Synthesis and *X*-Ray Crystal and Molecular Structure of the Palladium–Molybdenum Carbonyl Cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\}\cdot 2THF$ (THF = Tetrahydrofuran; Cp = η^5-cyclopentadienyl)

T. A. Stromnova, I. N. Busygina, S. B. Katser, A. S. Antsyshkina, M. A. Porai-Koshits, and I. I. Moiseev*

N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Leninskii Prospect, 31, Moscow, U.S.S.R.

The anionic octanuclear cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\}\cdot 2THF$ (THF = tetrahydrofuran; Cp = η^5-cyclopentadienyl) with a completely planar metal core, contains palladium in an unusual formal oxidation state +1/2 and has been obtained by the reaction of $Pd_4(CO)_4(OAc)_4$ with $Na[CpMo(CO)_3]$, and structurally characterized by *X*-ray diffraction.

Low molecular weight palladium clusters containing the metal in the formal oxidation states 0 and +1 are well known,[1] while there are only a few examples of Pd complexes with an intermediate formal oxidation state (+2/3).[2,3] We have successfully synthesized the first example of a cluster where Pd has a formal oxidation state of (+1/2).

The reaction of $Pd_4(CO)_4(OAc)_4$ (**1**) (containing a rectangular metal core)[4] with a large excess of $Na[CpMo(CO)_3]$ in THF (Cp = η^5-cyclopentadienyl; THF = tetrahydrofuran) produces the dimer $[CpMo(CO)_3]_2$ and a number of palladium–molybdenum complexes which are stable only in an inert atmosphere. From the THF–benzene–hexane mixture a complex of the composition $Na_2\{Pd_4[CpMo(CO)_3]_4\}\cdot 2THF$ (**2**) was isolated as dark-brown crystals. The i.r. spectrum of (**2**) displays bands corresponding to co-ordinated carbonyl groups at 2000, 1945, 1900, 1870, and 1830 cm^{-1}. Its ^1H n.m.r. spectrum in dimethylformamide contained a singlet at δ 4.763 (C_5H_5), but no metal hydride signals. The structure of the complex (**2**) was determined by *X*-ray diffraction.†

The structural unit of the crystal contains the centrosymmetric anion $\{Pd_4[CpMo(CO)_3]_4\}^{2-}$ (Figure 1), two sodium cations, and two THF molecules. Unlike complex (**1**), where the Pd–Pd distances are 2.663(1) and 2.909(1) Å, the cluster (**2**) has a square planar configuration [Pd–Pd 2.675—2.691(2)

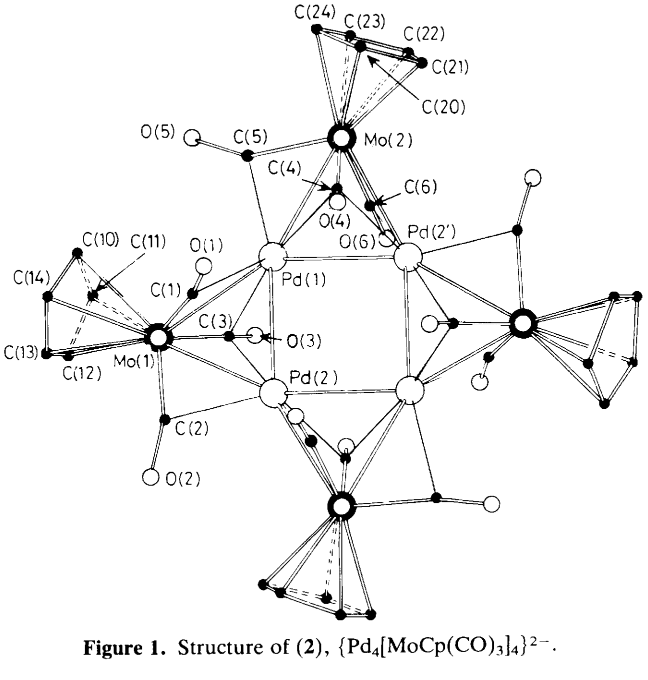

Figure 1. Structure of (**2**), $\{Pd_4[MoCp(CO)_3]_4\}^{2-}$.

