

than that in the planar chelate N<sub>4</sub> complex bis(3-methyl-1-phenyl-5-*p*-tolylformazyl)nickel(II) (Dale, 1967) or in the macrocyclic N<sub>4</sub>-coordinated Ni complex related to (1) by R<sup>1</sup>R<sup>1</sup>-bridging (Hanić, Handlović & Lindgren, 1972). It is also 0.025 Å longer than the Ni–N distance in the planar chelate O<sub>2</sub>N<sub>2</sub> complex bis(*N*-isopropyl-3-methylsalicylaldiminato)nickel(II) (Braun & Lingafelter, 1966) but shorter than those of 1.970 and 1.974 Å in the pseudotetrahedral chelate O<sub>2</sub>N<sub>2</sub> complexes bis(*N*-isopropylsalicylaldiminato)nickel(II) (Fox, Orioli, Lingafelter & Sacconi, 1964) and bis(*N*-isopropyl-3-ethylsalicylaldiminato)nickel(II) (Braun & Lingafelter, 1967). The chelate ring systems are symmetrical with average C–N and C–C distances of 1.336 and 1.392 Å. They are inclined to one another at 67.7° and make respective interplanar angles of 46.6 and 42.5° with their *p*-chlorophenyl and 34.4 and 35.4° with their phenyl substituents. The thermal motions of the phenyl substituents on C(3) and C(6) are more pronounced than those on N(1) and N(4), thereby correlating with NMR evidence for thermally excited rotation of the former phenyl rings on the basis of the temperature dependence of their <sup>1</sup>H NMR shifts (Knorr, Weiss, Polzer & Bischler, 1975). An important stabilizing factor favouring the tetrahedral ground state must be the interaction between the phenyl rings on N(1) and N(4). These make an interplanar angle of 16.5° to one another at a distance between their plane normals of 4.07 Å. Seven of the constituent C atoms are at intermolecular distances of less than 4.0 Å from

members of the other phenyl group. Nevertheless, rotation of such phenyl groups in (2) is fast in solution on the NMR time scale.

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## Dicarbonyl( $\eta$ -triphenylphosphoniumcyclopentadienylide)cobalt(I) Tetracarbonylcobaltate(–I)

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**Abstract.** [Co(C<sub>23</sub>H<sub>19</sub>P)(CO)<sub>2</sub>][Co(CO)<sub>4</sub>], C<sub>29</sub>H<sub>19</sub>Co<sub>2</sub>O<sub>6</sub>P, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.777 (2), *b* = 16.797 (6), *c* = 16.799 (5) Å,  $\beta$  = 96.11 (2)°, *Z* = 4, *M<sub>r</sub>* = 611.80, *D<sub>x</sub>* = 1.48 Mg m<sup>-3</sup>, *R* = [ $\sum w|\Delta F|^2 / \sum wF_o^2$ ]<sup>1/2</sup> = 0.0535 based on 3155 independent reflections. The structure consists of two  $\sigma$ -bonded carbonyl groups and the cyclopentadienylide moiety  $\pi$ -bonded to the cobalt(I) to form the cation with square-

planar coordination [the carbonyl–Co–carbonyl bond angle in the cation is 94.5 (3)°] and a tetrahedral [Co(CO)<sub>4</sub>]<sup>–</sup> anion.

**Introduction.** Intensity data (15706 total reflections, 4823 independent reflections, 3155 with intensities greater than three standard deviations above background) were collected to  $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$  using a

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Table 1. Atomic parameters ( $\times 10^5$  for Co, P;  $\times 10^4$  for C, O;  $\times 10^3$  for H)

