Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1**(**3**), 92–94

Mendeleev Communications

Unexpected Oxidation of a Coordinated Phosphine Ligand. Synthesis and Molecular Structure of $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$

Natal'a Yu. Kozitsyna,[a] **Arkadii M. Ellern,**[a] **Mikhail Yu. Antipin,**[b] **Yurii T. Struchkov**[b] **and Il'a I. Moiseev***[a]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, 117907 Moscow, USSR*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, 127334 Moscow, USSR*

The reaction of $[Pd(OAc)_2(PPh_3)]_2$ with HCO_2H includes the transfer of an O atom from the carboxylic ligand to the P atom and cleavage of the P—Ph bond accompanied by transfer of the Ph group from PPh_3 ligand to the palladium atom; the structure of the complex formed, $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$, has been resolved by X-ray analysis.

Reduction of bis(triphenylphosphine)tetraacetatodipalladium **1** with molecular hydrogen has been found to give a number of complexes containing a Pd—Pd bond.[1] Both the direction of reaction and the nature of the compounds formed were assumed to depend essentially on both the nature of the acidic ligands in the Pd coordination sphere and on the nature of the reductant.[1,2] In our work, the reduction of complex **1** with formic acid was studied to elucidate the process of Pd cluster formation.

The interaction of complex **1** (0.1 mmol) with HCO_2H (5 ml) (12 h at 20 °C under Ar atmosphere) was found to give hydride complex $[Pd_2(PPh_2)H_x]_n$ **2** as the main product (60–70% based on Pd).[3] Complex **2** was isolated from the reaction mixture after HCO_2H removal and dissolution of the residue in benzene followed by precipitation with hexane and washing with ether. In addition, the light-brown complex $[Pd(\mu\text{-}O_2PPh_2)(C_6H_5)(PPh_3)]_2$ **3** was obtained in 8–10% yield based on Pd by slow crystallization of the united mother solutions. The reaction was found by GLC data to give rise to AcOH (2 mol/mol Pd) and C_6H_6 (0.9 mol/mol PPh_3). Evolution of CO_2 and H_2 was

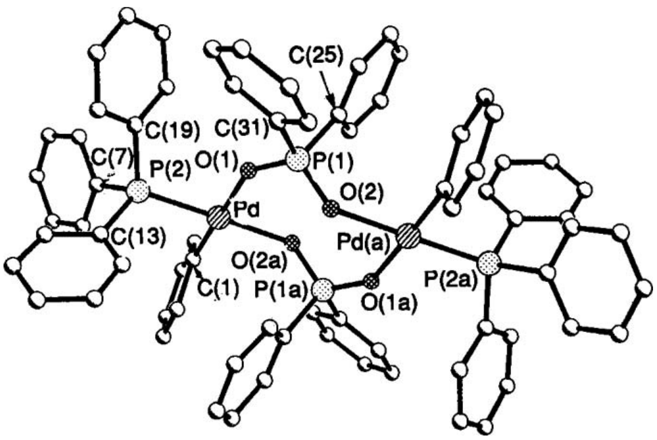


Fig. 1 A view of the structure of **3**. Selected distances (Å) and angles (°): Pd—O(1) 2.115(6), Pd—P(2) 2.213(4), Pd—O(2a) 2.100(9), Pd—C(1) 1.93(1), P(1)—O(1) 1.482(6), P(1)—O(2) 1.516(9); P(2)—Pd—O(2a) 177.9(2), O(1)—Pd—C(1) 178.3(4), P(2)—Pd—C(1) 87.2(4), P(2)—Pd—O(1) 93.1(3), O(2a)—Pd—C(1) 91.0(5), O(2a)—Pd—O(1) 88.7(3), Pd—O(1)—P(1) 143.4(6), O(1)—P(1)—O(2) 116.9(4), P(1)—O(2)—Pd(a) 233.6(5).

observed throughout the reaction time, seemingly as a result of HCO_2H decomposition catalysed by the Pd complexes.

