

Synthesis and characterization of a tricobalt cluster with μ_3 *tert*-butylcarbyne and PSe ligands

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Letter

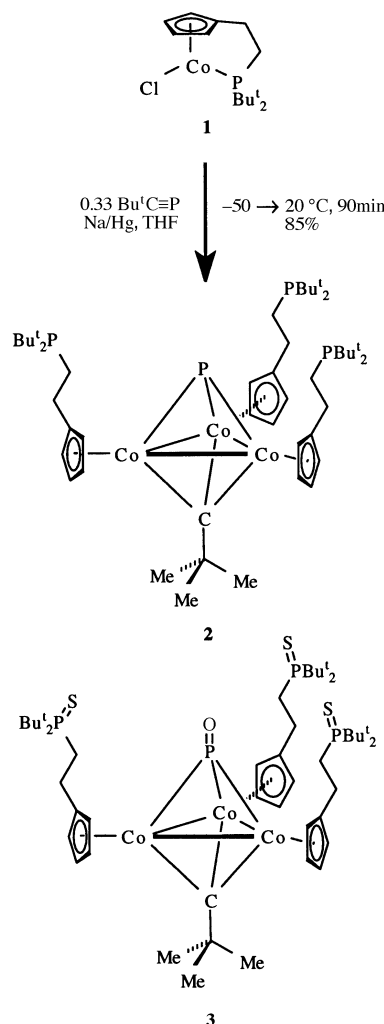
μ_3 -Phosphido cluster **2**, which is readily accessible from the cobalt chelate **1** by treatment with *tert*-butylphosphaethyne, reacts with red selenium to give the moderately air- and light-sensitive tetraselenide **4** with μ_3 *tert*-butylcarbyn and μ_3 PSe ligands in 48% yield. The crystal structure of **4** is reported and compared to those of closely related clusters.

We recently reported that the P,C triple bond of *tert*-butylphosphaethyne can be broken by treatment with the chelate complex **1** to form the phosphido-carbyne cluster **2** (Scheme 1) in good yield under mild reaction conditions. Cluster **2** was oxidized with oxygen or sulfur to obtain clusters with a PO or a PS ligand; the PO cluster **3** has been characterized spectroscopically as well as by an X-ray structure analysis.¹ Complexes with phosphorus oxide^{2–7} or sulfide^{8–14} ligands are rare, and the chemistry of phosphorus monoxide complexes has recently been reviewed.^{15,16} One way to obtain phosphorus chalcogenide complexes is by the oxidation of phosphido complexes with oxygen or sulfur. Very recently Weigel *et al.*¹⁷ reported on the corresponding oxidation using selenium with the resulting formation of a PSe cluster. In this communication we report on our closely related independent results concerning the synthesis and characterization of the PSe carbyne cluster **4**.^{18,19}

To find out how far the selenation of the phosphido cluster could be carried, **2** was treated with red selenium in the presence of a small amount of triethylamine. After column chromatography and crystallization from diethyl ether, phosphorus selenide complex **4** with all four phosphorus atoms selenized was obtained in 48% yield from **1** as red, transparent crystals with an edge length of up to 5 mm. **4** is air-stable but decomposes within a few hours in air when exposed to light. Although **4** was characterized by the usual spectroscopic methods and a correct combustion analysis, some expected signals could not be detected in the NMR spectra. These include the signals of the carbyne carbon atom in the ¹³C NMR spectrum, the signal of the phosphorus atom of the PSe ligand in the ³¹P NMR spectrum and the signal of the central selenium atom in the ⁷⁷Se NMR spectrum. The reason presumably is an interaction with the three neighbouring cobalt quadrupole nuclei and prolonged relaxation times as a result of the symmetry of the cluster. In principle, it might be possible to overcome this problem by measurement of variable temperature NMR spectra in some cases. However, the long acquisition times required did not render this a reasonable alternative. The P=Se absorption in the IR spectrum could not be assigned beyond doubt as it had to be expected to be near to the lower limit of detection (*cf.* ref. 17). In addition to the main fraction, minor amounts of incompletely sele-

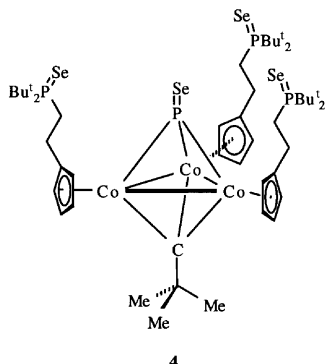
nized clusters were obtained, which were characterized by mass spectrometry only.

