Crystal and Molecular Structure of the Bis(tetramethylammonium) Octa-μ_3-carbonyl-hexacarbonyl-*octahedro*-dinickeltetracobaltate(2−)

By **Vincenzo G. Albano,* Gianfranco Ciani,** and **Paolo Chini,** Istituto di Chimica Generale ed Inorganica, Università degli Studi, via Venezian 21, Milano 20133, Italy

Crystals of the title compound $(NMe_4)_2[Co_4Ni_2(CO)_{14}]$, are trigonal, $a = 11{\cdot}283(6)$, $c = 21{\cdot}106(12)$ Å (hexagonal axes), space group $R\bar{3}$, $Z = 3$. The structure was determined by Patterson and Fourier methods from *X*-ray counter data and refined by full-matrix least-squares calculations to R 0·033 for 725 significant reflections.

The anion has S_6 crystallographic symmetry. The metal atoms are statistically distributed at the corners of a lightly stretched octahedron, with independent M–M distances 2·487(1) and 2·519(1) Å. Six of the carbonyl ligands are bonded in terminal positions and eight are bridging on the octahedron faces. The M–C and C–O distances for the linear groups are 1·757(3), 1·129(5) Å and the mean values for the bridging ones 2·10(1), 1·154(7) Å. The molecular geometry of the anion is compared with those of the isoelectronic species $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$.

An increasing number of carbonyl cluster complexes are being prepared which contain metals belonging to different groups or periods. Structural research on these compounds can be a source of new information on metal–metal bonds, preferred geometries of the ligands, and growth mechanisms of the clusters.

Of particular interest in this respect is the possibility of comparison among isoelectronic species such as $Co_6(CO)_{16}$,[1,2] $[Co_6(CO)_{15}]^{2-}$ (refs. 3 and 4), $[Co_6(CO)_{14}]^{4-}$ (refs. 5 and 6), and $[Co_4Ni_2(CO)_{14}]^{2-}$ (ref. 7). In the

---

[1] P. Chini, *Inorg. Chem.*, 1969, **8**, 1206.

[2] V. G. Albano, P. Chini, and V. Scatturin, *Chem. Comm.*, 1968, 163.

[3] P. Chini and V. G. Albano, *J. Organometallic Chem.*, 1968, **15**, 433.

[4] V. G. Albano, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1968, **15**, 423.

[5] P. Chini, V. G. Albano, and S. Martinengo, *J. Organometallic Chem.*, 1969, **16**, 471.

[6] V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1969, **16**, 461.

[7] P. Chini, A. Cavalieri, and S. Martinengo, *Co-ordination Chem. Rev.*, 1972, **8**, 3.

solid state the pure cobalt species have different ligand geometries, and, for the third one, at least a second structure exists in solution.[5] We report here the *X*-ray structure of $[Co_4Ni_2(CO)_{14}]^{2-}$ which may clarify the roles played by number of ligands, anionic charge, and, possibly, the nickel positions in the cluster in determining the stable stereochemistry.

The chemical behaviour of this anion is substantially different from that of the pure cobalt species. Redox reactions which interconvert $Co_6(CO)_{16}$, $[Co_6(CO)_{15}]^{2-}$, and $[Co_6CO)_{14}]^{4-}$, invariably bring about the fragmentation of $[Co_4Ni_2(CO)_{14}]^{2-}$. Some information on the bond strengths in these anions could be obtained by comparison of the metal–metal and –carbonyl distances.

EXPERIMENTAL

Precession photographs, taken with different crystals, displayed S_6 $\bar{3}$ Laue symmetry characteristic of the trigonal system, and enabled the unit cell parameters to be determined.

Crystal Data.—$C_{22}H_{24}Co_4Ni_2N_2O_{14}$, $M = 893{\cdot}14$, Trigonal, $a = b = 11{\cdot}283(6)$, $c = 21{\cdot}106(12)$ Å (hexagonal axes), $U = 2326{\cdot}9$ Å^3, $D_m = 1{\cdot}92(2)$ (by flotation), $Z = 3$, $D_c = 1{\cdot}91$, $F(000) = 1338$. Space group $R3$ (No. 146) or $R\bar{3}$ (No. 148). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, μ(Mo-K_α) $= 34{\cdot}25$ cm^{-1}.