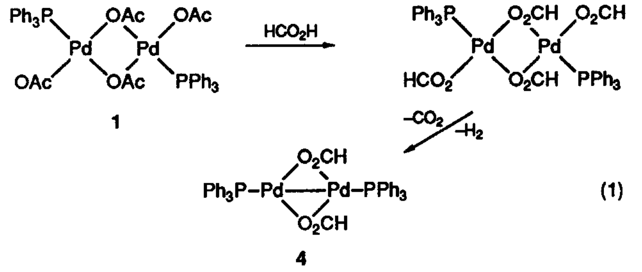
The structure of the centrosymmetrical dimeric complex **3** was proved by X-ray diffraction.† The Pd^{II} atoms are bridged by two diphenylphosphinate groups (Fig. 1). The mean Pd—Pd distance of 5.35 Å excludes the direct interaction between them. The coordination of the Pd-atoms is close to an ideal plane-square: the metal atoms and their nearest neighbours are coplanar to within 0.020 Å. The central 8-membered ring has a chair-like conformation. The atoms of the 'angular' fragment P(1), O(1), Pd and O(2a) are coplanar to within 0.03 Å and their plane is tilted to the central plane P(1), O(2), P(1a), O(2a) at an angle of 47.3°.

The geometrical parameters of complex **3** have the expected values and are close to those of the similar complex $[Pd_2(\mu\text{-}O_2CMe)_2(C_6H_5)_2(PPh_3)_2]$ with a bridging acetate ligand.[4] However, the central ring of the latter complex has a boat-like conformation, and the Pd···Pd distance is decreased to 3.079 Å. The Pd—O(1) and Pd—O(2a) bonds are *trans*-oriented with respect to the Ph- and Ph_3P-substituents and their lengths are almost equal [2.115(6) and 2.100(9) Å]. The Ph-ligand is oriented approximately normal to the coordination plane of the Pd atoms. The difference between the P(1)—O(1) [1.482(6) Å] and P(1)—O(2) [1.516(9) Å] distances is 0.034(9) Å. This value suggests that P(1)—O(1) is a multiple bond and Pd—O(1) a coordinative bond. Nevertheless, the Pd—O bond lengths are almost equal (see above), which may be explained by the electronic influence of the Ph_3P and Ph *trans*-substituents.

It is noteworthy that complex **3** was formed by an unusual redox reaction in which phosphorus(III) was oxidized to phosphorus (V) in spite of the presence of a strong reductant, formic acid. The only source of O atoms added to the P atom on formation of complex **3** under the reaction conditions (Ar atmosphere, reagents carefully purified from O_2) appeared to be a carboxylate ligand.

Let us consider some possible reactions which could lead to complexes **2** and **3**. Reactions involving P—C bond cleavage are well known in the chemistry of tertiary phosphine complexes.[1,5] These reactions are normally assumed to involve a decrease in the oxidation state of the metal atom in an intermediate step. When complex **1** was converted to **3**, the Pd—Ph fragment was also formed indicating the intermediate formation of a low-valent palladium complex capable of insertion into the P—C bond of the triphenylphosphine ligand.

Dissolution of complex **1** in HCO_2H was found by GLC to be followed by immediate substitution of the acetate ligands with formate ones. Further decarboxylation of the formate ligands and reduction of palladium could give rise to a complex containing Pd^I, $(PPh_3)Pd(O_2CH)_2Pd(PPh_3)$ **4** [eqn. (1)].



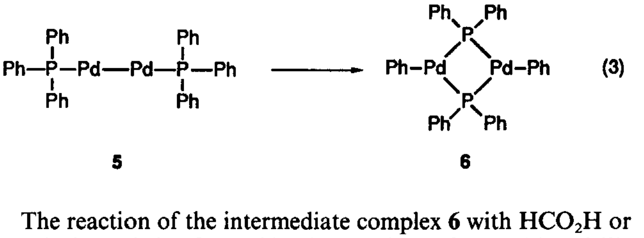
(1)

In contrast to the relatively stable $(Ph_3P)_2Pd_2(OAc)_2$ which was obtained by reaction of complex **1** with H_2,[1] complex **4** could undergo decarboxylation again, forming the Pd^0 complex **5** as shown by [eqn. (2)].

$$\mathbf{4} \xrightarrow[-H_2]{-2CO_2} \underset{\mathbf{5}}{(Ph_3P)_2Pd_2} \qquad (2)$$

Complex **5** was found to be the product of hydrogenation of **1** in CH_2Cl_2 solution.[1] The preparation of **5** was found to be poorly reproducible; CH_2Cl_2 or an admixture may have been responsible for the stabilization of **5**. We have not found direct evidence for the formation of **5** in our study. However, the transformation of complex **1** to **2** and **3** may be understood easily in terms of a mechanism involving steps (1) and (2) with intermediate formation of complex **5**.

