TABLE V

CENTRAL RING BOND DISTANCES (Å) AND ANGLES (DEG) (AVERAGE VALUES) OF 10-PHENOXARSINE CHLORIDE AND 10-PHENOXARSINE SULFIDE

	As–C	C–C	C–O	C–As–C	As–C–C	O–C–C	C–O–C
Sulfide	1.94 (1)	1.38 (1)	1.38 (2)	94.8 (4)	123.9 (2)	126.0 (8)	125.0 (5)
Chloride	1.93 (2)	1.38 (1)	1.40 (2)	94.6 (7)	123 (3)	124 (2)	124 (1)

the central-ring bond distances and bond angles. The comparison reveals that the 20° dihedral angle change toward planarity in the sulfide molecule has occurred with only slight changes in the central ring bond distances and angles. Further structural investigations are anticipated in order to elucidate the electronic factors which govern these dihedral angle changes.

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Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. VI.[1] Crystal Structure of Phenylmethinyltricobalt Hexacarbonyl–Mesitylene, $(C_6H_5)CCo_3(CO)_6 \cdot \pi\text{-}C_6H_3(CH_3)_3$

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The crystal and molecular structure of $(C_6H_5)CCo_3(CO)_6$–π-mesitylene, a product of the direct reaction of $(C_6H_5)CCo_3(CO)_9$ with mesitylene, has been determined. Crystals are orthorhombic, space group D_{2h}^{16}-*Pnma*, with four molecules in a unit cell of dimensions $a = 19.259$ (3), $b = 13.088$ (2), $c = 8.731$ (1) Å. Molecular symmetry C_s-m is required. X-Ray data were collected by counter methods in association with a four-circle diffractometer using Mo Kα radiation. All atoms were treated anisotropically in a full-matrix least-squares refinement to a conventional R factor of 0.057 for the 969 reflections having $|F^2| > \sigma|F^2|$. The molecular structure is derived from the parent $YCCo_3(CO)_9$ structure by replacement of the three CO groups attached to one of the Co atoms of the Co_3 triangle by one molecule of mesitylene. The plane of the mesitylene ring is approximately normal to the line joining the nearest Co atom to the centroid of the tetrahedral Co_3C group. Co–Co bond lengths are in the range 2.441 (2)–2.477 (3) Å and the mean Co–C(mesitylene) length is 2.15 (3) Å.

Introduction

When methinyltricobalt enneacarbonyls of general composition $YCCo_3(CO)_9$ (Y = alkyl or aryl) are heated with various arenes, complexes of composition $YCCo_3(CO)_6 \cdot$arene are obtained.[2] These complexes are distinct from the various linked cluster compounds[1,3–5] which are obtained when Y is Cl or Br. Evidence from nmr and infrared spectra was equivocal on the mode of attachment of the arene molecule, but replacement of the three carbonyl groups of one cobalt atom was indicated. The compound in which Y = phenyl and the arene is mesitylene was selected for detailed structure analysis, a preliminary account of which has been given.[6]

Experimental Section

An analyzed sample of $C_6H_5CCo_3(CO)_6 \cdot$mesitylene was kindly supplied by Dr. B. H. Robinson. The crystals, obtained by fractional sublimation, were large black prisms from which smaller fragments, suitable for X-ray diffraction, had to be cut.

Crystallographic Data.[7]—$Co_3C_{22}O_6H_{17}$, mol wt 553.7, is orthorhombic with $a = 19.259$ (3), $b = 13.088$ (2), $c = 8.731$ (1) Å; $V = 2201$ Å^3; $d_{obsd} = 1.64$ (5) g/cm^3; $Z = 4$; $d_{calcd} = 1.67$ g/cm^3; μ(Mo Kα) = 23.6 cm^{-1}. The two space groups consistent with observed systematic absences of X-ray reflections ((0kl) for $k + l$ odd and (hk0) for h odd) are C_{2v}^9-$Pn2_1a$ and D_{2h}^{16}-*Pnma*. Choice of the centrosymmetric *Pnma* was finally made on the basis of the Patterson function and the successful structure refinement.

Unit cell dimensions and their estimated standard deviations were obtained at room temperature (23 ± 2°) with Mo Kα_1 radiation (λ 0.7093 Å) by least-squares refinement of the setting angles of 12 high-angle reflections for the crystal mounted on a Hilger-Watts four-circle diffractometer. The experimental density was obtained by flotation of crystals in aqueous zinc bromide solution.