TABLE 1

Final positional and thermal [a] parameters [b] ($\times 10^4$)

Atom	x	y	z	b_{11}	b_{13}	b_{13}	b_{22}	b_{23}	b_{33}
M	1359(0)	1163(0)	490(0)	75(0)	68(0)	−19(0)	78(0)	−17(0)	24(0)
C(1)	2717(3)	2407(3)	944(2)	87(2)	86(4)	−10(3)	94(3)	−10(3)	25(1)
O(1)	3588(3)	3240(4)	1224(2)	151(4)	69(7)	−72(3)	158(4)	−54(3)	44(1)
C(2)	260(3)	2186(3)	422(2)	100(3)	84(4)	−3(3)	73(2)	−2(2)	27(1)
O(2)	426(2)	3232(2)	594(1)	96(2)	85(2)	−4(2)	68(1)	−8(2)	28(0)
C(3)	0	0	1207(4)	125(5)	125(5)	0	125(5)	0	25(2)
O(3)	0	0	1752(2)	133(3)	133(3)	0	133(3)	0	18(1)
N	0	0	3465(2)	71(3)	71(3)	0	71(3)	0	23(1)
C(4)	0	0	4166(4)	167(7)	167(7)	0	167(7)	0	24(2)
C(5)	1118(3)	1336(3)	3222(2)	72(3)	40(4)	0(3)	65(3)	0(3)	37(1)
Atom	x	y	z	B					
H(1)	1020	258	4340	4·0					
H(2)	1162	1297	2703	4·0					
H(3)	917	2158	3362	4·0					
H(4)	2102	1540	3424	4·0					

[a] The form of the anistropic thermal ellipsoid is exp-$(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$. [b] Estimated standard deviations are given in parentheses here and in subsequent Tables.

Intensity Measurements.—For the collection of intensity data, a trigonal polyhedral crystal ($0{\cdot}26 \times 0{\cdot}26 \times 0{\cdot}32$ mm) was mounted on a Pailred linear equi-inclination diffractometer with the *c* axis (that of maximum elongation) coincident with the ω axis of the instrument. Intensity data for two octants were collected within $2\theta \leqslant 50°$, by use of graphite monochromatized Mo-K_α radiation. Intensities were monitored by the ω-scan technique at a rate of $1{\cdot}0°$ min^{-1} with stationary-crystal–stationary-counter background counts of 40 s taken on each side of the scan. Increasing scan ranges, from 1·6 to 2·8°, were used for ω with increasing μ. 1532 Reflections, in the reciprocal lattice levels *hk*0—21, were collected. Three standard reflections, sampled after completion of each layer, revealed no crystal decay. The integrated intensities were corrected for Lorentz and polarization factors; the latter was evaluated taking account of the partial polarization of the incident beam.[8] The calculated transmission coefficients, obtained with the Busing and Levy method,[9] were found to be in the range 0·58—0·61 and the absorption corrections were performed by use of an 8^3 sampling of the crystal. No extinction corrections were made. After merging of the equivalent reflections, 725 independent observed reflections were obtained, all having $\sigma(I)/I \leqslant 0{\cdot}25$, and were used in the solution and refinement of the structure.

Determination and Refinement of the Structure.—The presence of three $(NMe_4)_2[Co_4Ni_2(CO)_{14}]$ units (using the hexagonal cell) in the space group $R3$ or $R\bar{3}$ indicated that only 1/3 or 1/6 of the formula was independent, and that the cobalt and nickel atoms were partially or totally disordered.