Thus, insertion of a Pd atom into a P—C bond of complex **5** may give rise to a complex containing both the diphenylphosphide group found in complex **2** and the Pd—Ph bond found in complex **3** [eqn. (3)].



(3)

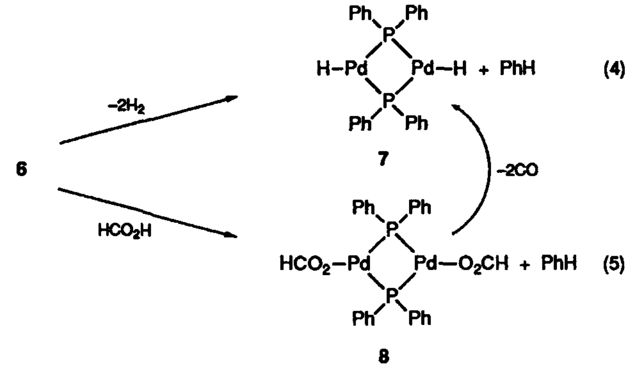
The reaction of the intermediate complex **6** with HCO_2H or H_2, the latter being formed by the reactions of eqns. (1) and (2), may be responsible for the formation of benzene (yield ~ 1 mol/mol PPh_3) and hydride complexes of type **2** [eqns. (4) and (5)]. Compound **7**, being the source of complex **2**, is assumed to be the catalyst for decarboxylation of HCO_2H [eqn. (6)].

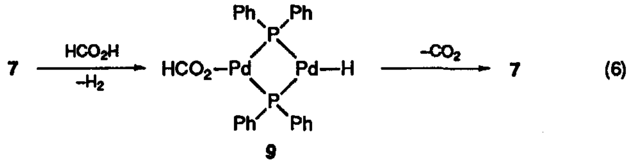
Thus, oxidative addition of the phosphine ligand to the Pd—Pd bond [eqn. (3)] followed by nucleophilic attack on the phosphorus atom of the formed diphenylphosphido group by the formate ligand, may give rise to complex **10**, as generalized by eqn. (7). A new ligand, formoxydiphenylphosphine, is prob-

---

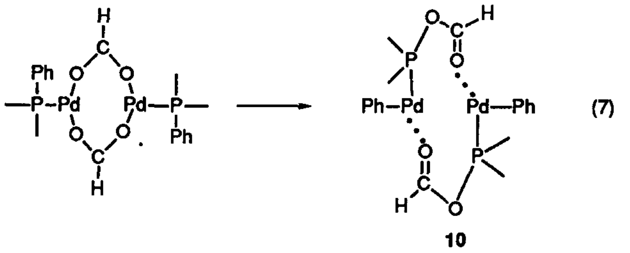
† *Crystal data* for **3**: $Pd_2P_2O_4C_{72}H_{60}$, $M_r = 1326.0$, triclinic, space group $P\bar{1}$, $T = 153$ K, $a = 10.057(6)$, $b = 12.769(7)$, $c = 12.862(7)$ Å, $\alpha = 112.00(6)$, $\beta = 104.24(7)$, $\gamma = 93.26(7)°$, $V = 1464(4)$ Å^3, $Z = 1$, $D_c = 1.504$ g cm^{-3}, μ(Mo-Kα) = 7.6 cm^{-1}, $F(000) = 676$. Using a 'Sintex P2$_1$' diffractometer, λ(Mo-Kα) = 0.7107 nm, graphite monochromator, $2\theta < 46°$ at 153 K, 1846 unique reflections with $F > 2\sigma(F_0)$ were collected of the total of 3043 independent reflections. The structure was solved by direct methods and refined by least-squares procedures in anisotropic block-diagonal approximation to $R = 0.051$, $R_w = 0.040$, GOF = 1.36. The positions of the H atoms were calculated geometrically and included in calculations with fixed coordinates and isotropic thermal parameters $U_{iso} = 0.08$ Å^2. All calculations were carried out using SHELX PLUS programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, *J. Chem. Soc., Chem. Commun.*