	x	y	z
Co(1)	9418 (9)	75948 (5)	1756 (5)
Co(2)	68281 (9)	64488 (5)	15693 (6)
P	20853 (16)	86290 (9)	19041 (9)
C(1)	1518 (8)	8056 (5)	9356 (5)
O(1)	1890 (7)	8384 (4)	8825 (4)
C(2)	805 (8)	2274 (4)	158 (4)
O(2)	1926 (5)	2202 (3)	369 (3)
C(3)	3436 (7)	2452 (5)	3686 (4)
O(3)	3631 (6)	3119 (3)	3828 (4)
C(4)	2024 (8)	1425 (4)	2552 (5)
O(4)	1285 (6)	1418 (3)	1977 (3)
C(5)	4728 (8)	1031 (4)	3209 (5)
O(5)	5749 (6)	759 (3)	3058 (4)
C(6)	2567 (8)	917 (5)	4214 (5)
O(6)	2165 (7)	533 (4)	4718 (4)
C(11)	1848 (6)	7741 (3)	1344 (3)
C(12)	2778 (8)	7427 (5)	824 (4)
C(13)	2298 (11)	6685 (5)	545 (6)
C(14)	1070 (11)	6527 (5)	843 (5)
C(15)	759 (8)	7184 (4)	1310 (4)
C(21)	3289 (6)	8448 (3)	2757 (3)
C(22)	3460 (6)	9017 (3)	3355 (4)
C(23)	4458 (7)	8906 (4)	3995 (4)
C(24)	5208 (7)	8242 (4)	4054 (4)
C(25)	5070 (7)	7675 (4)	3473 (4)
C(26)	4088 (6)	7766 (3)	2818 (4)
C(31)	2761 (6)	-609 (3)	1310 (4)
C(32)	4029 (7)	-282 (4)	1538 (4)
C(33)	4515 (7)	334 (4)	1069 (5)
C(34)	3756 (8)	584 (4)	401 (5)
C(35)	2524 (7)	255 (4)	162 (5)
C(36)	1991 (7)	-345 (4)	606 (4)
C(41)	511 (6)	8906 (3)	2252 (3)
C(42)	118 (7)	330 (4)	7962 (4)
C(43)	1313 (8)	148 (4)	7612 (5)
C(44)	1907 (8)	636 (4)	7119 (5)
C(45)	1322 (8)	1368 (4)	6932 (5)
C(46)	115 (8)	1593 (4)	7229 (4)
H(12)	352 (6)	769 (3)	80 (4)
H(13)	263 (6)	639 (4)	21 (4)
H(14)	47 (7)	609 (4)	62 (5)
H(15)	3 (5)	727 (3)	152 (3)
H(22)	288	947	333
H(23)	462	931	440
H(24)	587	816	450
H(25)	565	722	351
H(26)	394	736	242
H(32)	458	952	200
H(33)	538	58	124
H(34)	411	100	9
H(35)	200	44	969
H(36)	114	943	42
H(42)	935	60	770
H(43)	174	965	773
H(44)	271	47	690
H(45)	176	172	659
H(46)	963	183	763

four-circle automated diffractometer with  $\theta$ - $2\theta$  step scans and graphite-monochromatized radiation (Mo  $K\alpha_1 = 0.70926$  Å). The  $2\theta$  step size ranged from  $0.08$  to  $0.12^\circ$ ; background counts were taken at  $\pm 1.2^\circ$  ( $2\theta$ )

from the peak centers. [For further details of the step-scan procedure see Baenziger, Foster, Howells, Howells, Vander Valk & Burton (1977).] Intensity data were corrected for Lorentz and polarization factors and for absorption [analytical method of de Meulenaer & Tompa (1965), as used in the program *ABSORB* as described by Templeton & Templeton (1973) with local adaptation by F. J. Hollander]. The linear absorption coefficient is  $1.355 \text{ mm}^{-1}$ ; the crystal bounding planes with distances from the center of the crystal are:  $\pm(001)$   $0.094$  mm,  $\pm(011)$   $0.088$  mm,  $\pm(100)$   $0.244$  mm, and  $(01\bar{1})$   $0.105$  mm. Absorption corrections ranged from  $1.20$  to  $1.40$ .

The yellow crystals were prepared by combining octacarbonyldicobalt with triphenylphosphonium-cyclopentadienylide in tetrahydrofuran under nitrogen. Addition of petroleum ether precipitated a yellow-red product which was recrystallized from a mixture of tetrahydrofuran and petroleum ether; m.p.  $397$ – $405$  K. The unit-cell dimensions were determined from 12 well centered reflections on the diffractometer. The density of the crystals was measured by flotation in toluene-carbon tetrachloride mixtures.