A three-dimensional Patterson function showed the peaks expected for an octahedron of metal atoms with M–M 2·5 Å. Since no deviation from the ideal geometry was detectable, the octahedron was assumed to be regular, and the space group $R\bar{3}$ was tentatively assumed (being indistinguishable from $R3$ as far as the ideal octahedral cluster is concerned). With the co-ordinates of the only independent metal atom, structure factors were computed and a Fourier synthesis revealed the positions of the carbonyl groups and of the cations. The peaks of these light atoms were all well resolved and showed no duplication. This was considered good evidence for space group $R\bar{3}$, in which the structure was successfully refined by full-matrix least-squares. A difference-Fourier map, computed before completion of the refinement, clearly showed the hydrogen atom positions of the tetramethylammonium cation. The co-ordinates of these atoms were determined by superimposition of a methyl group model on the experimental peaks, assuming C–H 1·10 Å and H–C–H 109° 28′. The contribution of hydrogen atoms to the structure factors was computed, but their positions were not refined. The final conventional R and weighted R' factors were 0·033 and 0·045, respectively $[R' = (\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2)^{1/2}]$. Weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ and, in the final stages of the refinement, A was 0·6, B −0·05, and C 0·0023, chosen so that the mean value of $w(F_o - k|F_c|)^2$ was practically

---

[8] W. L. Bond, *Acta Cryst.*, 1959, **12**, 375.

[9] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

constant over all ranges of F_o and sin θ/λ. Atomic scattering factors were taken from ref. 10 for hydrogen, and from ref. 11 for the other species. For the cobalt–nickel factors weighted mean values were used. The real part of the anomalous scattering was taken into account.[12]

The final difference-Fourier synthesis was rather flat with some residual peaks not exceeding $\pm 0{\cdot}4$ eÅ^{-3}, mainly around the metal atom positions.

Table 1 reports the final parameters of the atoms with their estimated standard deviations. Bond distances and angles are reported in Table 2. The final list of observed and computed structure factors moduli is given in Supplementary Publication No. SUP 20761 (2 pp., 1 microfiche).*

TABLE 2

Bond distances (Å) and angles (deg) within anion and cation

M(1)–M(2)	2·487(1)	M(1)–C(1)–O(1)	177·7(5)
M(1)–M(5)	2·519(1)	M(1)–C(2)–O(2)	135·1(3)
M(1)–C(1)	1·757(3)	M(3)–C(2)–O(2)	138·5(3)
M(1)–C(2)	2·078(5)	M(5)–C(2)–O(2)	133·1(5)
M(3)–C(2)	2·008(4)	M(1)–C(2)–M(3)	74·9(1)
M(5)–C(2)	2·126(5)	M(1)–C(2)–M(5)	75·0(1)
M(1)–C(3)	2·086(6)	M(3)–C(2)–M(5)	73·6(1)
C(1)–O(1)	1·129(5)	M(1)–C(3)–O(3)	136·5(2)
C(2)–O(2)	1·157(5)	M(1)–C(3)–M(3)	73·2(3)
C(3)–O(3)	1·151(9)	M(1)–M(2)–M(6)	60·4(1)
N–C(4)	1·480(9)	C(1)–M(1)–M(3)	138·5(1)
N–C(5)	1·491(5)	C(1)–M(1)–M(2)	134·4(2)
O(3) · · · H(2)	2·44	C(1)–M(1)–M(6)	131·5(1)
		C(1)–M(1)–M(5)	135·3(2)
		C(4)–N–C(5)	110·1(3)
		C(5)–N–C(5′)	108·9(4)