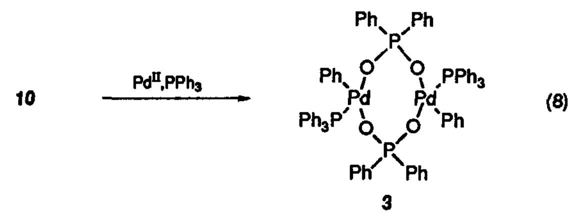
Mendeleev Commun., 1991, 1(3), 92–94





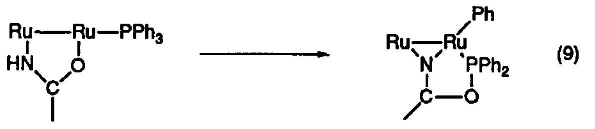
ably formed in this step. This ligand seems to be more liable than PPh_3 to both undergoing reactions of type (7) and to oxidation by the initial Pd^{II} complexes to produce Ph_2PO_2H or the corresponding anion. Moreover, an additional molecule of PPh_3 released as a result of the transformation of complex **1** to **2**, may be coordinated to Pd [eqn. (8)].





Related reactions may explain the course of phenylation of styrene by $Pd(OAc)_2/PPh_3$ where Ph_2PO_2H was formed,[6] and also the reaction of $[Pd_3(O_2CMe)_6]$ with PPh_3, where complex $[Pd_2(\mu\text{-}O_2CMe)_2(C_6H_5)_2(PPh_3)_2]$ was obtained.[4] In these systems methanol or styrene, accordingly, could play the role of reducing agent.

Cleavage of the P—C bond and nucleophilic attack by the coordinated PhCONH ligand on the PPh_2 group were observed in the course of the reaction of $[Ru_2(PhCONH)_4Cl]$ with PPh_3 to yield $[Ru_2Ph_2(PhCONH)_2\{Ph_2POC(Ph)N\}_2]$,[7] as depicted schematically by eqn. (9).



A similar process has also been observed during the reaction of $Pt(PPh_3)_3$ with RCNO resulting in the formation of $[Pt(OPPh_2)(RCN)(Ph)(PPh_3)]$.[8]

Received in USSR, 29th January 1991
Received in UK, 11th March 1991; *Com. 1/00466B*

References

1 A. A. Berenblyum, A. G. Kniznik, S. L. Mund and I. I. Moiseev, *J. Organomet. Chem.*, 1982, **234**, 219.
2 T. I. Bakunina, S. V. Zinchenko, V. A. Khutoryanskii, O. V. Burlakova, G. V. Ratovskii and F. K. Schmidt, *Metallorg. Khim.*, 1990, **3**, 462.
3 N. Yu. Kozitsyna and I. I. Moiseev, to be published.
4 M. B. Hursthouse, O. D. Sloan, P. Thornton and N. P. C. Walker, *Polyhedron*, 1986, **5**, 1475.
5 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 1713.
6 T. Yamane, K. Kikukawa, M. Takagi and T. Matsuda, *Tetrahedron*, 1973, **29**, 955; K. Kikukawa, M. Takagi and T. Matsuda, *J. Organomet. Chem.*, 1982, **235**, 243; T. Sakakura, T.-A. Kobayashi, T. Hayashi, Y. Kawabata, M. Tanaka and I. Ogata, *J. Organomet. Chem.*, 1984, **267**, 171.
7 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *J. Am. Chem. Soc.*, 1984, **106**, 6409.
8 W. Beck, M. Keubler, E. Leidl, U. Nagee and M. Schaal, *J. Chem. Soc., Chem. Commun.*, 1981, 446.