New Carbide Clusters in the Cobalt Subgroup. Part 13.[1] Synthesis and Chemical Characterization of the Anions $[Co_6C(CO)_{14}]^-$, $[Co_6C(CO)_{15}]^{2-}$, and $[Co_8C(CO)_{18}]^{2-}$, and Crystal Structure of μ_6-Carbido-ennea-μ-carbonyl-hexacarbonyl-*polyhedro*-hexacobaltate(2−) as its Benzyltrimethylammonium Salt; a Comparison with Isostructural Species ‡

Secondo Martinengo,* Donatella Strumolo, and (the late) Paolo Chini
Centro CNR di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione and Dipartimento di Chimica Inorganica e Metallorganica, Via G. Venezian 21, 20133 Milano, Italy
Vincenzo G. Albano † and Dario Braga
Istituto Chimico "G' Ciamician" dell' Universita', Via F. Selmi 2, 40126 Bologna, Italy

The anions $[Co_6C(CO)_{15}]^{2-}$ and $[Co_8C(CO)_{18}]^{2-}$ have been prepared starting from compounds such as $[Co_3C(CO)_9Cl]$, $Na[Co(CO)_4]$, and $[Co_4(CO)_{12}]$, and $[Co_6C(CO)_{14}]^-$ has been obtained from $[Co_6C(CO)_{15}]^{2-}$ by oxidation with $FeCl_3$ or iodine. The chemistry and relationships between these anions are discussed. The molecular structure of $[Co_6C(CO)_{15}]^{2-}$ has been determined by single-crystal *X*-ray crystallography. It is monoclinic, space group *C*2/*c*, with $a = 21.752(2)$, $b = 11.350(1)$, $c = 18.099(2)$ Å, $\beta = 112.28(1)°$, and $Z = 4$. The structure has been solved from 2 184 reflections, collected by counter methods, and refined by least-squares calculations to $R = 0.074$. The dianion has idealized D_{3d} symmetry and contains a trigonal prism of cobalt atoms, whose cavity accommodates an interstitial carbon atom. The structural parameters are carefully compared with those of the isostructural anions $[Rh_6C(CO)_{15}]^{2-}$ and $[M_6N(CO)_{15}]^-$ (M = Co or Rh) to show how the metal atoms, the interstitial species, and the anionic charge affect the bond parameters.

We have already reported in brief on the synthesis of anions $[Co_6C(CO)_{15}]^{2-}$,[2] $[Co_6C(CO)_{14}]^-$,[3] and $[Co_8C(CO)_{18}]^{2-}$,[3] and the *X*-ray structural characterization of $[Co_6C(CO)_{14}]^-$ [4] and $[Co_8C(CO)_{18}]^{2-}$.[5] We report here full details of the synthesis and chemical characterization of these anions and the *X*-ray structure of the anion $[Co_6C(CO)_{15}]^{2-}$ as its benzyltrimethylammonium salt.

In the vast family of carbonyl clusters there are few strictly isostructural species containing different metal atoms and/or ligands. A comparative structural analysis of such species has never been attempted because the elucidation of new geometries was the major aim. However, further information can be obtained from a comparison of bond parameters in isostructural and isoelectronic species and correlated to spectroscopic and reactivity data. An exceptional set of related species is given by the anions of general formula $[M_6C(CO)_{15}]^{2-}$ and $[M_6N(CO)_{15}]^-$ (M = Co or Rh), characterized by 90 valence electrons. These species have D_{3h} symmetry and contain a prismatic framework of metal atoms encapsulating an isolated heteroatom. Six carbonyl ligands are bonded linearly, one per metal atom, and nine bridge the prism edges. The rhodium carbido-carbonyl anion was characterized first,[6] while the nitrido-species have been prepared and analysed very recently.[7,8] A careful comparison of the bond parameters of all these species shows how the metal atoms, the interstitial species, and the anionic charge affect the bond parameters.

Results and Discussion

Synthesis and Chemical Characterization of $[Co_6C(CO)_{15}]^{2-}$. —The compound was prepared by the reaction of $[Co_3C(CO)_9Cl]$ with $Na[Co(CO)_4]$ according to equation (1). This reaction was originally carried out in tetrahydrofuran (thf)

$$[Co_3C(CO)_9Cl] + 3Na[Co(CO)_4] \longrightarrow Na_2[Co_6C(CO)_{15}] + NaCl + 6CO \quad (1)$$

or propan-2-ol giving 40—50% yields.[2] It has now been found that di-isopropyl ether is a better solvent because the product separates out as soon as it is formed due to its low solubility. However, the starting $Na[Co(CO)_4]$ is also poorly soluble in this solvent (although more so than the hexanuclear product) and for this reason a temperature of 60 °C and a good dispersion of the $Na[Co(CO)_4]$ are required to speed up the reaction. The $Na[Co(CO)_4]$ is used in a slight excess (3—5%) in order to avoid the side formation of other polynuclear anions such as $[Co_6C(CO)_{14}]^-$ and $[Co_8C(CO)_{18}]^{2-}$.[3-5] At the end of the reaction the precipitate contains also NaCl and the unreacted $Na[Co(CO)_4]$; this crude product can be used as such for the synthesis of other cobalt clusters such as $[Co_{13}C_2(CO)_{24}]^{4-}$ and $[Co_{11}C_2(CO)_{22}]^{3-}$.[9,10] Purification is achieved through precipitation of the potassium salt from water, and metathesis with bulky cations.

We also attempted the direct synthesis from CCl_4 and $[Co(CO)_4]^-$ in various solvents and at different temperatures according to reaction (2). The expected anion was observed but in lower yields and with more impurities.

$$CCl_4 + 6[Co(CO)_4]^- \longrightarrow [Co_6C(CO)_{15}]^{2-} + 4Cl^- + 9CO \quad (2)$$

Solutions of the red-brown $[Co_6C(CO)_{15}]^{2-}$ are quickly oxidized in air, while crystals of the $[NMe_3(CH_2Ph)]^+$ and $[N(PPh_3)_2]^+$ salts are stable in air for a few days. The salts of bulky cations are easily soluble in MeCN and acetone. In thf only the larger cations $[N(PPh_3)_2]^+$ and $[NMe_3(CH_2Ph)]^+$ give soluble salts, while the smaller ones $[NEt_4]^+$ and $[NMe_4]^+$ give moderately soluble products.

