Iron, Cobalt and Nickel Carbide--Carbonyl Clusters by CO Scission

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Iron, cobalt and nickel carbide–carbonyl clusters by CO scission

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A new approach to the synthesis in good yields of known cobalt and iron carbide–carbonyl clusters by CO cleavage in mild conditions is reported. Cleavage of CO results from attaching an acetyl or benzoyl carbocation to the oxygen atom, and by transfer of electrons from an external source. This synthetic approach to carbide molecular clusters may be of some significance with respect to the formation of carbide atoms on to metal crystallites.

Attempts to synthesize nickel carbide clusters with the same approach have only been partly successful. The new $[Ni_9C(CO)_{17}]^{2-}$ and $[Ni_8C(CO)_{16}]^{2-}$ have been obtained more conveniently from the reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4. The related reaction of $[Ni_6(CO)_{12}]^{2-}$ with $Co_3(CO)_9CCl$ results in the formation of the mixed-metal carbide cluster $[Co_3Ni_9C(CO)_{20}]^{3-}$. This compound is degraded under a carbon monoxide and hydrogen mixture (25 °C, 1 atm) to $Ni(CO)_4$, $[Co(CO)_4]^-$ and ethane. Intermediate formation of $[Co_3Ni_7(C{-}C)(CO)_{15}]^{3-}$, in which the two carbide atoms show an interatomic separation of 1.43 Å, or of a related species, would provide a possible pathway for C–C bond formation.

1. INTRODUCTION

Cluster chemistry has often provided models for individual steps that may be involved as transient intermediates in a catalytic sequence. For instance, the recent characterization of a series of hexanuclear clusters of the cobalt subgroup (e.g. $[M_6(CO)_{15}H]^-$ (M = Co, Rh), $[Rh_6(CO)_{15}(C({=}O){-}X)]^-$ (X = R, OR, NHR) and $[Rh_6(CO)_{14}(\eta_3\text{-}C_3H_4)]^-$ (Chini 1980)) has shown that also a higher nuclearity cluster can at least carry the functional groups that are presumably required in oxo-synthesis. Thus the hydroformylation of olefins catalysed by cobalt carbonyl derivatives is commonly accepted to occur through a sequence of steps such as (Pino *et al.* 1977):

$$\begin{tikzcd} \mathrm{HCo(CO)_3} \arrow[r, shift left, "\text{olefin}"] & \mathrm{R{-}Co(CO)_3} \arrow[l, shift left] \arrow[r, shift left, "\mathrm{CO}"] & \mathrm{R{-}C({=}O){-}Co(CO)_3} \arrow[l, shift left] \arrow[r, "\mathrm{H_2}"] \arrow[ll, bend left] & \text{aldehydes.} \end{tikzcd}$$

Support for the above mechanism stems also from the isolation and characterization of a series of monomeric compounds such as $HCo(CO)_4$, $R{-}Co(CO)_4$ and $R{-}C({=}O){-}CO(CO)_4$, which are believed to be the 18-electron counterparts of the 16-electron active intermediates of the above sequence (Pino *et al.* 1977). In this connection, it may appear significant that a key cluster model such as $[Rh_6(CO)_{15}(C({=}O){-}R)]^-$ has been initially obtained from

$$3Rh_4(CO)_{12} + 2CH_2{=}CH{-}CH_3 + 2H_2O \xrightarrow[\mathrm{H_2\ (1\ atm)}]{\mathrm{THF,\ 25\ ^\circ C}} 2[Rh_6(CO)_{15}(C({=}O){-}C_3H_7)]^- + 2H(THF)^+ + 2CO + 2CO_2, \quad (1)$$

and that reaction (1) in apolar solvents results in stoichiometric hydroformylation of olefins (Chini *et al.* 1972), and becomes catalytic on starting from $Co_2Rh_2(CO)_{12}$.

The search for other cluster models for hydroformylation originated the present work, which resulted in finding a ready CO cleavage reaction that may be of some significance for the formation of surface carbide atoms on metal crystallites.

