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# Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. III.[1] Crystal Structure and Reaction Studies of Bis(methinyltricobalt enneacarbonyl)acetylene ($Co_6(CO)_{18}C_4$)

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The compound $Co_6(CO)_{18}C_4$ is one product of the reaction of $ClCCo_3(CO)_9$ with mesitylene. Its crystal and molecular structure has been determined by three-dimensional X-ray analysis. Crystals are triclinic, space group $P\bar{1}$ with one centrosymmetric molecule in a cell of dimensions $a$ = 8.87 (1), $b$ = 12.61 (2), $c$ = 7.97 (1) Å; $\alpha$ = 106.9 (2), $\beta$ = 111.7 (1), $\gamma$ = 70.1 (1)°. X-Ray data were collected by conventional film techniques using Co K$\alpha$ radiation and the intensities of 1088 reflections above background were measured photometrically. The structure was refined anisotropically by full-matrix least-squares procedures to a conventional $R$ factor of 0.047. The structure is composed of discrete molecules formed by the insertion of a carbon–carbon triple bond between two identical $-CCo_3(CO)_9$ units. In the linear carbon chain, C—C≡C—C, at the center of the molecule, the C—C and C≡C bond lengths are 1.37 (1) and 1.24 (2) Å, respectively. The mean Co—Co bond length is 2.47 (1) Å. The optimum experimental conditions for formation of $Co_6(CO)_{18}C_4$ and related compounds from arenes and $YCo_3(CO)_9$ compounds are given and a number of reactions of $Co_6(CO)_{18}C_4$ and derivatives are reported and discussed.

## Introduction

From the reaction products of chloro- and bromomethinyltricobalt enneacarbonyl, $YCCo_3(CO)_9$, with various arenes, have been isolated the compounds $Co_5(CO)_{15}C_3H$,[1] $Co_6(CO)_{18}C_4$, and $Co_8(CO)_{24}C_6$.[5,6] All three compounds have proved to possess novel molecular structures all of which include the $-CCo_3(CO)_9$ structural unit originally discovered in $CH_3CCo_3(CO)_9$.[7]

Neither $CH_3CCo_3(CO)_9$, $C_6H_5CCo_3(CO)_9$, nor $FCCo_3(CO)_9$ produces similar products but give instead arene complexes $RCCo_3(CO)_6$(arene) and acetylene derivatives $(RC{\equiv}CR)Co_4(CO)_{10}$.[5] Yields are higher with $BrCCo_3(CO)_9$ than with $ClCCo_3(CO)_9$. These observations suggest that cleavage of the apical C–Y bond and formation of the electron-deficient species $CCo_3(CO)_9$ is the crucial step.

The arene must play an active part in the reactions as these compounds are not formed by thermal treatment of $BrCCo_3(CO)_9$ alone nor in reactions in hydrocarbon and other solvents. On the other hand the acetylene residue is not necessarily formed from the arene since it has been shown that the acetylene group in $(RC{\equiv}CR)Co_4(CO)_{10}$ (prepared from $CH_3CCo_3(CO)_9$) is derived entirely from the parent cluster.[8]

## Experimental Section

All reactions and manipulations were performed under nitrogen with dried solvents. The methinyltricobalt enneacarbonyls were prepared by published methods.[9] It should be noted that the preparation of $BrCCo_3(CO)_9$ from $CBr_4$ always gives a product containing small quantities of $HCCo_3(CO)_9$ which can only be removed by repeated separations on silica gel plates.

**Preparation of $Co_6(CO)_{18}C_4$.**—The orange-brown band obtained on chromatographic separation of the product from the reaction of $ClCCo_3(CO)_9$ with mesitylene[1] was removed and eluted with acetone–pentane; the solvent was removed *in vacuo*. Recrystallization of the brown solid from petroleum ether (bp 30–40°) gave small dark crystals of bis(methinyltricobalt enneacarbonyl)acetylene; yield 52 mg. *Anal.* Calcd for $C_{22}O_{18}Co_6$: C, 29.17; H, 0.0; Co, 39.04; CO, 55.66. Found: C, 29.23; H, 0.18; Co, 39.2; CO, 54.63.

The compound is air stable and soluble in organic solvents without decomposition. It will sublime at 90° (0.05 mm) but only with extensive decomposition. For this reason a mass spectrum was not obtained but both infrared and nmr spectra indicated the absence of hydrogen in the compound.

**General Conditions for the Preparation of $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$ from Arenes.**—Table I illustrates the effect on the yield if the tricobalt cluster compound (Br or Cl), arene, temperature, and reaction time are varied. Yields of the $Co_5$, $Co_6$, and $Co_8$ compounds are quoted per 1 g of tricobalt cluster.

TABLE I

| Y in $YCCo_3$-$(CO)_9$ | Arene | Temp, °C | Time, min | mg | | | |
|---|---|---|---|---|---|---|---|
| | | | | $Co_5$ | $Co_6$ | $Co_8$ | Dimer[a] |
| Cl | $C_6H_3(CH_3)_3$ | 154 | 10 | 18 | 37 | ... | ... |
| Cl, Br | $C_6H_3(CH_3)_3$ | 154 | 120 | Decomposition to cobalt | | | |
| Cl | $C_6H_3(CH_3)_3$ | 130 | 120 | 7 | 32 | 5 | Trace |
| Cl | $C_6H_3(CH_3)_3$ | 130 | 30 | 4 | 51 | ... | ... |
| Cl | *p*-$C_6H_4(CH_3)_2$ | 130 | 30 | 8 | 41 | ... | ... |
| Br | *p*-$C_6H_4(CH_3)_2$ | 125 | 30 | 23 | 130 | 12 | 30 |
| Br | $C_6H_5(CH_3)$ | 118 | 20 | 3 | Trace | ... | 100 |
| Br | $C_6H_5(CH_3)$ | 90 | 60 | Trace | ... | ... | 200[b] |

[a] $[Co_3(CO)_9C]_2$. [b] $[Co_3(CO)_9C]_2CO$ is also formed: G. Allegra, R. Ercoli, and E. M. Peronaci, *Chem. Commun.*, 549 (1966).

Yields are increased if the cluster is added gradually to the boiling or heated arene. Most samples of $Co_5(CO)_{15}C_3H$ contain trace quantities of $Co_5(CO)_{15}C_3CH_3$[1] as the two compounds have similar $R_f$ values on the plates.

The above reactions may also be carried out in sealed tubes and by this means it is possible to obtain the compounds in very low yields using benzene as a solvent.

In another preparation, $BrCCO_3(CO)_9$ (1.0 g in 10 ml of *m*-xylene) was added slowly to a solution of $Co_2(CO)_6(C_2H_2)$ (0.25 ml) in *m*-xylene (5 ml) at 110–115° over a period of 30 min.

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(1) Part II: R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197 (1970).

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(5) B. H. Robinson, J. L. Spencer, and R. Hodges, *Chem. Commun.*, 1480 (1968).

(6) R. J. Dellaca and B. R. Penfold, *Acta Crystallogr., Sect., A*, **25**, S170 (1969).

(7) P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

(8) B. H. Robinson and J. L. Spencer, unpublished results.

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

Chromatographic separation of the reaction mixture in the usual way gave $Co_5(CO)_{15}C_3H$ (0.015 g), $Co_6(CO)_{18}C_4$ (0.010 g), and $[Co_3(CO)_9C]_2$ (>0.11 g). When the same reaction was carried out in refluxing heptane (98°) complete decomposition occurred. Likewise, if the $Co_2(CO)_6(C_2H_2)$ was replaced by acetylene (bubbled through the solution), the result again was complete decomposition.

**Miscellaneous Preparations of $Co_5(CO)_{15}C_3H$ and $Co_6(CO)_{18}C_4$.**—(a) Cobalt carbonyl (10 g), tetrahydrofuran (50 ml), and trichlorofluoromethane (50 ml) were stirred at 40° for 4 hr. The solvent was removed *in vacuo* and the residue was sublimed at 50° (0.1 mm) to remove the volatile fluoromethinyltricobalt enneacarbonyl (1.93 g). The brown residue left after the sublimation was dissolved in hexane. Chromatographic separation as outlined previously yielded $Co_5(CO)_{15}C_3H$ (together with a small quantity of $Co_5(CO)_{15}C_3F$) (0.050 g), $Co_6(CO)_{18}C_4$ (0.022 g), and $Co_8(CO)_{24}C_6$ (0.005 g). It is thought that the vacuum sublimation markedly reduced the yield of these compounds because they are thermally unstable at 50° (0.1 mm).

$Co_5(CO)_{15}C_3F$ was detected only in the mass spectrum of $Co_5(CO)_{15}C_3H$.[1] It is unlikely that hydrogen exchange had occurred in the mass spectrometer (other evidence suggests that the fluorine is labile) as the analytical figures show that the amount of fluoride impurity must have been small. *Anal.* Calcd for $C_{18}O_{15}Co_5H$: C, 28.76; H, 0.13. Calcd for $C_{18}O_{15}Co_5F$: C, 28.05; H, 0.00. Found: C, 29.06; H, 0.21.

Tetrahydrofuran may be replaced by methanol and the compounds have been detected (tlc and infrared) in the preparations of $BrCCo_3(CO)_9$ and $HCCo_3(CO)_9$ from $Co_2(CO)_8$ and $CBr_4$ and $CHCl_3$, respectively, in tetrahydrofuran.

(b) In an attempt to prepare $Co_5(CO)_{15}C_3F$, $BrCCo_3(CO)_9$ (1.0 g) and hexafluorobenzene (1 ml) were allowed to react in a sealed tube at 100° for 10 min. The contents of the tube were extracted with pentane and the products separated on three 20 × 20 cm silica gel plates. Six bands in the following order were observed: (1) purple, $HCCo_3(CO)_9$ (*Anal.* Calcd for $C_{10}O_9Co_3H$: C, 27.15; H, 0.23. Found: C, 27.13; H, 0.34); (2) purple, $Co_3(CO)_9CBr$; (3) purple-gray, $Co_5(CO)_{15}C_3H$ (mass spectral analysis[1]); (4) brown, $Co_6(CO)_{18}C_4$ (ir spectra and analysis); (5) brown, $Co_8(CO)_{24}C_6$ (ir spectra and analysis); (6) brown, $[Co_3(CO)_9C]_2CO$ (analysis).

Hydrogen-containing impurities were not evident in the $^1H$ nmr or the mass spectrum of the hexafluorobenzene and $BrCCO_3(CO)_9$. Presumably hydrogen exchange had occurred during the working up.

(c) Tetrafluoroethylene and cobalt carbonyl were allowed to react according to the method of Beveridge and Clark.[10] A chromatographic separation of the products yielded, besides $Co_3(CO)_9CCF_3$, the dimer $[Co(CO)_9C]_2$, $[Co_3(CO)_9C]_2CO$, and $Co_6(CO)_{18}C_4$ (identified by analysis and infrared spectrum). There was no indication of any other hexane- or benzene-soluble product. We suggest that the brown "unknown" cobalt carbonyl reported as a product of this reaction by Beveridge and Clark is in fact $Co_6(CO)_{18}C_4$.

**An Attempted Preparation of $Co_6(CO)_{18}C_4$.**—Sodium acetylide was prepared in the usual way from acetylene and a solution of sodium in liquid ammonia. The ammonia was removed and the vessel was charged with $BrCCo_3(CO)_9$ (2 mol to 1 mol of $NaC{\equiv}CH$) and benzene (25 ml).

The mixture was refluxed for 30 min and stirred at room temperature for a further 3 hr. The benzene was removed *in vacuo* and the residue was extracted with hexane. A qualitative tlc separation showed the presence of $BrCCo_3(CO)_9$ and $HCCo_3(CO)_9$ only.

It is possible that $Co_6(CO)_{18}C_4$ could be made by the reaction $9Co_2(CO)_8 + 2Cl_3C{-}C{\equiv}C{-}CCl_3 \rightarrow 2Co_6(CO)_{18}C_4 + 36CO + 6CoCl_2$, but we have been unable to isolate the acetylene intermediate. The direct reaction of acetylenes with methinyltricobalt enneacarbonyls does not yield similar compounds.[11]

**Triphenylphosphine Derivatives of $Co_6(CO)_{18}C_4$.**—A solution of $Co_6(CO)_{18}C_4$ (0.065 g, 0.068 mmol) in benzene was added to a stirred solution of tetrakis(triphenylphosphine)platinum(0) (0.087 g, 0.07 mmol) in benzene (10 ml) at 20°. A reaction occurred almost instantaneously, but the solution was stirred for a further 5 min. The benzene was removed *in vacuo* and the residue was extracted with 6 ml of ether and spread on two 20 × 20 cm silica gel plates.

Elution of the plates with benzene–hexane gave three bands, the first due to unreacted $Co_6(CO)_{18}C_4$. The second band was removed and eluted with acetone. Brown needles of (triphenylphosphine)tetracarbonhexacobalt heptadecacarbonyl[12] crystallized from the acetone solution at 0°. *Anal.* Calcd for $C_{39}H_{15}Co_6O_{17}P$: C, 41.10; H, 1.32; mol wt 1140. Found: C, 42.27; H, 1.84; mol wt 1000 (benzene). The compound was stable in air and soluble without decomposition in all organic solvents tested except alcohols.