---

* For correspondence on synthesis and chemical characterization.

† For correspondence on structural characterization.

‡ *Supplementary data available:* structure factors, from the editorial office. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Table 1. I.r. data for salts of $[Co_6C(CO)_{15}]^{2-}$

Cation	Solvent	$\tilde{\nu}_{CO}/cm^{-1}$
Na^+	thf	1 983vs, 1 859w (sh), 1 830s, 1 791mw (sh), 1 745w
K^+	thf	1 985vs, 1 860w, 1 831s, 1 815m (sh), 1 795mw (sh), 1 749w
$[NEt_4]^+$, $[NMe_3(CH_2Ph)]^+$	thf	2 008vw (sh), 1 981vs, 1 859w, 1 826s, 1 814s, 1 774mw (sh), 1 750w (sh)
$[N(PPh_3)_2]^+$	thf	1 979vs, 1 970s (sh), 1 860vw, 1 824s, 1 782mw
All these	MeCN	1 987vs, 1 824s, 1 780mw

The i.r. spectrum of the anion $[Co_6C(CO)_{15}]^{2-}$ depended on both the solvent and the counter cation. The cation effect is remarkable in thf solution, as shown in Table 1. In MeCN solution no counter-cation effect is observed, and all the salts isolated have the same spectrum. In Figure 1 the spectra of $[NMe_3(CH_2Ph)]_2[Co_6C(CO)_{15}]$ in thf (*a*) and in MeCN (*b*) solution are compared.

We have already reported that $[Co_6C(CO)_{15}]^{2-}$ slowly reacts with CO in thf to give mainly the paramagnetic anion $[Co_6C(CO)_{14}]^-$, $[Co(CO)_4]^-$, traces of $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, and derivatives of the $[Co_3C(CO)_9X]$ species.[3] These species have now been identified by i.r. or mass spectroscopy as $[\{Co_3C(CO)_9\}_2CO]$,[11] $[Co_3(CO)_9(CH)]$,[12] and $[Co_5(CO)_{15}(C_3H)]$.[13] The presence of the last two species is somewhat surprising and could not be explained without assuming that some of the reaction intermediates are able to interact with traces of water or with the solvent. When the reaction with CO is carried out in the presence of Cl^- ions, slow decomposition of the cluster to $[Co_3C(CO)_9Cl]$ and $[Co(CO)_4]^-$ is observed according to the reverse of reaction (1); at longer reaction times $[Co_3C(CO)_9Cl]$ also decomposes.

Synthesis and Chemical Characterization of $[Co_8C(CO)_{18}]^{2-}$.—We have already reported [3] that the $[Co_8C(CO)_{18}]^{2-}$ anion can be prepared by condensation of $[Co_6C(CO)_{15}]^{2-}$ with $[Co_4(CO)_{12}]$ in di-isopropyl ether according to equation (3).

$$[Co_6C(CO)_{15}]^{2-} + 0.5[Co_4(CO)_{12}] \longrightarrow [Co_8C(CO)_{18}]^{2-} + 3CO \quad (3)$$

We have now found that the intermediate isolation of $[Co_6C(CO)_{15}]^{2-}$ is unnecessary as $[Co_4(CO)_{12}]$ can be added directly to the mixture used to prepare the hexanuclear dianion [equation (1)] to give $[Co_8C(CO)_{18}]^{2-}$ in the single-step reaction (4). Reaction (4) was carried out under the same experimental conditions as (1). A slight excess of $[Co_4(CO)_{12}]$ was used to ensure complete transformation into $[Co_8C(CO)_{18}]^{2-}$. Also, in this case the ether-solvated sodium salt $Na_2[Co_8C(CO)_{18}]$ separates out as a black crystalline powder together with NaCl and traces of $Na[Co(CO)_4]$. Purification is carried out through precipitation of the K^+, Cs^+, or bulky organic cation salts.

$$[Co_3C(CO)_9Cl] + 3Na[Co(CO)_4] + 0.5[Co_4(CO)_{12}] \longrightarrow Na_2[Co_8C(CO)_{18}] + NaCl + 9CO \quad (4)$$

Although reaction (3) appears as a simple condensation, a close monitoring of the reaction, performed in thf, shows that the first stage consists of the redox reaction (5). Condensation between the products of reaction (5) and the remaining $[Co_4(CO)_{12}]$ takes place subsequently giving the anion $[Co_8C(CO)_{18}]^{2-}$.

$$[Co_6C(CO)_{15}]^{2-} + 0.25[Co_4(CO)_{12}] \longrightarrow [Co_6C(CO)_{14}]^- + [Co(CO)_4]^- \quad (5)$$

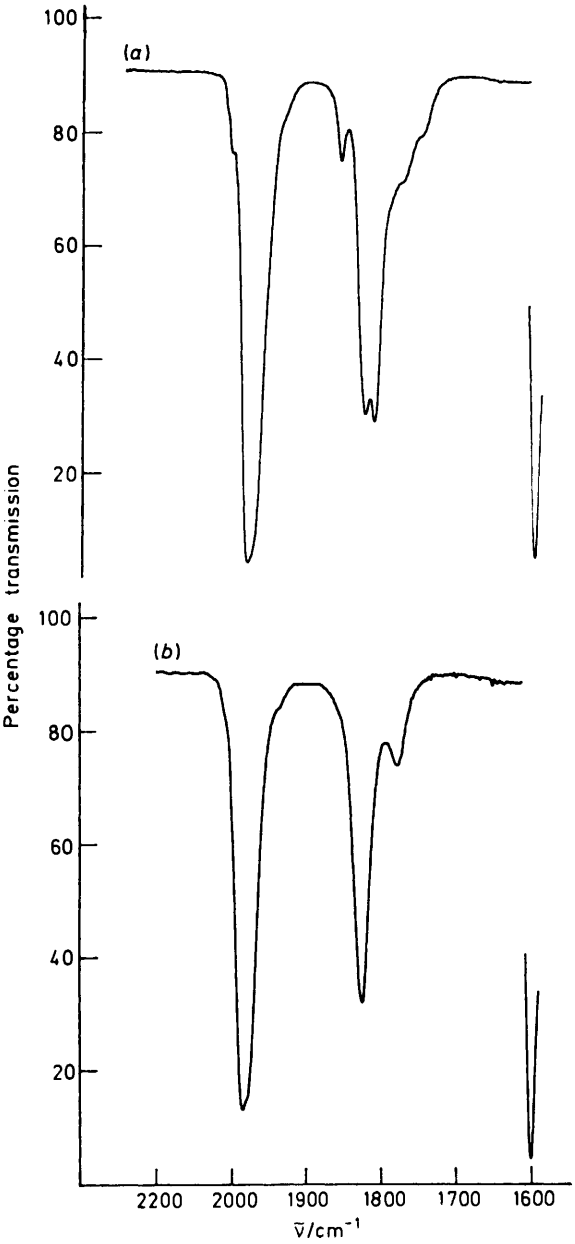

Figure 1. I.r. spectra of $[NMe_3(CH_2Ph)]_2[Co_6C(CO)_{15}]$ in thf solution (*a*) and in MeCN solution (*b*)

