Cationic Palladium(II)–Diphosphine Complexes as Catalysts for the Carbonylation of Alkenes to Ketones

Carmelina Pisano,[a] Giambattista Consiglio,*[a] Angelo Sironi[b] and Massimo Moret[b]

[a] *Eidgenössische Technische Hochschule, Technisch-Chemisches Laboratorium, CH-8092 Zürich, Switzerland*
[b] *Istituto di Chimica Strutturistica ed Inorganica dell'Università, Via Venezian 21, I-20133 Milano, Italy*

Cation palladium complexes of the type [(dppp)Pd(solvent)$_2$][X]$_2$ **2** [X = non or weakly coordinating anion; dppp = 1,3-bis(diphenylphosphino)propane] are active catalysts for the carbonylation to ketones, *e.g.*, for the selective formation of *E*-1,5-diphenylpent-l-en-3-one from styrene; in the presence of water and depending on the acidity conditions dimerisation to the much less catalytically active [(dppp)Pd(μ-OH)$_2$Pd(dppp)]X$_2$ **3** takes place, the structure of which was determined by X-ray crystallography.

Catalytic systems consisting of palladium compounds modified by weakly (or non) coordinating anions and by phosphorus or nitrogen ligands have attracted a great deal of interest due to the high activity that they exhibit for many reactions.[1–12] We have found that the catalytic system obtained *in situ* from [Pd(MeCN)$_4$][BF$_4$]$_2$ (prepared by oxidation of palladium sponge with NOBF$_4$[13]) and dppp [1,3-bis(diphenylphosphino)propane] promotes a highly selective formation of 1,5-diphenylpentan-3-one from styrene under hydroformylation conditions (200 atm of an equimolar mixture of hydrogen and carbon monoxide).[6] The paucity of systems able to catalyse the synthesis of ketones from substrates other than ethylene and propylene[14,15] prompted us to attempt the synthesis of cationic palladium complexes that can be used directly as catalyst precursors.

In the reaction of (dppp)PdCl$_2$ **1** with silver tetrafluoroborate in MeCN or tetrahydrofuran (thf) (Scheme 1) the corresponding bis-solvento complexes [(dppp)Pd(MeCN)$_2$]-[BF$_4$]$_2$ **2a** and [(dppp)Pd(thf)$_2$][BF$_4$]$_2$ **2b** form. However, when wet methanol is used as the solvent the bis-aquo

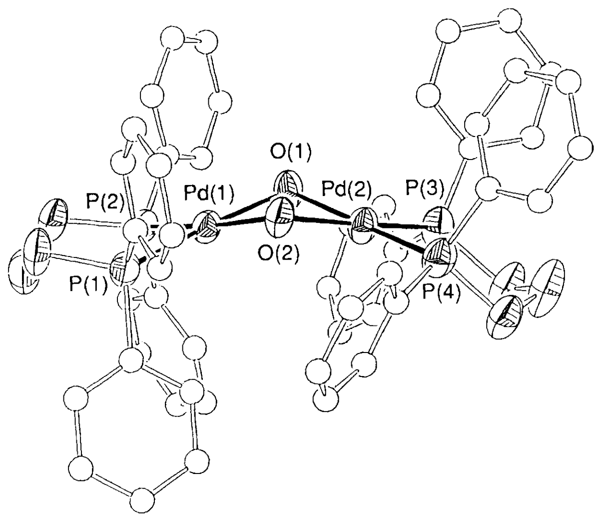
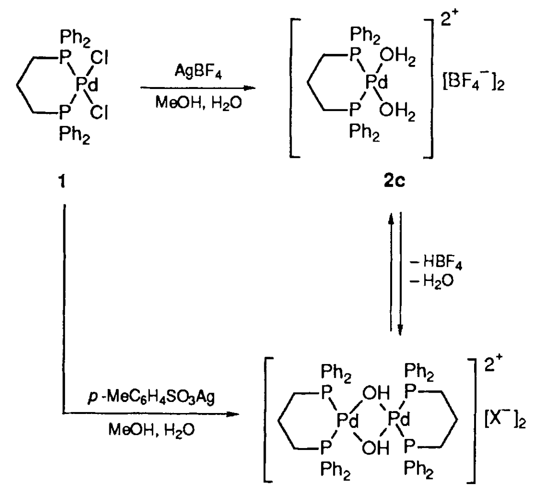


Fig. 1 ORTEP view of the $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]^{2+}$ cation (for clarity all the *B* values of the phenyl carbon atoms have been set to 2.0 $Å^2$). Relevant bond lengths (Å) and angles (°), averaged over the two independent molecules in the asymmetric unit (in parentheses is reported the standard error of mean), are: Pd–O 2.081(4), Pd–P 2.230(1), Pd···Pd 3.098(2), Pd-P-Pd 96.2(2), P-Pd-P 92.2(8), O-Pd-O 77.5(3), P-Pd-O(*trans*) 172.2(6), P-Pd-O(*cis*) 95.1(7). The dihedral angle between the two Pd coordination planes is 33.3(8)°.