2. SYNTHESIS OF COBALT AND IRON CARBIDE CLUSTERS BY CO SCISSION

The reaction of a carbonylanion with acyl chloride has been shown in the past to afford either mononuclear (e.g. $R–C(=O)–Co(CO)_4$) or polynuclear acyl derivatives (e.g. $[Rh_6(CO)_{15}(C(=O)–R)]^-$). In attempting the synthesis of a hexanuclear cobalt acyl derivative, we investigated the reaction of $[Co_6(CO)_{15}]^{2-}$ with acetyl chloride. Unexpectedly, this reaction did not result in the formation of the $[Co_6(CO)_{15}(C(=O)–CH_3)]^-$ acyl derivative nor the corresponding $[Co_6(CO)_{15}(–CH_3)]^-$ alkyl derivative, generated by decarbonylation of the former. The resulting brown compound showed an intense e.s.r. signal with $g = 2.013$, and on the basis of its spectroscopic and chemical behaviour it has been identified as the previously characterized paramagnetic $[Co_6C(CO)_{14}]^-$ carbide derivative, whose structure (Albano *et al.* 1980) is shown in figure 1.

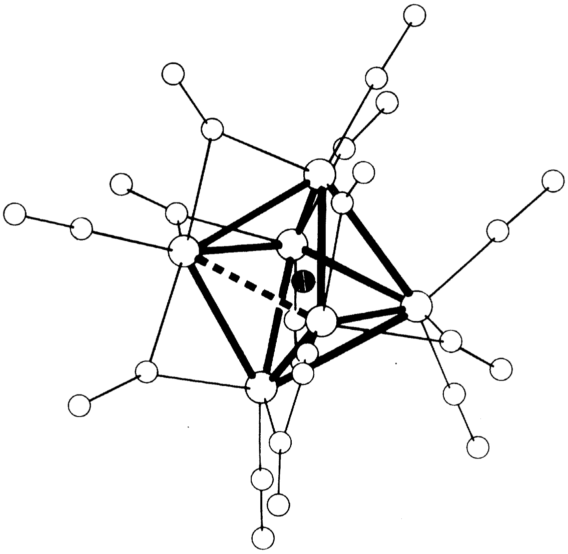


FIGURE 1. Structure of $[Co_6C(CO)_{14}]^-$ (Albano *et al.* 1980).

The reaction of $[Co_6(CO)_{15}]^{2-}$ with CH_3COCl follows this apparent stoichiometry:

$$3[Co_6(CO)_{15}]^{2-} + 2CH_3COCl(+CO) \longrightarrow 2[Co_6C(CO)_{14}]^- + 4[Co(CO)_4]^- + 2Co^{2+} + 2Cl^- + 2CH_3COO^-. \quad (2)$$

As reported previously (Albano *et al.* 1976), the octahedral $[Co_6C(CO)_{14}]^-$ is readily converted into the prismatic $[Co_6C(CO)_{15}]^{2-}$ in the presence of basic reagents. Therefore reaction (2) can also be used to synthesize the latter direct, by a slight modification of the isolation procedure. Both $[Co_6C(CO)_{14}]^-$ and $[Co_6C(CO)_{15}]^{2-}$ have been isolated in 50–60% yields (calculated from the starting compound $K_2[Co_6(CO)_{15}]$), and reaction (2) represents an alternative route to these interstitial carbides, which have previously been synthesized by reaction of $Co_3(CO)_9CCl$ with $[Co(CO)_4]^-$ (Albano *et al.* 1974).

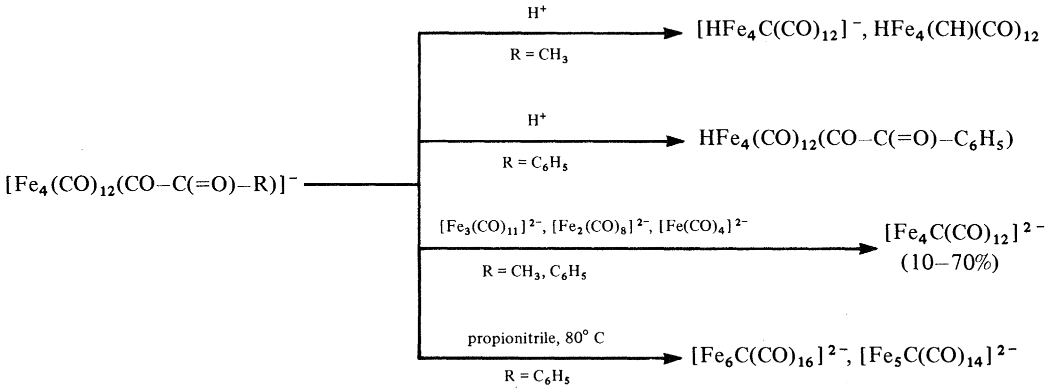
This unexpected result, represented by reaction (2), could have been due to ready CO scission, probably occurring with a $[Co_6(CO)_{14}(CO{-}C({=}O){-}CH_3)]^-$ transient adduct, related to the previously reported $[Fe_3(CO)_{10}(\mu_2\text{-}CO{-}C({=}O){-}CH_3)]^-$, where the acetyl carbocation is attached to the oxygen atom of a double-bridging carbonyl group (Hodali & Shriver 1979). This hypothesis led us to investigate a reaction analogous to (2) with the $[Fe_4(CO)_{13}]^{2-}$ dianion, which has recently been shown to give $[Fe_4(CO)_{12}(\mu_3\text{-}CO{-}CH_3)]^-$ and the corresponding $HFe_4(CO)_{12}(\mu_3\text{-}\eta_2\text{-}CO{-}CH_3)$ adduct, on reaction with methylating agents such as CH_3SO_3F (Holt *et al.* 1980; Dawson *et al.* 1980).