The structure was solved using the program package *MULTAN* (Germain, Main & Woolfson, 1971) to locate the Co and P atoms, and electron density difference maps to locate all the remaining atoms. H atoms were observed in the difference maps, but during refinement they were fixed at  $0.95$  Å from the C atoms of the phenyl groups. Full-matrix least-square refinements were carried out by the locally written least-square program, *FMLS*. The function minimized was  $RS = \sum w(|F_o| - |F_c|)^2$ . The weight,  $w$ , is  $1/S_F^2$ , where  $S_F$  was the larger of the two quantities: (1) the propagated error due to counting statistics; (2) the error estimated from the scatter of independently measured equivalent reflections. Scattering factors for Co, P and C are from *International Tables for X-ray Crystallography* (1968); the H atom scattering factors are those of Stewart, Davidson & Simpson (1965). Anomalous-dispersion terms were included for Co and P.

Positional parameters are given in Table 1.\* Bond distances and angles are given in Table 2. A view of the molecule looking down the normal to the cyclopentadiene plane is shown in Fig. 1.

**Discussion.** The triphenylphosphoniumcyclopentadienylide is  $\pi$  bonded to Co<sup>I</sup>. The carbonyl-Co-carbonyl bond angle is  $94.5(3)^\circ$ , and the projection of a square plane about Co which includes these carbonyl

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34084 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

Co—C(1)	2.080 (6)	Co—C(3)	1.751 (7)
Co—C(2)	2.018 (7)	Co—C(4)	1.756 (9)
Co—C(13)	2.074 (8)	Co—C(5)	1.752 (8)
Co—C(14)	2.112 (8)	Co—C(6)	1.746 (8)
Co—C(15)	2.052 (8)		
		C(3)—O(3)	1.158 (7)
		C(4)—O(4)	1.144 (8)
		C(5)—O(5)	1.149 (8)
		C(6)—O(6)	1.165 (8)
	<i>R</i> = 2	<i>R</i> = 3	<i>R</i> = 4
C(R1)—C(R2)	1.384 (8)	1.372 (8)	1.452 (9)
C(R2)—C(R3)	1.385 (9)	1.413 (9)	1.397 (9)
C(R3)—C(R4)	1.334 (8)	1.345 (9)	1.341 (9)
C(R4)—C(R5)	1.361 (8)	1.346 (9)	1.378 (9)
C(R5)—C(R6)	1.390 (9)	1.388 (8)	1.382 (10)
C(R6)—C(R1)	1.383 (7)	1.405 (8)	1.395 (10)
C(1)—Co(1)—C(2)			94.5 (3)
C(2)—Co(1)—[C(12)—C(13)] <sub>center</sub>			104.3 (4)
[C(12)—C(13)] <sub>center</sub> —Co(1)—[C(14)—C(15)] <sub>center</sub>			55.7 (4)
[C(14)—C(15)] <sub>center</sub> —Co(1)—C(1)			103.5 (4)
Co(1)—C(1)—O(1)			177.8 (8)
Co(1)—C(2)—O(2)			178.9 (7)
C(3)—Co(2)—C(4)	107.0 (3)		
C(3)—Co(2)—C(5)	109.2 (3)	Co(2)—C(3)—O(3)	177.5 (7)
C(3)—Co(2)—C(6)	111.2 (4)	Co(2)—C(4)—O(4)	179.2 (7)
C(4)—Co(2)—C(5)	107.7 (3)	Co(2)—C(5)—O(5)	179.5 (7)
C(4)—Co(2)—C(6)	112.6 (3)	Co(2)—C(6)—O(6)	177.2 (7)
C(5)—Co(2)—C(6)	109.1 (4)		
C(11)—P—C(21)	108.8 (3)	P—C(11)—C(12)	125.6 (5)
C(11)—P—C(31)	110.0 (3)	P—C(11)—C(15)	129.5 (5)
C(11)—P—C(41)	109.2 (3)	C(15)—C(11)—C(12)	104.9 (6)
C(21)—P—C(31)	108.6 (3)	C(11)—C(12)—C(13)	108.8 (8)
C(21)—P—C(41)	107.6 (3)	C(12)—C(13)—C(14)	109.0 (8)
C(31)—P—C(41)	112.5 (3)	C(13)—C(14)—C(15)	107.4 (8)
		C(14)—C(15)—C(11)	109.6 (8)
	<i>R</i> = 2	<i>R</i> = 3	<i>R</i> = 4
C(R6)—C(R1)—C(R2)	119.7 (5)	119.7 (6)	118.9 (5)
C(R1)—C(R2)—C(R3)	119.4 (6)	118.9 (6)	116.1 (6)
C(R2)—C(R3)—C(R4)	120.4 (6)	120.4 (7)	124.3 (7)
C(R3)—C(R4)—C(R5)	121.3 (6)	121.2 (7)	119.3 (8)
C(R4)—C(R5)—C(R6)	119.9 (6)	120.8 (7)	120.7 (7)
C(R5)—C(R6)—C(R1)	119.1 (6)	118.9 (6)	120.6 (6)
P—C(R1)—C(R2)	119.0 (5)	120.4 (5)	120.8 (5)
P—C(R1)—C(R6)	121.3 (5)	119.9 (5)	120.2 (5)