The stability towards air of solutions and crystals of the salts of $[Co_8C(CO)_{18}]^{2-}$ as well as the solubility are similar to those of the anion $[Co_6C(CO)_{15}]^{2-}$, the only difference being that all the salts of $[Co_8C(CO)_{18}]^{2-}$ are readily soluble in thf.

The i.r. spectrum of the $[NMe_3(CH_2Ph)]^+$ salt in thf solution shows bands at 2 040vw, 1 991vs, 1 950m (sh), and 1 810m cm^{-1} (Figure 2). No relevant counter-cation or solvent effects have been observed except generally small shifts (± 4 cm^{-1}) and the appearance in the spectra of the sodium and potassium salts of an additional very weak broad absorption at 1 760 cm^{-1}.

In thf solution the dianion $[Co_8C(CO)_{18}]^{2-}$ reacts with CO to give the paramagnetic $[Co_6C(CO)_{14}]^-$, $[Co(CO)_4]^-$, $[Co_2(CO)_8]$, and some $[Co_4(CO)_{12}]$, *i.e.* the mixture of intermedi-

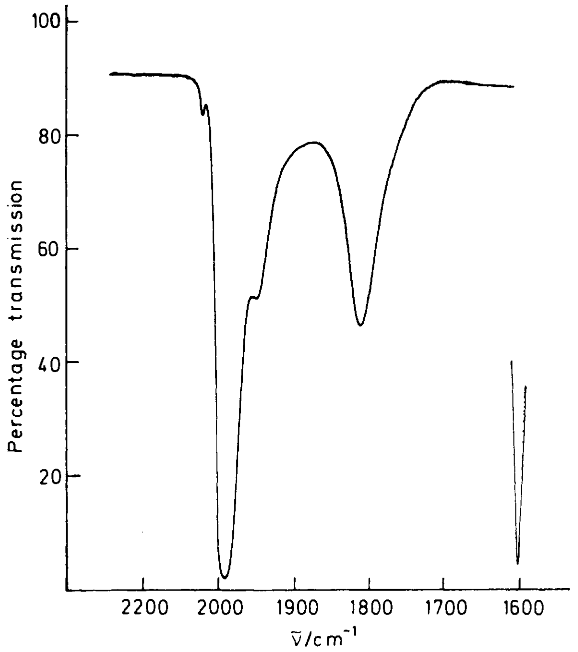

Figure 2. The i.r. spectrum of $[NMe_3(CH_2Ph)]_2[Co_8C(CO)_{18}]$ in thf solution

ate products observed in the synthesis (3) after reaction (5), the only difference being the presence, besides $[Co_4(CO)_{12}]$, of $[Co_2(CO)_8]$. Unlike the $[Co_6C(CO)_{15}]^{2-}$ case, no $[Co_3C(CO)_9X]$ species could be detected in the reaction of $[Co_8C(CO)_{18}]^{2-}$ with CO.

Synthesis and Chemical Characterization of $[Co_6C(CO)_{14}]^-$. —We have already mentioned that the anion $[Co_6C(CO)_{14}]^-$ is formed in the reactions of $[Co_6C(CO)_{15}]^{2-}$ with CO[3] or with $[Co_4(CO)_{12}]$ [see equation (5)]; however, these reactions are not useful for preparative purposes, as attempts to isolate the anion from the mixture with $[Co(CO)_4]^-$ result in the precipitation of a mixture of $[Co_6C(CO)_{15}]^{2-}$ and $[Co_8C(CO)_{18}]^{2-}$. We have also reported[3] a synthetic method starting from $[Co_3C(CO)_9Cl]$ and $Na[Co(CO)_4]$ in a 1 : 2 mol ratio in diethyl ether solution which gave rather low yields. We have subsequently found that a better synthesis is possible by oxidation of $[Co_6C(CO)_{15}]^{2-}$ with $FeCl_3$ according to equation (6). Iodine can also be used as an oxidant; the

$$[Co_6C(CO)_{15}]^{2-} + Fe^{3+} \longrightarrow [Co_6C(CO)_{14}]^- + Fe^{2+} + CO \quad (6)$$

reaction was performed in acetone at room temperature. The yields are rather good, 75—85%. The resulting product can be obtained as pure black-brown crystals from thf–benzene or -toluene. Recently a completely different synthesis of this anion starting from $[Co_6(CO)_{15}]^{2-}$ and acetyl chloride was reported.[14]

Solutions of $[Co_6C(CO)_{14}]^-$ are not stable in air, but crystals are stable for a few days. Salts of bulky cations are readily soluble in thf and acetone, moderately soluble in methanol, and insoluble in benzene and toluene. The i.r. spectrum of the $[NEt_4]^+$ salt in thf solution has no particular features, and shows bands at 2 060vw, 2 010vs, and 1 855m cm^{-1}. Magnetic measurements and e.s.r. data have already been reported.[3,15]

