

## Reaction of $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$ with Tricyclohexylphosphine and Structure of $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$ . Toluene. $\mu_4$ -Phenylphosphinidene Rotation as a Consequence of Thermodynamic Product Control

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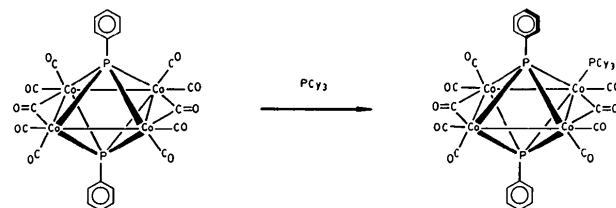
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**Abstract.** Di- $\mu$ -carbonyl-heptacarbonyl-bis( $\mu_4$ -phenylphosphinidene)-(tricyclohexylphosphine)tetracobalt(I)(4Co–Co)–toluene (1/1),  $[\text{Co}_4(\text{CO})_9(\text{C}_6\text{H}_5\text{P})_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]\cdot\text{C}_7\text{H}_8$ ,  $\text{C}_{39}\text{H}_{43}\text{Co}_4\text{O}_9\text{P}_3\cdot\text{C}_7\text{H}_8$ ,  $M_r = 1076.57$ , monoclinic,  $P2_1$ ,  $a = 10.634$  (1),  $b = 20.674$  (4),  $c = 12.189$  (2) Å,  $\beta = 112.44$  (1)°,  $V = 2476.8$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.443$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 14.59$  cm<sup>-1</sup>,  $F(000) = 1104$ ,  $T = 295$  K,  $R = 0.044$  for 2976 independent reflections. The rectangular array of Co atoms is planar and is capped by a pair of  $\mu_4$ -phenylphosphinidene groups to give a *closo* polyhedral core. The substitution of a CO ligand by a  $\text{PCy}_3$  (where Cy = cyclohexyl) ligand causes a  $\sim 0.13$  Å elongation of the non-carbonyl-bridged Co–Co bond adjacent to the  $\text{PCy}_3$  group in addition to a  $\sim 90^\circ$  twist in one of the  $\mu_4$ -phenylphosphinidene groups. The adopted structure of  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  is discussed with respect to thermodynamic product control.

**Introduction.** The reaction of phosphines with the tetracobalt cluster  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$  has been extensively studied in the last few years. Efficient CO substitution by phosphines has been shown to arise from both paramagnetic and diamagnetic cluster species. For example, facile electron-transfer chain (ETC) catalysis is observed from the coordinatively unsaturated cluster  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2^-$ . The chain-carrying cluster in this ETC reaction is readily obtained from  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2^-$  following the one-electron reduction of  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$  and dissociative CO loss (Richmond & Kochi, 1986*a*, 1987*a*). However, the majority of reports describe associative thermal reactions of  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$  with phosphines (Ryan, Pittman, O'Connor & Dahl,

1980; Richmond & Kochi, 1986*b*, 1987*b*; Schulman, Richmond, Watson & Nagl, 1989). In this genre of cluster it has been suggested that thermodynamic product control is important in determining the disposition of the  $\mu_4$ -phenylphosphinidene groups relative to the ancillary phosphine ligands in poly-substituted clusters (Don, Richmond, Watson & Nagl, 1989*a,b*). If severe intramolecular contacts exist between the ancillary phosphines and the cluster, a  $\mu_4$ -phenylphosphinidene group twists away from its preferred bisection of the carbonyl-bridged Co–Co bonds. All of the structurally characterized clusters have involved bis-, tris- and tetrakis-substituted clusters that adopt solid-state structures with minimized intramolecular contacts between the phosphine ligands and the  $\mu_4$ -phenylphosphinidene groups. The generality of thermodynamic product control has not, however, been tested with monosubstituted derivatives. Accordingly, we have studied the reaction of  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$  with  $\text{PCy}_3$  and report the single-crystal X-ray determination of  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  which establishes the disposition of the  $\mu_4$ -phenylphosphinidene group *cis* to the  $\text{PCy}_3$  ligand.



**Experimental.** To 0.50 g of  $\text{Co}_4(\text{CO})_{10}(\mu_4\text{-PPh})_2$  (0.68 mmol) in 100 ml of THF was added 0.21 g of  $\text{PCy}_3$  (0.75 mmol), followed by the addition of a few drops of 0.25 M sodium benzophenone ketyl solution (THF). The solution was stirred for several

