon(CO)$ region of the IR spectrum correspond to the terminal carbonyls attached to cobalt [$\upsilon(CO)$: 2038 and 2004 cm^{-1}], to one terminal carbonyl attached to molybdenum [$\upsilon(CO)$: 1984 cm^{-1}] and to two bridging carbonyl groups [$\upsilon(CO)$: 1837 and 1780 cm^{-1}]. Resonances for CH, Ph and Cp groups are present in the ^{1}H-NMR spectrum: signal integration indicates that these ligands are present in a 1:1:2 ratio. As expected, the ^{1}H-NMR spectrum shows two resonances for the chemically non-equivalent Cp groups. The phenyl and proton resonances of the alkyne ligand agree well those observed for cluster **5**. A similar butterfly cluster with a Co_3MoC_2 core, $[Co_3Mo(\mu_4\text{-}PhC_2H)(\eta^5\text{-}C_5H_4Me)(CO)_9]$, has been obtained by Chetcuti et al. [14] from the reaction of the tetrahedral heterometallic compound $[Co_3Mo(\eta^5\text{-}C_5H_4Me)(CO)_{11}]$ with PhC_2H. No mechanism for the formation of the by-product $[Co_3Mo(\mu_4\text{-}PhC_2H)(\eta^5\text{-}C_5H_5)_2(CO)_7]$ **6** is obvious to us. However, **6** contains a CpCo unit, indicating that the side reaction involves some fragmentation. A possible intermediate in the formation of **6** is the tetrahedral cluster $[Co_3Mo(\eta^5\text{-}C_5H_5)_2(CO)_n]$ which could result from the recombination of carbonyl–cobalt and molybdenum fragments. Indeed, it is well known that the opening of one edge of a tetrahedral cluster on reaction with alkyne is a common route to alkyne-stabilised butterfly clusters [14,15].

The main feature of the reaction of Scheme 1 is the facile formation of the μ_3-alkylidyne mixed-trinuclear complex **3** as the major product. This contrasts sharply with previous results on the reactions of $[Co_2(\mu\text{-}R^1C_2R^2)(CO)_6]$ **1** with various metal carbonyl compounds. As outlined above the products of these reactions depend on the character of the coordinated alkyne in **1** and the nature of the carbonyl reagent. When **1** contains a disubstituted alkyne, $R^1C_2R^2$, all carbonyl reagents of general type $[M(CO)_xL_y]_n$ give rise to *closo*-octahedral '$M_2Co_2C_2$' clusters by condensation of the μ-alkyne-bridged dicobalt derivative with a 'M–M' carbonyl unit. We have synthesised by this route many *closo*-tetrametallic '$M_2Co_2C_2$' clusters: $[Co_2Fe_2(\mu_4\text{-}RC_2R)Cp_2(\mu_3\text{-}CO)_2(CO)_4]$ ($R = CF_3$, CO_2Me), $[Co_2Mo_2(\mu_4\text{-}RC_2R)\ Cp_2(\mu_3\text{-}S)_2(CO)_4]$ ($R = CF_3$) and $[Co_4(\mu\text{-}RC_2R)Cp_2(\mu\text{-}CO)(CO)_4]$ are typical examples ([2]b–d). Morris and co-workers have reported the related preparation of the mixed-metal μ_4–η^2 alkyne species $[Co_2Mo_2(\mu_4\text{-}PhC_2Ph)(\mu_3\text{-}CPh)_2Cp_2(CO)_4]$ by reaction of a dicobalt μ-alkyne complex with a dimolybdenum alkyne complex $[Mo_2(\mu\text{-}PhC_2Ph)Cp_2(CO)_4]$ [16]. In contrast, when a terminal alkyne is present in **1** it rearranges to form a multiply-bridging vinylidene ligand. The metal framework in the product cluster depends on the metal carbonyl reagent: e.g. μ_4-vinylidene mixed-metal compounds with a butterfly skeleton $[Co_3Fe(\mu_4\text{-}C{=}CHR)(\mu\text{-}CO)_2(CO)_7]$ ($R = CF_3$, Ph) are formed from $[Co_2(\mu\text{-}RC_2H)(CO)_6]$ and $[Fe_2Cp_2(CO)_4]$ ([2]c), whereas μ_3-vinylidene mixed trinuclear complexes $[Co_2Fe(\mu_3\text{-}C{=}CHR)(CO)_9]$ ($R = H$, Ph) result from $[Co_2(\mu\text{-}RC_2H)(CO)_6]$ and $[Fe_3(CO)_{12}]$ ([4]a). In the latter case the initial product was the corresponding μ_3-alkyne cluster, which then rearranged to the μ_3-vinylidene on heating. No evidence for the formation of μ_3-vinylidene mixed-trinuclear or μ_4-vinylidene mixed-tetranuclear complexes was obtained in the present work; moreover, given the thermal stability of such species ([2]c[4]a) and the conditions of the reaction it is unlikely that they were formed as intermediates. The formation here of μ_3-alkylidyne compounds by reacting $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_6]$ with the molybdenum carbonyl complex $[Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp]$ contrasts strongly with results for similar reactions and probably arises from the facile fragmentation of $[Cp(CO)_2\text{-}Mo{\equiv}Mo(CO)_2Cp]$ into mononuclear dicarbonylmolybdenum units [17] which then govern the mechanism of the reaction. This is a further illustration of how the metal carbonyl reagent can control the nature of the product.