The third band was treated in the same way to give bis(triphenylphosphine)tetracarbonhexacobalt(0) hexadecacarbonyl as brown needles. *Anal.* Calcd for $C_{56}H_{30}Co_6O_{16}P_2$: C, 48.92; H, 2.18. Found: C, 49.51; H, 2.79.

The same two complexes could be prepared directly by heating a solution of $Co_6(CO)_{18}C_4$ with triphenylphosphine in hexane under reflux for 30 min. However the yields were very small as compared with those from the room-temperature reaction because of breakdown to $[Co(CO)_3(C_6H_5)_3P)]_2$ and $[Co(CO)_3((C_6H_5)_3P)_2][Co(CO)_4]$.

**Tricyclohexylphosphine Complexes of $Co_6(CO)_{18}C_4$.**—Tricyclohexylphosphine (0.05 g) was added to a stirred solution of $Co_6(CO)_{18}C_4$ in hexane (25 ml) and the temperature of the solution was raised over 15 min to 66°. After 10 min at 66° the solution was cooled and the solvent was removed *in vacuo*. The residue was extracted with pentane and separated on silica gel plates.

The first brown band was removed and eluted with hexane. Brown prisms of tricyclohexylphosphinetetracarbonhexacobalt(0) heptadecacarbonyl were obtained from the hexane solution at 0°; yield, 0.094 g. *Anal.* Calcd for $C_{39}H_{33}Co_6O_{17}P$: C, 40.41; H, 2.84. Found: C, 41.43; H, 3.32. The complex had properties similar to those of the triphenylphosphine derivative. A second purple-brown band was treated in the same manner to give small brown crystals of bis(tricyclohexylphosphine)tetracarbonhexacobalt(0) hexadecacarbonyl; yield, 0.012 g. *Anal.* Calcd for $C_{56}H_{66}Co_6O_{16}P_2$: C, 47.66; H, 4.68. Found: C, 48.24; H, 4.92.

**Reaction of Diethylphenylphosphine with $Co_6(CO)_{18}C_4$.**—Diethylphenylphosphine (0.083 g, 0.050 mmol) and $Co_6(CO)_{18}C_4$ (0.11 g, 0.012 mmol) in hexane (25 ml) were stirred for 30 min at 20°. The solvent was removed *in vacuo* and the residue was spread and developed with hexane–benzene on four 20 × 20 cm silica gel plates.

Five bands developed in the following order: (1) brown (unreacted $Co_6(CO)_{18}C_4$); (2) dark brown (presumably $Co_6(CO)_{17}C_4(C_6H_5(C_2H_5)_2P)$; (3) dark brown; (4) red; (5) lavender.

**Infrared Spectra.**—Solution and mull spectra were obtained in the region 5000–200 $cm^{-1}$ on a Perkin-Elmer 225 spectrophotometer using, where appropriate, sodium chloride, potassium bromide, and polythene cells.

**Crystallographic Data.**[13]—$Co_6(CO)_{18}C_4$, mol wt 906, is triclinic with $a$ = 8.87 (1), $b$ = 12.61 (2), $c$ = 7.97 (1) Å; $\alpha$ = 106.9 (2), $\beta$ = 111.7 (1), $\gamma$ = 70.1 (1)°; $V$ = 765 Å$^3$; $d_{obsd}$ = 1.96 (2) g/cm$^3$; $Z$ = 1; $d_{calcd}$ = 1.967 g/cm$^3$; $\mu$(Co K$\alpha$) = 62.1 $cm^{-1}$.

The crystal structure has been refined successfully in space group $P\bar{1}$ with all atoms occupying the general twofold set of equivalent positions. This implies a molecular center of symmetry.

Unit cell dimensions and their estimated standard deviations were obtained from a least-squares refinement on $\sin^2 \theta$. Input

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[10] A. D. Beveridge and H. C. Clark, *J. Organometal. Chem.*, **11**, 603 (1968).

[11] T. Matheson and B. H. Robinson, to be published.

[12] This nomenclature is used for convenience throughout this section instead of the alternative acetylene description.

[13] Here and throughout this paper, the uncertainties given in parentheses are estimated standard deviations in the least significant digits quoted.

data were the distances between Friedel pairs of reflections on calibrated zero-level precession photographs taken with Polaroid film and Mo K$\alpha$ radiation ($\lambda$ 0.7107 Å) at room temperature (20 ± 2°). The experimental density was obtained using a suitably calibrated density gradient tube with $CH_3I$ and $CCl_4$ as media. A Delaunay reduction gave parameters $a' = 8.87$, $b' = 12.80$, $c' = 7.97$ Å; $\alpha' = 109.6$, $\beta' = 111.7$, $\gamma' = 96.0°$ where the reduced cell (primed) is related to the nonreduced primitive cell (unprimed) by the transformations $a^{*\prime} = -a^*$, $b^{*\prime} = b^*$, $c^{*\prime} = b^* - c^*$. The data were indexed in the nonreduced cell and all results are reported in terms of this cell.

The crystal used for the primary data collection was plate-shaped with approximate dimensions 0.4 mm (parallel to $a$) × 0.3 mm × 0.1 mm. X-Ray intensities were recorded from this crystal at room temperature on a two-dimensionally integrating equiinclination Weissenberg camera using Fe-filtered Co K$\alpha$ radiation. The plateaus of the integrated spots and adjacent background areas were measured using a single-beam photometer and a galvanometer calibrated to indicate intensities directly. The levels ($nkl$), with $n$ = 0–5, were investigated, and, within these, intensities were assigned to 1088 reflections judged to be above the threshold of observation. Both halves of the Weissenberg films were measured for nonzero levels. Corrections were made for spot extension while spot contraction was assumed to be self-corrected in the integration process. Corrections for crystal absorption, using the Gaussian quadrature method, produced transmission factors varying between 0.25 and 0.50.

Intensities from a second crystal oscillating about the [$\bar{1}$10] axis were used to place the primary data on a common scale. A total of 105 reflections from the zero and first upper level were measured and processed as for the first crystal except that no corrections were made for spot extension. The crystal dimensions were 0.3 × 0.1 × 0.1 mm and transmission factors ranged from 0.33 to 0.64. Interlevel scale factors for the first crystal were obtained but the two data sets were not merged.

Only observed reflections were used in the refinement process. Following final refinement, structure factor calculations for the unobserved reflections in the reciprocal lattice region investigated showed that for the 212 reflections treated as "unobserved" only 10 $F_c$ values were greater than $F_{\min}$ and none was as great as $2F_{\min}$.

All calculations except the final stages of the refinement were carried out on an IBM 360/44 computer with 16K words of core storage and twin-disk drives. For the final refinement a 360/67 with a large core was available. Programs used have been described in part I of this series.

## Structure Determination and Refinement

The distribution of vectors in a sharpened three-dimensional Patterson function strongly indicated space group P$\bar{1}$ which with a single molecule of $Co_6(CO)_{18}C_4$ in the unit cell requires a center of symmetry. Initial values for the coordinates of the three independent cobalt atoms were obtained from the vector map. Two successive electron density difference maps followed by partial least-squares refinement cycles then revealed all carbon and oxygen atoms.

In all least-squares calculations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight $w$ was determined by the empirical formula of Cruickshank:[14] $w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$. Coefficients which gave reasonable constancy of average values of the minimized function over the full $F_o$ range at the end of the refinement were $A = 12.9$, $B = -0.43$, $C = 0.018$, and $D = -4.2 \times 10^{-5}$. The normal tabulations of atomic scattering factors[15] for Co, C, and O were used, those for Co only being corrected for anomalous dispersion, values for $\Delta f'$ and $\Delta f''$ of $-2.19$ and 0.74 electrons, respectively, being interpolated from Cromer's tables.[16]

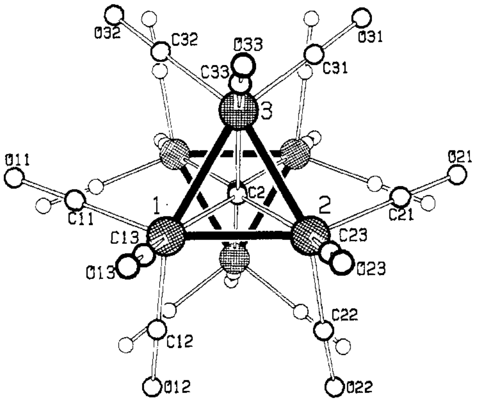

Figure 1.—The $Co_6(CO)_{18}C_4$ molecule viewed normal to the $Co_3$ triangles.

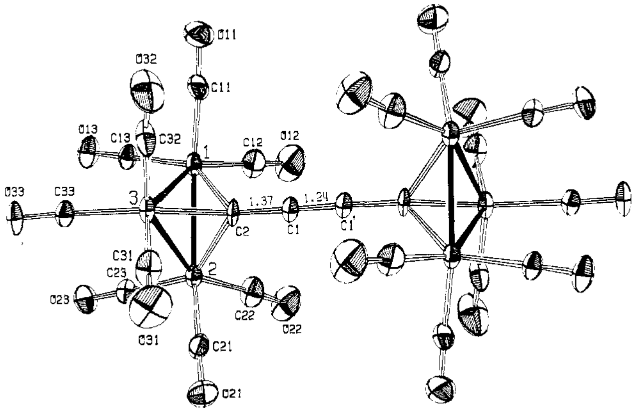

Figure 2.—A general perspective view of the $Co_6(CO)_{18}C_4$ molecule showing anisotropic thermal ellipsoids for individual atoms.

Full-matrix isotropic refinement, with a separate scale factor for each Weissenberg level, converged with $R_1$ and $R_2$[17] at 0.136 and 0.166, respectively. A difference map computed at this stage contained peaks of height up to 2.5 e$^-$/Å$^3$ close to the cobalt positions. Also the isotropic thermal parameters of most of the atoms in carbonyl groups were relatively large (up to 11.5 Å$^2$). It seemed reasonable therefore to resume the refinement using an ellipsoid (six parameters) rather than a sphere as the thermal model for each atom. It was at this point that absorption corrections were applied and all of the primary data were placed upon a common scale as earlier described. In the final refinement cycles a variable parameter, $C$, was introduced to correct for the effect of secondary extinction, the form of the correction being as proposed by Zachariasen,[18] $F$ (corrected) $= F_o(1 + CI)$, where $I$ is the uncorrected intensity. Simultaneous refinement of all 209 variable

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[14] D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Oxford, 1965, p 114.

[15] "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

[16] D. T. Cromer, *Acta Crystallogr.*, **18**, 511 (1965).

[17] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

[18] W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

TABLE II

POSITIONAL AND THERMAL[a] PARAMETERS FOR $Co_6(CO)_{18}C_4$

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co(1) | 0.5405 (2) | 0.2513 (1) | 0.1456 (2) | 0.0127 (6) | 0.0067 (1) | 0.0180 (4) | −0.0007 (2) | 0.0057 (3) | −0.0017 (2) |
| Co(2) | 0.6596 (3) | 0.1937 (1) | 0.4483 (2) | 0.0138 (6) | 0.0065 (1) | 0.0200 (4) | −0.0012 (2) | 0.0073 (3) | −0.0006 (2) |
| Co(3) | 0.8212 (2) | 0.2756 (1) | 0.3494 (2) | 0.0117 (5) | 0.0058 (1) | 0.0249 (4) | −0.0012 (2) | 0.0086 (3) | −0.0020 (2) |
| C(1) | 0.534 (1) | 0.4508 (7) | 0.466 (1) | 0.011 (2) | 0.0068 (7) | 0.019 (2) | −0.002 (1) | 0.006 (2) | −0.002 (1) |
| C(2) | 0.602 (1) | 0.3414 (7) | 0.386 (1) | 0.011 (2) | 0.0060 (7) | 0.022 (2) | 0.000 (1) | 0.010 (2) | −0.003 (1) |
| C(11) | 0.506 (2) | 0.3356 (8) | −0.012 (2) | 0.028 (3) | 0.0066 (9) | 0.025 (3) | 0.002 (1) | 0.010 (2) | 0.002 (1) |
| C(12) | 0.326 (2) | 0.2678 (13) | 0.123 (2) | 0.018 (5) | 0.0192 (17) | 0.020 (3) | −0.002 (2) | 0.001 (3) | −0.001 (2) |
| C(13) | 0.596 (1) | 0.1114 (9) | 0.001 (1) | 0.015 (3) | 0.0083 (9) | 0.021 (2) | −0.004 (1) | 0.007 (2) | −0.002 (1) |
| C(21) | 0.778 (2) | 0.2094 (9) | 0.685 (2) | 0.017 (3) | 0.0109 (10) | 0.021 (3) | −0.002 (1) | 0.008 (2) | −0.000 (1) |
| C(22) | 0.467 (2) | 0.1948 (12) | 0.477 (2) | 0.018 (6) | 0.0149 (14) | 0.034 (4) | −0.007 (2) | 0.008 (3) | −0.001 (2) |
| C(23) | 0.745 (1) | 0.0400 (9) | 0.372 (1) | 0.018 (3) | 0.0079 (10) | 0.026 (3) | −0.002 (1) | 0.010 (2) | 0.001 (1) |
| C(31) | 0.958 (2) | 0.3148 (10) | 0.569 (2) | 0.021 (3) | 0.0115 (11) | 0.032 (4) | −0.008 (2) | 0.008 (3) | −0.006 (2) |
| C(32) | 0.837 (2) | 0.3743 (10) | 0.240 (2) | 0.021 (3) | 0.0076 (10) | 0.056 (5) | 0.000 (1) | 0.020 (3) | 0.002 (2) |
| C(33) | 0.956 (1) | 0.1435 (8) | 0.259 (1) | 0.017 (3) | 0.0077 (9) | 0.021 (2) | −0.003 (1) | 0.008 (2) | −0.001 (1) |
| O(11) | 0.484 (1) | 0.3872 (7) | −0.121 (1) | 0.056 (3) | 0.0106 (8) | 0.034 (2) | 0.002 (1) | 0.018 (2) | 0.006 (1) |
| O(12) | 0.189 (2) | 0.2797 (14) | 0.110 (2) | 0.019 (4) | 0.0378 (23) | 0.044 (4) | −0.006 (2) | 0.005 (3) | 0.004 (2) |
| O(13) | 0.631 (1) | 0.0268 (6) | −0.090 (1) | 0.030 (2) | 0.0095 (7) | 0.033 (2) | −0.005 (1) | 0.016 (2) | −0.007 (1) |
| O(21) | 0.852 (1) | 0.2173 (8) | 0.837 (1) | 0.031 (2) | 0.0184 (11) | 0.022 (2) | −0.005 (1) | 0.003 (2) | 0.002 (1) |
| O(22) | 0.351 (2) | 0.1944 (12) | 0.500 (2) | 0.024 (4) | 0.0295 (17) | 0.049 (3) | −0.012 (2) | 0.014 (3) | 0.003 (2) |
| O(23) | 0.799 (1) | −0.0534 (6) | 0.321 (1) | 0.036 (2) | 0.0062 (6) | 0.039 (2) | 0.001 (1) | 0.015 (2) | 0.002 (1) |
| O(31) | 1.046 (2) | 0.3431 (10) | 0.713 (2) | 0.038 (3) | 0.0248 (16) | 0.040 (3) | −0.021 (2) | 0.002 (3) | −0.007 (2) |
| O(32) | 0.846 (2) | 0.4400 (9) | 0.174 (2) | 0.047 (4) | 0.0129 (10) | 0.107 (6) | −0.002 (1) | 0.039 (4) | 0.017 (2) |
| O(33) | 1.042 (1) | 0.0609 (6) | 0.207 (1) | 0.023 (2) | 0.0086 (7) | 0.042 (2) | 0.003 (9) | 0.018 (2) | −0.002 (1) |

