Boat-shaped Co$_6$ Carbonyl Cluster Derivatives Containing a Semi-interstitial P Atom and Bridging Thiolate or Heterocyclic Phosphido Ligands

Xiang Hu,* Qi-Wang Liu, Shu-Tang Liu, Li-Ping Zhang and Bao-Shan Wu

Department of Chemistry, Inner Mongolia University, Huhhot 010021, PR China

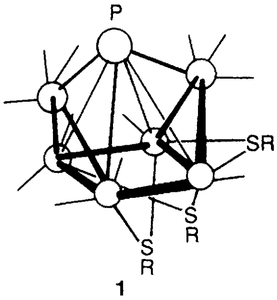
Reactions of MeSPCl$_2$, EtSPCl$_2$ and Cl$\overline{\mathrm{PSCH_2CH_2S}}$, respectively with Co$_2(CO)_8$ in the presence of zinc powder give the Co$_6$ clusters [Co$_6$(μ_6-P)(μ-SMe)$_3$(CO)$_{12}$] **1**, [Co$_6$(μ_6-P)(μ-SEt)$_3$(CO)$_{12}$] **2** and [Co$_6$(μ_6-P)(μ_4-SCH$_2$CH$_2$S)(μ-$\overline{\mathrm{PSCH_2CH_2S}}$)(CO)$_{12}$] **3** respectively; in **1** six Co atoms form a boat-shaped array consisting of a basal square of four cobalt atoms with two opposite edges bridged by two apical Co atoms, with the metal arrangement surrounding a semi-interstitial P atom, and with two μ-SMe ligands bridging underneath the basal square and another bridging μ-SMe side-linked to the basal square.

There is a limited range of core geometries associated with Co$_6$ carbonyl clusters. Closed structures include the compact octahedral arrangement and a few looser trigonal prismatic cages {*e.g.* [Co$_6$(μ_6-C)(μ_3-S)$_2$(CO)$_{12}$],[1] and PPN[Co$_6$(μ_6-N)(CO)$_{15}$],[2] which contain interstitial carbon or nitrogen atoms}. Open structures can be obtained by the insertion of the bulky P atom or a C$_2$ group, two examples being [Co$_6$(μ_6-P)(μ-CO)$_2$(CO)$_{14}$]$^-$,[3] **4**, and [Co$_6$(μ_6-C$_2$)(μ_4-S)(μ-CO)$_6$(CO)$_8$],[4] **5**. In **4**, the six metal atoms form a twisted boat arrangement surrounding a semi-interstitial P atom. In **5**, the six metal atoms form a boat-shaped open array which contains a Co$_4$ square with two opposite edges bridged by two cobalt atoms; the metal arrangement surrounds a semi-interstitial dicarbide group. Here, the C$_2$ unit is inserted into a trigonal-prismatic Co$_6$ array by breaking an edge and widening the distance between the two apical Co atoms. We report here the synthesis and characterization of three more boat-shaped Co$_6$ carbonyl clusters which contain a semi-interstitial P atom and bridging thiolate or heterocyclic phosphido ligands.

The reaction of MeSPCl$_2$ and EtSPCl$_2$ with Co$_2$(CO)$_8$ (toluene, 30–43 °C, 13 h) in the presence of zinc powder afforded, *inter alia*, the products [Co$_4$(μ_4-PSMe)$_2$(μ-CO)$_2$(CO)$_8$], [Co$_6$(μ_6-P)(μ-SMe)$_3$(CO)$_{12}$] **1**, [Co$_4$(μ_4-PSEt)$_2$-(μ-CO)$_2$(CO)$_8$], [Co$_6$(μ_6-P)(μ-SEt)$_3$(CO)$_{12}$], **2**, and [Co$_7$(μ_7-S)(μ_4-PSEt)(μ-SEt)$_2$(μ-CO)$_2$(CO)$_{12}$],[5] **6**, respectively. The structure of the Co$_7$ cluster **6** has been reported elswhere.[5] The yields of **1** and **2** are 4 and 7% respectively after chromatography (benzene–light petroleum) and recrystallization (*n*-C$_6$H$_{14}$–CH$_2$Cl$_2$). The reaction of Cl$\overline{\mathrm{PSCH_2CH_2S}}$ with Co$_2$(CO)$_8$ (toluene, 30–43 °C, 13 h) in the presence of zinc powder gave [Co$_6$(μ_6-P)(μ_4-SCH$_2$CH$_2$S)(μ-$\overline{\mathrm{PSCH_2CH_2S}}$)(CO)$_{12}$] **3** after similar separation and purification in 13% yield.[6] Analytical data (C, H, P) and IR (ν_{CO}), ^{1}H NMR and MS spectra of the three Co$_6$ clusters **1–3** are consistent with the proposed structures.† The molecular structure of **1** is shown in Fig. 1.‡

Cluster **1** has C_s symmetry, with a mirror plane through P(1), Co(3), Co(4), S(2) and bisecting the Co(1)–Co(1′) and Co(2)–Co(2′) sides of the Co$_4$ base. The boat-shaped open array of Co$_6$ atoms contains a Co$_4$ basal square with two opposite edges bridged by two apical Co atoms and the metal atoms surround a semi-interestitial P atom. The Co$_6$P framework could be viewed as arising from insertion of a P atom into a trigonal-prismatic Co$_6$ array by breaking a square edge and widening the distance between the two apical Co atoms.