Reaction of $[Fe_4(CO)_{13}]^{2-}$ in anhydrous THF with a slight excess of acetyl chloride affords the new red-violet $[Fe_4(CO)_{12}(CO{-}C({=}O){-}CH_3)]^-$ adduct:

$$[Fe_4(CO)_{13}]^{2-} + R{-}COCl \longrightarrow [Fe_4(CO)_{12}(CO{-}C({=}O){-}R)]^- + Cl^- \qquad (3)$$

($R = CH_3, C_6H_5$). This compound has been isolated in *ca.* 90% yield as crude product, and its crystallization has been hampered by decomposition to the starting $[Fe_4(CO)_{13}]^{2-}$ and $[HFe_4(CO)_{13}]^-$ on standing in solution. When acetyl chloride is replaced by benzoyl chloride, reaction (3) is very slow and requires several hours for completion. The reaction is accelerated at 50–60 °C; however, long reaction time and warming favour the concurrent formation of other products. Very pure samples of $[Fe_4(CO)_{12}(CO{-}C({=}O){-}C_6H_5)]^-$ are readily available by performing reaction (3) at 18 °C and under u.v. radiation. The benzoyl adduct shows a much greater stability than the corresponding acetyl derivative, and has been recrystallized from THF-heptane as the tetrasubstituted ammonium or phosphonium salt. Both the acetyl and benzoyl adducts are supposed to be structurally related to the corresponding methyl adduct previously characterized (Holt *et al.* 1980; Dawson *et al.* 1980).

As shown in scheme 1, the acyl adducts have been converted into iron carbide derivatives by several routes. The proton-induced formation of a carbide derivative (side 1) parallels the previously reported synthesis of $[HFe_4C(CO)_{12}]^-$ and $HFe_4(CH)(CO)_{12}$ from $[Fe_4(CO)_{13}]^{2-}$ and HSO_3CF_3, which probably occurs through the $HFe_4(CO)_{12}(CO{-}H)$ as intermediate (Holt *et al.* 1981; Whitmire & Shriver 1981). The greatest stability of the benzoyl adduct is also shown by its conversion to the corresponding $HFe_4(CO)_{12}(CO{-}C({=}O){-}C_6H_5)$ by reaction with acid (side 2).



Scheme 1

The $[Fe_4(CO)_{12}(CO{-}C({=}O){-}R)]^-$ ($R = CH_3$, C_6H_5) derivatives are stable in the presence of excess $[Fe_4(CO)_{13}]^{2-}$; however, reaction with the more reduced $[Fe_3(CO)_{11}]^{2-}$, $[Fe_2(CO)_8]^{2-}$ or $[Fe(CO)_4]^{2-}$ gives rise to a mixture of products containing increasing amounts of the previously reported $[Fe_4C(CO)_{12}]^{2-}$ dianion (Tachikawa & Muetterties 1980). When $[Fe(CO)_4]^{2-}$ is used as reducing agent, yields up to 70–80% of $[Fe_4C(CO)_{12}]^{2-}$ have been obtained. The use of an iron carbonyl anion as reducing agent can, however, be detrimental to the selectivity of the reaction; $[Fe_4(CO)_{12}(CO{-}C({=}O){-}R)]^-$ has been almost quantitatively converted into $[Fe_4C(CO)_{12}]^{2-}$ by reduction with sodium-ketyl:

$$[Fe_4(CO)_{12}(CO{-}C({=}O){-}R)]^- + 2Na \xrightarrow{\text{THF, }Ph_2CO} [Fe_4C(CO)_{12}]^{2-} + R{-}COO^- + 2Na^+. \quad (4)$$

The $[Fe_4C(CO)_{12}]^{2-}$ dianion has previously been synthesized by degradation of preformed $[Fe_5C(CO)_{14}]^{2-}$, and its structure is schematically represented in figure 2 (Tachikawa & Muetterties 1980). Reaction (4) represents a convenient alternate synthesis of this interesting compound and, by subsequent protonation, for the related $[HFe_4C(CO)_{12}]^-$ and $HFe_4(CH)(CO)_{12}$ (Tachikawa & Muetterties 1980).