[a] The expression used for the atomic temperature factor was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

parameters finally reduced $R_1$ and $R_2$ to values of 0.047 and 0.059.[19] Final positional and thermal parameters with esd's are listed in Table II, rms amplitudes of atom vibrations in Table III, and observed and calculated structure amplitudes in Table IV.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

| Atom | Min | Intermed | Max |
|---|---|---|---|
| Co(1) | 0.169 (3) | 0.212 (4) | 0.275 (2) |
| Co(2) | 0.179 (3) | 0.225 (4) | 0.259 (2) |
| Co(3) | 0.159 (3) | 0.210 (3) | 0.287 (2) |
| C(1) | 0.18 (1) | 0.20 (2) | 0.27 (1) |
| C(2) | 0.12 (2) | 0.22 (2) | 0.29 (1) |
| C(11) | 0.19 (1) | 0.26 (2) | 0.34 (2) |
| C(12) | 0.21 (2) | 0.26 (3) | 0.41 (2) |
| C(13) | 0.20 (2) | 0.22 (2) | 0.29 (1) |
| C(21) | 0.21 (2) | 0.25 (2) | 0.30 (1) |
| C(22) | 0.22 (5) | 0.28 (2) | 0.36 (2) |
| C(23) | 0.21 (2) | 0.25 (2) | 0.27 (1) |
| C(31) | 0.20 (2) | 0.26 (2) | 0.37 (2) |
| C(32) | 0.20 (2) | 0.27 (2) | 0.39 (2) |
| C(33) | 0.20 (2) | 0.25 (2) | 0.28 (1) |
| O(11) | 0.25 (1) | 0.29 (1) | 0.46 (1) |
| O(12) | 0.25 (2) | 0.35 (2) | 0.54 (2) |
| O(13) | 0.19 (1) | 0.31 (1) | 0.37 (1) |
| O(21) | 0.24 (1) | 0.32 (1) | 0.39 (1) |
| O(22) | 0.24 (3) | 0.36 (1) | 0.46 (1) |
| O(23) | 0.20 (1) | 0.33 (1) | 0.37 (1) |
| O(31) | 0.20 (2) | 0.40 (1) | 0.47 (1) |
| O(32) | 0.26 (1) | 0.33 (2) | 0.54 (2) |
| O(33) | 0.16 (1) | 0.33 (1) | 0.36 (1) |

## Description of Structure and Discussion

The crystal structure consists of well-separated molecules of $Co_6(CO)_{18}C_4$, no intermolecular contact being shorter than 2.96 Å. A view of the molecule projected onto the plane of one of the $Co_3$ triangles is shown in Figure 1 and a general perspective view showing anisotropic thermal ellipsoids is given in Figure 2. (Parentheses have been omitted from atom labels in order to simplify the diagrams but the numbering scheme is the same as in Table II.) Bond lengths and angles are listed in Tables V and VI, with nonbonded contacts in Table VII. No attempt was made to correct the distances for the effects of thermal motion. The only values likely to be affected significantly are the C–O bond lengths and these are not of great chemical interest. The molecule possesses a center of symmetry (at the center of the bond C(1)–C(1′)), required by the space group but, as can be readily observed form Figure 1, the idealized molecular symmetry is $D_{3d}$-$\bar{3}$m.

The basic structural feature of the molecule is the $CCo_3(CO)_9$ group based on a $CCo_3$ tetrahedron, which has previously been observed in $CH_3CCo_3(CO)_9$,[7] $[Co_3(CO)_9C]_2CO$,[20] $Co_3(CO)_{10}BH_2N(C_2H_5)_3$,[21] $CH_3CCo_3(CO)_8P(C_6H_5)_3$,[22] and $Co_5(CO)_{15}C_3H$[1] and also in our current studies of $Co_8(CO)_{24}C_6$[23] and $C_6H_5CCo_3(CO)_6[(C_6H_3)(CH_3)_3]$.[23] In the present compound two $CCo_3(CO)_9$ units are linked by a C≡C bridge so that the central part of the molecule consists of a linear C—C≡C—C chain. Average values of bond lengths and angles in the $CCo_3(CO)_9$ unit are in good agreement with those found in the related compounds mentioned above. The average axial Co–C(carbonyl) distance of 1.82 (1) Å is longer than the average equatorial Co–

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(19) The influence on the refinement of anisotropic thermal and extinction paramerers and absorption corrections may be judged by the behavior of $R_1$ as follows: only Co atoms anisotropic, 0.092; absorption and extinction corrections and additional eight O atoms anisotropic, 0.068; all remaining atoms anisotropic, 0.047.

(20) G. Allegra and S. Valle, *Acta Crystallogr., Sect. B*, **25**, 107 (1969).

(21) F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2265 (1968).

(22) M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *ibid.*, **9**, 362 (1970).

(23) Structures to be reported in forthcoming publications in this series.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $Co_6(CO)_{18}C_4$