The crystal used for all unit cell and intensity measurements was approximately a cube of edge 0.25 mm and its ten faces were identified as (011), $(0\bar{1}\bar{1})$, (201), $(\bar{2}0\bar{1})$, $(12\bar{1})$, $(\bar{1}21)$, and the forms {210}. The procedures for the collection of intensity data from the four-circle diffractometer using a θ–2θ scan technique were essentially as described in detail in part V of this series.[1] The crystal mosaicity was 0.10°. The scan range was 1.28° in 2θ and the reciprocal lattice was explored out to 2θ = 45° beyond which there were very few intensities above background. All independent hkl reflections out to this limit were recorded followed by all $\bar{h}\bar{k}\bar{l}$ reflections for which $I(hkl) > \sigma[I(hkl)]$. Absorption corrections were applied using a Gaussian integration method and transmission coefficients were in the

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[1] Part V: M. D. Brice and B. R. Penfold, *Inorg. Chem.*, **11**, 1381 (1972).

[2] B. H. Robinson and J. L. Spencer, *J. Chem. Soc. A*, 2045 (1971).

[3] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197, 2204 (1970).

[4] R. J. Dellaca and B. R. Penfold, *ibid.*, **10**, 1269 (1971).

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

[6] M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *Chem. Commun.*, 72 (1971).

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

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $(C_6H_5)CCo_3(CO)_6 \cdot \pi\text{-}C_6H_3(CH_3)_3$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.11138 (10)	0.25	0.0298 (2)	0.00174 (6)	0.0041 (1)	0.0099 (3)	0	−0.0002 (1)	0
Co(2)	0.19053 (7)	0.15537 (10)	0.1959 (2)	0.00186 (4)	0.0038 (1)	0.0115 (2)	0.00025 (7)	−0.00003 (9)	0.0002 (1)
O(1)	0.2962 (5)	0.1233 (7)	−0.043 (1)	0.0040 (4)	0.0105 (9)	0.031 (2)	−0.0009 (5)	0.0068 (8)	−0.006 (1)
O(2)	0.1117 (4)	−0.0337 (7)	0.169 (1)	0.0034 (3)	0.0064 (7)	0.023 (2)	−0.0014 (4)	0.0011 (6)	−0.0020 (9)
O(3)	0.2557 (5)	0.1250 (7)	0.496 (1)	0.0057 (4)	0.0092 (8)	0.020 (2)	0.0008 (4)	−0.0043 (8)	0.0012 (10)
C(1)	0.2561 (6)	0.1370 (8)	0.052 (1)	0.0026 (4)	0.0039 (8)	0.021 (2)	0.0003 (5)	0.0007 (8)	−0.001 (1)
C(2)	0.1428 (6)	0.0412 (9)	0.179 (1)	0.0023 (4)	0.0058 (9)	0.014 (2)	0.0013 (5)	−0.0007 (8)	0.002 (1)
C(3)	0.2313 (6)	0.1357 (9)	0.377 (2)	0.0030 (4)	0.0045 (9)	0.020 (2)	0.0009 (5)	0.0004 (9)	0.002 (1)
C(4)	0.1191 (7)	0.25	0.244 (2)	0.0022 (5)	0.0024 (10)	0.011 (3)	0	−0.0006 (10)	0
C(5)	0.0626 (7)	0.25	0.358 (2)	0.0017 (5)	0.0046 (11)	0.011 (3)	0	0.0009 (9)	0
C(6)	0.0340 (6)	0.1613 (9)	0.413 (1)	0.0032 (5)	0.0051 (8)	0.018 (2)	−0.0009 (6)	0.0020 (8)	−0.002 (1)
C(7)	−0.0223 (6)	0.1617 (10)	0.517 (1)	0.0039 (5)	0.0070 (10)	0.016 (2)	−0.0017 (6)	0.0023 (9)	0.003 (1)
C(8)	−0.0500 (9)	0.25	0.563 (2)	0.0027 (7)	0.007 (2)	0.015 (4)	0	−0.0003 (11)	0
C(9)	0.1224 (9)	0.25	−0.215 (2)	0.0039 (7)	0.010 (2)	0.005 (3)	0	−0.000 (1)	0
C(10)	0.0965 (6)	0.1537 (8)	−0.170 (1)	0.0032 (4)	0.0047 (8)	0.011 (2)	−0.0017 (6)	−0.0013 (7)	0.001 (1)
C(11)	0.0361 (6)	0.1605 (9)	−0.078 (1)	0.0029 (4)	0.0048 (8)	0.017 (2)	−0.0016 (6)	−0.0023 (8)	0.003 (1)
C(12)	0.0020 (9)	0.25	−0.028 (2)	0.0032 (6)	0.0024 (10)	0.017 (3)	0	−0.003 (1)	0
C(13)	0.1271 (7)	0.0536 (9)	−0.222 (1)	0.0049 (5)	0.0044 (9)	0.018 (2)	0.0018 (6)	−0.0011 (10)	−0.005 (1)
C(14)	−0.0618 (8)	0.25	0.072 (2)	0.0008 (5)	0.010 (2)	0.019 (4)	0	0.0009 (10)	0