The crystals of **4** were suitable for an X-ray structural analysis (Fig. 1, 2). In contrast to the corresponding PO cluster **3**,¹ **4** displays ideal C₃ symmetry. The P,Se bond length



Scheme 1

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of the PSe ligand is 2.084(3) Å, which is shorter than the value of 2.1129(19) Å for the P,Se bonds in the non-coordinated side arms, and which corresponds to the value of 2.0924(11) Å observed by Weigel *et al.*¹⁷ With regard to the cluster skeleton, there are no significant differences between the structures of the PO cluster **3**¹ and **4**. The Co₃Co distances are 2.4696(10) Å. The bond length from the coordinated phosphorus atom to the cobalt atoms is 2.1138(19) Å, which is slightly longer than the corresponding bond distance of the PO cluster [2.0941(13)–2.0964(13) Å] but similar to the corresponding values observed by Weigel *et al.*¹⁷ The distance of the carbyne ligand to the cobalt atoms in **4** is also similar to that in **3**: in **4**

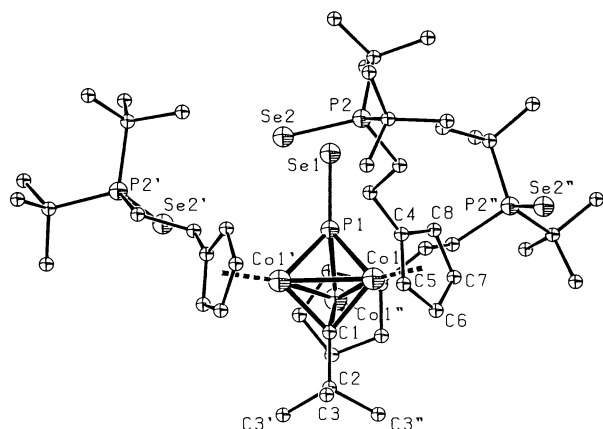


Fig. 1 Crystal structure of the PSe cluster **4**. Selected bond lengths (Å) and angles (°): Co1—Co1' 2.4696(10), Se1—P1 2.084(3), Se2—P2 2.1129(19), Co1—P1 2.1138(19), Co1—C1 1.895(7), Co1—C4 2.069(7), Co1—C5 2.079(7), Co1—C6 2.107(6), Co1—C7 2.088(6), Co1—C8 2.077(6), C1—C2 1.524(14), C2—C3 1.536(7); P1—Co1—C1 88.8(2), Se1—P1—Co1 137.58(5)

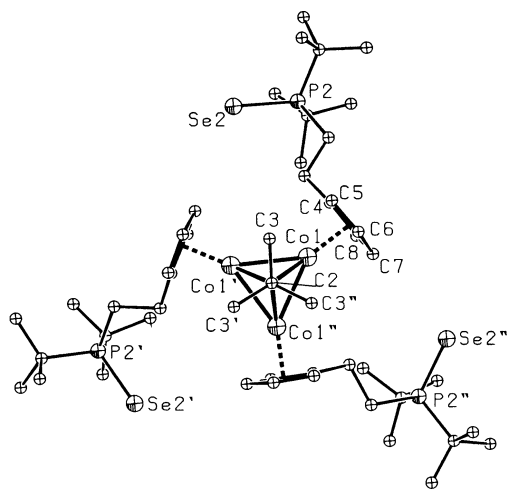


Fig. 2 Crystal structure of the PSe cluster **4** viewed down the C2—C1 axis of the carbyne ligand

it is 1.895(7) Å, whereas the distances in **3** are between 1.885(4) and 1.890(5) Å. The Co₃C₃Co angle in **4** measures 81.4°, and the corresponding angles in PO cluster **3** have values between 81.3 and 82.1°. The top view of the structure (Fig. 2) clearly shows that the carbyne ligand prefers a staggered conformation with respect to the cyclopentadienyl ligands.

Investigations concerning the use of the PSe groups in **4** as ligands and as centers of reactivity are underway in our laboratory.¹³

Experimental

General

Unless otherwise indicated all operations were carried out under argon using standard Schlenk techniques. Benzene-d₆, diethyl ether, petroleum ether and THF were distilled from sodium–potassium alloy with a small amount of benzophenone. DTA/TG: Thermobalance L 81 (Linseis) under argon. ¹H NMR: Bruker AM 400 (400.1 MHz). ¹³C NMR: Bruker AM 400 (100.1 MHz). ³¹P NMR: Bruker AM 400 (162 MHz). ⁷⁷Se NMR: Bruker AM 400 (76.3 MHz). NMR samples were prepared under argon and sealed under vacuum. IR: Perkin-Elmer FTIR spectrometers 580 and 1710. FAB-MS: VG Autospec. Elemental analyses: Heraeus CHN-Rapid.