| K | L | OBS | CALC |
|---|---|---|---|
| **** H = 0 **** | | | |
| -2 | 0 | 133 | 139 |
| -3 | 0 | 21 | 19 |
| -4 | 0 | 63 | 66 |
| -5 | 0 | 23 | 22 |
| -6 | 0 | 26 | 26 |
| -7 | 0 | 7 | 6 |
| -8 | 0 | 8 | 5 |
| -9 | 0 | 17 | 16 |
| -10 | 0 | 10 | 9 |
| -11 | 0 | 15 | 14 |
| 0 | -1 | 37 | 36 |
| 1 | -1 | 68 | 76 |
| 2 | -1 | 30 | 31 |
| 3 | -1 | 6 | 5 |
| 5 | -1 | 22 | 22 |
| 6 | -1 | 57 | 61 |
| 7 | -1 | 12 | 12 |
| 8 | -1 | 51 | 52 |
| 9 | -1 | 23 | 21 |
| 10 | -1 | 28 | 29 |
| 11 | -1 | 19 | 19 |
| 12 | -1 | 20 | 21 |
| -1 | -1 | 91 | 96 |
| -2 | -1 | 34 | 36 |
| -3 | -1 | 81 | 88 |
| -4 | -1 | 12 | 11 |
| -5 | -1 | 56 | 60 |
| -7 | -1 | 28 | 27 |
| -8 | -1 | 19 | 19 |
| 0 | -2 | 8 | 7 |
| 1 | -2 | 7 | 4 |
| 2 | -2 | 19 | 18 |
| 3 | -2 | 42 | 43 |
| 4 | -2 | 6 | 6 |
| 5 | -2 | 46 | 47 |
| 6 | -2 | 20 | 19 |
| 7 | -2 | 30 | 29 |
| 8 | -2 | 28 | 30 |
| 9 | -2 | 26 | 27 |
| 10 | -2 | 26 | 25 |
| 11 | -2 | 12 | 13 |
| 12 | -2 | 12 | 12 |
| -1 | -2 | 19 | 18 |
| -2 | -2 | 9 | 8 |
| -3 | -2 | 31 | 29 |
| -4 | -2 | 19 | 18 |
| -5 | -2 | 6 | 5 |
| -6 | -2 | 31 | 32 |
| -7 | -2 | 15 | 13 |
| -8 | -2 | 7 | 6 |
| -11 | -2 | 22 | 20 |
| 0 | -3 | 32 | 32 |
| 1 | -3 | 51 | 53 |
| 2 | -3 | 37 | 35 |
| 4 | -3 | 34 | 35 |
| 5 | -3 | 26 | 25 |
| 6 | -3 | 15 | 15 |
| 7 | -3 | 21 | 20 |
| 8 | -3 | 7 | 5 |
| 9 | -3 | 15 | 15 |
| -1 | -3 | 45 | 47 |
| -2 | -3 | 17 | 18 |
| -3 | -3 | 77 | 83 |
| -5 | -3 | 49 | 48 |
| -7 | -3 | 13 | 13 |
| -10 | -3 | 11 | 10 |
| 0 | -4 | 35 | 35 |
| 1 | -4 | 21 | 19 |
| 2 | -4 | 17 | 13 |
| 3 | -4 | 35 | 33 |
| 4 | -4 | 18 | 18 |
| 7 | -4 | 25 | 25 |
| 8 | -4 | 8 | 6 |
| 9 | -4 | 17 | 16 |
| 10 | -4 | 7 | 7 |
| -1 | -4 | 33 | 32 |
| -2 | -4 | 48 | 50 |
| -3 | -4 | 24 | 23 |
| -4 | -4 | 57 | 60 |
| -5 | -4 | 16 | 16 |
| -6 | -4 | 49 | 51 |
| -8 | -4 | 25 | 25 |
| -9 | -4 | 8 | 8 |
| 0 | -5 | 10 | 9 |
| 1 | -5 | 12 | 11 |
| 2 | -5 | 26 | 26 |
| 3 | -5 | 26 | 25 |
| 4 | -5 | 40 | 40 |
| 5 | -5 | 30 | 29 |
| 6 | -5 | 27 | 26 |
| 7 | -5 | [illegible] | 18 |
| 8 | -5 | 14 | 13 |
| 9 | -5 | 12 | 11 |
| 11 | -5 | 8 | 8 |
| -1 | -5 | 15 | 14 |
| -2 | -5 | 18 | 17 |
| -3 | -5 | 23 | 22 |
| -4 | -5 | 23 | 24 |
| -5 | -5 | 14 | 16 |
| -6 | -5 | 17 | 17 |
| -7 | -5 | 23 | 23 |
| -8 | -5 | 9 | 10 |
| 0 | -6 | 18 | 17 |
| 1 | -6 | 13 | 13 |
| 2 | -6 | 25 | 25 |
| 3 | -6 | 16 | 16 |
| 4 | -6 | 30 | 30 |
| 5 | -6 | 9 | 9 |
| 6 | -6 | 16 | 15 |
| 8 | -6 | 11 | 10 |
| -1 | -6 | 12 | 11 |
| -2 | -6 | 8 | 7 |
| -3 | -6 | 10 | 10 |
| -6 | -6 | 11 | 11 |
| 0 | -7 | 12 | 11 |
| 2 | -7 | 9 | 9 |
| 3 | -7 | 9 | 9 |
| 5 | -7 | 7 | 7 |
| -2 | -7 | 13 | 12 |
| -3 | -7 | 4 | 4 |
| -4 | -7 | 6 | 7 |
| 1 | -8 | 4 | 4 |
| 3 | -8 | 5 | 5 |
| **** H = 1 **** | | | |
| 0 | 0 | 55 | 55 |
| 1 | 0 | 127 | 94 |
| 2 | 0 | 44 | 43 |
| 3 | 0 | 5 | 4 |
| 4 | 0 | 51 | 51 |
| 5 | 0 | 19 | 18 |
| 6 | 0 | 9 | 9 |
| 7 | 0 | 19 | 18 |
| 9 | 0 | 17 | 15 |
| 10 | 0 | 7 | 7 |
| 11 | 0 | 6 | 5 |
| 12 | 0 | 9 | 9 |
| -1 | 0 | 90 | 94 |
| -2 | 0 | 36 | 35 |
| -3 | 0 | 62 | 64 |
| -4 | 0 | 6 | 5 |
| -5 | 0 | 51 | 53 |
| -7 | 0 | 11 | 10 |
| -8 | 0 | 20 | 18 |
| -9 | 0 | 8 | 9 |
| -10 | 0 | 14 | 12 |
| -11 | 0 | 14 | 12 |
| 0 | 1 | 37 | 36 |
| 1 | 1 | 23 | 22 |
| 2 | 1 | 4 | 4 |
| 3 | 1 | 46 | 46 |
| 4 | 1 | 7 | 7 |
| 5 | 1 | 27 | 27 |
| 6 | 1 | 21 | 20 |
| 7 | 1 | 20 | 21 |
| 8 | 1 | 46 | 46 |
| 9 | 1 | 8 | 7 |
| 10 | 1 | 23 | 22 |
| -1 | 1 | 17 | 14 |
| -2 | 1 | 5 | 1 |
| -3 | 1 | 26 | 24 |
| -5 | 1 | 9 | 9 |
| -6 | 1 | 5 | 4 |
| -7 | 1 | 13 | 14 |
| -8 | 1 | 9 | 8 |
| -9 | 1 | 25 | 25 |
| -10 | 1 | 12 | 11 |
| -11 | 1 | 23 | 23 |
| 0 | 2 | 139 | 153 |
| 1 | 2 | 24 | 24 |
| 2 | 2 | 62 | 65 |
| 3 | 2 | 48 | 47 |
| 4 | 2 | 17 | 16 |
| 5 | 2 | 20 | 21 |
| 6 | 2 | 21 | 20 |
| 7 | 2 | 17 | 17 |
| 8 | 2 | 24 | 23 |
| 9 | 2 | 22 | 21 |
| 10 | 2 | 10 | 9 |
| -1 | 2 | 43 | 45 |
| -2 | 2 | 9 | 10 |
| -3 | 2 | 40 | 40 |
| -4 | 2 | 21 | 19 |
| -5 | 2 | 31 | 32 |
| -6 | 2 | 7 | 6 |
| -7 | 2 | 18 | 17 |
| -8 | 2 | 20 | 19 |
| -9 | 2 | 7 | 7 |
| -11 | 2 | 5 | 5 |
| 0 | 3 | 60 | 63 |
| 1 | 3 | 37 | 38 |
| 2 | 3 | 53 | 54 |
| 4 | 3 | 45 | 46 |
| 5 | 3 | 27 | 27 |
| 6 | 3 | 34 | 35 |
| 7 | 3 | 6 | 6 |
| -1 | 3 | 37 | 37 |
| -2 | 3 | 60 | 62 |
| -4 | 3 | 27 | 26 |
| -5 | 3 | 11 | 12 |
| -8 | 3 | 7 | 5 |
| -9 | 3 | 15 | 14 |
| -10 | 3 | 6 | 6 |
| -11 | 3 | 10 | 10 |
| 1 | 4 | 47 | 49 |
| -1 | 4 | 37 | 38 |
| -3 | 4 | 7 | 7 |
| -4 | 4 | 6 | 5 |
| -6 | 4 | 22 | 22 |
| -8 | 4 | 24 | 25 |
| -10 | 4 | 16 | 16 |
| 0 | 5 | 6 | 3 |
| -3 | 5 | 29 | 29 |
| -5 | 5 | 30 | 29 |
| -7 | 5 | 22 | 22 |
| -8 | 5 | 10 | 8 |
| -9 | 5 | 12 | 12 |
| -1 | 6 | 8 | 7 |
| -2 | 6 | 12 | 11 |
| -3 | 6 | 7 | 7 |
| -4 | 6 | 5 | 5 |
| -6 | 6 | 5 | 6 |
| -7 | 6 | 9 | 9 |
| 0 | -1 | 79 | 81 |
| 1 | -1 | 68 | 65 |
| 2 | -1 | 36 | 30 |
| 3 | -1 | 17 | 15 |
| 4 | -1 | 5 | 5 |
| 5 | -1 | 37 | 37 |
| 6 | -1 | 25 | 25 |
| 7 | -1 | 33 | 33 |
| 8 | -1 | 19 | 19 |
| 9 | -1 | 30 | 30 |
| 10 | -1 | 22 | 22 |
| 12 | -1 | 12 | 13 |
| -1 | -1 | 89 | 96 |
| -2 | -1 | 13 | 13 |
| -3 | -1 | 141 | 154 |
| -4 | -1 | 34 | 35 |
| -5 | -1 | 46 | 46 |
| -6 | -1 | 40 | 40 |
| -7 | -1 | 22 | 20 |
| -8 | -1 | 36 | 36 |
| -9 | -1 | 14 | 13 |
| -10 | -1 | 7 | 8 |
| -11 | -1 | 6 | 6 |
| 0 | -2 | 6 | 3 |
| 1 | -2 | 8 | 5 |
| 2 | -2 | 21 | 20 |
| 3 | -2 | 120 | 129 |
| 4 | -2 | 44 | 45 |
| 5 | -2 | 64 | 65 |
| 6 | -2 | 30 | 30 |
| 7 | -2 | 65 | 68 |
| 8 | -2 | 9 | 9 |
| 9 | -2 | 48 | 48 |
| 10 | -2 | 8 | 8 |
| 11 | -2 | 17 | 17 |
| 13 | -2 | 8 | 9 |
| -1 | -2 | 35 | 32 |
| -2 | -2 | 43 | 42 |
| -3 | -2 | 41 | 41 |
| -4 | -2 | 50 | 50 |
| -5 | -2 | 23 | 22 |
| -6 | -2 | 48 | 48 |
| -7 | -2 | 35 | 36 |
| -8 | -2 | 20 | 18 |
| -9 | -2 | 10 | 10 |
| -10 | -2 | 7 | 6 |
| -11 | -2 | 6 | 6 |
| 0 | -3 | 37 | 35 |
| 1 | -3 | 29 | 27 |
| 2 | -3 | 58 | 58 |
| 3 | -3 | 8 | 8 |
| 4 | -3 | 70 | 72 |
| 6 | -3 | 47 | 47 |
| 8 | -3 | 43 | 44 |
| 10 | -3 | 16 | 15 |
| 11 | -3 | 7 | 8 |
| 12 | -3 | 5 | 4 |
| -2 | -3 | 5 | 5 |
| -3 | -3 | 16 | 14 |
| -4 | -3 | 10 | 9 |
| -5 | -3 | 5 | 5 |
| -7 | -3 | 28 | 26 |
| -9 | -3 | 11 | 11 |
| -10 | -3 | 5 | 5 |
| 0 | -4 | 23 | 24 |
| 1 | -4 | 23 | 22 |
| 3 | -4 | 24 | 25 |
| 4 | -4 | 26 | 23 |
| 5 | -4 | 23 | 22 |
| 6 | -4 | 7 | 6 |
| 7 | -4 | 12 | 10 |
| 12 | -4 | 5 | 6 |
| -1 | -4 | 17 | 16 |
| -2 | -4 | 20 | 19 |
| -4 | -4 | 29 | 29 |
| -5 | -4 | 34 | 33 |
| -7 | -4 | 17 | 17 |
| -8 | -4 | 16 | 14 |
| -9 | -4 | 9 | 10 |
| 0 | -5 | 9 | 8 |
| 1 | -5 | 12 | 11 |
| 2 | -5 | 8 | 8 |
| 3 | -5 | 15 | 14 |
| 4 | -5 | 32 | 30 |
| 6 | -5 | 22 | 21 |
| 8 | -5 | 9 | 9 |
| 11 | -5 | 8 | 8 |
| -1 | -5 | 13 | 13 |
| -3 | -5 | 30 | 29 |
| -4 | -5 | 12 | 11 |
| -5 | -5 | 23 | 23 |
| -6 | -5 | 19 | 17 |
| -7 | -5 | 27 | 28 |
| -8 | -5 | 11 | 11 |
| 1 | -6 | 35 | 34 |
| 3 | -6 | 39 | 37 |
| 5 | -6 | 35 | 34 |
| 7 | -6 | 14 | 14 |
| 8 | -6 | 9 | 10 |
| -1 | -6 | 25 | 25 |
| -2 | -6 | 6 | 6 |
| -3 | -6 | 15 | 14 |
| -5 | -6 | 6 | 5 |
| -6 | -6 | 15 | 15 |
| 0 | -7 | 23 | 22 |
| 1 | -7 | 6 | 6 |
| 2 | -7 | 20 | 19 |
| 4 | -7 | 14 | 13 |
| 5 | -7 | 6 | 4 |
| 6 | -7 | 11 | 10 |
| 8 | -7 | 7 | 6 |
| -2 | -7 | 16 | 14 |
| -4 | -7 | 10 | 11 |
| 1 | -8 | 7 | 7 |
| 2 | -8 | 4 | 4 |
| 3 | -8 | 3 | 4 |
| 4 | -8 | 4 | 4 |
| -1 | -8 | 11 | 10 |
| **** H = 2 **** | | | |
| 0 | 0 | 14 | 13 |
| 1 | 0 | 31 | 30 |
| 2 | 0 | 32 | 33 |
| 3 | 0 | 10 | 8 |
| 4 | 0 | 30 | 29 |
| 6 | 0 | 41 | 42 |
| 7 | 0 | 27 | 27 |
| 8 | 0 | 37 | 38 |
| 9 | 0 | 19 | 18 |
| 10 | 0 | 26 | 26 |
| 11 | 0 | 7 | 7 |
| 12 | 0 | 10 | 10 |
| -1 | 0 | 19 | 20 |
| -2 | 0 | 42 | 38 |
| -3 | 0 | 21 | 22 |
| -4 | 0 | 21 | 21 |
| -5 | 0 | 9 | 8 |
| -6 | 0 | 23 | 24 |
| -7 | 0 | 13 | 13 |