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

range 0.59–0.67. Following this the equivalent forms were averaged and yielded a set of 969 data for each of which $F_o^2 \geqslant \sigma(F_o^2)$ and which were used for the structure solution and refinement. Final structure factor calculations for the 547 reflections for which $F_o^2 < \sigma(F_o^2)$ showed that only one had $|F_o^2 - F_c^2| > 2\sigma(F_o^2)$.

Structure Solution and Refinement.—The disposition of Co–Co vectors (c = 2.5 Å) in a three-dimensional Patterson function strongly indicated a mirror plane normal to the b axis and hence space group *Pnma* rather than $Pn2_1a$. This was confirmed by the subsequent satisfactory refinement. Parameters for the two independent Co atoms, one of which must lie on the crystallographic mirror plane, were derived from the vector map, and two subsequent difference Fourier maps preceded by intermediate least-squares refinement then revealed all remaining nonhydrogen atoms.

In all least-squares calculations the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weight w being taken as $4F_o^2/[\sigma(F_o^2)]^2$. At the end of the refinement the value of the empirical parameter p in the expression for $\sigma(I)$,[1] the estimated standard deviation in the measured intensity, was adjusted to 0.075 to achieve approximate constancy of the minimized function over the full range of intensity. The usual tabulations[8] of atomic scattering factors for Co, C, and O were used, those for Co only being corrected for anomalous dispersion; values of $\Delta f'$ and $\Delta f''$ were interpolated from Cromer's tables.[9]

Isotropic least-squares refinement converged with values for the agreement factors R_1 and R_2 0.077 and 0.069.[10] All atoms were then assigned anisotropic vibrational parameters, and the subsequent refinement reduced R_1 and R_2 to 0.060 and 0.054. A further difference Fourier map showed all nonmethyl hydrogen atoms clearly resolved, and in all subsequent structure factor calculations these H atoms were included at their ideal positions (d(C–H) = 1.06 Å, B = 5 Å^2), but none of their parameters were varied. After adjustment of the weighting scheme as described above, two final least-squares cycles converged with R_1 and R_2 0.057 and 0.056. There was no evidence for secondary extinction. A final difference Fourier map showed no peak higher than 0.7 e/Å^3 nor any trough deeper than −0.5 e/Å^3. Final positional and thermal parameters are listed in Table I, root-mean-square amplitudes of vibration of atoms in Table II, and observed and calculated structure factors for all 969 reflections used in the refinement in Table III.[11]

All calculations were carried out on an IBM 360/44 computer with 32K words of core storage. The programs used have been described in part V of this series.[1]

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermediate	Max
Co(1)	0.179 (4)	0.189 (3)	0.197 (3)
Co(2)	0.174 (3)	0.193 (3)	0.211 (2)
O(1)	0.18 (2)	0.28 (1)	0.42 (1)
O(2)	0.20 (1)	0.26 (1)	0.31 (1)
O(3)	0.22 (1)	0.29 (1)	0.36 (1)
C(1)	0.18 (2)	0.22 (2)	0.28 (2)
C(2)	0.16 (2)	0.24 (2)	0.26 (2)
C(3)	0.18 (2)	0.24 (2)	0.29 (2)
C(4)	0.15 (3)	0.19 (3)	0.22 (3)
C(5)	0.17 (3)	0.20 (3)	0.21 (3)
C(6)	0.20 (2)	0.22 (2)	0.30 (2)
C(7)	0.16 (2)	0.29 (2)	0.30 (2)
C(8)	0.22 (3)	0.24 (3)	0.25 (3)
C(9)	0.13 (4)	0.27 (2)	0.29 (3)
C(10)	0.16 (2)	0.20 (2)	0.28 (2)
C(11)	0.16 (2)	0.20 (2)	0.30 (2)
C(12)	0.14 (3)	0.18 (3)	0.30 (3)
C(13)	0.14 (2)	0.26 (2)	0.33 (2)
C(14)	0.12 (4)	0.27 (3)	0.29 (2)