A mixture of $[Fe_6C(CO)_{16}]^{2-}$ (Churchill *et al.* 1971), $[Fe_5C(CO)_{14}]^{2-}$ (Hsieh & Mays 1972), and other unidentified products have been obtained when $[Fe_4(CO)_{12}(CO{-}C({=}O){-}C_6H_5)]^-$ is heated at 70–90 °C in propionitrile solution (side 4). Owing to difficulties encountered in

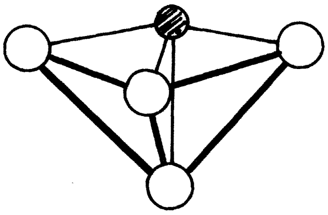


FIGURE 2. Schematic representation of the structure of $[Fe_4C(CO)_{12}]^{2-}$ (Tachikawa & Muetterties 1980).

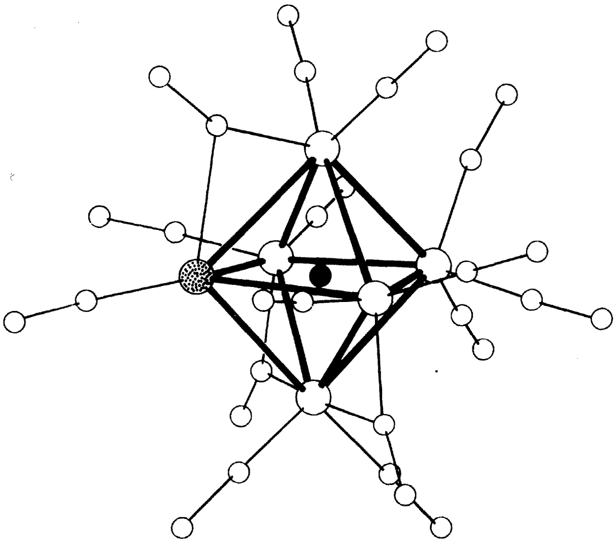


FIGURE 3. Structure of $[Fe_5PtC(CO)_{15}]^{2-}$.

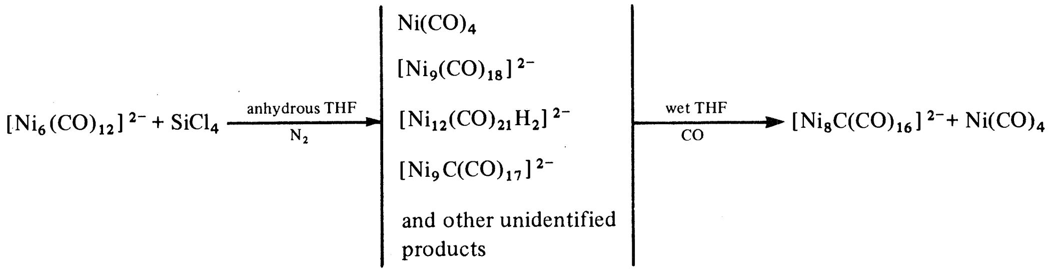
the separation of this complex mixture, this direct synthetic route to hexanuclear and pentanuclear carbide clusters has not been further investigated.

Identification of the products shown in scheme 1 is based on the complete correspondence of their spectroscopic and chemical behaviour with those previously reported for these compounds. The carbide nature of the product of reaction (4) has been also confirmed by its reaction with Pt salts, and by the X-ray characterization of the resulting $[Fe_5PtC(CO)_{15}]^{2-}$. The structure of this mixed-metal carbide cluster is shown in figure 3. The isolation of a carbide derivative in side 3 of scheme 1 confirms that intermediate formation of an acyl adduct, and its ready reduction either by $[Co_6(CO)_{15}]^{2-}$ or $[Co(CO)_4]^-$, may be also at the origin of $[Co_6C(CO)_{14}]^-$ in reaction (2).