Furthermore, in an attempt to assess the influence of the substituent R in the coordinated terminal alkyne H–C≡C–R of **1** on the reactivity of the complexes, we have reacted the trifluoromethyl compound $[Co_2(\mu\text{-}CF_3C{\equiv}CH)(CO)_6]$ with $[Mo_2Cp_2(CO)_4]$. No μ_3-perfluoroalkylidyne compound could be isolated by this procedure. Instead, a mixed-metal bimetallic compound **7a** was formed according to the metal-exchange process described by Eq. (1). A related μ-hexafluorobut-2-yne molybdenum–cobalt dinuclear complex $[CoMoCp(\mu\text{-}CF_3C_2CF_3)(CO)_5]$ **7b** has been previously reported [18].

$$[Co_2(\mu\text{-}CF_3C_2H)(CO)_6] + [Mo_2Cp_2(CO)_4]$$
$$\rightarrow [CoMoCp(\mu\text{-}CF_3C_2H)(CO)_6] + 1/2[Mo_2Cp_2(CO)_4]$$
$$+ .... \ \mathbf{7a} \qquad (1)$$



7a

At present it is difficult to propose a definitive mechanism for the formation of **3**, as we have been unable to isolate any intermediates.

The mechanism of μ_3-alkylidyne cluster formation ($\mathbf{1} + \mathbf{2} \rightarrow \mathbf{3}$) involves the transformation of the H–C≡C–Ph ligand in **1** into the alkylidyne ligand 'C–CH_2Ph' in **3**. This transformation requires an additional hydrogen atom and, as the reaction was performed in THF, we propose that this hydrogen atom is abstracted by a preformed radical from the solvent (or residual water). Indeed, it is well known that THF is an excellent hydrogen atom donor [19]. Some support for a radical pathway to the trinuclear cluster **3** is afforded by previous demonstrations of radical involvement in the formation of transition metals clusters [20]. Therefore, we propose addition of hydrogen and mononuclear dicarbonylmolybdenum radicals to a neutral biradical species derived from **1**. The resulting alkenyl intermediate can then be transformed into the μ_3-alkylidyne cluster **3** by concomitant internal hydrogen migration and Mo–Co bond formation. Parallels for such a transformation are readily found in the many known examples of conversion of alkenyl to alkylidyne ligands on di- or tri-nuclear complexes of transition metals [21]. The migration of an acetylenic hydrogen appears to be an essential step in the formation of $[Co_2Mo(\mu\text{-}CCH_2Ph)(CO)_8]$ **3** from $[Co_2(\mu\text{-}R^1C{\equiv}CR^2)(CO)_6]$ **1** since the reaction does not proceed if **1** contains a disubstituted acetylene. An alternative mechanism involving the μ_3-alkylidyne tricobalt complex $[Co_3(\mu_3\text{-}CCH_2Ph)(CO)_9]$ as an intermediate has been considered. $[Co_3(\mu_3\text{-}CCH_2Ph)(CO)_9]$ can be obtained by treatment of **1a** with sulfuric acid in methanol [22] and its subsequent reaction with $CpMo(CO)_2$ fragments could give **3**. However, this mechanism can be ruled out since it requires the yield of **3** to be greater than 100%. The dimolybdenum cluster **4** may result from a metal-exchange between complex **3** and $CpMo(CO)_2$ fragments.

In recent years many mixed-trinuclear μ_3-alkylidyne complexes have been reported and three effective methods for their rational synthesis have been developed: (*a*) Stone and co-workers reacted alkylidyne metal complexes $[M({\equiv}CR)Cp(CO)_2]$ (M = Mo, W) with transition metal (M′) carbonyls (M′ = Co, Fe, Mo) to give trinuclear clusters $[M'_2M(\mu_3\text{-}CR)Cp_x(CO)_n]$ (R = Me, C_6H_4Me-4) [23]; (*b*) Vahrenkamp and co-workers applied the metal-exchange process using homotrinuclear μ_3-alkylidyne compounds and carbonyl reagents to obtain complexes related to **3**, such as $[Co_2Mo(\mu_3\text{-}CR)Cp(CO)_8]$ (R = Me, Ph, CO_2Me, CO_2Ph) [24]; (*c*) Mathieu treated bridged dinuclear vinyl-iron complex anions with metal carbonyls ([5]c). The reaction of $[Co_2(\mu\text{-}PhC{\equiv}CH)(CO)_6]$ with $[Mo_2Cp_2(CO)_4]$ represents a novel fourth route to μ^3-alkylidyne mixed-metal trinuclear clusters. It is based on the ability of $[(CO)_2CpMo{\equiv}MoCp(CO)_2]$ to generate mononuclear dicarbonyl molybdenum radicals, thereby opening a path which favours the formation of a μ_3-benzylidyne ligand.

*2.2. Reaction of $[Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)Co(CO)_3]$ **7b** with $[CoCp(CO)_2]$*

The cobalt–molybdenum alkyne complex **7b** can be conveniently prepared in 55–60% yield by heating $[Co_2(\mu\text{-}CF_3C_2CF_3)(CO)_6]$ with $[Mo_2Cp_2(CO)_4]$ in tetrahydrofuran. It contains a dimetallic MoCo center whose reactivity could be expected to differ from that of the dicobalt center in **1**. With suitable metal carbonyls it is therefore a promising starting material for the production of alkyne clusters of greater nuclearity.