| -9 | 0 | 9 | 8 |
| -10 | 0 | 7 | 7 |
| 0 | 1 | 49 | 51 |
| 1 | 1 | 6 | 4 |
| 2 | 1 | 45 | 48 |
| 3 | 1 | 38 | 41 |
| 4 | 1 | 14 | 13 |
| 5 | 1 | 48 | 52 |
| 7 | 1 | 46 | 48 |
| 9 | 1 | 47 | 48 |
| 10 | 1 | 10 | 10 |
| 11 | 1 | 20 | 22 |
| -1 | 1 | 20 | 13 |
| -2 | 1 | 23 | 21 |
| -3 | 1 | 11 | 11 |
| -4 | 1 | 41 | 42 |
| -5 | 1 | 23 | 23 |
| -6 | 1 | 28 | 28 |
| -7 | 1 | 11 | 11 |
| -8 | 1 | 14 | 13 |
| 0 | 2 | 17 | 17 |
| 1 | 2 | 69 | 72 |
| 2 | 2 | 21 | 21 |
| 3 | 2 | 37 | 39 |
| 4 | 2 | 17 | 16 |
| 5 | 2 | 11 | 7 |
| 6 | 2 | 31 | 31 |
| 8 | 2 | 30 | 29 |
| 9 | 2 | 14 | 13 |
| 10 | 2 | 18 | 19 |
| -1 | 2 | 52 | 54 |
| -2 | 2 | 50 | 51 |
| -3 | 2 | 46 | 49 |
| -4 | 2 | 32 | 33 |
| -5 | 2 | 37 | 36 |
| -6 | 2 | 22 | 23 |
| -7 | 2 | 14 | 14 |
| -8 | 2 | 10 | 10 |
| -9 | 2 | 15 | 15 |
| 0 | 3 | 55 | 58 |
| 1 | 3 | 34 | 36 |
| 2 | 3 | 44 | 45 |
| -1 | 3 | 34 | 34 |
| -2 | 3 | 28 | 26 |
| -3 | 3 | 31 | 31 |
| -4 | 3 | 23 | 23 |
| -5 | 3 | 20 | 19 |
| -6 | 3 | 15 | 15 |
| -8 | 3 | 15 | 15 |
| -9 | 3 | 11 | 12 |
| -10 | 3 | 14 | 14 |
| 0 | 4 | 42 | 43 |
| 1 | 4 | 14 | 14 |
| 2 | 4 | 27 | 25 |
| -1 | 4 | 6 | 8 |
| -5 | 4 | 9 | 9 |
| -6 | 4 | 10 | 10 |
| -7 | 4 | 11 | 11 |
| -8 | 4 | 12 | 12 |
| -9 | 4 | 17 | 16 |
| 0 | 5 | 8 | 8 |
| -1 | 5 | 7 | 6 |
| -3 | 5 | 18 | 17 |
| -5 | 5 | 11 | 11 |
| -6 | 5 | 10 | 10 |
| -8 | 5 | 10 | 10 |
| -2 | 6 | 12 | 12 |
| -4 | 6 | 7 | 7 |
| 0 | -1 | 41 | 41 |
| 1 | -1 | 30 | 25 |
| 2 | -1 | 6 | 4 |
| 3 | -1 | 14 | 12 |
| 4 | -1 | 32 | 32 |
| 5 | -1 | 29 | 30 |
| 6 | -1 | 25 | 26 |
| 7 | -1 | 14 | 14 |
| 8 | -1 | 23 | 22 |
| 9 | -1 | 8 | 8 |
| 10 | -1 | 8 | 7 |
| 11 | -1 | 10 | 10 |
| -1 | -1 | 41 | 42 |
| -2 | -1 | 87 | 93 |
| -3 | -1 | 28 | 28 |
| -4 | -1 | 58 | 62 |
| -5 | -1 | 23 | 24 |
| -6 | -1 | 43 | 44 |
| -7 | -1 | 40 | 40 |
| -8 | -1 | 26 | 25 |
| -9 | -1 | 8 | 8 |
| -10 | -1 | 8 | 8 |
| 0 | -2 | 21 | 21 |
| 1 | -2 | 13 | 12 |
| 2 | -2 | 30 | 31 |
| 3 | -2 | 21 | 20 |
| 4 | -2 | 74 | 78 |
| 5 | -2 | 9 | 6 |
| 6 | -2 | 44 | 47 |
| 8 | -2 | 31 | 32 |
| 10 | -2 | 12 | 13 |
| 11 | -2 | 11 | 11 |
| -1 | -2 | 33 | 33 |
| -2 | -2 | 31 | 31 |
| -3 | -2 | 64 | 69 |
| -4 | -2 | 11 | 9 |
| -5 | -2 | 64 | 69 |
| -6 | -2 | 19 | 19 |
| -7 | -2 | 35 | 37 |
| -8 | -2 | 7 | 5 |
| -9 | -2 | 24 | 24 |
| -10 | -2 | 5 | 5 |
| 0 | -3 | 16 | 15 |
| 1 | -3 | 17 | 16 |
| 2 | -3 | 25 | 25 |
| 3 | -3 | 72 | 77 |
| 4 | -3 | 49 | 51 |
| 5 | -3 | 46 | 48 |
| 6 | -3 | 29 | 32 |
| 7 | -3 | 38 | 40 |
| 8 | -3 | 17 | 16 |
| 9 | -3 | 29 | 30 |
| -1 | -3 | 26 | 25 |
| -3 | -3 | 10 | 9 |
| -4 | -3 | 42 | 43 |
| -6 | -3 | 48 | 49 |
| -7 | -3 | 7 | 5 |
| -8 | -3 | 23 | 22 |
| -9 | -3 | 8 | 8 |
| 0 | -4 | 45 | 45 |
| 1 | -4 | 26 | 26 |
| 2 | -4 | 51 | 53 |
| 3 | -4 | 27 | 27 |
| 4 | -4 | 37 | 38 |
| 5 | -4 | 45 | 47 |
| 6 | -4 | 31 | 33 |
| 7 | -4 | 29 | 30 |
| 8 | -4 | 13 | 13 |
| 11 | -4 | 5 | 6 |
| 12 | -4 | 9 | 8 |
| -1 | -4 | 11 | 11 |
| -2 | -4 | 25 | 25 |
| -4 | -4 | 11 | 9 |
| -6 | -4 | 14 | 13 |
| -8 | -4 | 6 | 6 |
| 0 | -5 | 20 | 20 |
| 1 | -5 | 9 | 8 |
| 2 | -5 | 25 | 25 |
| 3 | -5 | 11 | 12 |
| 4 | -5 | 18 | 18 |
| 6 | -5 | 9 | 6 |
| 8 | -5 | 5 | 7 |
| 10 | -5 | 6 | 6 |
| 11 | -5 | 10 | 10 |
| -1 | -5 | 25 | 24 |
| -3 | -5 | 17 | 17 |
| -5 | -5 | 6 | 6 |
| -6 | -5 | 14 | 15 |
| -7 | -5 | 5 | 5 |
| 0 | -6 | 18 | 17 |
| 2 | -6 | 17 | 16 |
| 3 | -6 | 8 | 8 |
| 4 | -6 | 17 | 15 |
| 5 | -6 | 15 | 16 |
| 6 | -6 | 10 | 9 |
| 7 | -6 | 7 | 7 |
| 8 | -6 | 7 | 6 |
| 9 | -6 | 6 | 6 |
| 10 | -6 | 9 | 9 |
| -2 | -6 | 15 | 13 |
| -3 | -6 | 6 | 6 |
| -5 | -6 | 8 | 7 |
| -6 | -6 | 7 | 8 |
| 0 | -7 | 21 | 21 |
| 1 | -7 | 14 | 14 |
| 2 | -7 | 19 | 19 |
| 3 | -7 | 13 | 12 |
| 4 | -7 | 13 | 13 |
| -1 | -7 | 17 | 17 |
| -2 | -7 | 10 | 10 |
| -3 | -7 | 14 | 14 |
| -4 | -7 | 8 | 8 |
| 0 | -8 | 11 | 12 |
| 1 | -8 | 11 | 12 |
| 2 | -8 | 6 | 6 |
| 3 | -8 | 9 | 9 |
| -1 | -8 | 10 | 12 |
| **** H = 3 **** | | | |
| 0 | 0 | 43 | 61 |
| 1 | 0 | 71 | 75 |
| 2 | 0 | 32 | 33 |
| 3 | 0 | 43 | 46 |
| 4 | 0 | 42 | 43 |
| 5 | 0 | 44 | 45 |
| 6 | 0 | 44 | 44 |
| 7 | 0 | 36 | 37 |
| 8 | 0 | 34 | 35 |
| 9 | 0 | 26 | 25 |
| 10 | 0 | 23 | 25 |
| 11 | 0 | 14 | 14 |
| -1 | 0 | 19 | 17 |
| -2 | 0 | 30 | 30 |
| -3 | 0 | 24 | 23 |
| -4 | 0 | 29 | 30 |
| -5 | 0 | 20 | 20 |
| -6 | 0 | 43 | 44 |
| -7 | 0 | 13 | 13 |
| -8 | 0 | 19 | 19 |
| -10 | 0 | 10 | 10 |
| 0 | 1 | 20 | 19 |
| 1 | 1 | 36 | 33 |
| 2 | 1 | 15 | 14 |
| 3 | 1 | 30 | 30 |
| 4 | 1 | 31 | 31 |
| 5 | 1 | 12 | 10 |
| 6 | 1 | 41 | 41 |
| 7 | 1 | 12 | 11 |
| 8 | 1 | 40 | 39 |
| 9 | 1 | 22 | 21 |
| 10 | 1 | 18 | 19 |
| -1 | 1 | 57 | 61 |
| -2 | 1 | 29 | 27 |
| -3 | 1 | 55 | 56 |
| -4 | 1 | 13 | 11 |
| -5 | 1 | 56 | 55 |
| -6 | 1 | 13 | 11 |
| -7 | 1 | 45 | 45 |
| -8 | 1 | 9 | 2 |
| -9 | 1 | 16 | 17 |
| 0 | 2 | 51 | 50 |
| 1 | 2 | 20 | 19 |
| 2 | 2 | 30 | 31 |
| 4 | 2 | 26 | 26 |
| 5 | 2 | 7 | 7 |
| 7 | 2 | 15 | 15 |
| 8 | 2 | 11 | 10 |
| 9 | 2 | 14 | 14 |
| -2 | 2 | 55 | 59 |
| -3 | 2 | 12 | 11 |
| -4 | 2 | 43 | 44 |
| -5 | 2 | 8 | 7 |
| -6 | 2 | 35 | 33 |
| -7 | 2 | 8 | 7 |
| -8 | 2 | 18 | 17 |
| -9 | 2 | 9 | 8 |
| 0 | 3 | 8 | 9 |
| 1 | 3 | 33 | 33 |
| 2 | 3 | 11 | 7 |
| -1 | 3 | 11 | 9 |
| -3 | 3 | 23 | 22 |
| -4 | 3 | 18 | 18 |
| -5 | 3 | 7 | 6 |
| -8 | 3 | 8 | 7 |
| -9 | 3 | 5 | 5 |
| 0 | 4 | 19 | 20 |
| 1 | 4 | 10 | 8 |
| -2 | 4 | 29 | 30 |
| -4 | 4 | 16 | 14 |
| -5 | 4 | 7 | 6 |
| -6 | 4 | 11 | 9 |
| -7 | 4 | 7 | 6 |
| -1 | 5 | 17 | 20 |
| -2 | 5 | 12 | 12 |
| -3 | 5 | 19 | 19 |
| -4 | 5 | 6 | 5 |
| -5 | 5 | 12 | 10 |
| 0 | -1 | 57 | 61 |
| 1 | -1 | 22 | 25 |
| 2 | -1 | 184 | 150 |
| 3 | -1 | 49 | 54 |
| 4 | -1 | 11 | 10 |
| 5 | -1 | 50 | 51 |
| 6 | -1 | 22 | 21 |
| 7 | -1 | 36 | 36 |
| 8 | -1 | 12 | 11 |
| 9 | -1 | 26 | 26 |
| 10 | -1 | 11 | 9 |
| 12 | -1 | 16 | 16 |
| -1 | -1 | 31 | 31 |
| -2 | -1 | 22 | 19 |
| -3 | -1 | 21 | 21 |
| -4 | -1 | 18 | 18 |
| -5 | -1 | 26 | 27 |
| -6 | -1 | 32 | 32 |
| -7 | -1 | 12 | 11 |
| -9 | -1 | 9 | 9 |
| 0 | -2 | 26 | 25 |
| 1 | -2 | 18 | 16 |
| 2 | -2 | 51 | 51 |
| 3 | -2 | 23 | 23 |
| 4 | -2 | 40 | 40 |
| 5 | -2 | 30 | 30 |
| 6 | -2 | 8 | 8 |
| 7 | -2 | 23 | 24 |
| 8 | -2 | 10 | 9 |
| 9 | -2 | 7 | 2 |
| 10 | -2 | 10 | 8 |
| 11 | -2 | 19 | 18 |
| 13 | -2 | 11 | 12 |
| -1 | -2 | 10 | 8 |
| -2 | -2 | 16 | 16 |
| -3 | -2 | 29 | 28 |
| -4 | -2 | 35 | 35 |
| -5 | -2 | 28 | 27 |
| -6 | -2 | 41 | 42 |
| -7 | -2 | 9 | 9 |
| -8 | -2 | 23 | 23 |
| -9 | -2 | 7 | 7 |
| -10 | -2 | 19 | 21 |
| 0 | -3 | 25 | 24 |
| 1 | -3 | 38 | 36 |
| 2 | -3 | 40 | 40 |
| 3 | -3 | 38 | 38 |
| 4 | -3 | 39 | 39 |
| 5 | -3 | 42 | 42 |
| 6 | -3 | 27 | 26 |
| 7 | -3 | 24 | 23 |
| 10 | -3 | 12 | 12 |
| 12 | -3 | 6 | 5 |
| 13 | -3 | 7 | 6 |
| -1 | -3 | 10 | 10 |
| -2 | -3 | 15 | 15 |
| -3 | -3 | 34 | 36 |
| -4 | -3 | 11 | 10 |
| -5 | -3 | 46 | 46 |
| -6 | -3 | 23 | 22 |
| -7 | -3 | 15 | 14 |
| -8 | -3 | 24 | 26 |
| -9 | -3 | 26 | 28 |
| 0 | -4 | 54 | 55 |
| 1 | -4 | 37 | 36 |
| 2 | -4 | 49 | 53 |
| 3 | -4 | 36 | 36 |
| 4 | -4 | 43 | 42 |
| 5 | -4 | 6 | 6 |
| 6 | -4 | 47 | 48 |
| 7 | -4 | 9 | 8 |
| 8 | -4 | 13 | 12 |
| 9 | -4 | 7 | 6 |
| 11 | -4 | 6 | 5 |
| 12 | -4 | 6 | 6 |
| 13 | -4 | 7 | 8 |
| -1 | -4 | 41 | 41 |
| -2 | -4 | 32 | 32 |
| -3 | -4 | 33 | 31 |
| -4 | -4 | 28 | 27 |
| -6 | -4 | 10 | 9 |
| -7 | -4 | 16 | 16 |
| -8 | -4 | 13 | 12 |
| 0 | -5 | 11 | 10 |
| 1 | -5 | 43 | 44 |
| 2 | -5 | 6 | 5 |
| 3 | -5 | 36 | 36 |
| 6 | -5 | 21 | 21 |
| 7 | -5 | 10 | 10 |
| 8 | -5 | 10 | 9 |
| 9 | -5 | 7 | 7 |
| 10 | -5 | 10 | 10 |
| 12 | -5 | 14 | 14 |
| -1 | -5 | 45 | 47 |
| -2 | -5 | 18 | 17 |
| -3 | -5 | 36 | 37 |
| -4 | -5 | 18 | 15 |
| -6 | -5 | 5 | 5 |
| 0 | -6 | 18 | 16 |
| 1 | -6 | 11 | 11 |
| 2 | -6 | 8 | 7 |