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Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	U
Co(1)	3767 (1)	6140	7643 (1)	27 (1)*
Co(2)	5157 (1)	6259 (1)	6358 (1)	31 (1)*
Co(3)	2908 (1)	6260 (1)	4371 (1)	33 (1)*
Co(4)	1416 (1)	6174 (1)	5555 (1)	33 (1)*
C(1)	3281 (9)	5442 (5)	8213 (7)	38 (4)*
O(1)	2890 (7)	4984 (3)	8499 (6)	57 (3)*
C(2)	5685 (9)	6067 (4)	8090 (8)	38 (4)*
O(2)	6688 (6)	5922 (4)	8841 (5)	52 (3)*
C(3)	6165 (11)	5642 (5)	6067 (9)	46 (4)*
O(3)	6841 (9)	5277 (4)	5883 (8)	82 (4)*
C(4)	6266 (10)	6926 (5)	6466 (8)	40 (4)*
O(4)	7051 (8)	7323 (4)	6523 (7)	66 (4)*
C(5)	3203 (11)	5626 (6)	3486 (9)	49 (4)*
O(5)	3404 (10)	5250 (4)	2917 (8)	84 (5)*
C(6)	3040 (11)	6968 (5)	3549 (9)	46 (4)*
O(6)	3181 (10)	7384 (4)	3007 (7)	76 (4)*
C(7)	972 (9)	6210 (6)	3834 (8)	49 (4)*
O(7)	14 (7)	6176 (5)	2975 (6)	75 (3)*
C(8)	524 (11)	5467 (5)	5682 (10)	54 (5)*
O(8)	-67 (10)	5045 (5)	5770 (10)	101 (5)*
C(9)	148 (11)	6758 (5)	5514 (8)	50 (4)*
O(9)	-715 (8)	7083 (5)	5445 (8)	85 (4)*
P(1)	3342 (2)	5614 (1)	5940 (2)	31 (1)*
Co(10)	3443 (10)	4732 (4)	5884 (8)	36 (4)*
C(11)	4431 (11)	4405 (5)	6735 (10)	51 (5)*
C(12)	4491 (15)	3727 (6)	6706 (11)	65 (6)*
C(13)	3542 (16)	3410 (5)	5842 (14)	74 (8)*
C(14)	2558 (15)	3730 (6)	4978 (12)	73 (6)*
C(15)	2468 (13)	4394 (5)	4994 (10)	62 (5)*
P(2)	3258 (2)	6839 (1)	6090 (2)	29 (1)*
C(20)	3108 (9)	7718 (5)	5959 (7)	35 (4)*
C(21)	3962 (9)	8082 (4)	5561 (8)	38 (4)*
C(22)	3841 (11)	8752 (5)	5485 (9)	49 (5)*
C(23)	2849 (12)	9059 (5)	5771 (9)	55 (5)*
C(24)	2005 (11)	8709 (4)	6153 (9)	54 (5)*
C(25)	2131 (10)	8039 (4)	6251 (8)	42 (4)*
P(3)	4029 (2)	6769 (1)	9268 (2)	28 (1)*
Co(30)	5355 (8)	6451 (4)	10690 (7)	30 (3)*
C(31)	5296 (10)	6726 (5)	11814 (8)	51 (4)*
C(32)	6563 (12)	6550 (5)	12877 (9)	58 (5)*
C(33)	6749 (11)	5829 (5)	13014 (9)	54 (4)*
C(34)	6710 (10)	5526 (5)	11864 (8)	49 (4)*
C(35)	5435 (10)	5706 (4)	10812 (8)	42 (4)*
C(40)	4617 (8)	7620 (4)	9161 (8)	33 (3)*
C(41)	4543 (10)	8129 (4)	10026 (10)	49 (4)*
C(42)	4811 (12)	8800 (5)	9645 (10)	62 (5)*
C(43)	6154 (12)	8817 (5)	9522 (10)	63 (5)*
C(44)	6332 (12)	8291 (5)	8740 (10)	62 (5)*
C(45)	6014 (10)	7635 (5)	9094 (9)	50 (4)*
C(50)	2485 (8)	6879 (4)	9615 (7)	32 (3)*
C(51)	1380 (9)	7270 (5)	8630 (8)	45 (4)*
C(52)	176 (11)	7417 (5)	8997 (11)	60 (5)*
C(53)	-415 (10)	6800 (7)	9256 (12)	79 (6)*
C(54)	647 (11)	6393 (6)	10175 (11)	73 (6)*
C(55)	1884 (9)	6271 (5)	9825 (9)	53 (4)*
C(60)	10306	9388	-1569	150
C(61)	9284	7965	2773	150
C(62)	10073	8288	1914	150
C(63)	10787	9020	1902	150
C(64)	10113	8571	2666	150
C(65)	10762	9374	585	150
C(66)	10951	9510	-429	150