The eight Co–Co bond lengths [2.461(6)–2.651(6) Å] and the six Co–P bond lengths [2.112(8)–2.261(7) Å] are consistent with the values found in many cobalt carbonyl clusters, including **4** and **5**. The apical Co(3) and Co(4) atoms bear three terminal carbonyl groups whereas the basal Co(1) and



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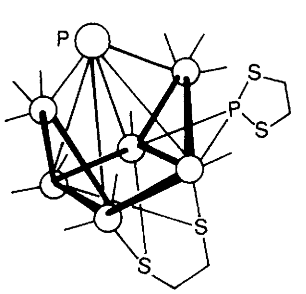

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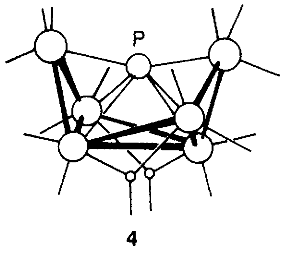

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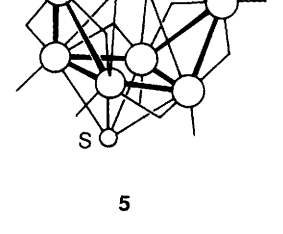

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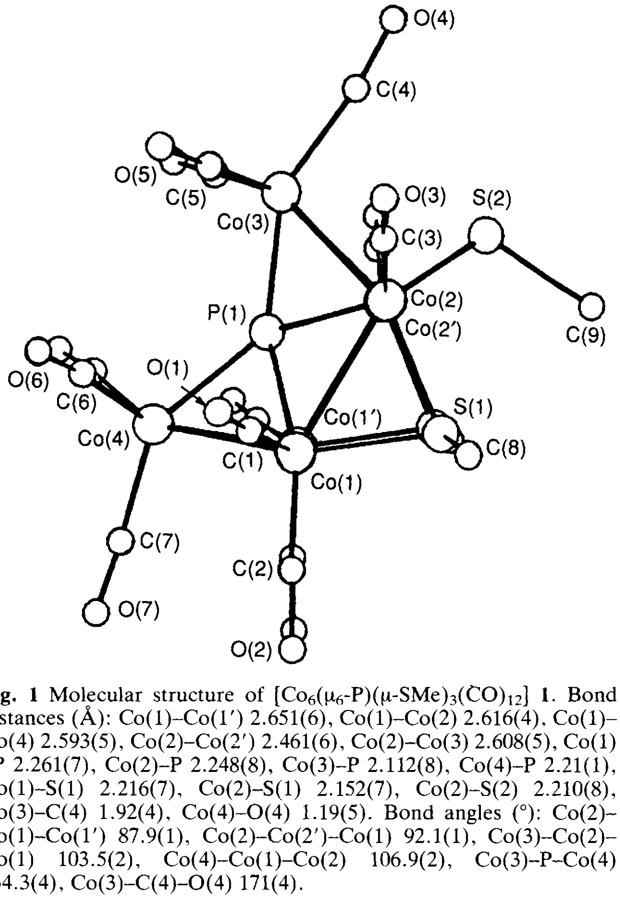
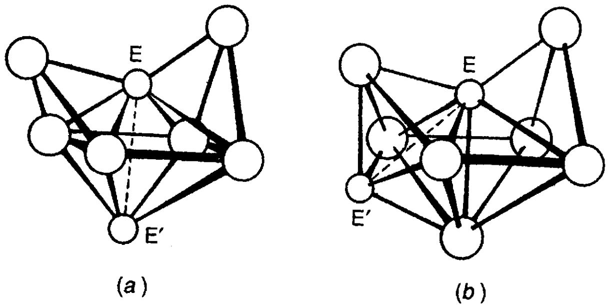


Fig. 1 Molecular structure of [Co$_6$(μ_6-P)(μ-SMe)$_3$(CO)$_{12}$] **1**. Bond distances (Å): Co(1)–Co(1′) 2.651(6), Co(1)–Co(2) 2.616(4), Co(1)–Co(4) 2.593(5), Co(2)–Co(2′) 2.461(6), Co(2)–Co(3) 2.608(5), Co(1)–P 2.261(7), Co(2)–P 2.248(8), Co(3)–P 2.112(8), Co(4)–P 2.21(1), Co(1)–S(1) 2.216(7), Co(2)–S(1) 2.152(7), Co(2)–S(2) 2.210(8), Co(3)–C(4) 1.92(4), Co(4)–O(4) 1.19(5). Bond angles (°): Co(2)–Co(1)–Co(1′) 87.9(1), Co(2)–Co(2′)–Co(1) 92.1(1), Co(3)–Co(2)–Co(1) 103.5(2), Co(4)–Co(1)–Co(2) 106.9(2), Co(3)–P–Co(4) 134.3(4), Co(3)–C(4)–O(4) 171(4).