| 5 | -6 | 13 | 13 |
| 6 | -6 | 9 | 9 |
| 7 | -6 | 14 | 14 |
| 9 | -6 | 13 | 13 |
| 10 | -6 | 6 | 6 |
| 11 | -6 | 12 | 12 |
| -1 | -6 | 9 | 9 |
| -2 | -6 | 19 | 19 |
| -3 | -6 | 8 | 8 |
| -4 | -6 | 14 | 14 |
| -5 | -6 | 7 | 7 |
| 1 | -7 | 16 | 15 |
| 3 | -7 | 11 | 11 |
| 4 | -7 | 7 | 8 |
| 6 | -7 | 14 | 14 |
| 7 | -7 | 6 | 6 |
| 8 | -7 | 7 | 7 |
| 9 | -7 | 6 | 7 |
| -1 | -7 | 15 | 15 |
| -2 | -7 | 17 | 16 |
| -3 | -7 | 6 | 7 |
| 0 | -8 | 14 | 15 |
| 2 | -8 | 8 | 8 |
| -1 | -8 | 4 | 4 |
| **** H = 4 **** | | | |
| 0 | 0 | 8 | 7 |
| 1 | 0 | 51 | 50 |
| 2 | 0 | 39 | 40 |
| 3 | 0 | 48 | 48 |
| 4 | 0 | 27 | 26 |
| 5 | 0 | 55 | 56 |
| 6 | 0 | 14 | 14 |
| 7 | 0 | 36 | 37 |
| 9 | 0 | 23 | 24 |
| 10 | 0 | 6 | 5 |
| -1 | 0 | 33 | 33 |
| -2 | 0 | 20 | 18 |
| -3 | 0 | 15 | 13 |
| -4 | 0 | 28 | 28 |
| -5 | 0 | 24 | 24 |
| -6 | 0 | 33 | 33 |
| -7 | 0 | 24 | 25 |
| -8 | 0 | 15 | 15 |
| -9 | 0 | 13 | 15 |
| 0 | 1 | 17 | 17 |
| 1 | 1 | 15 | 14 |
| 2 | 1 | 49 | 48 |
| 3 | 1 | 18 | 19 |
| 4 | 1 | 12 | 11 |
| 5 | 1 | 14 | 13 |
| 6 | 1 | 12 | 11 |
| 7 | 1 | 20 | 19 |
| 8 | 1 | 8 | 8 |
| 9 | 1 | 7 | 8 |
| -1 | 1 | 16 | 15 |
| -2 | 1 | 21 | 20 |
| -3 | 1 | 35 | 35 |
| -4 | 1 | 31 | 31 |
| -5 | 1 | 30 | 31 |
| -6 | 1 | 38 | 37 |
| -7 | 1 | 15 | 14 |
| -8 | 1 | 14 | 14 |
| -9 | 1 | 9 | 10 |
| 0 | 2 | 21 | 20 |
| 1 | 2 | 22 | 22 |
| 2 | 2 | 7 | 5 |
| 3 | 2 | 30 | 29 |
| 7 | 2 | 25 | 25 |
| -1 | 2 | 20 | 19 |
| -2 | 2 | 17 | 17 |
| -3 | 2 | 23 | 23 |
| -5 | 2 | 21 | 21 |
| -7 | 2 | 10 | 11 |
| 0 | 3 | 6 | 5 |
| 1 | 3 | 10 | 10 |
| 2 | 3 | 12 | 12 |
| -1 | 3 | 12 | 12 |
| -3 | 3 | 16 | 15 |
| -5 | 3 | 16 | 15 |
| -6 | 3 | 9 | 8 |
| -7 | 3 | 10 | 11 |
| 0 | 4 | 7 | 8 |
| 1 | 4 | 12 | 12 |
| -1 | 4 | 25 | 27 |
| -2 | 4 | 10 | 11 |
| -3 | 4 | 24 | 26 |
| -4 | 4 | 8 | 9 |
| -5 | 4 | 19 | 20 |
| -6 | 4 | 7 | 7 |
| -1 | 5 | 5 | 5 |
| -2 | 5 | 17 | 17 |
| -3 | 5 | 8 | 9 |
| -4 | 5 | 13 | 15 |
| 0 | -1 | 67 | 63 |
| 1 | -1 | 37 | 37 |
| 2 | -1 | 71 | 66 |
| 3 | -1 | 17 | 18 |
| 4 | -1 | 65 | 65 |
| 5 | -1 | 7 | 6 |
| 6 | -1 | 55 | 57 |
| 7 | -1 | 7 | 5 |
| 8 | -1 | 27 | 27 |
| 9 | -1 | 5 | 4 |
| 10 | -1 | 9 | 9 |
| 11 | -1 | 9 | 9 |
| 13 | -1 | 8 | 9 |
| -1 | -1 | 11 | 11 |
| -2 | -1 | 41 | 40 |
| -3 | -1 | 17 | 17 |
| -4 | -1 | 7 | 7 |
| -5 | -1 | 23 | 22 |
| -6 | -1 | 6 | 5 |
| -7 | -1 | 8 | 9 |
| -9 | -1 | 22 | 23 |
| 0 | -2 | 14 | 13 |
| 1 | -2 | 60 | 60 |
| 2 | -2 | 17 | 17 |
| 3 | -2 | 72 | 73 |
| 4 | -2 | 7 | 6 |
| 5 | -2 | 40 | 39 |
| 6 | -2 | 18 | 18 |
| 7 | -2 | 7 | 7 |
| 9 | -2 | 8 | 7 |
| 10 | -2 | 19 | 19 |
| 12 | -2 | 17 | 18 |
| 13 | -2 | 8 | 8 |
| -1 | -2 | 86 | 87 |
| -3 | -2 | 39 | 37 |
| -6 | -2 | 19 | 20 |
| -7 | -2 | 10 | 10 |
| -9 | -2 | 12 | 12 |
| 0 | -3 | 6 | 6 |
| 1 | -3 | 34 | 33 |
| 2 | -3 | 4 | 3 |
| 3 | -3 | 26 | 27 |
| 4 | -3 | 8 | 6 |
| 5 | -3 | 38 | 37 |
| 6 | -3 | 15 | 15 |
| 7 | -3 | 6 | 7 |
| 8 | -3 | 8 | 7 |
| 9 | -3 | 30 | 31 |
| 10 | -3 | 10 | 9 |
| 11 | -3 | 20 | 21 |
| 12 | -3 | 11 | 11 |
| 13 | -3 | 5 | 6 |
| -1 | -3 | 22 | 21 |
| -2 | -3 | 5 | 4 |
| -3 | -3 | 12 | 12 |
| -5 | -3 | 26 | 27 |
| -7 | -3 | 18 | 17 |
| 1 | -4 | 39 | 40 |
| 3 | -4 | 39 | 39 |
| 4 | -4 | 8 | 8 |
| 5 | -4 | 13 | 12 |
| 6 | -4 | 12 | 12 |
| 9 | -4 | 8 | 8 |
| 10 | -4 | 6 | 4 |
| 11 | -4 | 8 | 7 |
| 12 | -4 | 6 | 5 |
| 13 | -4 | 6 | 6 |
| -1 | -4 | 29 | 29 |
| -2 | -4 | 12 | 12 |
| -3 | -4 | 29 | 31 |
| -4 | -4 | 8 | 6 |
| -5 | -4 | 6 | 5 |
| -6 | -4 | 15 | 15 |
| -7 | -4 | 6 | 5 |
| 0 | -5 | 48 | 49 |
| 1 | -5 | 14 | 14 |
| 2 | -5 | 34 | 35 |
| 3 | -5 | 17 | 16 |
| 4 | -5 | 18 | 18 |
| 5 | -5 | 6 | 5 |
| 7 | -5 | 6 | 7 |
| 9 | -5 | 9 | 10 |
| 11 | -5 | 10 | 10 |
| -1 | -5 | 15 | 16 |
| -2 | -5 | 54 | 55 |
| -3 | -5 | 7 | 6 |
| -4 | -5 | 19 | 20 |
| -6 | -5 | 21 | 22 |
| 0 | -6 | 18 | 18 |
| 1 | -6 | 20 | 19 |
| 2 | -6 | 5 | 5 |
| 3 | -6 | 20 | 20 |
| 6 | -6 | 26 | 28 |
| 7 | -6 | 6 | 6 |
| 8 | -6 | 13 | 14 |
| 9 | -6 | 12 | 12 |
| 10 | -6 | 7 | 8 |
| 11 | -6 | 10 | 10 |
| -1 | -6 | 30 | 31 |
| -2 | -6 | 16 | 15 |
| -3 | -6 | 21 | 22 |
| -4 | -6 | 8 | 8 |
| -5 | -6 | 17 | 21 |
| 1 | -7 | 6 | 6 |
| 2 | -7 | 6 | 7 |
| 3 | -7 | 14 | 14 |
| 4 | -7 | 8 | 8 |
| 5 | -7 | 16 | 17 |
| 6 | -7 | 13 | 13 |
| 7 | -7 | 11 | 12 |
| 8 | -7 | 13 | 12 |
| 9 | -7 | 4 | 6 |
| 10 | -7 | 11 | 13 |
| -1 | -7 | 5 | 5 |
| -2 | -7 | 5 | 6 |
| -3 | -7 | 7 | 7 |
| 0 | -8 | 5 | 5 |
| 2 | -8 | 5 | 6 |
| 3 | -8 | 7 | 7 |
| 5 | -8 | 9 | 9 |
| 7 | -8 | 7 | 8 |
| -1 | -8 | 5 | 6 |
| **** H = 5 **** | | | |
| 0 | 0 | 18 | 18 |
| 1 | 0 | 7 | 6 |
| 2 | 0 | 11 | 10 |
| 3 | 0 | 14 | 14 |
| 4 | 0 | 14 | 13 |
| 5 | 0 | 8 | 7 |
| 6 | 0 | 21 | 22 |
| 7 | 0 | 7 | 8 |
| 9 | 0 | 12 | 13 |
| 10 | 0 | 12 | 11 |
| 11 | 0 | 11 | 10 |
| -1 | 0 | 13 | 12 |
| -3 | 0 | 20 | 19 |
| -5 | 0 | 23 | 23 |
| -6 | 0 | 6 | 7 |
| -7 | 0 | 19 | 19 |
| 1 | 1 | 31 | 32 |
| 2 | 1 | 24 | 24 |
| 3 | 1 | 36 | 37 |
| 5 | 1 | 18 | 17 |
| 6 | 1 | 16 | 16 |
| 7 | 1 | 9 | 9 |
| 9 | 1 | 8 | 9 |
| 10 | 1 | 9 | 10 |
| -1 | 1 | 13 | 13 |
| -2 | 1 | 11 | 10 |
| -3 | 1 | 10 | 9 |
| -4 | 1 | 17 | 16 |
| -6 | 1 | 12 | 12 |
| -8 | 1 | 7 | 8 |
| 0 | 2 | 28 | 27 |
| 1 | 2 | 7 | 7 |
| 2 | 2 | 52 | 54 |
| 3 | 2 | 6 | 6 |
| -2 | 2 | 12 | 11 |
| -5 | 2 | 10 | 9 |
| -7 | 2 | 9 | 10 |
| 0 | 3 | 14 | 15 |
| 1 | 3 | 12 | 12 |
| 2 | 3 | 10 | 11 |
| -1 | 3 | 9 | 9 |
| -2 | 3 | 18 | 18 |
| -4 | 3 | 22 | 23 |
| -6 | 3 | 20 | 23 |
| -1 | 4 | 18 | 19 |
| -2 | 4 | 6 | 5 |
| -3 | 4 | 16 | 18 |
| -4 | 4 | 7 | 8 |
| -5 | 4 | 11 | 13 |
| 0 | -1 | 10 | 9 |
| 1 | -1 | 52 | 53 |
| 2 | -1 | 15 | 16 |
| 3 | -1 | 74 | 66 |
| 4 | -1 | 13 | 15 |
| 5 | -1 | 16 | 15 |
| 7 | -1 | 17 | 17 |
| 8 | -1 | 14 | 13 |
| 11 | -1 | 9 | 9 |
| -1 | -1 | 40 | 38 |
| -2 | -1 | 22 | 21 |
| -3 | -1 | 22 | 22 |
| -4 | -1 | 15 | 13 |
| -6 | -1 | 15 | 15 |
| -8 | -1 | 19 | 20 |
| 0 | -2 | 69 | 71 |
| 1 | -2 | 24 | 24 |
| 2 | -2 | 63 | 57 |
| 3 | -2 | 47 | 44 |
| 4 | -2 | 37 | 39 |
| 5 | -2 | 18 | 18 |
| 6 | -2 | 17 | 16 |
| 7 | -2 | 9 | 8 |
| 8 | -2 | 14 | 14 |
| 9 | -2 | 12 | 10 |
| 11 | -2 | 13 | 13 |
| 12 | -2 | 10 | 9 |
| -1 | -2 | 24 | 24 |
| -2 | -2 | 65 | 68 |
| -3 | -2 | 31 | 30 |
| -4 | -2 | 35 | 36 |
| -6 | -2 | 7 | 6 |
| -7 | -2 | 7 | 6 |
| 0 | -3 | 41 | 41 |
| 1 | -3 | 14 | 13 |
| 2 | -3 | 38 | 39 |
| 3 | -3 | 10 | 9 |
| 4 | -3 | 4 | 3 |
| 5 | -3 | 21 | 21 |
| 6 | -3 | 24 | 23 |
| 7 | -3 | 23 | 23 |
| 8 | -3 | 20 | 19 |
| 9 | -3 | 23 | 24 |
| 10 | -3 | 17 | 17 |
| 11 | -3 | 19 | 19 |
| -1 | -3 | 21 | 20 |
| -2 | -3 | 50 | 46 |
| -3 | -3 | 40 | 38 |
| -4 | -3 | 14 | 14 |
| -5 | -3 | 20 | 20 |
| -6 | -3 | 13 | 12 |
| -7 | -3 | 9 | 10 |
| 0 | -4 | 22 | 21 |
| 3 | -4 | 6 | 6 |
| 5 | -4 | 18 | 17 |
| 6 | -4 | 45 | 47 |
| 7 | -4 | 8 | 8 |
| 8 | -4 | 35 | 36 |
| 9 | -4 | 6 | 5 |
| 10 | -4 | 16 | 16 |
| 12 | -4 | 10 | 10 |
| -1 | -4 | 13 | 12 |
| -2 | -4 | 10 | 8 |
| 0 | -5 | 24 | 24 |
| 1 | -5 | 14 | 14 |
| 2 | -5 | 23 | 21 |
| 4 | -5 | 13 | 12 |
| 5 | -5 | 13 | 12 |
| 7 | -5 | 20 | 18 |
| 9 | -5 | 7 | 8 |
| 10 | -5 | 11 | 11 |
| -1 | -5 | 22 | 22 |
| -2 | -5 | 21 | 20 |
| -3 | -5 | 19 | 19 |
| -5 | -5 | 16 | 17 |
| -6 | -5 | 6 | 8 |
| 0 | -6 | 12 | 11 |
| 1 | -6 | 15 | 16 |
| 3 | -6 | 5 | 1 |
| 4 | -6 | 6 | 5 |
| 5 | -6 | 10 | 10 |
| 6 | -6 | 9 | 9 |
| 7 | -6 | 15 | 14 |
| 8 | -6 | 8 | 8 |
| 10 | -6 | 9 | 8 |
| -1 | -6 | 23 | 24 |
| -2 | -6 | 10 | 9 |
| -3 | -6 | 20 | 18 |
| -4 | -6 | 12 | 14 |
| 1 | -7 | 14 | 14 |
| 3 | -7 | 20 | 20 |
| 4 | -7 | 8 | 8 |
| 5 | -7 | 19 | 19 |
| 6 | -7 | 7 | 7 |
| 7 | -7 | 17 | 17 |
| 9 | -7 | 10 | 11 |
| -2 | -7 | 7 | 8 |
| 0 | -8 | 8 | 11 |
| 2 | -8 | 17 | 20 |
| 4 | -8 | 16 | 16 |
| 5 | -8 | 5 | 4 |
| 6 | -8 | 11 | 13 |
| 7 | -8 | 6 | 8 |