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

hours at room temperature, after which time TLC examination (benzene/petroleum ether, 8:2 v/v) revealed ~70% conversion to the monosubstituted cluster Co<sub>4</sub>(CO)<sub>9</sub>(μ<sub>4</sub>-PPh)<sub>2</sub>(PCy<sub>3</sub>). Chromatography over silica gel using benzene/petroleum ether (8:2 v/v) afforded pure Co<sub>4</sub>(CO)<sub>9</sub>(μ<sub>4</sub>-PPh)<sub>2</sub>(PCy<sub>3</sub>) which was recrystallized from toluene/heptane (1:1 v/v) at 253 K to give 0.41 g (61% yield) of dark red Co<sub>4</sub>(CO)<sub>9</sub>(μ<sub>4</sub>-PPh)<sub>2</sub>(PCy<sub>3</sub>). Crystals suitable for X-ray diffraction analysis were selected from this

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

Co(1)—Co(2)	2.544 (2)	Co(1)—Co(4)	2.806 (1)
Co(2)—Co(3)	2.677 (1)	Co(3)—Co(4)	2.526 (1)
Co(1)—P(1)	2.232 (2)	Co(1)—P(2)	2.277 (2)
Co(2)—P(2)	2.263 (3)	Co(2)—P(1)	2.239 (3)
Co(3)—P(2)	2.318 (2)	Co(3)—P(1)	2.231 (3)
Co(4)—P(1)	2.241 (3)	Co(4)—P(2)	2.275 (2)
Co(1)—P(3)	2.296 (2)	P(1)—P(2)	2.543 (3)
Co(1)—C(1)	1.763 (10)	Co(1)—C(2)	1.906 (9)
Co(2)—C(2)	2.006 (9)	Co(2)—C(3)	1.788 (12)
Co(2)—C(4)	1.785 (10)	Co(3)—C(5)	1.798 (12)
Co(3)—C(7)	1.910 (9)	Co(3)—C(6)	1.809 (11)
Co(4)—C(8)	1.782 (12)	Co(4)—C(7)	1.968 (9)
Co(4)—C(9)	1.796 (12)		
Co(2)—Co(1)—Co(4)	88.0 (1)	Co(1)—Co(2)—Co(3)	91.6 (1)
Co(2)—Co(3)—Co(4)	91.3 (1)	Co(1)—Co(4)—Co(3)	89.1 (1)
P(1)—Co(1)—P(2)	68.7 (1)	P(1)—Co(2)—P(2)	68.8 (1)
P(1)—Co(3)—P(2)	68.0 (1)	P(1)—Co(4)—P(2)	68.6 (1)
P(1)—Co(1)—P(3)	173.4 (1)	P(2)—Co(1)—P(3)	105.6 (1)
Co(1)—C(1)—O(1)	174.8 (7)	Co(1)—C(2)—O(2)	144.6 (9)
Co(2)—C(2)—O(2)	133.8 (9)	Co(2)—C(3)—O(3)	176.6 (1)
Co(2)—C(4)—O(4)	174.8 (10)	Co(3)—C(5)—O(5)	177.4 (12)
Co(3)—C(6)—O(6)	175.0 (11)	Co(3)—C(7)—O(7)	141.2 (9)
Co(4)—C(7)—O(7)	137.4 (9)	Co(4)—C(8)—O(8)	177.0 (13)
Co(4)—C(9)—O(9)	174.4 (10)	Co(1)—C(2)—Co(2)	81.1 (3)
Co(3)—C(7)—Co(4)	81.3 (3)		

recrystallization. Crystal dimensions 0.15 × 0.28 × 0.35 mm; Nicolet R3m/μ update of P<sub>2</sub>, diffractometer; data collected in the ω-scan mode (3 ≤ 2θ ≤ 45°), scan rate 4 to 29.3° min<sup>-1</sup>, graphite-monochromated Mo Kα radiation, lattice parameters from a least-squares refinement of 25 reflections (38.64 ≤ 2θ ≤ 44.96°), angles measured by a centering routine; Laue symmetry and intensity statistics consistent with the space group P<sub>2</sub><sub>1</sub>; monitored reflections 135 and 207 showed a 25% decay, data corrected by linear interpolation using check reflections and the 15 reflections in the automatic centering routine when appropriate; 4300 total reflections, 3366 independent reflections measured (-11 ≤ h ≤ 10, 0 ≤ k ≤ 22, 0 ≤ l ≤ 14), R<sub>merge</sub> = 0.007, 2976 ≥ 3σ(I); Lorentz-polarization corrections and a ψ-scan-based empirical absorption correction (transmission factors 0.66 to 0.787); structure solved by direct methods; block-cascade least-squares refinement; H atoms located in difference map but allowed to ride at fixed distance from attached atom, single isotropic thermal parameters were refined for the phenyl H atoms and for the cyclohexyl H atoms; the structure contained a molecule of toluene which was slowly lost during data collection leading to a number of disordered solvent peaks in the difference maps. The seven largest peaks were refined and then fixed, but no attempt was made to constrain a toluene molecule. Final R = 0.044, wR = 0.059 for 498 parameters and 2976 reflections (R = 0.0517, wR = 0.0609 for all data), S = 1.045, (Δ/σ)<sub>max</sub> = 0.021, (Δ/σ)<sub>av</sub> = 0.006; largest peaks in final difference map +0.53 and -0.48 e Å<sup>-3</sup>; ∑w(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup> minimized with w = [σ<sup>2</sup>(F<sub>o</sub>) + 0.000024F<sub>c</sub><sup>2</sup>]<sup>-1</sup>; extinction correction F\* = F<sub>c</sub>/[1.0 + 4.1 (3) × 10<sup>-6</sup>F<sub>c</sub><sup>2</sup>/sin(2θ)]<sup>0.25</sup> applied. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30