The anion $[Co_6C(CO)_{14}]^-$ is less reactive towards CO than $[Co_6C(CO)_{15}]^{2-}$ and $[Co_8C(CO)_{18}]^{2-}$ in accordance with its lower negative charge. In thf solution after 4 d only 40—50% of the original product has reacted. In the presence of halide ions the reaction with CO is more rapid, giving $[Co_3C(CO)_9Cl]$ and $[Co(CO)_4]^-$. The $[Co_6C(CO)_{14}]^-$ anion can be converted back into $[Co_6C(CO)_{15}]^{2-}$ by the action of reductants; however, in order to obtain good yields the reduction should be performed under CO in order to provide the missing molecule. On the other hand we have already mentioned that the anion $[Co_6C(CO)_{15}]^{2-}$ reacts with CO. It is possible to overcome this by taking advantage of the different solubilities of the salts of $[Co_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{14}]^-$ with bulky cations in methanol, which is higher for the monoanion. This difference can be greatly enhanced by adding a salt of the cation, which makes the dianion practically insoluble. It is therefore possible, under these conditions, to perform reduction under CO, as the $[Co_6C(CO)_{15}]^{2-}$ anion separates out as soon as it is formed. For example, stirring with zinc powder under CO in methanol a mixture of $[NEt_4][Co_6C(CO)_{14}]$ with $[NEt_4]Br$ (in excess of the 1 : 1 molar ratio) results in slow separation of the red $[NEt_4]_2[Co_6C(CO)_{15}]$ in nearly quantitative yield.

We have also found that a cleaner and faster reduction can be performed by treating the above mixture with alkali-metal hydroxides in MeOH solution; in this case the reductant is the CO itself, according to reaction (7). Reduction is quantitative, and gives directly the crystalline salts of $[Co_6C(CO)_{15}]^{2-}$ with bulky cations. The effectiveness of this reduction method has recently been confirmed by its use to obtain also $[Co_6C(CO)_{15}]^{2-}$ from a new synthesis of $[Co_6C(CO)_{14}]^-$.[14] This well known reduction through the action of hydroxides on carbonyls,[16] which has been widely used in rhodium and iridium cluster chemistry, has been little used for cobalt and it is probably worth wider application.

$$2[Co_6C(CO)_{14}]^- + 4OH^- + 3CO \longrightarrow 2[Co_6C(CO)_{15}]^{2-} + 2H_2O + CO_3^{2-} \quad (7)$$

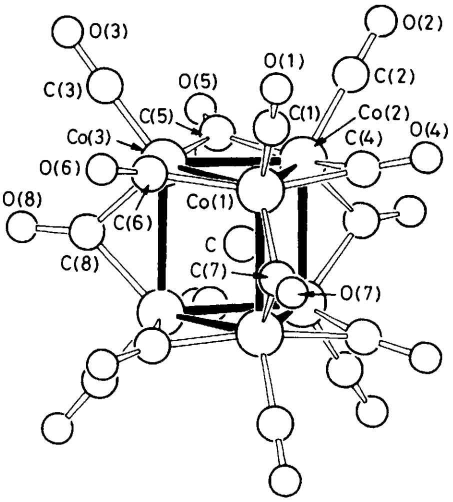

Figure 3. The structure of the dianion $[Co_6C(CO)_{15}]^{2-}$, showing atom labelling. Unlabelled atoms are related by the two-fold symmetry axis passing through carbonyl C(8)–O(8) and the centre of the opposite square face

The Structure of $[Co_6C(CO)_{15}]^{2-}$.—The structure depicted in Figure 3 is similar to that of the isoelectronic species and we will therefore not describe it in detail. The anion possesses D_{3h} idealized symmetry and C_2 crystallographic symmetry. The

Table 2. Average bond values (Å) for prismatic anions $[M_6C(CO)_{15}]^{2-}$ and $[M_6N(CO)_{15}]^{-}$ (M = Rh or Co)

	Carbides		Nitrides	
	Rh	Co	Rh	Co
M–M (basal)	2.776	2.537	2.763	2.517
M–M (inter-basal)	2.817	2.575	2.828	2.564
M–M (average)	2.790	2.550	2.785	2.533
M–C,N (average)	2.134	1.95	2.130	1.938
C,N radius	0.739	0.675	0.738	0.672
M–C (terminal)	1.89	1.75	1.863	1.71
C–O (terminal)	1.13	1.14	1.134	1.16
M–C (basal, bridging)	2.12	1.97	2.117	1.96
C–O (basal, bridging)	1.14	1.16	1.151	1.17
M–C (inter-basal, bridging)	2.04	1.90	2.050	1.90
C–O (inter-basal, bridging)	1.17	1.18	1.158	1.19

discussion will be devoted to a comparative analysis of the average bond parameters reported in Table 2.

The average Co–Co distances [2.550(2) in the carbide and 2.533(2) Å in the nitride] show a slight (0.017 Å) but significant shrinkage of the metal-atom framework upon the decrease in charge. The shortening is more marked in the basal edges (0.020 Å) than in the inter-basal ones (0.011 Å). The same effect is present in the rhodium species, but is less evident because the shortening of the basal edges (0.018 Å) is almost offset by a lengthening of the inter-basal ones (0.011 Å). The greater shortening of the basal edges upon halving of the anionic charge is in keeping with our feeling, previously expressed,[17–19] that the basal triangles are the most basic sites in these prismatic anions, as demonstrated by their selective capping by electrophilic fragments such as $[Cu(MeCN)]^+$, Ag^+, H^+, and $[Rh(CO)_2]^+$ in $[Cu_2Rh_6C(CO)_{15}(MeCN)_2]$,[17] $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$,[18] $[HRh_6C(CO)_{15}]^-$,[19] and $[Rh_{14}C_2(CO)_{33}]^{2-}$,[1] respectively. This is represented in Figure 4, which shows space-filling diagrams[20] of the anion $[Co_6C(CO)_{15}]^{2-}$. As one can see, while the rectangular faces appear almost completely covered by the ligands, the metal atoms are exposed on the triangular faces. This situation is perfectly reproduced on the surface of the rhodium analogue $[Rh_6C(CO)_{15}]^{2-}$ in which lengthenings of the carbon–carbon contacts are observed consistent with the enlargement of the metal-atom polyhedron. In both cases the ligands seem ' pushed away ' from the triangular faces which can be taken as an evidence of a partial accumulation of cluster electron density on that site.

The apparent radii of the interstitial carbon and nitrogen atoms are not significantly different. Very probably a compensation occurs between the smaller covalent radius of nitrogen and a larger population of its orbitals due to the higher electronegativity with respect to carbon. The shrinkage of the cobalt atom in the nitride with respect to the carbide is confirmed by some shortening of the Co–C(carbonyl) distances, particularly for the linear groups (0.04 Å). This shortening is accompanied by a slight lengthening of the C–O distances. At first sight the M–C and C–O distances follow the normal trend, but we must point out that, quite unexpectedly, this effect takes place in spite of the halved anionic charge and the shift of the CO stretching modes to higher wavenumbers.