ligands intersects the C(2)—C(3) and C(4)—C(5) bonds of the cyclopentadiene ring. The angle carbonyl—Co—[C(2)—C(3) center] is 104.3°, [C(2)—C(3) center]—Co—[C(4)—C(5) center] is 55.7°, and the [C(4)—C(5) center]—Co—carbonyl angle is 103.5°, totalling 358°. These bond angles imply that *dsp*<sup>2</sup> square-planar coordination occurs about Co<sup>I</sup> involving four electrons from the cyclopentadienyliide system. The coordinated bonds from the ylide are slightly (but not significantly) longer than the distances observed in the uncoordinated ylide (Ammon, Wheeler & Watts, 1973): 1.376 (4) and 1.392 (4) Å for the uncoordinated ylide *vs* 1.395 (10) and 1.406 (10) Å in the coordinated ylide. There has been a significant change

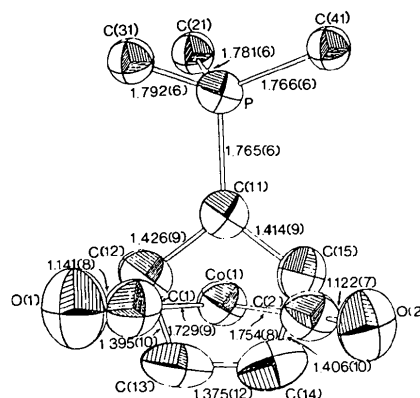


Fig. 1. A view of the dicarbonyl( $\eta$ -triphenylphosphonium)cyclopentadienyliide)cobalt(I) cation along the perpendicular to the plane of the cyclopentadiene ring.

in the P—C ylide bond distance. In the uncoordinated ligand it is 1.718 (4) Å (Ammon, Wheeler & Watts, 1973), indicating substantial double-bond character. In this Co complex the P—C distance is 1.765 (6) Å. For comparison, in a  $\sigma$ -bonded triphenylphosphonium-cyclopentadienyliide complex with mercuric iodide, the P—C distance is 1.748 (7) Å (Baenziger, Flynn & Holy, 1978).

The tetracarbonylcobaltate anion is a very regular tetrahedral anion with the six tetrahedral bond angles ranging from 107.0 (3) to 112.6 (3)°, and Co—C distances ranging from 1.746 (8) to 1.756 (9) Å. The thermal parameters for the atoms in the carbonyl groups are very uniform. The cations are arranged in a roughly square lattice array buckled  $\pm \frac{1}{10}$  about the plane  $x = 0$  with the cation centers approximately at  $y = \frac{1}{4}$  and  $\frac{3}{4}$ . The anions form an even more distorted array buckled  $\pm \frac{1}{8}$  about the plane  $x = \frac{1}{2}$  such that staggered lines of alternating cations and anions proceed along the  $x$  direction.

The ylide cobalt carbonyl complex is an interesting compound because of its extraordinary catalytic properties in solution (Holy, 1979). Substituted acetylenic compounds are cyclotrimerized by this compound to the corresponding substituted benzene compounds with essentially no other derived products, in contrast to the catalytic activity of CpCo(CO)<sub>2</sub> in which several other products are formed in amounts nearly equivalent to the substituted benzene compound.