Heating **7b** with two equivalents of $[CoCp(CO)_2]$ under reflux in octane solution caused a reaction which was readily monitored by a change in colour from red orange to dark green over a period of 2 h. The product, the new mixed-tetranuclear compound **8**, was isolated by column chromatography as an air-stable black solid in fairly good yield. The complex **8** was characterized by a combination of elemental analyses, and ^1H and $^{13}C\{1H\}$-NMR spectroscopy (Table 1) which is consistent with the formula [$Co_3MoCp_3(CF_3C_2CF_3)(CO)_4$], **8**. The reaction is described by Eq. (2). It is interesting to note that when **7b** was treated under similar conditions with 1 equivalent of either dicobalt octacarbonyl or [$FeCp(CO)_2]_2$ no reaction was observed over a period of 12 h.

$$\begin{aligned}&[Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)Co(CO)_3] + 2[CoCp(CO)_3]\\ &+ 2[CoCp(CO)_2]\\ &\rightarrow [Co_3MoCp_3(CF_3C_2CF_3)(\mu\text{-}CO)(CO)_3] + 5CO\ \mathbf{7b}\end{aligned} \tag{2}$$

Compound **8** is a Co_3Mo cluster. A structure based on a tetrahedral arrangement of the metal atoms, only three of which interact with the alkyne, is not expected from normal electron-counting procedures. We therefore consider it much more likely that **8** has a structure similar to that of the fully characterized heterotetrametallic butterfly cluster [$Co_2Mo_2Cp_2(\mu_4\text{-}PhC_2H)(\mu\text{-}CO)_4(CO)_4$] **5** ([9]a) with all four metal atoms interacting with the alkyne (Fig. 1). The similarity of the spectroscopic data for **5** and **8** (Table 1, Section 3 and ref. [9]a) reinforces this view.

The IR spectrum of **8** showed υ(CO) bands at frequencies characteristic of terminal, semibridging and bridging carbonyl ligands. Both ^{1}H- and ^{13}C-NMR spectra indicated the presence of three cyclopentadienyl rings; this implies that the one CpCo group is on a wing-tip and the other in a hinge position. We suggest that the molybdenum atom also resides on a wing-tip, the usual position for the unique metal atom in butterfly-type alkyne clusters with M_3M' metallic cores ([14,15]a). At room temperature the ^{13}C-NMR spectrum of **8** revealed a four-line pattern in the carbonyl region. The observation of broad resonances at 255.6, 200.5 and 194.8 ppm was indicative of carbonyl ligands bonded to cobalt. The peak at lowest field was assigned to the CO bridging the Mo–Co edge and the others were assigned to terminal CO ligands bonded to Co. A further sharp resonance at 247.4 ppm was ascribed to the Mo-bonded carbonyl which may weakly semibridge to Co.

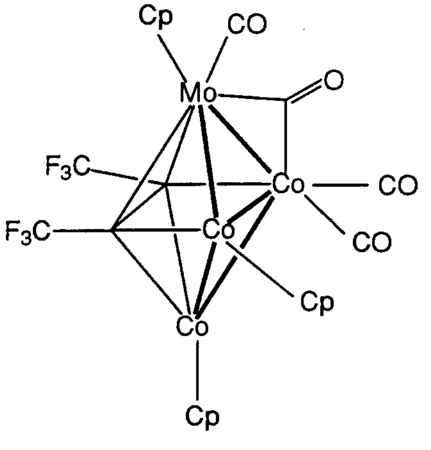


Fig. 1. Structure of complex 8.

Compound **8** can be viewed as a 60-electron, seven skeletal electron-pair Co_3MoC_2 *closo*-octahedron, according to Wade-Mingos theory [25]. Complexes of this type are known and it is interesting to compare the synthesis of **8** with that of the related butterfly-type alkyne clusters with M_3M' metallic cores. The first complexes with this arrangement were the isomeric clusters [$Ru_3Fe(\mu_4\text{-}R^1C_2R^2)(CO)_{12}$] ($R^1 = R^2 =$ Ph, Me; $R^1 =$ Ph, $R^2 =$ Me) that were formed from the reaction of alkynes $R^1C{\equiv}CR^2$ with the tetrahedral compound [$Ru_3Fe(\mu\text{-}H)_2(CO)_{13}$] by inserting the alkyne into a Ru–Ru bond; the single iron atom was either in the hinge position or on a wing-tip ([15]a). More recently Chetcuti and co-workers have reported the synthesis of the mixed-tetranuclear complex [$Co_3M'Cp'(\mu_4\text{-}PhC_2H)(\mu\text{-}CO)_2(CO)_7$] ($M' =$ Mo, W; $Cp' = C_5H_4Me$) by a similar procedure [14]. Another synthetic route to butterfly-type alkyne M_3M' clusters uses thermal or photochemical activation of suitable metal (M')-carbonyl reagents, e.g. [$M'Cp'(CO)_2$] ($M' =$ Rh, Co; $Cp' = C_5H_5$, C_5Me_5), for the expansion of trinuclear compounds, e.g. either alkyne-bridged trinuclear (M) clusters or trinuclear bis(μ_3-alkylidyne) complexes, to the corresponding tetranuclear cluster [$Fe_3RhCp(\mu_4\text{-}MeC_2Me)(CO)_9$] [26] or [$Fe_3CoCp'(\mu\text{-}FC_2F)(CO)_9$] ($Cp' = C_5Me_5$) [27] containing [M'] building blocks. The formation of **8** from the reaction of [$CoCp(CO)_2$] with a dinuclear μ-alkyne compound is therefore unprecedented. It is significant that a regiospecific cluster product was obtained here and that no isomers were detected in solution by NMR.

2.3. Reaction of [$Co_2(\mu\text{-}CF_3C_2CF_3)(CO)_6$] **1b** with [$Mo_2Cp_2(\mu\text{-}CO)(\mu\text{-}PPh_2)_2$]

As we have already noted, the reactivity of dicobalt alkyne complexes [$Co_2(\mu\text{-}R^1C_2R^2)(CO)_6$] **1** depends greatly on the substituents of the alkyne, as well as on the carbonyl reagents. We have previously shown that **1** reacts with the Mo=Mo thiolato complex [$Mo_2Cp_2(\mu\text{-}SMe)_2(CO)_2$] to give *closo*-octahedral [$Co_2Mo_2Cp_2(\mu_4\text{-}R^1C_2R^2)(\mu_3\text{-}S)_2(CO)_4$] ($R^1 = R^2 = CF_3$; $R^1 =$ Ph, CF_3 and $R^2 =$ H; $R^1 = CF_3$, Ph and $R^2 =$ Me) ([2]b). We now consider whether the reactions of **1** with a dimolybdenum carbonyl complex containing a multiple Mo–Mo bond and a different bridging ligand parallel those of the Mo=Mo thiolato compound. For this study we chose the phosphino compound [$Mo_2Cp_2(\mu\text{-}CO)(\mu\text{-}PPh_2)_2$] (Mo≡Mo) previously reported by Mays [28].