3. Synthesis of carbide nickel clusters

The ready CO cleavage reactions (2) and (4) of §2 led us to investigate the possible extension of this synthetic approach to carbide clusters of the metals of nickel subgroup. Although a Ni_3C binary bulk phase is known (Nakagura 1957), there have been no reports in the literature on the synthesis of carbide molecular clusters of nickel.

When reacting both $[Ni_5(CO)_{12}]^{2-}$ or $[Ni_6(CO)_{12}]^{2-}$ with acylchloride, we observed only oxidation to $[Ni_9(CO)_{18}]^{2-}$. Similar results have been obtained also when starting from $[Pt_6(CO)_{12}]^{2-}$. It therefore seems probable that the presence of more basic face-bridging carbonyl groups and steric crowding of the carbonyl ligands around the metal core of the cluster are important requirements to avoid side-reactions and obtain the formation of acyl adducts, in which the acyl carbocation is attached to the oxygen atom of a carbonyl group.



Scheme 2

To our knowledge the first genuine example of carbide synthesis by CO splitting induced by coordination of a Lewis acid to the oxygen atom of a carbonyl group was probably the fortuitous synthesis of $[Rh_6C(CO)_{15}]^{2-}$, while attempting the synthesis of a related $[Rh_6Si(CO)_{15}]^{2-}$ by reaction of $[Rh(CO)_4]^-$ with $SiCl_4$ (Chini *et al.* 1973). This result, on the basis of the known transformation of $(CH_3)_3Si–Co(CO)_4$ into $Co_3(CO)_9(\mu_3\text{-}CO–Si(CH_3)_3)$ (Ingle *et al.* 1973), may be due to a CO splitting reaction related to (2), and suggested this different approach to carbide–nickel clusters. As shown in scheme 2, the reaction of $[Ni_6(CO)_{12}]^{2-}$ in anhydrous THF with $SiCl_4$ resulted in a very complicated mixture of products. However, the subsequent degradation of this mixture under carbon monoxide in wet THF converted most of the nickel carbonyl anions into $Ni(CO)_4$, and allowed the isolation, in low yield, of a red species, which has been characterized as $[Ni_8C(CO)_{16}]^{2-}$. Despite past failures in the synthesis of carbide nickel clusters by reduction of $Ni(CO)_4$ with alkali in methanol and in the presence of small amounts of $CHCl_3$ or CCl_4, carbide nickel clusters do exist and, since the experiment shown in scheme 2, have been synthesized in good yields by the classical reaction between a preformed carbonyl anion and CCl_4 (Chini *et al.* 1974), such as the following:

$$2[Ni_6(CO)_{12}]^{2-} + CCl_4(+CO) \xrightarrow{THF,\ N_2} [Ni_9C(CO)_{17}]^{2-} + 2Ni(CO)_4 + Ni^{2+} + 4Cl^-. \quad (5)$$

The $[Ni_9C(CO)_{17}]^{2-}$ and $[Ni_8C(CO)_{16}]^{2-}$ dianions are related by the degradation-condensation equilibrium

$$[Ni_9C(CO)_{17}]^{2-} + 3CO \underset{N_2}{\overset{CO}{\rightleftharpoons}} [Ni_8C(CO)_{16}]^{2-} + Ni(CO)_4. \quad (6)$$

The right-hand side of this equilibrium, combined with the stability of $[Ni_8C(CO)_{16}]^{2-}$ toward further degradation under CO, is probably responsible for the isolation of this compound in the experiment represented in scheme 2.

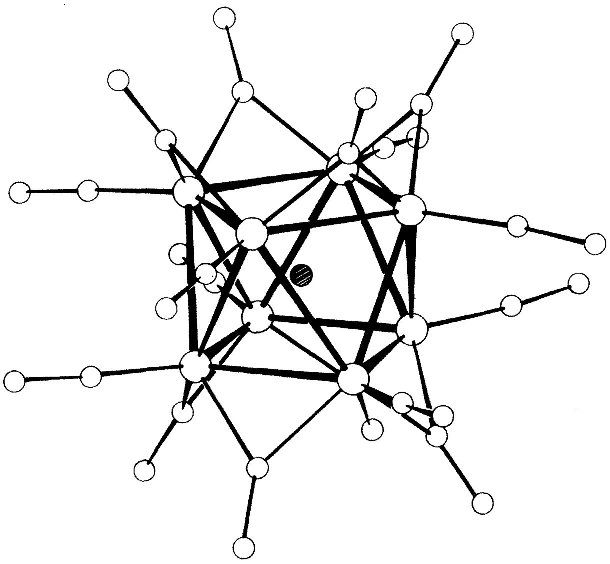


Figure 4. Structure of $[Ni_8C(CO)_{16}]^{2-}$.