TABLE V

BOND DISTANCES (Å)[a]

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.465(5) | Co(1)–C(2) | 1.91(1) |
| Co(1)–Co(3) | 2.485(4) | Co(2)–C(2) | 1.92(1) |
| Co(2)–Co(3) | 2.462(4) | Co(3)–C(2) | 1.93(1) |
| Av | 2.470(10) | Av | 1.92(1) |
| Co(1)–C(11) | 1.75(1) | C(11)–O(11) | 1.16(1) |
| Co(1)–C(12) | 1.79(2) | C(12)–O(12) | 1.14(2) |
| Co(2)–C(21) | 1.78(1) | C(13)–O(13) | 1.12(1) |
| Co(2)–C(22) | 1.80(2) | C(21)–O(21) | 1.14(1) |
| Co(3)–C(31) | 1.77(2) | C(22)–O(22) | 1.11(1) |
| Co(3)–C(32) | 1.78(2) | C(23)–O(23) | 1.12(1) |
| Av | 1.78(2) | C(31)–O(31) | 1.15(1) |
| | | C(32)–O(32) | 1.14(1) |
| Co(1)–C(13) | 1.82(1) | C(33)–O(33) | 1.13(1) |
| Co(2)–C(23) | 1.83(1) | Av | 1.13(1) |
| Co(3)–C(33) | 1.82(1) | | |
| Av | 1.82(1) | C(1)–C(1)′ | 1.24(2) |
| | | C(1)–C(2) | 1.37(1) |

[a] Mean values of bonds assumed chemically equivalent are indicated and their associated uncertainties are rms deviations given by the expression $(\Sigma^n(x_i - \bar{x})^2/n)^{1/2}$, where there are $n$ observations. The estimated standard deviations of individual bonds were calculated using variances and covariances in positional parameters and variances only in cell parameters.

C(carbonyl) distance of 1.78 (2) Å as previously observed.[21,22] In contrast to the situation in $Co_5(CO)_{15}C_3H$,[1] the CO groups attached to one $Co_3$ cluster are well separated from those attached to the second cluster. Thus the average dihedral angle between planes defined by the equatorial CO groups and the Co atom to which they are attached[24] and the $Co_3$ plane is 28°, *i.e.*, very close to the values observed in $CH_3CCo_3(CO)_9$ (29°) and $Co_3(CO)_{10}BH_2N(C_2H_5)_3$ (32°) where there is only a single cluster. A significant reduction had been observed for some of these angles in $Co_5(CO)_{15}C_3H$[1] as a result of intramolecular nonbonded repulsions.

The most interesting structural feature of $Co_6(CO)_{18}C_4$ is the $C_4$ chain containing a formal triple carbon–carbon bond in a unique environment. The two independent C—C distances are 1.24 (2) Å for C(1)—C(1′) and 1.37 (1) Å for C(1)—C(2). The angle C(2)—C(1)≡C(1′) is not significantly different from 180°.

The observations that C(1)—C(1′) is about 0.04 Å longer than the triple bond in simple acetylenes and

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[24] These planes were calculated in two ways: (a) as mean planes involving Co, two C, and two O atoms; (b) as the exact planes containing only Co, O, O. The individual dihedral angles with the $Co_3$ plane for the two methods of calculation did not differ by more than 0.2°.

TABLE VI

BOND ANGLES (DEG)[a]

| | | | |
|---|---|---|---|
| Co(1)–Co(2)–Co(3) | 60.6(1) | C(11)–Co(1)–Co(2) | 155.0(4) |
| Co(2)–Co(3)–Co(1) | 59.8(1( | C(12)–Co(1)–Co(3) | 148.1(4) |
| Co(3)–Co(1)–Co(2) | 59.7(1) | C(21)–Co(2)–Co(1) | 153.4(4) |
| Av | 60.0 | C(22)–Co(2)–Co(3) | 151.4(5) |
| | | C(31)–Co(3)–Co(1) | 150.9(4) |
| C(11)–Co(1)–C(12) | 98.1(7) | C(32)–Co(3)–Co(2) | 152.2(4) |
| C(21)–Co(2)–C(22) | 96.9(6) | Av | 151.8 |
| C(31)–Co(3)–C(32) | 97.7(7) | | |
| Av | 97.6 | C(13)–Co(1)–Co(2) | 99.3(4) |
| | | C(13)–Co(1)–Co(3) | 101.8(4) |
| C(11)–Co(1)–C(13) | 97.4(5) | C(23)–Co(2)–Co(1) | 98.2(4) |
| C(12)–Co(1)–C(13) | 102.7(6) | C(23)–Co(2)–Co(3) | 100.5(4) |
| C(21)–Co(2)–C(23) | 100.1(5) | C(33)–Co(3)–Co(1) | 100.3(4) |
| C(22)–Co(2)–C(23) | 101.5(6) | C(33)–Co(3)–Co(2) | 99.5(4) |
| C(31)–Co(3)–C(33) | 101.1(5) | Av | 99.9 |
| C(32)–Co(3)–C(33) | 100.4(5) | | |
| Av | 100.5 | C(2)–Co(1)–Co(2) | 50.1(3) |
| | | C(2)–Co(1)–C(3) | 50.1(3) |
| C(11)–Co(1)–C(2) | 107.2(5) | C(2)–Co(2)–Co(3) | 50.5(3) |
| C(12)–Co(1)–C(2) | 98.8(5) | C(2)–Co(2)–Co(1) | 49.7(3) |
| C(21)–Co(2)–C(2) | 105.7(5) | C(2)–Co(3)–Co(2) | 50.0(3) |
| C(22)–Co(2)–C(2) | 101.5(6) | C(2)–Co(3)–Co(1) | 49.2(3) |
| C(31)–Co(3)–C(2) | 103.0(5) | Av | 49.9 |
| C(32)–Co(3)–C(2) | 103.6(5) | | |
| Av | 103.6 | Co–C–O | |
| | | 9 independent angles | |
| C(13)–Co(1)–C(2) | 144.5(5) | all within the range | 177–179° |
| C(23)–Co(2)–C(2) | 142.8(4) | | |
| C(33)–Co(3)–C(2) | 143.1(5) | C(1)–C(2)–Co(1) | 133.6(8) |
| Av | 143.5 | C(1)–C(2)–Co(2) | 133.0(8) |
| | | C(1)–C(2)–Co(3) | 129.3(8) |
| C(11)–Co(1)–Co(3) | 98.7(5) | Av | 132.0 |
| C(12)–Co(1)–Co(2) | 96.2(5) | | |
| C(21)–Co(2)–Co(3) | 97.0(4) | Co(1)–C(2)–Co(2) | 80.2(4) |
| C(22)–Co(2)–Co(1) | 98.2(5) | Co(1)–C(2)–Co(3) | 80.6(3) |
| C(31)–Co(3)–Co(2) | 97.3(5) | Co(2)–C(2)–Co(3) | 79.5(3) |
| C(32)–Co(3)–Co(1) | 97.6(5) | Av | 80.1 |
| Av | 97.5 | | |
| | | C(2)–C(1)–C(1)′ | 178(1) |

[a] See footnote to Table V. Rms deviations are not given for mean values of chemically equivalent angles because these far exceed the standard deviations of individual values.

TABLE VII

SELECTED NONBONDED CONTACTS (Å)

| | | | |
|---|---|---|---|
| Intramolecular | | | |
| C(11)···C(12) | 2.67 | C(11)···C(13) | 2.69 |
| C(21)···C(22) | 2.68 | C(12)···C(13) | 2.82 |
| C(31)···C(32) | 2.67 | C(21)···C(23) | 2.77 |
| | | C(22)···C(23) | 2.81 |
| C(13)···C(23) | 3.02 | C(31)···C(33) | 2.77 |
| C(13)···C(33) | 3.18 | C(32)···C(33) | 2.77 |
| C(23)···C(33) | 3.10 | | |
| | | C(11)···C(32) | 2.99 |
| | | C(12)···C(22) | 2.92 |
| | | C(21)···C(31) | 2.90 |
| Intermolecular | | | |
| O(11)···O(32) | 2.96 | O(31)···O(32) | 2.99 |
| O(11)···O(11) | 2.98 | O(12)···O(32) | 3.16 |

that C(1)–C(2) is about 0.09 Å shorter than the single bond in dimethylacetylene and related compounds[25] are both consistent with some delocalization of the $\pi$-electron density from C(1)–C(1′) to C(1)–C(2).

Partial double-bond character in C(1)–C(2) would be expected to be accompanied by a reduction in the bond orders of the Co–C(2) bonds below unity and hence a lengthening of these bonds. The Co–C(apical) bonds in all the related compounds studied so far fall within the range 1.89–1.92 Å. The values in the present compound (1.92 (1) Å) and in $Co_5(CO)_{15}C_3H$ (1.92 (2) Å) are in fact longer than in $CH_3CCo_3(CO)_9$ (1.90 (2) Å) and in $CH_3CCo_3(CO)_8P(C_6H_5)_3$ (1.91 (1) Å) in neither of which can there be any double-bond character in the C(apical)–C bonds. This difference although in the direction expected is not statistically significant. It is however of the magnitude expected, bearing in mind that there is not just one Co–C bond but three of them and that the expected reduction in the multiplicity of each bond would be only one-third of any increase in the multiplicity of the C(apical)–C bond. Further discussion of this point will be deferred to later papers in this series.

**Infrared Spectrum.**—The infrared spectrum of $Co_6(CO)_{18}C_4$ is given in Table VIII. Few of the possible vibrational frequencies are observed because of the high symmetry of the molecule. Five carbonyl stretching modes were found, the number predicted ($3\ E_u + 2\ A_{2u}$) from the overall molecular symmetry. Unfortunately it has not been possible to obtain a Raman spectrum of this compound and thus no assignment can be given for the ($C\equiv C$) mode.

TABLE VIII

INFRARED SPECTRUM (CM$^{-1}$) OF $Co_6(CO)_{18}C_4$[a,b]

| | | | |
|---|---|---|---|
| 4198 vw | $\nu$(CO) overtone and combination bands | 593 s | $\nu$(Co–C) and $\delta$(Co–C–O) |
| 4172 vw | | 579 s | |
| 4142 vw | | 525 s | |
| 4135 vw, sh | | 502 vs | |
| 4087 vw, sh | | 491, 463 m | |
| 4077 vw | | 438, 407 m | |
| 4070 vw, sh | | 389, 357 m | |
| 4020 vw | | | |
| 2107.3 w | $\nu$(CO) | | |
| 2090.4 s | | | |
| 2065.0 vs | | | |
| 2037.3 s | | | |
| 1983.0 vw | | | |
| 1382 m | $\nu$($C\equiv C$) | | |

[a] From 5000 to 800 cm$^{-1}$ in $CCl_4$ or *n*-octane (2200–1950 cm$^{-1}$); from 800 to 200 cm$^{-1}$ in Nujol mull. [b] Frequencies in the range 2200–1950 cm$^{-1}$ are accurate to ±0.2 cm$^{-1}$; the remainder, to ±1 cm$^{-1}$.