Reaction between an excess of the dicobalt alkyne complex **1b** with the dimolybdenum compound [$Mo_2Cp_2(\mu\text{-}CO)(\mu\text{-}PPh_2)_2$] under reflux in octane solution was judged complete after 2 h from monitoring by

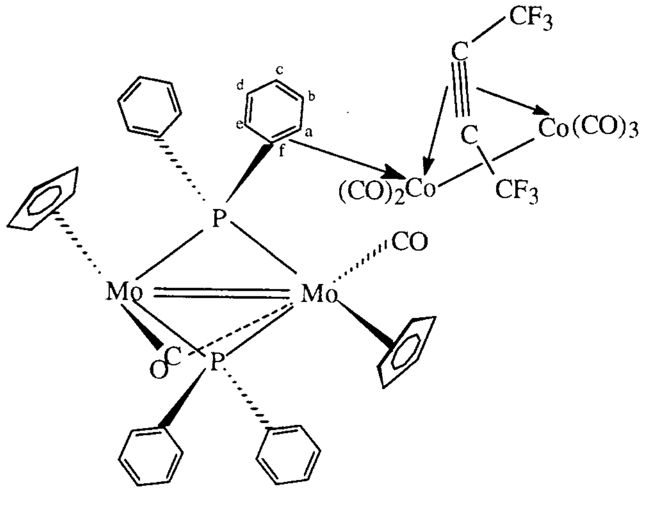
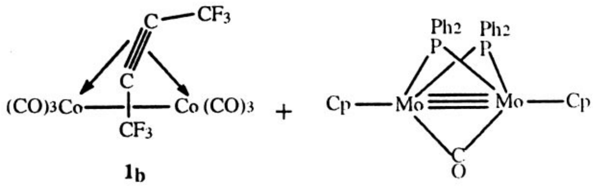


Fig. 2. Structure of complex 9.

^{19}F-NMR spectroscopy. The new product, the tetranuclear complex [Mo$_2$Cp$_2$(μ-PPh$_2$) {μ-PPh$_2$Co$_2$(μ-CF$_3$C$_2$CF$_3$)(CO)$_5$}(CO)$_2$] **9** was isolated as an air-stable red brown solid in moderate yield (Eq. (3)). In addition, two compounds formed in appreciable yields were identified by IR and ^{1}H-NMR spectroscopy as the previously characterized species [Cp(CO)Mo(μ-PPh$_2$)$_2$Mo(CO)Cp] (Mo=Mo) and [Cp(CO)Mo(μ-PPh$_2$)$_2$ Mo(O)Cp] (Mo=Mo) [28].



1b

$\longrightarrow$ [Mo$_2$Cp$_2$(μ-PPh$_2$){μPPH$_2$Co$_2$(μ-CF$_3$C$_2$CF$_3$)(CO)$_5$}(CO)$_2$] + ··· (3)

9

The characterization of the new tetranuclear complex **9** was accomplished by a combination of elemental analysis, mass spectrometry, and IR and NMR (^{1}H, ^{31}P, ^{19}F and ^{13}C) spectroscopy. The proposed structure for **9** is shown in Fig. 2.

Analysis of **9** indicated that cobalt and molybdenum were present. Although the molecular ion peak (M$^+$) was not detected, the FAB mass spectrum was otherwise very informative regarding the formulation of **9**. The heating curve showed clearly that **9** decomposed into two fragments. The first fragment gave in the mass spectrum a peak at m/z 420, with successive loss of five carbonyl groups, that corresponds to [Co$_2$(CF$_3$C$_2$CF$_3$)(CO)$_5$]. The second appeared at m/z 326 and corresponds to [MoCp(PPh$_2$)]. The observed mass pattern is therefore in accord with **9** having the assigned structure.

IR υ(CO) bands were observed in the IR spectrum of **9** in regions characteristic of both terminal and semibridging ligands. The observation of some high-energy υ(CO) stretches implied that cobalt was present, a conclusion confirmed by the marked similarity of the high-energy υ(CO) region of **9** with those of various dicobalt complexes [L(CO)$_2$Co(μ-R^{1}C$_2$R^2) Co(CO)$_3$] [29]. The low energy υ(CO) pattern of **9** [υ(CO) at 1890 and 1845 cm^{-1}] strongly resembled that of the dinuclear complex [Cp(CO)Mo(μ-PPh$_2$)$_2$Mo(CO)Cp] (Mo=Mo) [28]. The IR thus strongly indicated that Co$_2$(CF$_3$C$_2$CF$_5$)(CO)$_5$ and Mo$_2$Cp$_2$(PPh$_2$)$_2$(CO)$_2$ fragments are present in **9**. Since the ^{19}F-NMR spectrum of **9** displayed only one signal, with a chemical shift close to that of the starting complex **1b**, there is little doubt that the two CF$_3$ groups are ligated to bridging alkyne carbon atoms as in **1b**.