A comparison of the metal–metal distances in cobalt and rhodium species shows that the radius of rhodium is 0.123 Å longer than that of cobalt. An independent assessment of the same quantity, obtained by comparison of equivalent metal–carbonyl distances in corresponding compounds, gives a rhodium radius 0.147 Å longer than that of cobalt. The apparent increase of the rhodium radius by 0.024 Å indicates that the rhodium–carbonyl interactions are weaker than the cobalt–carbonyl ones. This effect is significant because it is accompanied by an average 0.02 Å shortening of the carbon–oxygen distances indicating a weaker π-back bonding in the rhodium species. In agreement with the structural evidence, the CO stretching frequencies for rhodium species lie at higher wavenumbers than do the corresponding ones of the cobalt species.

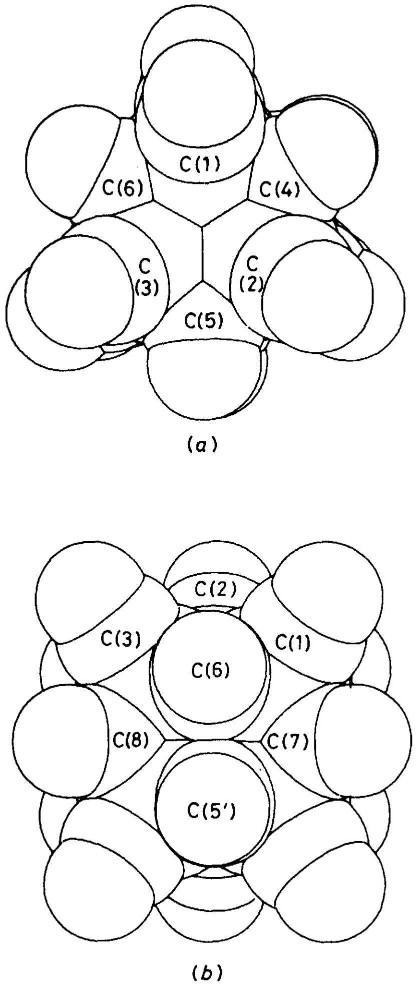

Figure 4. Space-filling diagrams of the anion $[Co_6C(CO)_{15}]^{2-}$ showing (*a*) the triangular face and (*b*) the square face of the prism. Van der Waals radii have been used with values of 1.6, 1.4, and 2.2 Å for C, O, and Co respectively. Relevant carbon–carbon contacts are: C(1) ··· C(2) 4.43, C(2) ··· C(3) 4.41, C(1) ··· C(3) 4.46, C(1) ··· C(6) 2.62, C(1) ··· C(7) 2.67, C(6) ··· C(7) 3.07, C(6) ··· C(8) 2.99, and C(6) ··· C(5′) 3.09 Å

Experimental

General.—All the operations were carried out under nitrogen using the Schlenk-tube technique. The solvents were distilled and stored under nitrogen. Water was degassed by pumping in vacuum and saturated with nitrogen. Di-isopropyl ether had to be freshly distilled, possibly immediately prior to use. The i.r. spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The compound $[Co_3C(CO)_9Cl]$ was prepared as reported in the literature.[21,22]

Synthesis of $[Co_6C(CO)_{15}]^{2-}$.—A suspension of finely powdered $Na[Co(CO)_4]$ (1 g, 5.15 mmol) in freshly distilled di-isopropyl ether (40 cm^3) was treated with $[Co_3C(CO)_9Cl]$ (0.79 g, 1.66 mmol) and vigorously stirred under nitrogen in an oil-bath at 60 °C for about 60—90 min. During heating the mixture was briefly degassed in vacuum every 15 min to remove the evolved CO, reintroducing nitrogen after evacuation. The sodium salt of the hexanuclear anion separated out as a reddish brown crystalline powder while the mother-liquor remained only slightly coloured. The suspension was left to cool at room temperature and then filtered; the product was washed with di-isopropyl ether in 10-cm^3 portions until the washings were colourless, and finally vacuum dried. This crude product consisted of the sodium salt of the hexanuclear anion containing some solvated ether, together with precipitated NaCl, traces of unreacted $Na[Co(CO)_4]$, and other impurities. Higher quantities of unreacted $Na[Co(CO)_4]$ were observed when it was not sufficiently well powdered and/or dispersed by stirring.

Potassium salt. Purification from the residual $Na[Co(CO)_4]$ was achieved through the potassium salt. The sodium salt was extracted from the septum with water (*ca.* 20 cm^3 in 5-cm^3 portions). The clear solution was briefly pumped in vacuum to eliminate the residual ether and then treated while stirring with solid deaerated KBr until saturation was reached (*ca.* 12 g). The potassium salt separated out as a finely crystalline red-brown powder which was left to crystallize for *ca.* 2 h. The product was filtered from the brown mother-liquor, washed with a saturated aqueous solution of KBr until the washings were nearly colourless, and then vacuum dried. This crude potassium salt was used for the subsequent metathesis with bulky cations. It could also be obtained in a pure state by extraction with tetrahydrofuran, which left the KBr undissolved, and evaporation to dryness in vacuum {yields 70—80% based on $[Co_3C(CO)_9Cl]$}. Metathesis with bulky cations was carried out in methanol. With smaller cations such as $[NMe_4]^+$ addition of water was necessary to complete precipitation.

Benzyltrimethylammonium salt. The above crude potassium salt (0.5 g) was dissolved in methanol (20 cm^3), filtered, and the clear solution treated dropwise with a solution of $[NMe_3(CH_2Ph)]Cl$ (2 g) in methanol (10 cm^3) while stirring to give a crystalline precipitate. This was filtered off, washed first with propan-2-ol then water, and vacuum dried (Found: C, 39.95; H, 2.60; Co, 31.8; N, 2.45. Calc. for $C_{36}H_{32}Co_6N_2O_{15}$: C, 39.8; H, 2.95; Co, 32.55; N, 2.60%). Crystals for *X*-ray analysis were obtained from tetrahydrofuran–propan-2-ol by the slow-diffusion technique.

