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The First Platinum–Cobalt Heteropentametallic Cluster: $Pt_3Co_2(CO)_4(\mu_2\text{-}CO)_5[P(C_2H_5)_3]_3$*

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Reactions between square planar substrates of the type PtL_2Cl_2 and the anion $Co(CO)_4^-$ have been shown to give metal–metal bonded complexes. Their molecular structure depends very much on the nature of L. If L is pyridine, a linear trimetallic chain Co–Pt(L_2)–Co [1] is obtained, whereas if L is triphenylphosphine PPh_3 a tetrametallic $Pt_2Co_2(CO)_5(\mu_2\text{-}CO)_3(PPh_3)_2$ (*5*) butterfly cluster is formed [2]. We have now investigated the influence of the more basic phosphine ligand L = PEt_3 upon the course of this reaction and found that it leads to the formation of a similar hetereotetrametallic cluster and of a new heteropentametallic cluster.

Four products were isolated [3] from the reaction of *cis*-$Pt(PEt_3)_2Cl_2$ with $NaCo(CO)_4$: $Co_2(CO)_7PEt_3$ (*1*), $Co_2(CO)_6(PEt_3)_2$ (*2*), $Pt_2Co_2(CO)_5$ $(\mu_2\text{-}CO)_3(PEt_3)_2$ (*3*) and $Pt_3Co_2(CO)_4$ $(\mu_2\text{-}CO)_5(PEt_3)_3$ (*4*). The molecular structure of (*4*) was established by a single crystal X-ray diffraction study [4] (Fig. 1). IR data for (*1*) and (*2*) are in agreement with the literature [5, 6] and those for (*3*) (Table I) are very similar to those found for (*5*) [2] indicating the same butterfly type of structure. The ν(CO) values for (*4*) (Table I) are indicative of both terminal and bridging CO groups.

The pentametallic core has a slightly distorted trigonal bipyramid structure with a *hetero*trimetallic basis Co(1)Pt(2)Co(2) and two apical Pt(1) and Pt(3) atoms [7]. A pseudo two fold axis goes through the P(2)–Pt(2)–C(1) atoms. Only few heteropentametallic transition metal clusters are known [8, 9], none of them involving platinum nor cobalt. Amongst them, only the $[M_2Ni_3(CO)_3(\mu_2\text{-}CO)_3]^{2-}$ (M = Cr, Mo, W) compounds [8] have a trigonal bipyramid structure but with a *homo*trimetallic basis (Ni_3). In (*4*), the metal–metal bond lengths are all considered as bonding distances and each metal atom has an 18 electron configuration. This confers to (*4*) a *closo* type of structure according to Wade's rules [10] whereas (*3*) is of the *arachno* type. Although the detailed reaction mechanism is unclear, we have shown that formation of (*3*) is favored at 45 °C whereas (*4*) is best obtained at 0 °C. We have checked that (*3*) cannot be formed in THF by thermal degradation of (*4*) at 45 °C.

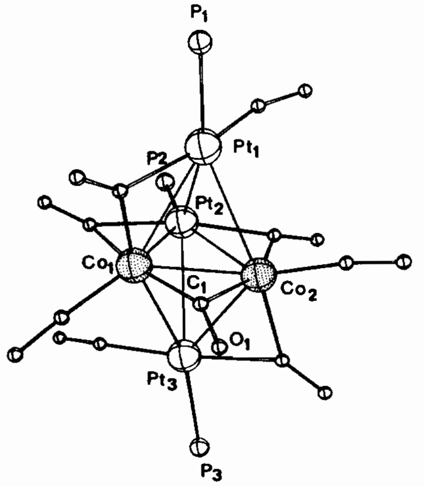

Figure 1. Structure of the molecule (*4*) with metal–metal bond lengths in [pm]:

Pt(1)–Co(1)	: 267 (1)
Pt(1)–Co(2)	: 287 (1)
Pt(1)–Pt(2)	: 288.5 (4)
Pt(2)–Co(1)	: 251 (1)
Pt(2)–Co(2)	: 250 (1)
Pt(2)–Pt(3)	: 289.2 (4)
Pt(3)–Co(1)	: 285 (1)
Pt(3)–Co(2)	: 264 (1)
Co(1)–Co(2)	: 249 (1)

TABLE I. IR Spectra in ν(CO) Region (cm^{-1}).