Multiplets in the phenyl region of the ^{1}H-NMR spectrum (Table 2) were observed, and two sharp singlets due to inequivalent cyclopentadienyl ligands were also noted. Signal integration revealed that the phenyl and cyclopendadienyl groups were in a 3:2 ratio. Furthermore, to a first approximation five signals appeared in the olefinic region of the spectrum; each was a doublet of doublets ($J_{\mathrm{H-H}} \approx J_{\mathrm{P-H}}$) and integrated to a single proton; they were assigned to Ha–He protons and were highfield relative to usual phenyl protons. These data suggest that one phenyl ring is π-bonded to a cobalt atom. This proposal was subsequently confirmed from the ^{13}C{^{1}H}-NMR spectrum at 293 K by the shift to higher field of five carbon atoms of one phenyl group relative to usual phenyl carbons. Selective proton decoupling experiments were performed at 293 K and showed that both Ha and He protons were correlated with only one hydrogen atom and with one phosphorus atom ($^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}}$ ca. 7 Hz), whereas Hb, Hc and Hd protons were each of them correlated to two hydrogen atoms ($^3J_{\mathrm{H-H}} = 6$–7 Hz). This coupling pattern for the ring protons of one phenyl group was confirmed by a 2D-COSY NMR experiment (see Fig. 3). ^{1}H–^{13}C 2D HETCOR experiments, optimized for $J_{\mathrm{C-H}} = 2$ and 7 Hz have been performed and the results of one of them ($J_{\mathrm{C-H}} = 7$ Hz, 298 K) are reported in Fig. 4. At this temperature the 1D ^{13}C spectrum showed between 90 and 110 ppm one signal appearing as a singlet, and the other four resonances appearing as doublets (Table 2). The common correlations allowed assignment of the resonances a, b, c, d and e to the carbon atoms bound to Ha, Hb, Hc, Hd and He, respectively. More detailed ^{13}C-NMR analysis help to confirm the structure of **9** by revealing the presence of Mo(CO) and Co(CO) groups. The ^{13}C{^{1}H}-NMR spectrum showed two sharp downfield resonances (δ 235.2, 233.7) assigned to the Mo–CO groups on the basis of a lack of quadrupole broadening. The remaining higher field ^{13}CO resonance (δ 195.5) was

Table 2
NMR (δ) data for **9**

^{1}H^{a,b}	^{13}C{^{1}H}^{a,b}	^{31}P{^{1}H}^{a,b}	^{19}F^a
8.0 (dd, $J_1 = 11$, $J_2 = 7.3$, 2H, Ph)	235.2 (t, $J_{P-C} = 13$, **C**O)	98.9 (d, $J_{P-P} = 9$)	-50.84 (m,)
7.1–7.6 (m, 13H, Ph)	233.7 (t, $J_{P-C} = 13$, **C**O)	91.9 (d, $J_{P-P} = 9$)	
6.51(dd, $J_{H-H} \approx J_{P-H} = 6.5$, 1H, He)	195.5 (s(br), **C**O)		
6.19(dd, $J_{H-H} \approx J_{H-H} = 6.5$, 1H, Hc)	145.3 (d, $J_{P-C} = 5.0$, **C**_ipso_)		
6.10(dd, $J_{H-H} \approx J_{H-H} = 6.5$, 1H, Hb)	144.9 (d, $J_{P-C} = 5.0$ **C**_ipso_)		
5.96(dd, $J_{H-H} \approx J_{H-H} = 6.5$, 1H, Hd)	134.3 (d, $J_{P-C} = 5.0$ **C**_ipso_)		
5.76(dd, $J_{H-H} \approx J_{P-H} = 6.5$, 1H, Ha)	127.6–139.8 (Ph)		
5.40(s, 5H, Cp)	126.7 (q, $J_{C-F} = 277$, **C**F$_3$)		
5.26 (s, 5H,Cp)	125.2 ($J_{P-C} = 15.5$, **C**f)		
	95.5 (d, $J_{P-C} = 8.5$, **C**e)		
	94.0 (d, $J_{P-C} = 15.5$, **C**a)		
	93.7 (s, Cc)		
	92.1 (d, $J_{P-C} = 9.0$, **C**b)		
	91.4 (d, $J_{P-C} = 6.5$, **C**d)		
	89.5 (s, C_5H_5)		
	89.0 (s, C_5H_5)		
	70.2 (q, $J_{C-F} = 35$, **C**–CF$_3$)		

[a] Chemical shifts (δ) in ppm measured in $CDCl_3$ at room temperature.
[b] J in Hz.

^{59}Co quadrupole broadened and was assigned to the two Co–CO groups.

Complex **9** is derived structurally from [(CO)$_3$Co(μ-CF$_3$C$_2$CF$_3$)Co(Co)$_3$] (Co–Co) **1b** by the replacement of a carbonyl ligand by a [Mo$_2$Cp$_2$(μ-PPh$_2$)$_2$(CO)$_2$] moiety which bonds to the Co atom through a phenyl C=C double bond. The dimolybdenum species [Mo$_2$Cp$_2$(μ-PPh$_2$)$_2$(CO)$_2$] (Mo=Mo) was readily formed from the carbonylation of the bridged-carbonyl reagent [Mo$_2$Cp$_2$(μ-CO)(μ-PPh$_2$)$_2$] (Mo≡Mo) [28]. Surprisingly, the direct reaction of [Mo$_2$Cp$_2$(μ-PPh$_2$)$_2$(CO)$_2$] (Mo(Mo) with **1b** did not give complex **9**. Displacement of CO at a cobalt atom in [(CO)$_3$Co(μ-R^{1}C$_2$R^2)Co(CO)$_3$](Co–Co) by a sulfur atom has been observed [30], but to the best of our knowledge such a displacement by a phenyl group is without precedent.