Both these two compounds have been isolated in a crystalline state as tetrabutylammonium salts, and their X-ray structures are reported in figures 4 and 5. Although the carbide atom in the Ni_3C bulk phase has been shown to occupy octahedral cavities in both $[Ni_8C(CO)_{16}]^{2-}$ and $[Ni_9C(CO)_{17}]^{2-}$, the carbide atoms are encapsulated in a square antiprismatic cage. The Ni–Ni average bond distance in these two compounds (2.55 Å†) is intermediate between Ni–Ni bond distance in bulk Ni metal (2.50 Å) and in Ni_3C binary carbide (2.63 Å) (Nakagura 1957).

4. Mixed Co–Ni carbide clusters

Reaction (7), formally analogous to reaction (5), has been used to synthesize mixed Co–Ni carbide clusters:

$$2[Ni_6(CO)_{12}]^{2-} + Co_3(CO)_9CCl \longrightarrow [Co_3Ni_9C(CO)_{20}]^{3-} + 3Ni(CO)_4 + Cl^- + CO. \quad (7)$$

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† 1 Å = 10^{-10} m = 10^{-1} nm.

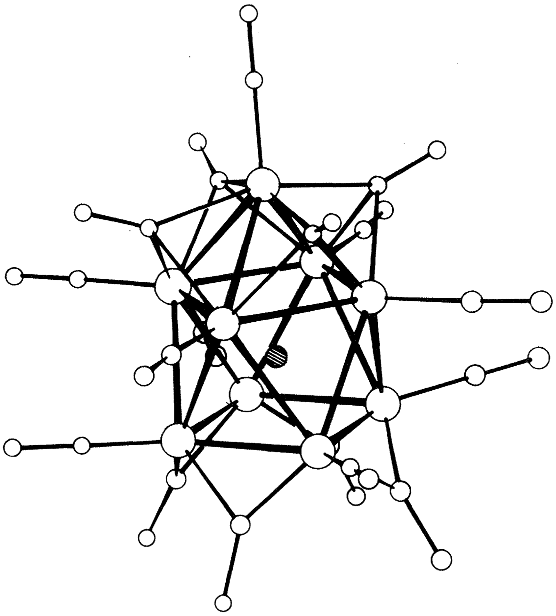

FIGURE 5. Structure of $[Ni_9C(CO)_{17}]^{2-}$.

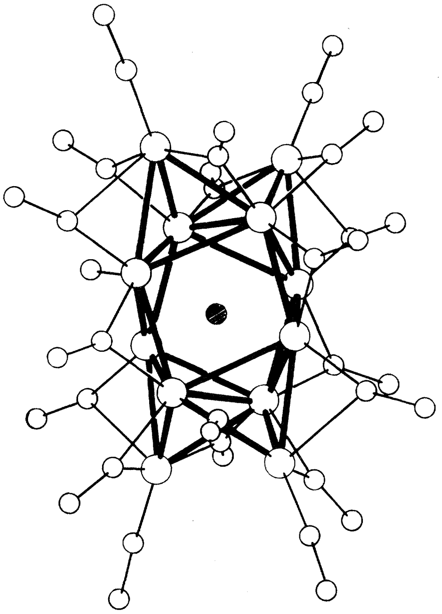

FIGURE 6. Structure of $[Co_3Ni_9C(CO)_{20}]^{3-}$.

As shown in figure 6, the structure of the $[Co_3Ni_9C(CO)_{20}]^{3-}$ is based on a tetracapped square antiprism of metal atoms. Cobalt and nickel atoms are not distinguishable and are probably randomly distributed. The most interesting chemical feature of this compound is that it differs from all the other carbide derivatives so far reported in that it is completely degraded by carbon monoxide (25 °C, 1 atm):

$$[Co_3Ni_9C(CO)_{20}]^{3-} + 28CO \longrightarrow 3[Co(CO)_4]^- + 9Ni(CO)_4 + \{C\}. \qquad (8)$$

The fate of the carbide atom in this reaction is still obscure, and the unusual unstability of $[Co_3Ni_9C(CO)_{20}]^{3-}$ under carbon monoxide is probably the consequence of the presence in this compound of the same number of cobalt atoms and free negative charges, and of the particular stability of both $[Co(CO)_4]^-$ and $Ni(CO)_4$.