(a) (b)

Fig. 2 (*a*) $Co_6(\mu_6\text{-}E)(\mu_4\text{-}E')$ and (*b*) $Co_7(\mu_7\text{-}E)(\mu_4\text{-}E')$ skeletons

Co(1′) have two and Co(2) and Co(2′) only one. One terminal carbonyl group, C(4)–O(4), in **1** has an unusually long Co–C(4) distance [1.92(4) Å].

Cluster **4** has two bridging CO groups in a position underneath the twisted basal Co_4 square, opposite to the semi-interstitial P atom above. Likewise, **5** contains a face-bridging μ_4-S atom, and **1** includes two bridging SMe groups in these underneath positions. The Co_6 boat-shaped array may require a semi-interstitial μ_6-E unit above the basal Co_4 square and also a μ_4-E′ unit (two bridging CO in **4**, S atom in **5** and two bridging SMe in **1**) below, to allow an attractive interligand E···E′ interaction[7] for stabilization of this type of Co_6 open structure. Another SMe ligand in **1** is side-linked to the basal Co_4 square and the symmetry of **1** (C_s) is then lowered from that of **5** (C_{2v}). Interestingly, the skeletal geometry of the $Co_7(\mu_7\text{-}S)(\mu_4\text{-}PSEt)$ part of cluster **6** also shows an $E(\mu_7\text{-}S)\cdots E'(\mu_4\text{-}PSEt)$ attractive interligand interaction, tilted to the side of the Co_4 base of the Co_7 unit [Fig. 2(*b*)]. The electron counts of **1**, **4** and **5** indicate that each Co atom in **4** and **5** satisfies the 18-electron rule, but the case is complicated in **1**. On average each Co atom obeys the 18 electron rule, but the valence electron numbers around Co(1), Co(1′) are $18\frac{1}{3}$ and around Co(2), Co(2′) and Co(3), Co(4) are $17\frac{5}{6}$, respectively. The electron deficiency of Co(2), Co(2′) may demand shorter Co(2)–Co(2′) [2.461(6) Å] and Co(2)–S(1) bond lengths [2.152(7) Å] to increase the electron density around the valence shell of Co(2), Co(2′) to balance the deficiency. In contrast, the electron surplus of Co(1), Co(1′) causes longer Co(1)–Co(1′) [2.651(6) Å] and Co(1)–S(1) bonds [2.216(7) Å].

During the reactions, the ligand precursors $RSPCl_2$ (R = Me, Et) and $Cl\overline{PSCH_2CH_2S}$ are cleaved to yield a variety of fragments as ligands, namely μ_7-S, μ_6-P, μ_4-PSR, μ_4-SCH_2CH_2S, μ-$\overline{PSCH_2CH_2S}$ and μ-SR. These are the essential constituents to build the novel Co_7 and Co_6 carbonyl clusters which contain semi-interstitial P or S atoms and bridging P or S-containing ligands.

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Footnotes

† *Selected spectroscopic data* for **1**: ν_{max}/cm^{-1} (CO) (n-C_6H_{14}–CH_2Cl_2) 2086m, 2053vs, 2042vs, 2030m, 1985w; ^1H NMR $\delta(CDCl_3)$ 1.26, 1.34 (2 × S, 2 × 3 H, SMe), 2.46 (s, 3 H, SMe); FD-MS *m/z* 861.5 (calc. 861.97). For **2**: ν_{max}/cm^{-1} (CO)(n-C_6H_{14}–CH_2Cl_2) 2085m, 2053vs, 2041vs, 2030m, 1984w; ^1H NMR δ ($CDCl_3$) 1.45 (m, 2 × 5 H, SEt), 2.68 (s, 5 H, SEt); FD-MS *m/z* 903.6 (calc. 904.06). For **3**: ν_{max}/cm^{-1} (CO) (n-C_6H_{14}–CH_2Cl_2) 2080m, 2051vs, 2031vs, 2029m, 2000w; ^1H NMR $\delta(CDCl_3)$ 1.52, 2.13, 2.55 (m, 2 × 2 H, SCH_2CH_2S), 3.60, 3.72 (d, 2 × 2 H, $PSCH_2CH_2S$); FD-MS: *m/z* 935.5 (calc. 936.00).

‡ *Crystal data* for **1**:$[C_{15}H_9Co_6O_{12}PS_3]$, M = 861.97, orthorhombic, space group $Pmn2_1$, a = 10.962(9), b = 9.634(5), c = 13.01(1) Å, V = 1374 $Å^3$, Z = 2, D_c = 2.08 g cm^{-3}, Rigaku AFC 5R diffractometer, $2\theta_{max} = 50°$, μ(Mo-Kα) = 38.67 cm^{-1}, crystal dimensions 0.40 × 0.30 × 0.2 mm, 810 observed data [$I \geqslant 3\sigma(I)$] from 1462 data measured were refined to R = 0.053, R_w = 0.059 (statistical weights). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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