Tetramethylammonium salt. The crude potassium salt (0.3 g) was dissolved in MeOH (15 cm^3), separated from KBr by filtration, and treated dropwise with a solution of NMe_4Cl (0.5 g) in MeOH (5 cm^3) while stirring. The stirred mixture was then treated dropwise with water (15—20 cm^3). The $[NMe_4]^+$ salt separated out as a dark red crystalline powder which was filtered off, washed with water, and vacuum dried.

Bis(triphenylphosphine)iminium salt. The potassium salt (0.13 g) in methanol (5 cm^3) was filtered off from KBr and slowly treated dropwise with a solution of $[N(PPh_3)_2]Cl$ (0.25 g) in MeOH (5 cm^3) while stirring. The finely crystalline dark red precipitate was filtered off, washed with water, and vacuum dried.

Reactions of $[Co_6C(CO)_{15}]^{2-}$.—*With* CO. The salt $[N(PPh_3)_2]_2[Co_6C(CO)_{15}]$ (0.334 g) was introduced in a thermostatted gas-volumetric apparatus under CO and dissolved in thf (14 cm^3). The solution was stirred at 26.3 °C while the CO absorption was monitored. After an induction period of about 1 h, absorption took place autocatalytically. After about 24 h the absorption ceased, about 2.1 mol of CO per mol of Co_6 having been absorbed. The i.r. spectrum of the solution showed bands typical of $[Co_6C(CO)_{14}]^-$ and $[Co(CO)_4]^-$, together with those of other minor products. To identify these products the solution was evaporated to dryness in vacuum, and the residue extracted by stirring with cyclohexane in 5-cm^3 portions until the extract was colourless (total *ca.* 15 cm^3). The i.r. spectrum of the extracted solution was rather complex, the presence of $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ being recognized from their absorption bands in the bridging CO stretching region. However, sometimes these species were absent (probably due to slow decomposition in thf). When present they were eliminated by evaporation to dryness of the extract, dissolution in MeOH, and evaporation to dryness again. The residue was dissolved in n-hexane (0.5 cm^3) and introduced into a silica gel chromatography column (diameter 12, height 120 mm) in n-hexane. Elution with n-hexane caused separation of three bands, the first very weak violet, the second brown, and the third orange. The first two contained $[Co_3(CO)_9(CH)]$ and $[Co_5(CO)_{15}(C_3H)]$, respectively, while the third, which was more easily eluted with hexane–benzene (2 : 1), contained $[\{Co_3C(CO)_9\}_2CO]$. These compounds were recognized from i.r. spectra and the pentanuclear one also from its mass spectrum. Another brown band of an unknown compound remained at the top of the column.

With CO *and* Cl^-. A stirred solution of $[NMe_3(CH_2Ph)]_2[Co_6C(CO)_{15}]$ (0.17 g) in thf (17 cm^3) under CO was treated with LiCl (0.1 g). After 20 h the i.r. spectrum showed the presence of bands due to $[Co_3C(CO)_9Cl]$ and $[Co(CO)_4]^-$. After 5 d all the $[Co_3C(CO)_9Cl]$ had disappeared and only i.r. bands due to $[Co(CO)_4]^-$ were present.

With $[Co_4(CO)_{12}]$. A solution of $[NEt_4]_2[Co_6C(CO)_{15}]$ (0.097 g, 0.093 mmol) in thf (5 cm^3) was treated with $[Co_4(CO)_{12}]$ (0.015 g, 0.026 mmol) and stirred under nitrogen. Monitoring of the reaction by i.r. spectroscopy showed that after 20—30 min the starting anion had disappeared, to give a mixture of $[Co_6C(CO)_{14}]^-$ and $[Co(CO)_4]^-$.

Synthesis of $[Co_8C(CO)_{18}]^{2-}$.—A mixture of finely powdered $Na[Co(CO)_4]$ (1.25 g, 6.44 mmol) with $[Co_3C(CO)_9Cl]$ (1 g, 2.10 mmol) and a slight excess of $[Co_4(CO)_{12}]$ (0.75 g, 1.31 mmol) was treated with di-isopropyl ether (40 cm^3) and vigorously stirred under nitrogen in an oil-bath at 60 °C for about 3 h. During heating the mixture was briefly degassed in vacuum every 15 min to remove the evolved CO, reintroducing nitrogen after every evacuation. The sodium salt of the octanuclear anion separated as a brown-black crystalline powder which after cooling at room temperature was filtered off, washed with di-isopropyl ether until the washings were colourless, and then vacuum dried. The crude product contained the ether-solvated sodium salt of the anion together with precipitated NaCl and other impurities. Purification was achieved through the potassium salt exactly as described for $[Co_6C(CO)_{15}]^{2-}$ using water (30 cm^3) and KBr (*ca.* 18 g); the yields were 75—85% based on $[Co_3C(CO)_9Cl]$.

Salts with bulky organic cations were obtained from the potassium salt by metathesis in methanol similar to that used for $[Co_6C(CO)_{15}]^{2-}$. For example the $[NMe_3(CH_2Ph)]^+$ salt was obtained by dissolving the potassium salt (0.3 g) in MeOH (20 cm^3) and adding dropwise a solution of $[NMe_3(CH_2Ph)]Cl$ (1 g) in MeOH (10 cm^3) and water (10 cm^3) while stirring; precipitation was completed by concentration in vacuum and the product filtered off, washed with water, and vacuum dried {Found: Co, 35.7%; $[NMe_3(CH_2Ph)]^+$, 22.8. Calc. for $C_{39}H_{32}Co_8N_2O_{18}$: Co, 36.6; $[NMe_3(CH_2Ph)]^+$, 23.3%}.