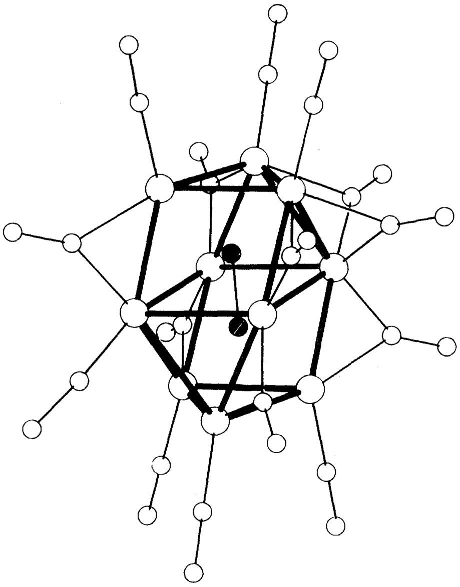

FIGURE 7. Structure of $[Co_3Ni_7C_2(CO)_{15}]^{3-}$.

When $[Co_3Ni_9C(CO)_{20}]^{3-}$ has been degraded under an atmosphere of carbon monoxide and hydrogen (1:1, 25 °C, 1 atm), the carbide atom has been almost selectively converted into ethane. A possible interpretation for the unexpected selective formation of ethane has been suggested by the subsequent isolation and characterization of the $[Co_3Ni_7C_2(CO)_{15}]^{3-}$ dicarbide, as a by-product of reaction (7). In this cluster the two interstitial carbide atoms present an interatomic separation (1.43 Å) shorter than those previously determined in $Rh_{12}C_2(CO)_{25}$ (1.48 Å) (Albano *et al.* 1978) and $[Co_{11}C_2(CO)_{22}]^{3-}$ (1.62 Å) (Albano *et al.* 1981). The intermediate degradation of $[Co_3Ni_9C(CO)_{20}]^{3-}$ to $[Co_3Ni_7(C\text{–}C)(CO)_{15}]^{3-}$, as represented in reactions (9) and (10), or to a structurally related species, would provide a possible pathway to C–C bond formation:

$$2[Co_3Ni_9C(CO)_{20}]^{3-} + 31CO \xrightarrow[25\ °C,\ 1\ atm]{CO+H_2} [Co_3Ni_7(C\text{–}C)(CO)_{15}]^{3-} + 3[Co(CO)_4]^- + 11Ni(CO)_4; \quad (9)$$

$$[Co_3Ni_7(C\text{–}C)(CO)_{15}]^{3-} + 25CO + 3H_2 \xrightarrow[25\ °C,\ 1\ atm]{CO+H_2} 3[Co(CO)_4]^- + 7Ni(CO)_4 + C_2H_6. \quad (10)$$

In agreement with this interpretation, reaction (10) has also been verified on starting from preformed $[Co_3Ni_7(C\text{–}C)(CO)_{15}]^{3-}$. The structure of this dicarbide is schematically shown in figure 7. The three-layer metal skeleton of this compound may be thought to derive from the rearrangement of either two interstitially occupied trigonal prismatic or octahedral moieties sharing a common edge, as shown in figure 8. Both these two undistorted arrangements may be found in binary transition metal carbides. Two trigonal prisms, condensed as shown in figure 8*a*, constitute the central part of the unit cell of the Cr_3C_2 binary phase (figure 9), in which, however, the C–C interatomic separation is 1.66 Å (Toth 1971). The metal arrangement found in $[Co_3Ni_7C_2(CO)_{15}]^{3-}$ indicates the higher degree of freedom of the finite metal array of the molecular clusters, and favours both a shortening of the C–C interatomic separation and expansion of the carbide atoms in a heptahedral cage.

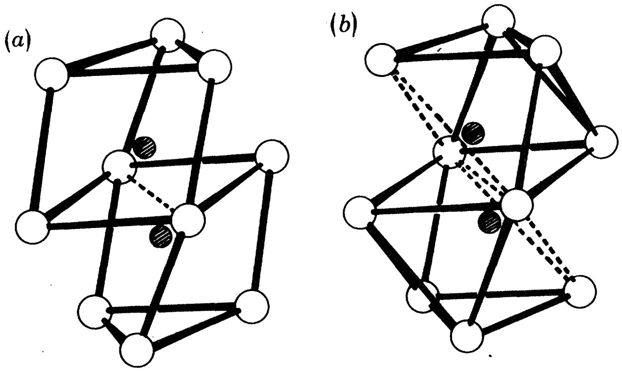

FIGURE 8. The $[Co_3Ni_7C_2(CO)_{15}]^{3-}$ metal skeleton as (*a*) two condensed trigonal prisms or as (*b*) two condensed octahedra.