Cluster 4

At –50 °C 44 mg (0.44 mmol) of *tert*-butylphosphaethyne is added to a solution of 432 mg (1.30 mmol) of the chloro chelate **1** in 30 mL of THF. After 5 min 25.0 g of sodium amalgam (2%) is added dropwise, and the mixture is allowed to warm to –45 °C. After stirring for 10 min the mixture is allowed to warm to 20 °C and is stirred at 20 °C for 1 h. The THF is condensed into a cold trap, and the residue is taken up with diethyl ether and filtered through a P4 frit covered with a 3 cm thick layer of Celite. The Celite is washed with diethyl ether until the solvent remains colourless. The diethyl ether is condensed into a cold trap, and the residue is purified by column chromatography (10 × 1 cm, silica gel, petroleum ether–diethyl ether 1 : 3). The obtained phosphido cluster **2** is dissolved in 50 mL of diethyl ether, and at 20 °C 205 mg (0.33 mmol) of red selenium and 30 mg of triethylamine are added. The mixture is stirred for 20 min, and the diethyl ether and the triethylamine are removed into a cold trap. The residue is taken up with petroleum ether–diethyl ether (3 : 1) and chromatographed (20 × 2 cm, silica gel, petroleum ether–diethyl ether 3 : 1). Crystallization of the product from diethyl ether yields 276 mg (0.21 mmol, 48%) of phosphorus selenide cluster **4** as deep red, transparent crystals, which are moderately air- and light-sensitive, m.p. (DTA/TG) 218.1 °C.

IR (KBr): $\bar{\nu}$ = 3050(w, Cp–H), 2960(s, –CH₂–, CH₃), 2920(s, –CH₂–, CH₃), 2868(s, –CH₂–, CH₃), 1652(w), 1636(w), 1472(m), 1388(w, Bu^t), 1316(w, Bu^t), 1260(w), 1176(w), 1072(m, Cp–R), 1020(m, Cp–R), 924(w), 864(w), 804(s, Cp), 720(m), 676(m), 648(m, C–Co₃), 624(m), 588(m), 500(w), cm^{–1}. ¹H-NMR (400 MHz, benzene-d₆): δ = 1.27 (d, 54H, 9-H, ³J_{P,H} = 14.7 Hz), 1.97–2.08 (m, 6H, 6-H), 2.41 (s, 9H, 12-H), 2.73–2.83 (m, 6H, 7-H), 4.72 [m, 6H, 2(5)-H or 3(4)-H], 4.98 [br s, 6H, 2(5)-H or 3(4)-H]. ¹³C-NMR (100 MHz, benzene-d₆): δ = 24.2 (d, C-6, ²J_{C,P} = 32.5 Hz), 26.1 (br s, C-12), 28.1 (d, C-9, ²J_{C,P} = 1.6 Hz), 36.8 (d, C-8, ¹J_{C,P} = 1.2 Hz), 37.0 (d, C-7, ¹J_{C,P} = 32.9 Hz), 62.3 (d, C-11, ¹J_{C,P} = 1.6 Hz), 83.4 [s, C-2(5) or C-3(4)], 87.7 [d, C-2(5) or C-3(4), ²J_{C,P} = 1.2 Hz], 102.4 (d, C-1, ³J_{C,P} = 16.5 Hz); signal of C-10 was not observed. ³¹P-NMR (162 MHz, benzene-d₆): δ = 78.3 [s, Se=P(Bu^t)₂, ¹J_{P,Se} = 715 Hz], the signal of P=Se was not observed. ⁷⁷Se-NMR (76.3 MHz, benzene-d₆): δ = –454 [d, Se=P(Bu^t)₂, ¹J_{P,Se} = 717 Hz], the signal for P=Se was not observed. MS (FAB, *o*-nitrobenzylalcohol). *m/z* (%): 1304 (10) [M⁺], 1275 (20), 1240 (11), 1115 (5), 964 (11),

899 (15), 376 (100) [Cp[#]CoSe⁺]. Anal. C₅₀H₈₇Co₃P₄Se₄ (1305): calcd C 46.03, H 6.72; found C 46.08, H 6.92.

Crystal structure analysis of 4

C₅₀H₈₇Co₃P₄Se₄, *M* = 1305 g mol⁻¹, deep red crystal, size 0.30 × 0.30 × 0.32 mm, crystal system trigonal, space group *R* $\bar{3}$ (no. 148), *a* = 17.48(1), *c* = 33.35(1) Å, *U* = 8824(2) Å³, *Z* = 6, μ = 34.5 cm⁻¹, ρ_{calc} = 1.47 g cm⁻³, $2\theta_{\text{max}}$ = 48.3°, MoK α radiation, λ = 0.71073 Å, diffractometer Stoe IPDS, 150 imaging plates, $\Delta\phi$ = 1.5°, *T* = 300 K, 21171 measured reflections, 3090 independent reflections, all used for refinement on *F*², numerical absorption correction, structure solution with direct methods (SHELXS-86), refinement with SHELXL-93, 184 free parameters, hydrogen atoms in geometrically calculated positions, *R*₁ = 0.046 [2109 reflections with *F*₀ > 4σ(*F*₀)], *wR*₂ = 0.092 (all data), minimal and maximal residual electron density -0.72, 0.87 e Å⁻³.

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