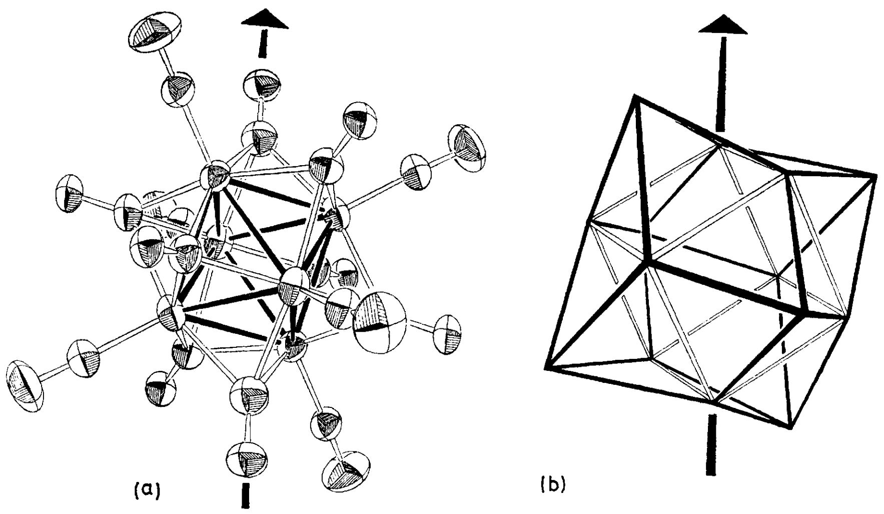

FIGURE 1 (a) ORTEP drawing of the anion showing thermal ellipsoids at 40% probability. (b) Polyhedron with 24 triangular faces obtained by connecting the carbon atoms. The black lines would define a rhombic dodecahedron if the concavities on the faces were ignored

Computations.—All computations were performed on a UNIVAC 1106 computer. For absorption correction a local programme was used, in which the directions of primary and diffracted beams are evaluated as recently described.[13] Counter data reduction and statistical analysis for weighting schemes were based upon Fortran programmes written by M. Sansoni. In addition, local versions of entries No. 7528, 7531, 7532, and 7535 in the 1966 'International World List of Crystallographic Programs' were used for Fourier analysis, structure-factor, and least-squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

MOLECULAR AND CRYSTAL STRUCTURE AND DISCUSSION

The $[Co_4Ni_2(CO)_{14}]^{2-}$ anion (Figure 1) consists of an octahedral metal atom cluster surrounded by fourteen carbonyl ligands, six of them linearly bonded, one *per* metal atom, and the other eight forming triple bridges above the octahedron faces. This ligand arrangement is closely similar to that found in $[Co_6(CO)_{14}]^{4-}$ and will be discussed later.

In the crystal, the anions lie around special positions with site-symmetry S_6 and the tetramethylammonium cations about positions of C_3 symmetry forming piles along the symmetry axes. Each anion is surrounded by eight cations and exhibits short contacts among oxygens of the bridging ligands and hydrogens in the range 2·44—2·48 Å. Figure 2 shows a drawing of the unit cell.

A consequence of the symmetry imposed by the space group is that cobalt and nickel are statistically distributed at the corners of the octahedral cluster, indicating that their positions have no influence on the overall geometry of the anion. It is impossible to define whether one or both the structural isomers, *i.e. cis* and

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full size copies.)

[10] J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, *A*, **24**, 321.

[12] 'International Tables for *X*-Ray Crystallography, vol. 3,' Kynoch Press, Birmingham, 1962.

[13] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

trans, are present in the crystal, but it must be pointed out that, whichever isomer is present, the deviations of the true molecular geometry from the crystal-imposed average geometry are negligible because all the atomic peaks in the Fourier synthesis are well defined and the thermal ellipsoids do not reveal improbable shapes or orientations.

The metal-atom cluster is best defined as a trigonal antiprism lightly stretched along the three-fold axis, the two independent M–M distances being 2·487(1) Å in the basal triangles and 2·519(1) Å between them. These values fall within the range of distances found in $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ (see Table 3). In $[Co_6(CO)_{14}]^{4-}$ the cluster is lightly squeezed, but in neither case can it be stated whether the deformations are true molecular features or crystal packing effects.