The absence of C–H vibrational modes is to be noted (no signals were found in the $^1H$ nmr spectrum), and so is also the high $\nu$(CO) mode at 2107 cm$^{-1}$, from which it may be inferred that the apical-$C\equiv CCCo_3(CO)_9$ group is an electron-withdrawing substituent.[1,8] These data will be discussed in more detail in a later paper.

**Derivatives of $Co_6(CO)_{18}C_4$.**—One point of considerable interest is whether the formal carbon–carbon triple bond in this compound reacts as an acetylene residue; alternatively the carbon chain could coordinate as a $-C-C\equiv C-C-$ unit or, less likely, an allene group.

Dicobalt octacarbonyl reacted with acetylenes to give a variety of products,[26] but it did not react with

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[25] "Tables of Interatomic Distances," Special Publication No. 18, The Chemical Society, London, 1965.

[26] R. S. Dickson and D. B. W. Yawney, *Aust. J. Chem.*, **22**, 533 (1969), and references therein.

$Co_6(CO)_{18}C_4$ under similar conditions. Likewise there was no evidence for platinum coordination using either $((C_6H_5)_3P)_4Pt$ or $((C_6H_5)_3P)_2PtCl_2$. Even more surprising is the resistance of the molecule to catalytic hydrogenation (20° (1 atm), 80° (100 atm)) since hydrogenation is usually so facile with acetylenes.[27] Examination of scale models shows that the triple bond is sterically protected by the equatorial carbonyl groups and this lack of reactivity even with small molecules like $H_2$ could well be a result of steric hindrance rather than electronic factors. Furthermore a reduction in the $C—C{\equiv}C$ bond angle from 180° such as would occur on coordination or hydrogenation would result in prohibitive carbonyl–carbonyl interactions. In this respect it is significant that $(CO)_9Co_3CC{\equiv}C(Co_2(CO)_6)C{\equiv}CCCo_3(CO)_9$ or $(Co_8(CO)_{24}C_6)$ is formed in these arene reactions but not $(CO)_9Co_3CC{\equiv}C(Co_2(CO)_6)CCo_3(CO)_9$.

Tetrakis(triphenylphosphine)platinum(0) unexpectedly proved to be a very useful source of triphenylphosphine and the derivatives $Co_6(CO)_{17}C_4((C_6H_5)_3P)$ and $Co_6(CO)_{16}C_4((C_6H_5)_3P)_2$ were readily prepared at 20°. In contrast temperatures above 60° are necessary for the direct reaction of triphenylphosphine and $Co_6(CO)_{18}C_4$. Subsequent work has shown that this reaction with $PtL_4$ (L = phosphine or arsine) compounds is general for metal carbonyls; the mechanism will be discussed elsewhere.[28] Other phosphine derivatives were isolated as it was anticipated that, with the lower symmetry, the $-C{\equiv}C-$ stretching frequency would be ir active. Also our experience with similar derivatives of the parent clusters $YCCo_3(CO)_9$ has shown their usefulness in studies of stability and electronic effects within the cluster.[11,29]

Table IX lists the derivatives together with their infrared spectra in the region 2150–1700 $cm^{-1}$. The maximum number of ligands able to be coordinated to the $-CCo_3(CO)_9$ unit both in $YCCo_3(CO)_9$ and in $Co_6(CO)_{18}C_4$ appears to be 3. These derivatives have similar chemical and physical properties to the $YCCo_3(CO)_9$ compounds and greater thermal and oxidative stability than $[Co_3(CO)_9C]_2$ derivatives; *i.e.*, the triple bond is a strong link.

The absence of bridging carbonyl vibrations in the spectra of $Co_6(CO)_{17}C_4L$ derivatives is noteworthy as bridging is found only with an electron-donating substituent on the apical carbon atom.[11] Their structure is probably one based on the replacement of an equatorial carbonyl group as in $CH_3CCo_3(CO)_8P(C_6H_5)_3$.[22]

It would appear from the infrared spectra that the three $Co_6(CO)_{16}C_4L_2$ derivatives have different structures. Bis-substituted $YCCo_3(CO)_9$ derivatives invariably have a structure with bridging carbonyl groups even if the $YCCo_3(CO)_8L$ compounds do not.[11] Therefore it is suggested that $Co_6(CO)_{16}C_4((C_2H_5)_2C_6H_5P)_2$ has a structure with both ligands coordinated to one $-CCo_3(CO)_7$ unit whereas there is one ligand molecule per $-CCo_3(CO)_8$ unit in $Co_6(CO)_{16}C_4((C_6H_5)_3P)_2$ and $Co_6(CO)_{16}C_4[(C_6H_{11})_3P]_2$. The latter compounds probably differ in the equatorial carbonyl groups replaced. A structure with two $(C_2H_5)_2C_6H_5P$ molecules coordinated to one cluster unit and one to the other is favored for $Co_6(CO)_{15}C_4((C_2H_5)_2C_6H_5P)_3$ because the presence of at least four bridging carbonyl vibrations shows that both cluster units have bridged configurations.

TABLE IX

INFRARED SPECTRA (2150–1700 $CM^{-1}$) OF PHOSPHINE DERIVATIVES (IN *n*-OCTANE)

| $Co_6(CO)_{17}C_4L$ | | $Co_6(CO)_{16}C_4L_2$ | | |
|---|---|---|---|---|
| L = $(C_6H_5)_3P$ | L = $(C_6H_{11})_3P$ | L = $(C_6H_{11})_3P$ | L = $(C_6H_5)_3P$ | L = $(C_2H_5)_2C_6H_5P$ |
| 2102 s | 2100 s | 2095 s | 2095 w | 2082 m |
| 2090 w | 2090 w | 2056 vs | 2084 s | 2066 vs |
| 2076 vs | 2074 s | 2052 vs | 2068 vs | 2038 s |
| 2058 br, vs | 2059 vs | 2042 w | 2057 m | 2022 s |
| | 2055 sh | 2034 s | 2043 vs | 2011 s |
| 2040 s | 2039 s | 2020 w | 2015 s | 1997 sh |
| 2025 s | 2024 s | 1998 s | | 1971 w |
| 2004 sh | 2014 sh | 1993 sh | | |
| 1997 sh | 1993 w | 1982 m | | |
| 1973 w | 1981 w | 1870 w | | |
| | | 1849 m | | |
| | | 1845 m | | |
| | | 1826 w | | |
| | | 1818 m | | |

| $Co_6(CO)_{15}C_4((C_2H_5)_2C_6H_5P)_3$ | | $Co_6(CO)_{14}C_4((C_2H_5)_2C_6H_5P)_4$ | | $Co_6(CO)_{13}C_4((C_2H_5)_2C_6H_5P)_5$ | |
|---|---|---|---|---|---|
| 2073 s | 1870 w | 2048 m | 1842 m | 2050 sh | (Solid) |
| 2045 vs | 1849 sh | 2038 s | 1818 m | 2035 s | |
| 2035 s | 1845 m | 2002 s | | 2006 s | 1826 s |
| 2029 sh | 1819 m | 1993 s | | 1988 s | 1813 s |
| 2019 s | | 1980 sh | | 1980 s | 1807 s |
| 2007 m | | 1953 w | | 1958 s | 1786 s |
| 1998 s | | 1845 m | | 1938 w | |
| 1968 w | | | | 1890 w | |
| | | | | 1851 m | |
| | | | | 1831 sh | |

It is not possible to postulate detailed structures for $Co_6(CO)_{14}C_4((C_2H_5)_2C_6H_5P)_4$ and $Co_6(CO)_{13}C_4((C_2H_5)_2C_6H_5P)_5$ at present as the configuration of a bridged $-CCo_3(CO)_n$ unit is unknown. However there are most likely two ligand molecules per $-CCo_3(CO)_7$ unit in $Co_6(CO)_{14}C_4((C_2H_5)_2C_6H_5P)_4$ arranged in a symmetrical fashion; note that there are only three bridging stretching vibrations and nine stretching frequencies in all. Further crystal structure studies are planned in order to settle a number of these points.

An interesting feature of complexes in which there are 3 mol of $(C_2H_5)_2C_6H_5P$ per $-CCo_3(CO)_6$ unit (as in $Co_6(CO)_{13}((C_2H_5)_2C_6H_5P)_5$) is that their solution spectra are broad and diffuse whereas their solid infrared and $^1H$ nmr spectra are relatively sharp. Ligand dissociation processes in solution could account for this behavior (mol wt: calcd for $Co_6(CO)_{13}C_4((C_2H_5)_2C_6H_5P)_5$, 1596; found (in chloroform), 1027).

A close examination of the infrared spectra between 2500 and 1600 $cm^{-1}$ has failed to reveal any bands other than those given in Table IX. It is concluded that the carbon–carbon triple bond stretch is lost in the wealth of carbonyl bands and assignment must await studies on isotopically substituted derivatives.

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[27] R. L. Augustine, "Catalytic Hydrogenation," Arnold, London, 1965.

[28] T. Matheson, B. H. Robinson, and J. L. Spencer, to be submitted for publication.

[29] B. H. Robinson and W. S. Tham, *J. Organometal. Chem.*, **16**, 45 (1969).

In conclusion, these chemical studies have shown that the carbon–carbon triple bond is a sterically protected group, that the triple bond can be regarded as an electron-withdrawing apical substituent of the $-CCo_3(CO)_9$ unit, and that the individual $-CCo_3(CO)_9$ clusters have chemical properties similar to those of the parent clusters, $YCCo_3(CO)_9$.

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# Dithiolene Complex Adducts. The Crystal and Molecular Structure of Tetra-*n*-propylammonium Bis(maleonitriledithiolato)-1,10-phenanthrolinecobaltate, $[(n-C_3H_7)_4N][Co(S_2C_2(CN)_2)_2(o\text{-phen})]$

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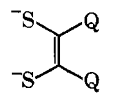
The crystal and molecular structure of the tetra-*n*-propylammonium salt of the *o*-phenanthroline adduct $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$ has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter techniques. The structure has been refined by least-squares methods to a conventional $R$ factor of 0.068 for 1490 nonzero reflections. The complex crystallizes in space group Pbca of the orthorhombic system in a unit cell of dimensions $a$ = 15.53 (2) Å, $b$ = 27.01 (3) Å, $c$ = 17.20 (2) Å, and $V$ = 7219 Å$^3$. The experimental density is 1.29 (3) g/cm$^3$; the calculated value is 1.30 g/cm$^3$ for $Z$ = 8. The coordination geometry about the cobalt ion is that of a tris-chelated octahedron with essentially $C_2$ molecular symmetry. The average Co–N distance is 2.01 (1) Å and the N–Co–N bond angle is 85.2 (5)°. The Co–S distances exhibit slight but significant differences depending on whether they are *trans* to an *o*-phenanthroline nitrogen atom in which case the average Co–S distance is 2.213 (5) Å or *trans* to another sulfur donor atom in which case the average distance is 2.247 (5) Å. The bond distances within the *o*-phenanthroline ligand range from 1.31 (2) to 1.48 (2) Å and follow approximately the individual bond orders predicted from simple valence bond considerations. All other bond distances, bond angles, and intermolecular contacts are normal.

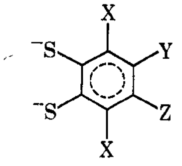
## Introduction

The cobalt and iron bis complexes of the 1,2-dithiolato ligand systems I and II are of particular interest



I

Q = CN, $CF_3$, $C_6H_5$, H, $CH_3$



II

X = Y = Z = H, Cl, $CH_3$, F
X = Y = H, Z = $CH_3$
X = H, Y = Z = $CH_3$

because of the structural differences which these systems can exhibit depending upon the overall oxidation state of the complex and the electron-withdrawing ability or π acidity of the particular ligand system.[1] Although I and II are represented in their classical dianion formulation, it is clear from the many studies which have been performed on them and their complexes that complexes of I and II exhibit extensive covalency and their ground states may be considered to be delocalized.[1c] To date, X-ray structural studies have shown that the complexes $Co(S_2C_2(CN)_2)_2^{2-}$ [2] and $Co(S_2C_6H_3(CH_3))_2^-$ [3] are truly monomeric in the solid, possessing essentially square-planar coordination geometries, whereas the related complexes $Co_2(S_2C_2(CF_3)_2)_4$,[4] $Co_2(S_2C_6Cl_4)_4^{2-}$,[5] and $Fe_2(S_2C_2(CN)_2)_4^{2-}$ [6] exist in the solid state as five-coordinate dimers in which the metal atom from one planar unit is bound to a fifth sulfur atom of a second such unit in the apical position of a square pyramid. Chemical and polarographic studies[7–11] together with the X-ray structure determinations have established that the more highly oxidized neutral complexes and those monoanionic systems with good π-acceptor ligands tend to form stable five-coordinate dimers while the more reduced dianionic systems and those monoanions with poor π-acceptor ligands exhibit little or no tendency to form the dimer structure. The tendency to-

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(1) For a comprehensive review of metal–1,2-dithiolene complexes, see (a) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); (b) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); (c) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

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