3. Experimental procedures

3.1. General procedures

All experiments were carried out under an inert argon atmosphere using Schlenk techniques. Solvents were freshly distilled from either sodium benzophenone or calcium hydride prior to use. Literature methods were used for the preparation of [Co$_2$(μ-R^{1}C$_2$R^2)(CO)$_6$] ($R^1 = R^2 = CF_3$; R^1 = Ph, CF$_3$ and R^2 = H) [31], [Mo$_2$Cp$_2$ (CO)$_6$] [32], [Mo$_2$Cp$_2$(CO)$_4$] [33] and [Mo$_2$Cp$_2$(μ-CO)(μ-PPh$_2$)$_6$] [28]. All other reagents were commercial grade and were used as obtained. Yields are either with respect to the starting complex **1** for the preparation of **3**, **4**, **5**, **6** and **7** or with respect to compound **7b** and [Mo$_2$Cp$_2$(CO)(PPh$_2$)$_2$] for the synthesis of **8** and **9**, respectively.

IR spectra were obtained with a Perkin–Elmer 1430 spectrophotometer in dichloromethane solutions in the υ(CO)region. The mass spectra were measured on a GC/MS Hewlett Packard 5595C. NMR spectra (^{1}H, ^{31}P, ^{19}F, ^{13}C) in CDCl$_3$ solution were recorded on a Jeol FX100 or a Brucker AC 300 and were referenced to Me$_4$Si, H$_3$(PO$_4$), CFCl$_3$ and Me$_4$Si, respectively. Chemical analyses were performed either by the 'Oceanographie Chimique' Laboratory or by the 'Spectroscopie Atomique' Laboratory at the University of Brest.

3.2. Reaction of the dicobalt complex [Co$_2$(μ-PhC$_2$H)(CO)$_6$] (**1a**) with [Mo$_2$Cp$_2$(CO)$_n$] ($n = 4, 6$)

1. In a typical procedure, a solution of **1a** (388 mg, 1 mmol) and 1 equivalent of [Mo$_2$Cp$_2$(CO)$_4$] in THF (30 ml) was heated under reflux for *ca* 12 h. The solution was then pumped to dryness, and the resulting solid was dissolved in a hexane/CH$_2$Cl$_2$ (ca. 9:1), and subjected to silica gel chromatography. Elution with hexane/CH$_2$Cl$_2$ (4:1) afforded two main bands (dark green and green, respectively) which were identified as **3** (328 mg, 63%) and **4** (40 mg, 6%), respectively. Further elution with hexane/CH$_2$Cl$_2$ (1.5:1) gave two bands (dark blue and red brown, respectively) yielding **5** (38 mg, 5%) and **6** (23 mg, 5%), respectively.
2. In a similar manner to (1) above, reaction of **1a** (388 mg, 1 mmol) with 1 equivalent of [Mo$_2$Cp$_2$(CO)$_6$] was conducted in refluxing THF for 22 h. After this solvent was removed in vacuo. Chromatography as in (1) afforded **3** (376 mg, 62%), **4** (53 mg, 8%) and **6** (23 mg, 5%).

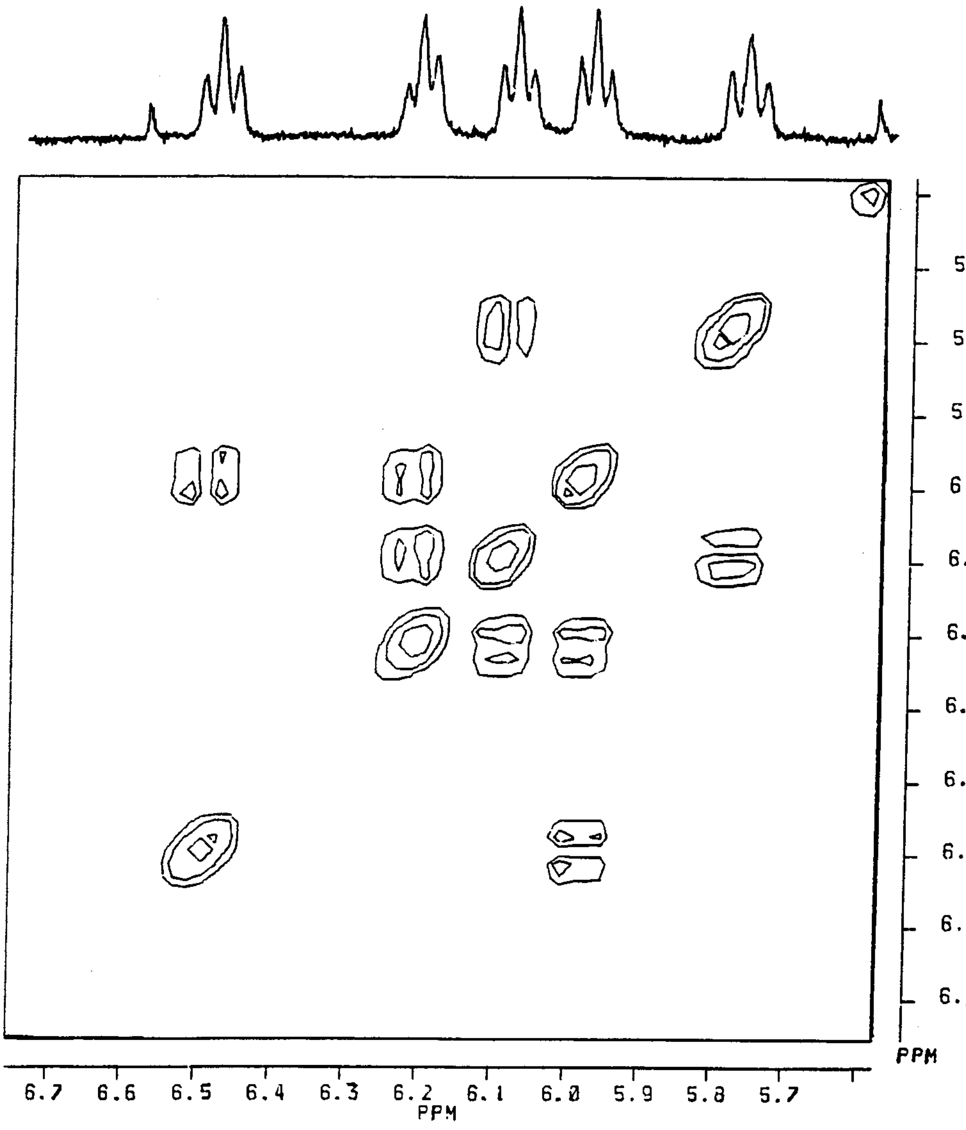


Fig. 3. COSY proton coupled 2D NMR spectrum of the olefinic region of 9.