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## Structure of Triphenyltin Bromide

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**Abstract.** (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnBr, *M<sub>r</sub>* = 429.92, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 19.082 (3), *b* = 9.763 (2), *c* = 18.739 (3) Å, β = 106.32 (8)°, *Z* = 8, *V* = 3350.3 Å<sup>3</sup>, μ(Mo *K*α) = 3.73 mm<sup>-1</sup>, *D<sub>c</sub>* = 1.704 Mg m<sup>-3</sup>, *R* = 0.052. The asymmetric unit contains two slightly distorted tetrahedral molecules. The mean parameters are: Sn–Br = 2.495 (2), Sn–C = 2.114 (8) Å; ∠Br–Sn–C = 105.2 (2), ∠C–Sn–C = 113.4 (3)°.

**Introduction.** We have recently reported the structures of Ph<sub>3</sub>PbX (Ph = C<sub>6</sub>H<sub>5</sub>, X = Cl, Br) (Preut & Huber, 1977) and Ph<sub>3</sub>GeBr (Preut & Huber, 1979). As part of our study of coordinative and structural correlations in organocompounds of Group IVb elements we have determined the crystal structure of Ph<sub>3</sub>SnBr. Data were collected with a crystal 0.34 × 0.23 × 0.18 mm.

Cell parameters were determined by least squares from 23 reflections on a Hilger & Watts Y290 automatic four-circle diffractometer with graphite-monochromatized Mo *K*α radiation and a scintillation counter. The intensities of 3988 reflections (*I* > 3σ) with 2 ≤ θ ≤ 28.1° were measured by the ω/2θ scan technique, with a scan width Δ2θ = (1.34 + 0.34 tan θ)° from background to background and a scan speed of 0.02° s<sup>-1</sup> in 2θ. Backgrounds were measured at each end of the scan range for 7 s. Five standard reflections were measured every fifty reflections during data collection and showed only random deviations. Lorentz and polarization corrections were applied, but no corrections were made for absorption. After averaging the equivalent reflections the data set contained 3292 unique reflections. The structure was solved by Patterson and Fourier methods and refined

by blocked-full-matrix least squares with *SHELX* (Sheldrick, 1976). During the refinement the phenyl rings were treated as rigid hexagons (∠C–C–C = 120°; C–C = 1.395, C–H = 1.080 Å) with individual isotropic temperature factors for the C atoms and one common temperature factor for the H atoms of one molecule. In the final stages of refinement, each reflection was assigned a weight *w*<sup>-1</sup> = σ<sup>2</sup>(*F<sub>o</sub>*) + 0.005*F<sub>o</sub>*<sup>2</sup> and reflections with *F<sub>o</sub>* < 4σ(*F<sub>o</sub>*) were omitted (757 reflections suppressed out of 3292). The refinement converged to *R* = ∑ Δ/∑ *F<sub>o</sub>* = 0.052 and *R<sub>w</sub>* = (∑ *w*<sup>1/2</sup> Δ/∑ *w*<sup>1/2</sup> *F<sub>o</sub>*) = 0.052 for 75 refined parameters.

The final coordinates are listed in Table 1 and bond distances and angles in Table 2. Fig. 1 shows the two molecules in the asymmetric unit, and the numbering of the atoms.†

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34090 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

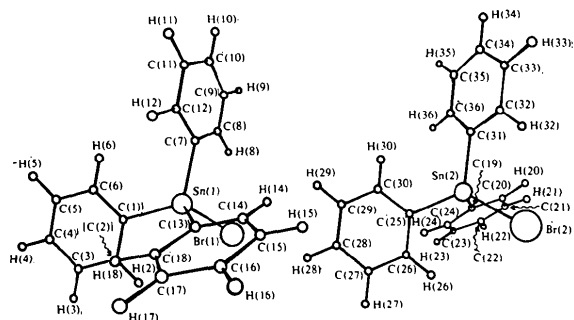


Fig. 1. The two molecules of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnBr in the asymmetric unit, showing the atom-numbering scheme.

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