This comparison represents a further confirmation of the relation between molecular carbide metal clusters and binary transition metal carbides (Tachikawa & Muetterties 1982; Chini 1980).

5. CONCLUSIONS

Several examples of intermolecular dual coordination of a metal-bound carbonyl group with a Lewis acid have been reported (Hamilton *et al.* 1981, and references therein). A significant example in cluster chemistry is given by the structure of $[Fe_4(CO)_{12}(CO{-}CH_3)]^-$ (Holt *et al.* 1980; Dawson *et al.* 1980), shown schematically in figure 10*a*. In molecular clusters intramolecular dual coordination of carbon monoxide has also been documented, e.g. $Mn_2(CO)_5(Ph_2P{-}CH_2{-}PPh_2)_2$ (Colton *et al.* 1975), $[HFe_4(CO)_{13}]^-$ (Manassero *et al.* 1976) (figure 10*b*) and $Nb_3Cp_3(CO)_7$ (Herrman *et al.* 1981).

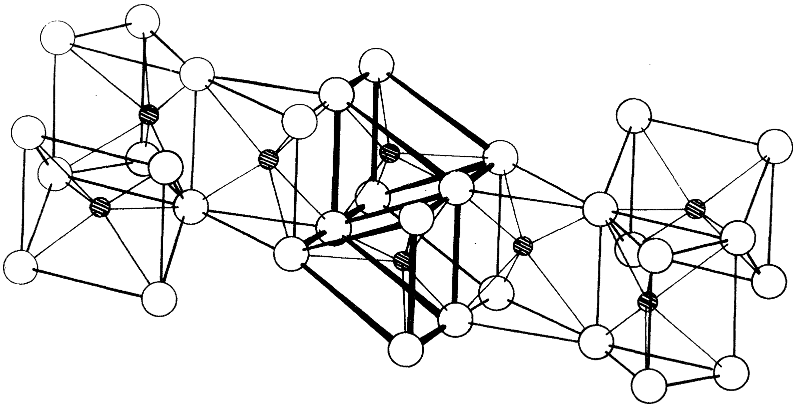

FIGURE 9. The unit cell of the Cr_3C_2 binary phase (Toth 1971). Bold bonds delineate two trigonal prisms condensed as in $[Co_3Ni_7(C{-}C)(CO)_{15}]^{3-}$ (figure 10*a*).

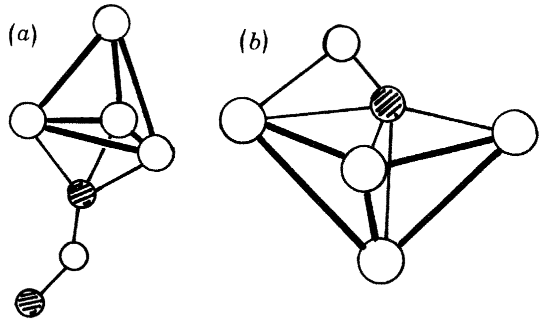

FIGURE 10. Schematic representation of (*a*) $[Fe_4(CO)_{12}(CO{-}CH_3)]^-$ (Holt *et al.* 1980; Dawson *et al.* 1980), and (*b*) $[HFe_4(CO)_{13}]^-$ (Manassero *et al.* 1976).

The high-yield synthesis of cobalt and iron carbide carbonyl clusters here reported confirms that intermolecular dual coordination of a carbonyl group bonded to a molecular cluster with a Lewis acid, such as acetyl or benzoyl carbocation, precedes a ready CO cleavage. In the described approach, CO splitting requires a transfer of electrons from an external source, and is probably favoured by the increase in metal coordination of the carbide atom and by delocalization of the C–O bond in the leaving carboxylate group.

Dual coordinations, related to those represented in figure 10, may also occur on metal crystallites either by interaction of the oxygen atom of a metal-bound carbonyl group with an acidic site of the support (Shriver 1981) or, directly, onto the crystallite metal surface, as well as at surface defects such as steps or adatoms (Chini 1979). The relevance of surface carbide atoms in methanation or Fischer–Tropsch reactions has been recently confirmed by isotopic studies (Sachtler *et al.* 1978).

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