3 (dark green solid). Anal. Found: Co, 19.1; Mo, 15.6. $C_{21}H_{12}Co_2MoO_8$ calc.: Co, 19.4; Mo, 15.8%.

4 (green solid). Anal. Found: Co, 9.0; Mo, 27.7. $C_{25}H_{17}CoMo_2O_7$ calc.: Co, 8.7; Mo, 28.2%.

5 (dark blue solid) was identified as $[Co_2Mo_2Cp_2(\mu_4\text{-}PhC_2H)(\mu\text{-}CO)_4(CO)_4]$ by ^{1}H-NMR and IR [9](a).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, 298K)$^{(*)}$, δ: 245.6 (s, 2 CO), 245.1 (s, 2 CO), 204.0(br, Co–CO's), 203.5 (br, Co–CO's), 199.5 (br, Co–CO's), 168.4 (s, **C**–Ph), 153.0 (s, C*ipso*(Ph)), 137.6 (s, C≡**C**H), 129.4–120.9(Ph), 96.8 (s, 2 C_5H_5).

$^{(*)}$ For comparison, $^{13}C\{^1H\}$-NMR ($CDCl_3$) of $[Co_2Mo_2Cp_2(\mu_4\text{-}MeC_2Me)(\mu\text{-}CO)_4(CO)_4]$, δ: 246.9 (s, 4 CO), 200 (br, 4 Co–CO's), 177.3 (s, 2 **C**–CH3), 97.2 (s, 2 $\mathbf{C}_5H_5$), 38.4 (s, 2 $\mathbf{C}H_3$).

6 (red brown solid) Anal. Found: C, 42.7; H, 2.4; Co, 25.3; Mo, 13.7. $C_{25}H_{16}Co_3MoO_7$ calc.: C, 42.8; H, 2.3; Co, 25.2; Mo, 13.7%.

3.3. Reaction of the dicobalt complex $[Co_2(\mu\text{-}CF_3C_2R)(CO)_6]$ (R = CF_3 (1b), H (1c)) with $[Mo_2Cp_2(CO)_4]$

1. In a similar reaction to the above, a solution of $[Co_2(\mu\text{-}CF_3C_2CF_3)(CO)_6]$ (**1b**) (890 mg, 2 mmol) and $[Mo_2Cp_2(CO)_4]$ (860 mg, 2 mmol) in THF (40 ml) was refluxed for ca. 48 h. Chromatography as above produced a red orange band eluted with hexane/CH_2Cl_2 (9:1) which yielded complex **7b** (590 mg, 57%) that was identified as $[Cp(CO)_2Mo(\mu\text{-}CF_3C_2CF_3)\ Co(CO)_3](Mo\text{–}Co)$ by comparison of its spectral data (IR, NMR) with those of an authentic sample which was prepared in low yield (17%) according to a method described previously [18]. Further elution with hexane/CH_2Cl_2 (4:1) served to remove a dark red band which was evaporated to yield $[Mo_2Cp_2(CO)_6]$ (0.70 g).