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† *Crystal data:* $C_{40}H_{36}Mo_4Na_2O_{14}Pd_4$, M = 1596.0, monoclinic, space group *C2/c*, a = 22.056(6), b = 12.125(2), c = 17.249(4) Å, β = 102.99(2)°, U = 4495(2) Å^3, Z = 4, D_c = 2.36 g cm^{-3}, $\lambda(Mo\text{-}K_\alpha)$ = 0.71069 Å, $\mu(Mo\text{-}K_\alpha)$ = 29.50 cm^{-1}. Intensity data were collected on a Syntex $P2_1$ diffractometer, 7167 independent reflections ($4° \leqslant 2\theta \leqslant 60°$), 3487 observed, with $I \geqslant 1.96\,\sigma(I)$. The data were corrected for Lorentz, polarization, and absorption (ψ scan) effects and the structure was solved by direct methods using the SHELX-76 program. Anisotropic least-squares refinement using unit weights gave a final agreement factor of R = 0.066. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Å]. Each of the Mo atoms forms an isosceles triangle with two Pd atoms [Pd–Mo 2.723—2.741(2) Å], all the metals atoms lying in the one plane. Pd–Mo distances are similar to those found in related compounds[5] and correspond to single bonds.

The environment of each Mo and Pd atom is similar to that in the known cluster $Pd_2Mo_2(Cp)_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2(PEt_3)_2$. The three carbonyl groups attached to each Mo atom form a trigonal pyramid with C–Mo–C angles of 92—109(1)°, and Mo–C distances 1.97—2.01(2) Å. The positions above the vertices are occupied by the cyclopentadienyl ligands which are oriented in such a way that the Cp ring planes form angles of 78.3 and 83.6° with the planar metal core [Mo–C 2.29—2.36(3) Å, C–C 1.34—1.44(5) Å]. The carbonyl carbon atoms attached to Mo approach Pd, one of them in a triply bridging mode, μ^3-CO [Pd–C 2.22—2.45(2) Å], and the other two as doubly bridging ligands, μ-CO [Pd–C 2.34—2.36(2) Å].

Thus, during the formation of the octanuclear cluster, not only are the acetate ligands displaced by the $CpMo(CO)_3^-$ anions, but the neutral CO molecules are also eliminated. The vacancies in the co-ordination sphere of the Pd are occupied by the Mo co-ordinated CO molecules which form the bridging ligands. However, the observed reaction is not restricted to the ligand substitution process. During the reaction the reduction of Pd(+1) atoms takes place apparently owing to the one-electron oxidation of the $[CpMo(CO)_3]^-$ anions. Assuming that the Mo atoms entering the complex retain their oxidation state of 0 as in the initial $Na[CpMo(CO)_3]$, the observed transformation can be formally described as the reduction of Pd(+1) to Pd(+1/2) according to equation (1).

$$\begin{aligned} &Pd_4(CO)_4(OAc)_4 + 6\ Na[CpMo(CO)_3] \\ &\quad \rightarrow Na_2[Pd_4Mo_4Cp_4(CO)_{12}] + 4\ CO \\ &\qquad + [CpMo(CO)_3]_2 + 4\ NaOAc \end{aligned} \tag{1}$$

In the planar rectangular cluster (**1**) the formation of the metal core involves 4 electrons from 4 Pd atoms in the d^9 configuration. These electrons occupy two bonding M.O.s. Occupation of the antibonding orbitals in the oxidation state Pd(+1/2) would lead to decomposition of the cluster or at least result in an increase in the metal–metal bond lengths. In contrast, in compound (**2**) two Pd–Pd distances are noticeably shorter than in (**1**). This suggests that electrons, which in the formal description belong to the Pd atom, are really delocalized through the CO groups of the bridging ligands in $[CpMo(CO)_3]^-$. The acceptor ability of carbonyl groups is known to stabilise such anions as $[M(CO)_n]^{n-}$.[6]

Thus, the transformation of the metal core from a rectangle to a square is due to the fact that, whereas the parent compound (**1**) is bridged by two types of ligand (OAc^- and CO), the final product (**2**) contains only strong acceptor bridging groups $[CpMo(CO)_3]^-$.

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References

1 N. K. Eremenko, E. G. Mednikov, and S. S. Kurasov, *Usp. Khim.*, 1985, **4**, 671.

2 L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd, and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1336.

3 A. L. Balch, J. R. Boehm, H. Hope, and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431.

4 I. I. Moiseev, T. A. Stromnova, M. N. Vargaftig, G. J. Mazo, L. G. Kuz'mina, and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, 1978, 27.

5 R. Bender, P. Braunstein, J-M. Jud, and Y. Dusaysoy, *Inorg. Chem.*, 1983, **22**, 3394; M. Pfeffer, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1980, **102**, 6338; P. Braunstein, J. Fischer, D. Matt, and M. Pfeffer, *ibid.*, 1984, **106**, 410.

6 I. I. Moiseev, *Zh. Vses. Khim. Ova.*, 1982, **27**, 309.