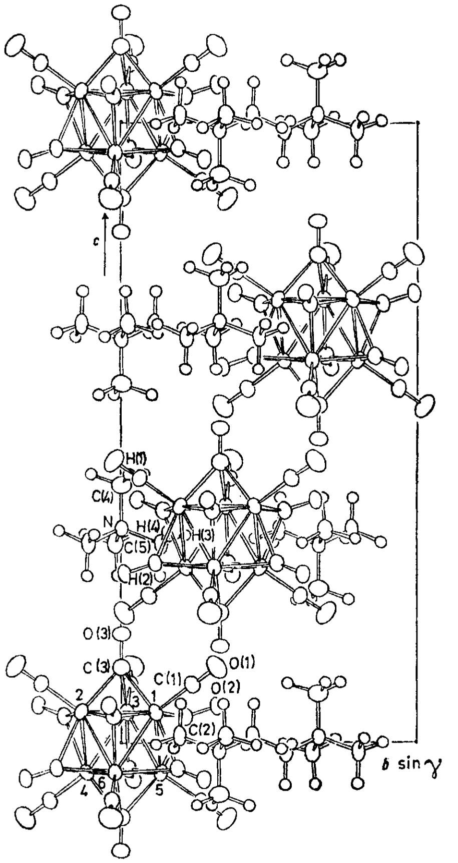

FIGURE 2 Perspective unit-cell drawing of the salt down the *a* axis. For sake of clarity the labelling is simplified and only the independent light atoms are numbered

The carbonyl ligands fall into three crystallographically independent classes: six terminal groups, two bridging groups on the three-fold axis, and the other six bridging the remaining octahedron faces. The M–C and C–O distances are normal and compare well with the corresponding values in $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$ (see Table 3). Whilst the ligand arrangement is almost equivalent to that found in $[Co_6(CO)_{14}]^{4-}$, the bond distances are closer to those found in $[Co_6(CO)_{15}]^{2-}$. One explanation is that the bond distances depend on the degree of π interactions, which are comparable to a greater extent in compounds having the same anionic charge. A closer comparison between bond distances in $[Co_6(CO)_{15}]^{2-}$ and $[Co_4Ni_2(CO)_{14}]^{2-}$ is hindered by the different geometries of the anions. Neglecting the influence of the geometry, the differences in bond lengths indicate a lesser back-donation in $[Co_4Ni_2(CO)_{14}]^{2-}$. This situation would be opposite from that expected on the basis of the diminished number of carbonyl groups, but would be in accord with the increased nuclear charge of the nickel atoms.

TABLE 3

Comparison of bond distances (Å) in some hexanuclear carbonyl anions

	M–M	M–C(term)	C–O(term)	M–C(face-br)	C–O(face-br)
$[Co_6(CO)_{15}]^{2-}$	2·47—2·52 (2·51) [a]	1·74 [a]	1·15 [a]	2·00	1·19 [a]
$[Co_6(CO)_{14}]^{4-}$	2·466—2·534 (2·50) [a]	1·70 [a]	1·17 [a]	2·97—2·31	1·21 [a]
$[Co_4Ni_2(CO)_{11}]^{2-}$	2·486, 2·521 (2·50) [a]	1·757	1·129	2·008—2·126	1·154 [a]

[a] Mean values.

The fourteen carbonyl groups are approximately disposed toward the vertices of a polyhedron with 24 triangular faces, which however can be idealized as a rhombic dodecahedron (Figure 1). The carbon–carbon contacts are approximately equal, mean 2·91 Å, while two types of oxygen–oxygen contacts are found, terminal–bridging and bridging–bridging, with mean values 3·92 and 4·23 Å.

The S_6 symmetry of the heteronuclear dianion in $(NMe_4)_2[Co_4Ni_2(CO)_{14}]$ seems to be exceptional when compared with the C_i symmetry of the homonuclear tetra-anion in $K_4[Co_6(CO)_{14}],6H_2O$, but can be rationalized. The main stereochemical difference between the two anions lies in the triple bridging carbonyl groups. The ligands which are strictly symmetric and moderately asymmetric in the former, are correspondingly moderately and strongly asymmetric in the latter. The low symmetry of $[Co_6(CO)_{14}]^{4-}$ may be partially explained in terms of the external interactions of the carbonyl ligands, mainly strong Coulombic attractions with the potassium cations and hydrogen bonds with water molecules. Another factor should however be considered: in the tetra-anion the carbonyl groups receive more negative charge *via* π back-donation and might prefer the looser structure obtainable with edge-bridging ligands. In fact the (centre-of-cluster)–oxygen distances for edge-bridging groups are 0·1—0·2 Å longer than for face-bridging groups, *i.e.* in the first case the anion has greater volume and the density of negative charge becomes smaller. With strongly asymmetric triple bridges, $[Co_6(CO)_{14}]^{4-}$ achieves the best compromise among the aforementioned factors, the bond interactions, and the packing efficiency which favours the most compact structure. Similar considerations explain the more regular structure of $[Co_4N_2(CO)_{14}]^{2-}$. Now we can imagine that in solution, where the crystal-packing forces are absent and many strong carbonyl-solvent interactions occur, a structure with six edge-bridging carbonyl groups becomes the most stable, giving the second isomeric form of $[Co_6(CO)_{14}]^4$.