Description of Structure and Discussion

In the crystalline state $C_6H_5CCo_3(CO)_6 \cdot C_6H_3(CH_3)_3$ consists of well-separated molecules; the shortest intermolecular contact not involving hydrogen is 3.34 Å. Figure 1 is a stereoscopic view of the whole molecule, while Figure 2, which is a projection of the asymmetric unit onto the crystallographic mirror plane, gives an indication of the directions of the principal axes of thermal motion. (Parentheses have been omitted from atom labels in these diagrams, for clarity, but the numbering scheme is the same as in Table I.) Intramolecular distances and angles are listed in Tables IV and V, respectively, with selected nonbonded contacts in Table VI. The mesitylene molecule has replaced the three carbonyl groups which are bonded to one cobalt atom of the parent compound $(C_6H_5)CCo_3(CO)_9$.

Few compounds are known in which an arene molecule (as distinct from say a cyclopentadienyl radical or a polyene molecule like cyclooctatetraene) is associated with a metal cluster. The only structure determination which has been reported is that of $Ru_6(CO)_{14}C \cdot$mesitylene[12] in which the mesitylene has replaced three CO groups of $Ru_6(CO)_{17}C$ and is π-bonded to a single Ru atom with a mean Ru–C(mesitylene) distance of 2.24 Å, or 0.10 Å greater than the mean Co–

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(8) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(9) D. T. Cromer, *Acta Crystallogr.*, **18**, 511 (1965).

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

(11) Table III containing structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1855. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(12) R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968).

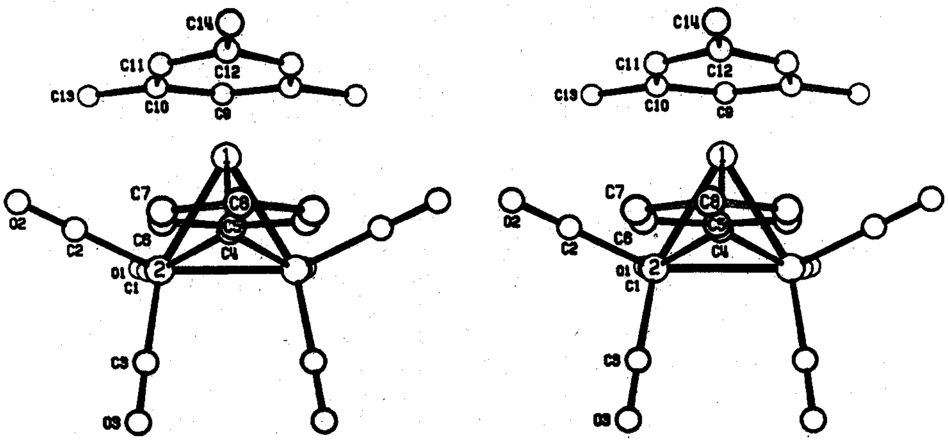

Figure 1.—A stereoscopic view of one molecule of $(C_6H_5)CCo_3(CO)_6$–π-mesitylene.

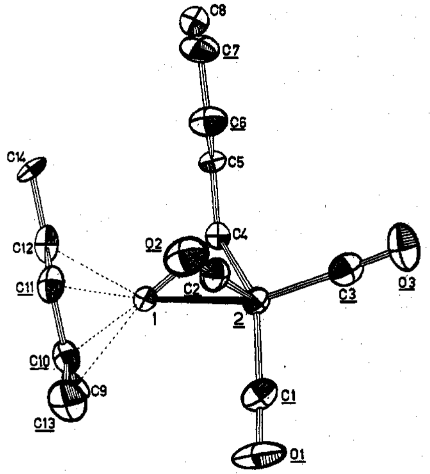

Figure 2.—The molecule $(C_6H_5)CCo_3(CO)_6$–π-mesitylene viewed in projection onto the crystallographic mirror plane showing atomic thermal ellipsoids. Atoms with underlined labels are related to other atoms in the molecule by the mirror plane.

