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Preliminary communication

A NEW HETERONUCLEAR CLUSTER COMPOUND: $[P(C_6H_5)_3]_2Pt_2Co_2(CO)_8$. SYNTHESIS AND CRYSTAL STRUCTURE

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Summary

The synthesis, spectroscopic features and crystal structure of a new heteronuclear cluster compound $[P(C_6H_5)_3]_2Pt_2Co_2(CO)_8$ of butterfly type are reported.

Although butterfly type homonuclear M_4 [1] and heteronuclear $M_1M'_3$ [2] cluster compounds are known (M and M′ represent different metals), few tetrametallic heteronuclear $M_2M'_2$ compounds have been prepared [3]. For one of these the crystal structure has been determined by X-ray diffraction [4].

$[P(C_6H_5)_3]_2Pt_2Co_2(CO)_8$ (I) was obtained by reaction of $Co(CO)_4^-$ with *cis*- or *trans*-$PtCl_2[P(C_6H_5)_3]_2$ in THF. It was isolated free from several byproducts ($Co_2(CO)_7P(C_6H_5)_3$ and $Co_2(CO)_6[P(C_6H_5)_3]_2$) by chromatography. Recrystallisation of I in a benzene—pentane mixture leads to well-formed dark red crystals (decomposition temperature, 250 °C). The infrared spectra show ν(CO) bands at 2058s, 2031s, 2009s, 1990s, 1983s, 1891m, 1841s and 1804 vs cm^{-1} (KBr pellets). Analysis and molecular weight measurements are consistent with a tetrametallic heteronuclear Pt_2Co_2 cluster.

Crystal data: crystals of I are triclinic, space group $P1$, a = 10.954(4), b = 11.090(4), c = 9.352(4) Å, α 98.40 (2)°, β 11.06 (3)°, γ 82.17 (2)°, Z = 1.4421 independent reflexions, collected with monochromated Mo-K_α radiation on a Picker automatic diffractometer, were used to solve the crystal structure by standard Patterson, Fourier and least-squares methods. The present R valueis 0.046.

The crystal structure consists of discrete molecules of I. A representation of the molecule with the atom numbering scheme is shown in Fig. 1 (phenyl groups are indicated only by their C bonded to P). Distances within the cluster containing the tetrahedral metal atoms are: Co(1)—Co(2) = 2.498(3), Co(1)—Pt(1) =

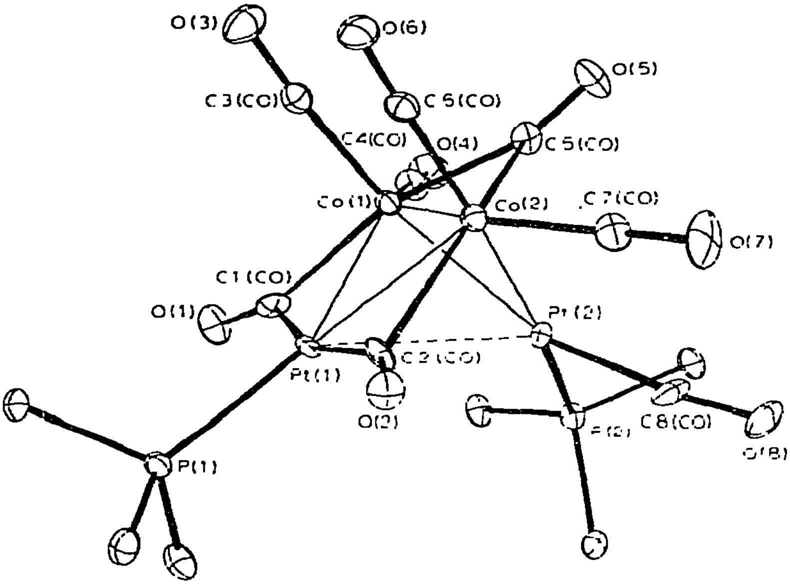

Fig. 1. Numbering scheme of the molecule $[P(C_6H_5)_3]_2Pt_2Co_2(CO)_8$ (I)

2.540(2), Co(2)—Pt(1) = 2.579(2), Co(1)—Pt(2) = 2.554(3), Co(2)—Pt(2) = 2.528(3) and Pt(1)—Pt(2) = 2.987(4) Å. Ligands are distributed among metal centers in the following way: one $P(C_6H_5)_3$ ligand is associated with each platinum atom and carbonyl group bridges Co(1)—Co(2), Pt(1)—Co(1) and Pt(1)—Co(2). The remaining carbonyl groups are attached terminally to Co(1), Co(2) and Pt(2). The cluster, excluding the phenyl rings, has a pseudomirror plane through Pt(1), Pt(2) and the middle of the Co(1)—Co(2) vector.

Since the Pt(1)—Pt(2) distance is greater by 0.4 Å than twice the covalent radius of platinum (1.30 Å [5]), the cluster has a butterfly configuration which is related to the tetrahedral $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$ [4] by flattening of the Pt_2Co_2 tetrahedron along its c_2 axis through the middle of the Co(1)—Co(2) vector.

The Pt(1)—C1(CO)—Co(1) and Co(1)—C5(CO)—Co(2) bridges are symmetric within a three-fold limit of the standard deviations but Pt(1)—C2(CO) and Co(2)—C2(CO) distances differ by 0.2 Å. This asymmetry is due essentially to steric hindrance by the C2(CO)/O(2) group. The platinum and cobalt atoms have 16 and 18 electron configurations respectively. The geometry of the $P(C_6H_5)_3$ groups is normal.

References

1 R.G. Vranka and L.F. Dahl, J. Amer Chem. Soc., 91 (1969) 1574;
L.F. Dahl and D.L. Smith, ibid., 84 (1962) 2450;
R. Mason and K.M. Thomas, J. Organometal. Chem., 43 (1972) C39;
R. Belford, H.P. Taylor and P. Woodward, J. Chem. Soc. (Dalton), (1972) 2425.
2 C.W. Bradford, W. Van Bronswijk, R.J.H. Clark and R.S. Nyholm, J. Chem. Soc. (A), (1970) 2889.
3 A.T.T. Hsieh and M.J. Mays, J. Organometal. Chem., 39 (1972) 157.
4 M.R. Churchill and M.V. Veidis, Chem. Commun., (1970) 529.
5 O. Kahn and M.F. Koenig, Données Fondamentales pour la Chimie, Herman, Paris, 1972, p. 21.