Table 3. Final positional parameters ($\times 10^4$) for $[NMe_3(CH_2Ph)]_2[Co_6C(CO)_{15}]$ with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	817(1)	2 778(1)	3 288(1)	H(3)	2 920	859	2 888
Co(2)	−364(1)	2 778(1)	3 248(1)	C(10)	4 128(4)	1 676(9)	3 438(7)
Co(3)	226(1)	845(1)	3 269(1)	H(4)	4 496	2 329	3 462
C(0)	0	2 140(1)	2 500	H(5)	4 064	1 074	2 952
C(1)	1 509(5)	3 215(8)	4 120(6)	H(6)	4 291	1 195	3 994
O(1)	1 981(4)	3 476(8)	4 662(5)	C(11)	3 703(6)	3 085(9)	4 114(7)
C(2)	−538(4)	3 291(8)	4 068(5)	H(7)	3 232	3 390	4 110
O(2)	−653(5)	3 621(9)	4 581(5)	H(8)	4 023	3 831	4 155
C(3)	426(4)	−133(8)	4 078(5)	H(9)	3 934	2 512	4 620
O(3)	524(4)	−783(8)	4 597(5)	C(12)	3 261(5)	3 077(9)	2 653(6)
C(4)	288(4)	4 092(8)	3 413(5)	H(10)	3 551	3 314	2 306
O(4)	324(4)	5 091(7)	3 585(6)	H(11)	2 739	3 164	2 289
C(5)	−633(4)	1 194(8)	3 372(5)	C(13)	3 057(3)	2 387(7)	1 890(4)
O(5)	−1 060(3)	682(6)	3 466(4)	C(14)	2 399(3)	2 007(7)	1 535(4)
C(6)	1 158(4)	1 117(8)	3 472(5)	C(15)	2 190(3)	1 392(7)	815(4)
O(6)	1 655(3)	623(6)	3 631(5)	C(16)	2 637(3)	1 157(7)	449(4)
C(7)	1 159(4)	3 396(8)	2 547(5)	C(17)	3 294(3)	1 537(7)	803(4)
O(7)	1 634(4)	3 907(6)	2 567(4)	C(18)	3 504(3)	2 152(7)	1 524(4)
C(8)	0	−377(9)	2 500	H(12)	2 053	2 188	1 819
O(8)	0	−1 443(8)	2 500	H(13)	1 681	1 098	540
N	3 536(4)	2 312(8)	3 407(5)	H(14)	2 475	0 681	−110
C(9)	3 026(4)	1 429(10)	3 399(8)	H(15)	3 641	1 355	520
H(1)	2 572	1 836	3 380	H(16)	4 013	2 446	1 799
H(2)	3 240	918	3 940				

* Atoms C(0), C(8), and O(8) are on the two-fold axis (*x* and *z* fixed); H atoms were refined by riding on the C atom to which they are attached.

Reaction of $[Co_8C(CO)_{18}]^{2-}$ *with* CO.—A 2% solution of $[NMe_3(CH_2Ph)]_2[Co_8C(CO)_{18}]$ in thf was stirred under CO. Monitoring of the reaction by i.r. spectroscopy showed that, within 15—20 min, the starting dianion disappeared to give a mixture of $[Co_6C(CO)_{14}]^-$ and $[Co(CO)_4]^-$ with neutral cobalt carbonyls. The latter were identified as $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ by evaporation to dryness of the solution, extraction of the residue with n-hexane, and i.r. analysis of the extract. No $[Co_3C(CO)_9X]$ species could be detected in this extract.

Synthesis of $[Co_6C(CO)_{14}]^-$.—*From* $[Co_6C(CO)_{15}]^{2-}$ *and* $FeCl_3$. A stirred solution of $[NEt_4]_2[Co_6C(CO)_{15}]$ (0.44 g, 0.42 mmol) in acetone (8 cm^3) under nitrogen was treated slowly dropwise with a 0.043 mol dm^{-3} solution of $FeCl_3$ in acetone until the i.r. bands of the starting dianion had disappeared and only those of the monoanion were present (about 12 cm^3 of solution was required, corresponding to a 25% excess). At the end of the reaction toluene (15 cm^3) was added and the solution pumped in vacuum until the acetone was eliminated. The precipitate was filtered off, washed with toluene, and vacuum dried. The dry mixture was washed with water to eliminate the co-precipitated $FeCl_2$ and $[NEt_4]Cl$ and then vacuum dried again (yield 75—85%). The product was recrystallized from tetrahydrofuran–toluene by the slow-diffusion technique (Found: Co, 39.4. Calc. for $C_{23}H_{20}Co_6NO_{14}$: Co, 39.8%). The $[PPh_4]^+$ salt was prepared in a similar way and crystallized from tetrahydrofuran–n-hexane.

From $[Co_6C(CO)_{15}]^{2-}$ *and iodine.* The synthesis was performed as described above, but starting from $[NMe_4]_2[Co_6C(CO)_{15}]$ (0.36 g) in acetone (20 cm^3) and using a 0.2 N solution of iodine in acetone in place of the $FeCl_3$. Also in this case an excess of about 25% of iodine was required. At the end of the reaction the solution was filtered from some precipitated $[NMe_4]I$ and evaporated to dryness. The residue was dissolved in thf (5 cm^3), filtered, and the product precipitated by dropwise addition of toluene (20 cm^3) while stirring followed by leaving to crystallize for about 1 h. Sometimes the $[NMe_4]^+$ salt separated out initially as an oil that crystallized on standing (yield 70—80%). Large crystals were obtained from tetrahydrofuran–toluene by the slow-diffusion technique.

Reduction of $[Co_6C(CO)_{14}]^-$ *to* $[Co_6C(CO)_{15}]^{2-}$.—A stirred mixture of $[NEt_4][Co_6C(CO)_{14}]$ (0.13 g) with $[NEt_4]Br$ (0.1 g) in methanol (10 cm^3) under CO was treated with a 0.9 mol dm^{-3} solution of NaOH in MeOH (4 cm^3). After a few minutes, red crystalline $[NEt_4]_2[Co_6C(CO)_{15}]$ precipitated and this process was complete in about 1 h. The precipitate was filtered off, washed with water, and vacuum dried. The yields were nearly quantitative.

Crystallography.—Crystals of $[NMe_3(CH_2Ph)]_2[Co_6C(CO)_{15}]$ were used for the structure analysis.

Crystal data. $C_{36}H_{32}Co_6N_2O_{15}$, $M = 1\,086.3$, monoclinic, $a = 21.752(2)$, $b = 11.350(1)$, $c = 18.099(2)$ Å, $\beta = 112.28(1)°$, $U = 4\,134.9$ Å^3, $D_m = 1.75$, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 2\,176$, space group $C2/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 23.2 cm^{-1}.