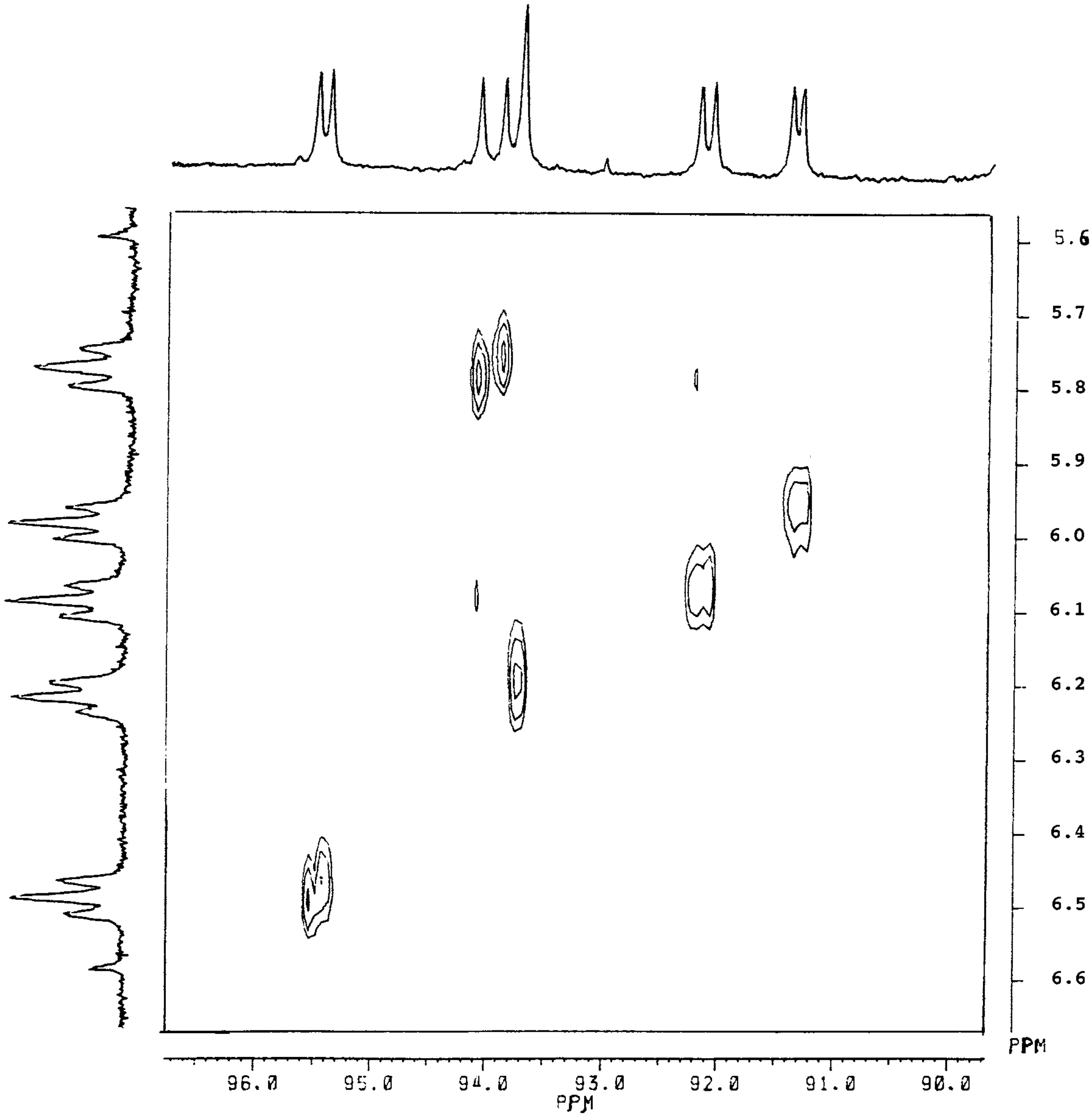


Fig. 4. Selected region of the ^{1}H–^{13}C 2D HETCOR spectrum (298 K, $CDCl_3$).

2. In a similar way, the reaction of $[Co_2(\mu-CF_3C_2H)(CO)_6]$ (**1c**) (1.00 g, 2.6 mmol) and $[Mo_2Cp_2(CO)_4]$ (1.27 g, 2.9 mmol) in refluxing THF for ca. 33h produced, on chromatography, two main bands. Complex **7a** was eluted with hexane/CH_2Cl_2 (9:1) as a orange band (246 mg, 21%). Further elution with hexane/CH_2Cl_2 (4:1) gave a dark red band due to $[Mo_2Cp_2(CO)_6]$ (1.05 g). Complex **7a** was identified as $[Cp(CO)_2Mo(\mu-CF_3C_2H)Co(CO)_3]$ (Mo–Co) by comparison of its NMR data with those of **7b** [18].

7a (orange solid). ^{1}H-NMR ($CDCl_3$), δ: 5.48 (s, C_5H_5), 5.69 (s, ≡C–**H**); ^{19}F-NMR ($CDCl_3$), δ: −50.41 (s).

3.4. Reaction of the molybdenum–cobalt complex $[CoMoCp(\mu-CF_3C_2CF_3)(CO)_5]$ (7b) with $[CoCp(CO)_2]$

A solution of complex **7b** (390 mg, 0.75 mmol) and $[CoCp(CO)_2]$ (270 mg, 0.75 mmol) in octane (30 ml) was heated to reflux for 2 h. Column chromatography of the residue produced a dark green band of **8** (380 mg, 69%) eluted with hexane/CH_2Cl_2 (1:1).

8 (black solid). Anal. Found: C, 37,4; Co, 24.0; H, 2,2; Mo, 12.6. $C_{23}H_{15}Co_3F_6MoO_4$. Calc.: C, 37,2; Co, 23.8; H, 2,04; Mo, 12.9%

*3.5. Reaction of the dicobalt complex [$Co_2(\mu$-$CF_3C_2CF_3)(CO)_6$] (**1b**) with [$Mo_2Cp_2(\mu$-$CO)(\mu$-$PPh_2)_2$]*

A mixture of **1b** (1.12g, 2.5 mmol) and [$Mo_2Cp_2(\mu$-$CO)(\mu$-$PPh_2)_2$] (0.60 g, 0.83 mmol) in octane (40 ml) was heated to reflux for 2 h. The solution was then pumped to dryness, and the resulting residue was stirred in hexane (10 ml) for 30 min. The solution was filtered to remove an insoluble green material, which was identified as [$Mo_2Cp_2(\mu$-$PPh_2)_2(CO)_2$] (Mo=Mo) (236 mg, 38% with respect to the dimolybdenum reagent) by comparison of its IR and NMR spectra with those of an authentic sample [28]. The filtrate was subjected to chromatography on silica gel. Elution with hexane/CH_2Cl_2 (2.5:1) gave a red brown band containing **9** (150 mg, 15.5%). Further elution with hexane–H_2Cl_2 (1:1) produced a red band of [$Mo_2Cp_2(O)(\mu$-$PPh_2)_2(CO)$] (Mo=Mo) (49 mg, 8%) which was identified by comparison of its spectral data with those of an authentic sample [28].

9 (red brown solid). Anal. Found: C, 46.4; H, 2.6; Co, 10.0; Mo, 16.2, $C_{45}H_{30}Co_2F_6Mo_2O_7P_2$ calc.: C, 46.3; H, 2.6; Co, 10.1; Mo, 16.4. IR (CH_2Cl_2): υ(CO) 2068s, 2010s, 1890 sh, 1845s, cm^{-1}.

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