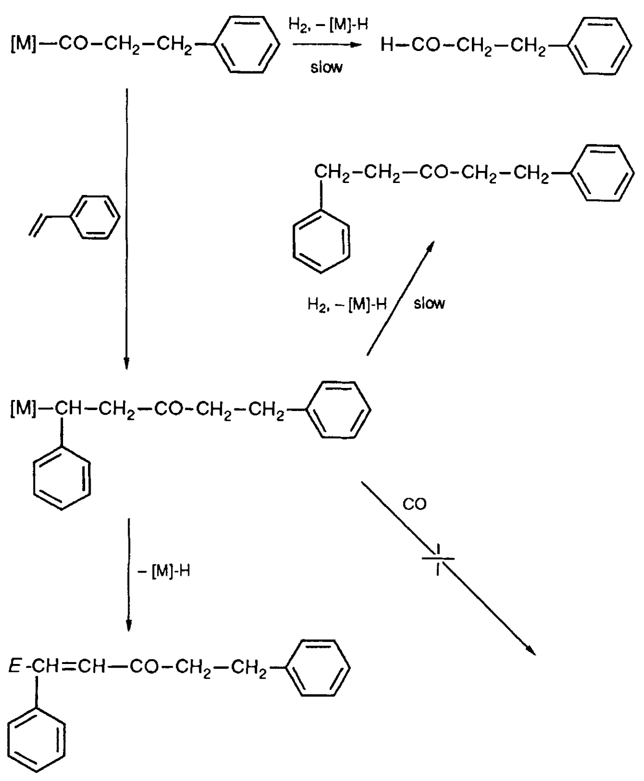
complex **2c** probably[12,16] forms. Compound **2c** seems to be unstable under neutral conditions. In fact, the addition of diethyl ether to solutions of **2c** in methanol results in the formation of yellow crystals of **3**†. A broad signal at δ −2.30 can be recognized in the ^1H NMR spectrum. This signal sharpens somewhat on lowering the temperature to −80 °C but remains unresolved; furthermore, it disappears by treating the solution with deuteriated water. Based on IR, multinuclear NMR and fast atom bombardment (FAB) mass spectroscopy we assigned the structure $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]X_2$ to compound **3**. This assignment is supported by single crystal X-ray analysis‡ (Fig. 1).

The crystal structure consists of a packing of dimeric palladium[1] dications (two per asymmetric unit) and BF_4^- anions, together with clathrated acetone molecules in the ratio 1:2:0.5, respectively. The palladium atoms possess an approximately square-planar coordination consisting of two μ^2-OH and one chelating dppp ligands (maximum deviation of the Pd atoms from the O_2P_2 planes 0.053 Å), as shown in Fig. 1. The O–Pd–O, P–Pd–P and Pd–O–Pd angles average, are respectively, 77.5, 92.2 and 96.2°. The two PdO_2P_2 square-planar moieties are folded along the O–O hinge (dihedral angles 34.0 and 32.4° for the two independent molecules). A similar folding has been observed in the $Pd_2(\mu\text{-}MeO)_2(hfacac)_2$[17] (26°)§ and $Pt_2(\mu\text{-}OH)_2(PEt_3)_4$[18] (36.4°) molecules and has normally been attributed to intermolecular interactions (but in the present case the μ^2-OH groups are not