TABLE IV

BOND DISTANCES (Å)[a]

Co(1)–Co(2)	2.441 (2)	C(5)–C(6)	1.37 (1)
Co(2)–Co(2′)	2.477 (3)	C(6)–C(7)	1.42 (2)
		C(7)–C(8)	1.33 (2)
Co(1)–C(4)	1.87 (2)	C–C(phenyl)	*1.37 (3)*
Co(2)–C(4)	1.90 (1)		
Co–C(bridge)	*1.89 (2)*	C(9)–C(10)	1.41 (1)
		C(10)–C(11)	1.42 (2)
Co(2)–C(1)	1.80 (1)	C(11)–C(12)	1.41 (2)
Co(2)–C(2)	1.76 (1)	C–C(mesitylene)	*1.41 (1)*
Co(2)–C(3)	1.79 (1)		
Co–CO	*1.78 (2)*	C(10)–C(13)	1.51 (2)
		C(12)–C(14)	1.50 (2)
Co(1)–C(9)	2.15 (2)	C–C(methyl)	*1.50 (1)*
Co(1)–C(10)	2.17 (1)		
Co(1)–C(11)	2.09 (1)	C(1)–O(1)	1.15 (1)
Co(1)–C(12)	2.17 (2)	C(2)–O(2)	1.15 (1)
Co–C(mesitylene)	*2.15 (3)*	C(3)–O(3)	1.14 (1)
		C–O	*1.15 (1)*

[a] Mean values of bonds assumed chemically equivalent are italicized and their associated uncertainties are root-mean-square 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.

TABLE V

BOND ANGLES (DEG)[a]

Co(2)–Co(1)–Co(2′)	61.0 (1)	C(1)–Co(2)–C(2)	101.3 (5)
Co(1)–Co(2)–Co(2)′	59.5 (1)	C(1)–Co(2)–C(3)	106.9 (5)
	60 (1)		*104 (3)*
C(4)–Co(1)–Co(2)	50.1 (3)	C(2)–Co(2)–Co(1)	93.2 (3)
C(4)–Co(2)–Co(1)	49.2 (4)	C(3)–Co(2)–Co(2)′	98.3 (4)
C(4)–Co(2)–Co(2)′	49.2 (3)		*96 (3)*
	49.5 (5)		
		Co(2)–C(1)–O(1)	177 (1)
C(5)–C(4)–Co(1)	128 (1)	Co(2)–C(2)–O(2)	180 (1)
C(5)–C(4)–Co(2)	133 (1)	Co(2)–C(2)–O(3)	178 (1)
	131 (3)		*178 (1)*
C(2)–Co(2)–C(3)	100.4 (5)	C(4)–Co(2)–C(2)	101.2 (5)
		C(4)–Co(2)–C(3)	102.6 (6)
C(6)–C(5)–C(6)′	116 (1)		*101.9* (7)
C(5)–C(6)–C(7)	122 (1)		
C(6)–C(7)–C(8)	120 (1)	C(4)–Co(2)–C(1)	138.6 (5)
C(7)–C(8)–C(7)′	120 (2)		
	120 (2)	C(10)–C(9)–C(10)′	126 (2)
		C(9)–C(10–C(11)	113 (1)
Co(1)–C(4)–Co(2)	80.7 (5)	C(10)–C(11)–C(12)	128 (1)
Co(2)–C(4)–Co(2)′	81.5 (6)	C(11)–C(12)–C(11)′	112 (2)
	81.1 (4)		*120* (7)
C(2)–Co(2)–Co(2)′	148.1 (3)	C(9)–C(10)–C(13)	124 (1)
C(3)–Co(2)–Co(1)	150.9 (4)	C(11–C(10)–C(13)	123 (1)
	150 (2)	C(11)–C(12)–C(14)	124 (1)
			124 (1)
C(1)–Co(2)–Co(1)	95.3 (4)		
C(1)–Co(2)–Co(2)′	97.7 (4)	C(4)–C(5)–C(6)	122.0 (7)
	97 (1)		

[a] See footnote to Table IV. Primed atoms are related by a mirror plane to the corresponding unprimed atoms.

TABLE VI

SELECTED INTRAMOLECULAR NONBONDED CONTACTS (Å)

C(1)···C(2)	2.75	C(3)···C(3′)	2.99
C(1)···C(3)	2.88	C(4)···C(12)	3.27
C(2)···C(3)	2.73	C(5)···C(14)	3.46
C(1)···C(1′)	2.96		

C(mesitylene) distance in the present structure. (Covalent radii for Ru and Co are 1.25 and 1.16 Å, respectively.) The mean Co–C distance of 2.14 (3) Å may be compared with an average Co–C(ring) distance of 2.07 Å for a number of "unperturbed" π complexes of cobalt as tabulated by Wheatley.[13] The Co atom is 1.61 Å from the center of the mesitylene ring. Aver-

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[13] P. J. Wheatley *Perspect. Struct. Chem.*, 1, 1 (1967).

age values for mesitylene bond lengths of 1.41 (1) Å within the ring and 1.50 (2) Å for C(ring)–C(methyl) indicate no significant change on coordination.