(*3*)	2050s	2032s	2012s	1981s	1967s	1870m	1810–1804 vs	
	2055s	2024s	1989s	1980sh	1870m	1820 vs		
(*4*)	2023s	1985s	1971vs	1940sh	1859w	1821s	1804s	1747ms
	2016s	1988sh	1980s	1948w	1860w	1825s	1807s	1761m

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Experimental

All reactions and manipulations were carried out under nitrogen. Solvents were dried and distilled under nitrogen before use. A THF solution (45 ml) of [$NaCo(CO)_4$], prepared from $Co_2(CO)_8$ [11] (1.37 g; 4 mmol), was filtered and added to a suspension of *cis*-$Pt(PEt_3)_2Cl_2$ (2 g; 4 mmol) in THF (20 ml) at room temperature. This mixture was stirred for 5 h and no gas evolution was detected. The residue obtained after filtration and evaporation under reduced pressure was chromatographed on a Kiesegel 60 Merck column.

Elution with pentane gives a red solution of (*1*) which was recrystallized from pentane at −78 °C. (*1*) seems to have been isolated here for the first time [5]: dark brown-red product, m.p.: 22–25 °C, yield: 0.11 g (6%). Further elution with: (i) toluene/pentane (1:4) gives a red solution of (*2*), yield: 0.3 g (15%); (ii) toluene/pentane (3:2) gives a red violet solution which afforded (*3*) (recrystallization from toluene/pentane or CH_2Cl_2/pentane): red violet crystals, m.p.: 87–88 °C (decomp.), yield 0.02 g (1% based on Pt, 0.5% based on Co); (iii) toluene gives a dark violet solution which afforded (*4*) (recrystallization from toluene/pentane or CH_2Cl_2/pentane): dark violet needles, m.p.: 158–159 °C, yield: 1.12 g (63% based on Pt, 21% based on Co); (iv) THF gives a red solution containing very small quantities of a so far unidentified complex.

The same experiment was carried out in the same manner at (i) 0 °C for 20 h affording (yield %): (*1*) 10%, (*2*) 11%, (*3*) (only detected by infrared spectroscopy), (*4*) 66% based on Pt, 22% based on Co. (ii) 45 °C for a 1 h affording: (*1*) 4%, (*2*) 27%, (*3*) 10% based on Pt, 5% based on Co, (*4*) 55% based on Pt, 18% based on Co.

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3 The compounds were characterized by C, H. P elemental analysis and IR spectroscopy.

4 Crystals of (*4*) are monoclinic, space group $P2_1/c$, $Z = 8$, $a = 23.107(5)$ Å, $b = 17.969(4)$ Å and $c = 20.881(5)$ Å, $\gamma = 115.6(1)°$, $V = 7818.9$ Å^3, $d_{calc.} = 2.225$ g/cm^3, $d_{obs.} = 2.20$ g/cm^3. 9724 reflections were recorded in the range $4° < 2\theta < 43°$ using graphite monochromated MoKα radiation. 2680 of these ($I > 3\sigma I$) were used in structure solution and refinement; present R = 0.075.

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7 The asymmetric unit contains two independent molecules of (*4*). The metal backbone and seven of the nine carbonyl groups have identical geometries in the two molecules; of the seven carbonyls, five are bridging groups (4 Pt(μ-CO)Co and 1 Co(μ-CO)Co) and one is terminally bonded to each Co atom. However, the two terminal carbonyl groups bonded to the apical platinum atoms would be bonded differently in the two molecules. This observation is probably an artifact arising from decomposition of the crystals during data collection (≅33%) and lack of resolution due to poor diffraction. We hope to obtain better resolution and overall quality of the structure by using an homologue containing a different ligand.

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