3 : X = BF_4^-
3′ : X = p-$MeC_6H_4SO_3^-$

Scheme 1



Scheme 2

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† Complex **3** was recrystallised from diethyl ether–acetone. Spectroscopic data: ^1H NMR (300 MHz, $CDCl_3$, Me_4Si int.): δ 7.5-7.26 (m, 40H; arom.), 2.73 (m, 8H, PCH_2), 2.01 (m, 4H, PCH_2CH_2), −2.3 (s, br., 1.50H); ^{31}P NMR (referenced to H_3PO_4, 81 MHz, $CDCl_3$): δ 15.2; ^{19}F NMR (referenced to $CFCl_3$ 188 MHz, $CDCl_3$): δ −150. IR (KBr): ν 3588 cm^{-1} (m). FAB mass spectrum [matrix: NOBA (3-nitrobenzylalcohol)]: 1070.4 $[(dppp)Pd(\mu\text{-}OH)_2Pd(dppp)]$; 1053.4 $[(dppp)Pd(\mu\text{-}OH)Pd(dppp)]$; 518.4 [(dppp)Pd]. Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **3**: $C_{54}H_{54}B_2F_8O_2P_4Pd_2 \cdot 1/2C_3H_6O$, M = 1274.4, triclinic, space group $P\bar{1}$ (No. 2), a = 13.522(5), b = 19.802(3), c = 21.751(4) Å, α = 81.31(1), β = 82.87(2), γ = 87.56(2)°, U = 5711.0 $Å^3$, $F(000)$ = 2576, Z = 4, D_c = 1.48 g cm^{-3}, Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 7.96 cm^{-1}. 19904 reflections with $3° \leq \theta \leq 25°$ were measured on a CAD4 automatic diffractometer at room temperature; data were corrected for absorption and Lorentz–polarization effects. 11027 independent reflections with $I > 3\sigma(I)$ were used in the structure refinements of two independent molecules in the asymmetric unit. All the atoms, except those of the phenyl rings and of the disordered anions, were refined anisotropically using SHELX; the phenyl groups and the BF_4^- anions were constrained to D_{6h} and T_d symmetry, respectively. The hydrogen atoms were not included in the calculations. The final R value was 0.054 (R_w = 0.059). 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.

§ Hhfacac = hexafluoropentane-2,4-dione.

involved in any hydrogen bond). The Pd···Pd distance is rather long [3.096(1) and 3.099(1) Å for the two independent molecules], and does not indicate a significant metal–metal interaction. The Pd–O bond lengths of 2.081(4) Å (on average) are significantly longer than those found in $Pd_2(\mu\text{-}MeO)_2(hfacac)_2$, 1.996(av) Å, which consequently has a shorter Pd··· Pd interaction 2.984(1) Å.

The analogous compound **3**′ which contains the toluene-*p*-sulphonate anion can be prepared in a similar way by treatment of **1** with the corresponding silver salt in wet methanol (Scheme 1). Preliminary experiments suggest that **2c** and **3** can interconvert depending on the acidity of the medium; in fact, formation of **2c** was observed when **3** was dissolved under acidic conditions. Compounds similar to **3** and **3**′ containing triphenylphosphine[19] or nitrogen ligands such as 1,10-phenanthroline or 1,1′-bipyridyl[20] have already been reported in the literature, though they were incompletely characterised. The easy formation of these dimeric complexes and their dependence on the acidity of the medium could have large implications for catalysis. In fact, it suggests possible reasons for the decrease in the productivity by increasing the concentration of the catalyst precursor, which has been observed in the synthesis of poly-oxo-trimethylene from ethene and carbon monoxide[21] by $[(dppp)Pd(CF_3CO_2)_2]$ and in the dimerisation of methyl acrylate[11] by the catalyst precursor $[PPh_3PdCl_2]_2$–$AgBF_4$. Moreover, in the synthesis of poly-oxo-trimethylene the productivity of the system increases by increasing the concentration of free trifluoroacetic acid; this increase flattening at higher concentrations.[21]

The carbonylation of styrene in thf using **2a** as the catalyst precursor at 77 °C under 160 atm of an equimolar mixture of carbon monoxide and hydrogen produces 1,5-diphenylpentan-3-one and *E*-1,5-diphenylpent-1-en-3-one (5:95 molar ratio) with a selectivity of ~99%; the conversion was 42% after 4 h. Remarkably the dimeric compound **3** gives only 4.5% conversion under the same reaction conditions, the selectivity of the reaction remaining the same. Very similar results as far as the selectivity is concerned were obtained using $[(dppp)Pd(p\text{-}MeC_6H_4SO_3)_2]$ **4** as the catalyst precursor at 110 °C under 20 atm of carbon monoxide and 1 atm of hydrogen. With the latter catalytic system an increase in the hydrogen partial pressure to 200 atm does not influence the ratio between saturated and unsaturated ketone but decreases the selectivity towards their formation (from 98% to 53%). Under these conditions about 45% of aldehydes (3-phenylpropanal and 2-phenylpropanal) are formed in an 83:17 molar ratio.

The results obtained in the above carbonylation can be interpreted according to Scheme 2. It is worth mentioning that catalytic systems related to **4** but containing nitrogen ligands like 1,10-phenanthroline or 1,1′-bipyridyl are able to promote the alternate copolymerization of styrene and carbon monoxide with formation of poly-(1-oxo-2-phenyltrimethylene) which has a high stereoregularity.[22,23] The copolymers obtained have a rather low molecular weight. Despite the fact that the nature of the end group has not been carefully analysed, the importance of the β-hydrogen elimination reaction similar to that observed in our synthesis of the ketones (Scheme 2) as a reason for chain termination cannot be disregarded.

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