Average values of bond lengths and angles within the $-CCo_3(CO)_6$ portion of the molecule are in general agreement with those observed in a range of similar compounds,[4] but the independent Co–Co bond lengths of 2.441 (2) Å for Co(1)–Co(2) and 2.477 (3) Å for Co(2)–Co(2′) differ significantly from each other. This is the first structure determination for this class of compound where there is a terminal aryl group attached to the bridging carbon atom. The C(bridge)–C(phenyl) bond length of 1.48 (2) Å is not inconsistent with the view expressed in part V of this series that the orbital used by the bridge carbon for this bond approximates to an sp hybrid. The normal to the phenyl ring is tilted by 6.6° away from the plane of the Co_3 triangle to bring the ring closer to the mesitylene molecule, but there appears to be no reason for this tilt other than the requirements of intermolecular packing.

The most interesting structural feature of the compound is the fact that the mesitylene molecule is π-bonded to a single Co atom in direct contrast to $C_6H_5CCo_3(CO)_6$–cyclooctatetraene[6] in which the polyene ring, having replaced the axial carbonyl of each Co atom in the parent compound, is π-bonded to all three Co atoms through three of its double bonds. A possible explanation is that the rigid phenyl ring cannot arrange itself so as to satisfy the electronic requirements of a triangle of bonded Co atoms. Alternatively, a configuration in which mesitylene is π-bonded to the Co_3 triangle might result in prohibitive interactions between the equatorial carbonyl groups and the mesitylene methyl groups. The normal to the plane of the mesitylene ring is tilted by 11.4° away from the Co_3 plane so that the mesitylene plane is approximately perpendicular to the line joining the nearest cobalt atom, Co(1), to the centroid of the CCo_3 group.

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New Penta- and Hexasubstituted Derivatives of Group VIb Metal Hexacarbonyls

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An attempt to obtain new zerovalent derivatives of group VIb metal hexacarbonyls has been made by studying the extensive ultraviolet irradiation of mixtures of metal carbonyls with the ligands n-$C_3H_7OPF_2$, $(CH_3O)_2PF$, $P(OCH_3)_3$, $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$ in pentane. This method is efficient for obtaining penta- or hexasubstituted derivatives which, in most cases, were isolated. Infrared and nmr data are reported for these complexes. The comparison of the most highly substituted derivatives obtainable with each metal and each ligand seems to indicate the possibility of differentiation between the steric and electronic stability factors.

Only a few hexasubstituted derivatives of group VI metal carbonyls with tertiary phosphorus ligands are known at the present time. These have been prepared essentially by two indirect methods: displacement of benzene from dibenzenemolybdenum by chelating phosphines $C_2H_4(PR_2)_2$[1] or by PF_3;[2] reduction of metal salts in the presence of the phosphines $C_2H_4[P(CH_3)_2]_2$,[3] PF_3,[2] or $PPhH_2$.[4]

Direct synthesis from molybdenum hexacarbonyl has been successful only with trifluorophosphine by either thermal or photochemical activation.[5] Similar attempts with chelating phosphines $C_2H_4(PR_2)_2$ and o-$C_6H_4(PR_2)_2$ lead only to the tetrasubstituted derivatives.[6]

No systematic study has been made of the possibility of synthesizing hexasubstituted derivatives directly from hexacarbonylmetals with a great variety of nonchelating phosphines. In addition to concerning itself with problems of synthesis, this study can also lead to experimental evidence for factors governing the obtainment of the higher substituted derivatives.

We have therefore used a great variety of trivalent phosphorus compounds with variable electron donor–acceptor power and steric crowding and we have, for each, attempted to synthesize the most highly substituted derivative possible. These ligands are n-$C_3H_7OPF_2$, $(CH_3O)_2PF$, $P(OCH_3)_3$, $CH_3P(OCH_3)_2$, $(CH_3)_2POCH_3$, and $P(CH_3)_3$. We have selected primarily methyl derivatives because of the potential value of their proton nmr spectra.

To carry out the substitution we have chosen photochemical activation by uv light because we have previously seen that this method is particularly well suited to the preparation of tetrasubstituted derivatives.[7]

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 225 spectrometer. The compounds were examined in hexadecane solution in the carbonyl stretching region and the spectra were calibrated by saturated water vapor lines.

Proton nmr spectra were taken on a Varian Associates Model

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