Microeclipse and Nova 4/c configuration; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 lists atomic positional parameters for  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  while Table 2 gives bond distances and valence angles.\* Fig. 1 is a drawing of the  $\text{PCy}_3$ -substituted cluster.

**Discussion.** The structure of  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  consists of four Co atoms in a planar, rectangular array and is capped by a pair of  $\mu_4$ -phenylphosphinidene groups to give a *closo* octahedral core commonly observed in this genre of cluster. Asymmetric carbonyl-bridged and non-carbonyl-bridged Co—Co bonds are observed as a result of the destabilizing effect of the large  $\text{PCy}_3$  ligand which possesses a cone angle of  $170^\circ$  (Tolman, 1977). At the site of  $\text{PCy}_3$  substitution the carbonyl-bridged Co—Co bond length is 2.544 (2) Å while the non-carbonyl-bridged Co—Co bond length is 2.806 (1) Å. These bond lengths are 0.018 (2) and 0.129 (1) Å longer than the opposite carbonyl-bridged and non-carbonyl-bridged Co—Co bonds, respectively. Similar bond-length alterations have been observed in  $\text{Co}_4(\text{CO})_8(\mu_4\text{-PPh})_2(\text{dmpe})$  (Schulman, Richmond, Watson & Nagl, 1989) and  $\text{Co}_4(\text{CO})_8(\mu_4\text{-PPh})_2(\text{Ph}_2\text{PCH}=\text{CHPh}_2)$  (Richmond & Kochi, 1987*a*) and are attributed to unfavorable P-ligand/cluster interactions which are minimized through Co—Co bond lengthening.

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53325 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

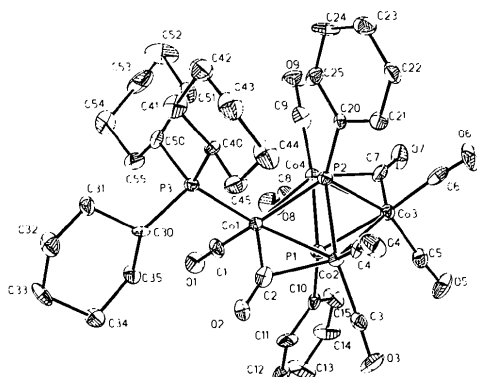


Fig. 1. Diagram of  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  with the thermal ellipsoids drawn at the 30% probability level. H atoms are omitted for clarity.

Another indication of unfavorable intramolecular  $\text{PCy}_3$ /cluster interactions is seen in the disposition of the  $\mu_4$ -phenylphosphinidene group that is *cis* to the  $\text{PCy}_3$ . The plane formed by the phenyl group bound to P(2) and the tetracobalt plane possesses a dihedral angle of  $81.8(7)^\circ$  which represents a tipping of  $8.1(6)^\circ$  between P(2)—C(20) and the normal to the tetracobalt plane. A near perpendicular relation of these planes is found in the parent cluster (Ryan & Dahl, 1975; Ryan, Pittman, O'Connor & Dahl, 1980). Furthermore, the twist angle between the  $\mu_4$ -phenylphosphinidene group is  $77.3(8)^\circ$ . The phenyl group associated with P(2) twists and tips from its preferred orientation (see above) as a result of close intramolecular contacts with the ancillary  $\text{PCy}_3$  ligand, consistent with previous reports on structurally similar  $\mu_4$ -phenylphosphinidene-capped clusters (Ryan, Pittman, O'Connor & Dahl, 1980; Richmond & Kochi, 1986*b*, 1987*b*).

The terminal Co—CO distances range from 1.763 (10) to 1.809 (11) Å while the bridging Co—CO distances are asymmetric, ranging from 1.906 (9) to 2.006 (9) Å. The remaining C—O, C—P and C—C distances are unexceptional and require no comment.

The reaction of  $\text{Co}_4(\text{CO})_9(\mu_4\text{-PPh})_2(\text{PCy}_3)$  with different phosphines is planned in order to test the generality of thermodynamic control in determining the location and stereochemistry of incoming phosphine ligands.

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