The anion affords another example of the particular stability of the octahedral carbonylic clusters with **86** valence electrons. These conditions can be fulfilled with different metals and a variable number and type of ligands, *e.g.* $[Fe_6(CO)_{16}C]^{2-}$ (ref. 14), $H_2Ru_6(CO)_{18}$,[15] $Ru(CO)_{17}C$,[16] $Ru_6(CO)_{14}(arene)C$,[17,18] $Co_6(CO)_{16}$,[1,2] $[Co_6(CO)_{15}]^{2-}$ (refs. 3 and 4), $[Co_6(CO)_{14}]^{4-}$ (refs. 5 and 6), $Co_2Rh_4(CO)_{16}$,[19,20] $Rh_6(CO)_{16}$,[21–23] $Rh_6(CO)_{16-x}L_x$ (L = substituted phosphines or arsines),[24,25] $[Rh_6(CO)_{15}X]^-$ (X = anionic ligand),[26,27] $[Rh_6(CO)_{15}]^{2-}$ (ref. 28), $[Rh_6(CO)_{14}]^{4-}$ (ref. 29), $Ir_6(CO)_{16}$,[30] $[Ir_{16}(CO)_{15}]^{2-}$ (ref. 30), and $[Co_4Ni_2(CO)_{14}]^{2-}$. As soon as the number of electrons changes, new structures are obtained for the metal-atom cluster, *i.e.* a trigonal prism with 90 electrons in $[Rh_6(CO)_{15}C]^{2-}$ (ref. 31), a bicapped rhombus with 82 electrons in $[Mo_2Ni_4(CO)_{14}]^{2-}$ (ref. 32), and a bicapped tetrahedron with 84 electrons in $Os_6(CO)_{18}$.[33]

We thank the Italian C.N.R. for financial support and Dr. P. L. Bellon for useful discussions.

[3/548 *Received*, 15*th March*, 1973]

---

[14] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, 1971, **93**, 3073.

[15] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Comm.*, 1970, 458

[16] A. Sirigu, M. Bianchi, and E. Benedetti, *Chem. Comm.*, 1969, 596.

[17] B. F. Jonson, R. D. Johnston, and J. Lewis, *J. Chem. Soc.* (*A*), 1968, 2865.

[18] R. Mason and W. R. Robinson, *Chem. Comm.*, 1968, 468.

[19] F. G. A. Stone and S. H. H. Chaston, Proc. XI I.C.C.C., Haifa, Sept. 1968.

[20] S. Martinengo, P. Chini, T. Salvatori, V. C. Albano, and F. Cariati, *J. Organometallic Chem.*, 1973, **59**, 379.

[21] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[22] P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 315.

[23] S. H. H. Chaston and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 500.

[24] B. F. G. Johnson, J. Lewis, and P. W. Robinson, *J. Chem. Soc.* (*A*), 1970, 1100.

[25] B. L. Booth, M. J. Else, R. Fields, and R. N. Haszeldine, *J. Organometallic Chem.*, 1971, **27**, 119.

[26] P. Chini, S. Martinengo, and G. Giordano, *Gazzetta*, 1972, **102**, 330.

[27] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 678.

[28] S. Martinengo and P. Chini, *Gazzetta*, 1972, **102**, 344.

[29] P. Chini and S. Martinengo, *Chem. Comm.*, 1969, 1092.

[30] L. Malatesta, G. Caglio, and M. Angoletta, *Chem. Comm.*, 1970, 532.

[31] V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.

[32] W. R. Costello and L. F. Dahl, unpublished research; preliminary information in ref. 23 of J. K. Ruff, R. P. White, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 2159.

[33] R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Amer. Chem. Soc.*, 1973, **95**, 3802.