A suitable crystal of dimensions 0.10 × 0.12 × 0.15 mm was mounted on a Philips PW 1100 diffractometer. Diffraction intensities were measured in the range $2 < \theta < 25°$, by the ω-scan method, with scan interval 1.2° and speed 0.3° s^{-1}. The background was measured on both sides of the reflections for a total time equal to the peak scanning time. 3 943 Reflections were collected, 2 184 of which $[F_o > 5\sigma(F_o)]$ were used for structure solution and refinement. The integrated intensities were reduced to F_o values, no absorption correction being applied. For all the computations the SHELX[23] package of crystallographic programs was used. Due to the isomorphism with $[NMe_3(CH_2Ph)]_2[Rh_6C(CO)_{15}]$ and to the predictable small differences in the positions of the heavy atoms, a set of metal-atom co-ordinates taken from the rhodium species was refined by least-squares calculations. A subsequent Fourier difference map revealed all the light atoms. During the refinement cycles both metal and light

Table 4. Selected distances (Å) and angles (°) of $[NMe_3(CH_2Ph)]_2$-$[Co_6C(CO)_{15}]$ with estimated standard deviations in parentheses

Co(1)–Co(2)	2.541(1)	C(3)–O(3)	1.15(1)
Co(1)–Co(3)	2.536(1)	C(4)–O(4)	1.17(1)
Co(2)–Co(3)	2.533(2)	C(5)–O(5)	1.16(1)
Co(1)–Co(2′)	2.574(2)	C(6)–O(6)	1.15(1)
Co(3)–Co(3′)	2.578(2)	C(7)–O(7)	1.17(1)
Co(1)–C(0)	1.95(1)	C(8)–O(8)	1.21(2)
Co(2)–C(0)	1.95(1)	N–C(9)	1.49(2)
Co(3)–C(0)	1.95(1)	N–C(10)	1.46(2)
Co(1)–C(1)	1.75(1)	N–C(11)	1.48(2)
Co(2)–C(2)	1.76(1)	N–C(12)	1.53(1)
Co(3)–C(3)	1.75(1)	C(12)–C(13)	1.50(1)
Co(1)–C(4)	1.95(1)	Co(1)–C(1)–O(1)	178(1)
Co(2)–C(4)	2.00(1)	Co(2)–C(2)–O(2)	179(1)
Co(2)–C(5)	1.93(1)	Co(3)–C(3)–O(3)	177(1)
Co(3)–C(5)	1.99(1)	Co(1)–C(4)–O(4)	142(1)
Co(1)–C(6)	2.01(1)	Co(2)–C(4)–O(4)	137(1)
Co(3)–C(6)	1.94(1)	Co(2)–C(5)–O(5)	141(1)
Co(1)–C(7)	1.90(1)	Co(3)–C(5)–O(5)	138(1)
Co(2′)–C(7)	1.92(1)	Co(1)–C(6)–O(6)	139(1)
Co(3)–C(8)	1.89(1)	Co(3)–C(6)–O(6)	141(1)
C(1)–O(1)	1.16(1)	Co(1)–C(7)–O(7)	138(1)
C(2)–O(2)	1.11(1)	Co(3)–C(8)–O(8)	137(1)

atoms of the dianion were treated anisotropically, while the cation atoms were refined isotropically. The phenyl ring was treated as a rigid group (C–C 1.395 Å, C–C–C 120°), and the hydrogen atoms were added in calculated positions. The final agreement indices were $R = 0.074$ and $R' = 0.093$. A final Fourier difference map showed residual peaks lower than 1.0 e Å^{-3} in proximity of the heavy atoms. The co-ordinates of all the refined atoms are reported in Table 3, bond distances and relevant angles in Table 4.

References

1 Part 12, S. Martinengo, D. Strumolo, P. Chini, V. G. Albano, and D. Braga, *J. Chem. Soc., Dalton Trans.*, 1984, 1837.

2 V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J. Chem. Soc., Chem. Commun.*, 1974, 299.

3 V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton, and S. Martinengo, *J. Am. Chem. Soc.*, 1976, **98**, 5027.

4 Part 6, V. G. Albano, P. Chini, G. Ciani, M. Sansoni, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1980, 163.

5 Part 5, V. G. Albano, P. Chini, G. Ciani, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1978, 463.

6 Part 1, V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1973, 651.

7 S. Martinengo, G. Ciani, A. Sironi, B. T. Heaton, and J. Mason, *J. Am. Chem. Soc.*, 1979, **109**, 7095.

8 R. Bonfichi, G. Ciani, A. Sironi, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1983, 253.

9 Part 9, V. G. Albano, D. Braga, P. Chini, G. Ciani, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 1982, 645.

10 Part 8, V. G. Albano, D. Braga, G. Ciani, and S. Martinengo, *J. Organomet. Chem.*, 1981, **213**, 293.

11 G. Allegra, E. Mostardini Peronaci, and R. Ercoli, *Chem. Commun.*, 1966, 549; G. Palyi, F. Piacenti, and L. Marko', *Inorg. Chim. Acta Rev.*, 1970, **4**, 109.

12 G. Bor, L. Marko', and B. Marko', *Chem. Ber.*, 1962, **95**, 333.

13 R. S. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, 1970, **9**, 2197.

14 A. Ceriotti, P. Chini, G. Longoni, and G. Piro, *Gazz. Chim. Ital.*, 1982, **112**, 353.

15 T. Beringhelli, F. Morazzoni, and D. Strumolo, *J. Organomet. Chem.*, 1982, **236**, 109.

16 P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, 1976, **14**, 285 and refs. therein.

17 V. G. Albano, D. Braga, S. Martinengo, P. Chini, M. Sansoni, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 1980, 52.

18 B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, V. G. Albano, and D. Braga, *J. Chem. Soc., Dalton Trans.*, 1983, 2175.

19 B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, R. J. Goodfellow, and I. H. Sadler, *J. Chem. Soc., Dalton Trans.*, 1982, 1499.

20 E. Keller, SCHAKAL Program, Graphical Representation of Molecular Models, University of Freiburg, 1978.

21 R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chim. Ind. (Milan)*, 1962, **44**, 1344.

22 C. L. Nivert, G. H. Williams, and D. Seyferth, *Inorg. Synth.*, 1980, **20**, 234.

23 G. M. Sheldrick, SHELX 75 System of Computer Programs, Cambridge, 1975.

Received 30*th January* 1984; *Paper* 4/159