Mendeleev Commun., 2002, 12(2), 47–48

Synthesis and structure of new triphenylphosphine π-complexes of palladium(0) with *p*-benzoquinone and their role in the oxidative carbonylation of alkynes

Alexander V. Kulik,*[a] Lev G. Bruk,[a] Oleg N. Temkin,[a] Vildar R. Khabibulin,[a] Vitaly K. Belsky[b] and Valery E. Zavodnik[b]

[a] *M. V. Lomonosov Moscow State Academy of Fine Chemical Technology, 117571 Moscow, Russian Federation. Fax: +7 095 434 8711; e-mail: lbruk@cityline.ru*

[b] *L. Ya. Karpov Institute of Physical Chemistry, 103064 Moscow, Russian Federation*

10.1070/MC2002v012n02ABEH001577

The complexes [Pd(η^2-Q)(PPh$_3$)$_2$]$_2$H$_2$Q and Pd$_2$(μ-η^2,η^2-Q)$_2$(PPh$_3$)$_2$ (where Q and H$_2$Q are *p*-benzoquinone and hydroquinone, respectively) were synthesised and structurally characterised, and their catalytic activity in the oxidative carbonylation of phenylacetylene to methyl phenylpropiolate was examined.

p-Benzoquinone is widely used as an oxidant in the reactions of unsaturated organic compounds catalysed by palladium compounds.[1–3] It can play different roles in the course of a catalytic reaction. In addition to the back oxidation of reduced catalysts, *p*-benzoquinone can participate in the reactions of organometallic intermediates. For example, it can contribute to the redox degradation of the allyl π-complexes of palladium without the formation[4] or with the formation of intermediate Pd^{0}Q complexes[5] (where Q is *p*-benzoquinone). It can also be responsible for the pathways of intermediate degradation. Thus, with the participation of PdCl$_2$[6(*a*)] and [Pd(CO)Cl]$_n$[6(*b*)] in the presence of *p*-benzoquinone, dimethyl oxalate was selectively produced in the oxidative carbonylation of methanol at atmospheric pressure and 40 °C and in the oxidative conversion of AcOHgCOOMe (dimethyl carbonate and methyl chloroformate, respectively, were the reaction products in the absence of *p*-benzoquinone).[6]

A number of hypotheses[7] were considered in studying the mechanism of the oxidative carbonylation of alkynes at C–H bonds in the Pd(OAc)$_2$–PPh$_3$–Q–MeOH system

$$\mathrm{RC{\equiv}CH + CO + MeOH + Q \xrightarrow{[Pd]} RC{\equiv}CCOOMe + H_2Q,} \qquad (1)$$

where H$_2$Q is hydroquinone. One of these hypotheses assumes that a Pd^0 complex with *p*-benzoquinone is formed, and this complex is active in the carbonylation. In the above system, Pd^0 complexes can be formed on the reduction of Pd(OAc)$_2$ in reactions with PPh$_3$,[8] CO and MeOH.

To our knowledge, Pd$^{\mathrm{II}}$ complexes with *p*-benzoquinone were not obtained previously. For Pd$^{\mathrm{I}}$, only the complex Pd$_2$SO$_4$·Q, which was identified by elemental analysis, IR and X-ray spectroscopy, and thermal analysis, is known.[9] The Pd^0 complexes with *p*-benzoquinone LPdQ (where L is a bidentate ligand or two monodentate ligands) are well known (L is bipy, phen,[10] cod or PPh$_3$[11]). However, the structures of only three compounds with chelate ligands {2,3,4,6-tetra-*O*-acetyl-1-[(2-diphenylphosphino)-benzylthio]-β-D-glucopyranose,[12] 2,2′-bipyridine,[13,14] and 4,5-diazafluoren-9-one (dafo)[14]} were found recently by X-ray diffraction analysis.

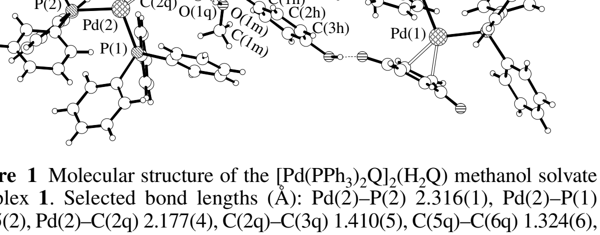


Figure 1 Molecular structure of the [Pd(PPh$_3$)$_2$Q]$_2$(H$_2$Q) methanol solvate complex **1**. Selected bond lengths (Å): Pd(2)–P(2) 2.316(1), Pd(2)–P(1) 2.345(2), Pd(2)–C(2q) 2.177(4), C(2q)–C(3q) 1.410(5), C(5q)–C(6q) 1.324(6), O(1q)···O(1h) 2.693(5), O(1q)···H(1h) 1.79(4), O(1q)···O(1m) 2.956(4), O(1q)···H(1m) 2.05(3); selected bond angles (°): O(1q)–H(1h)–O(1h) 179.3(3), O(1q)–H(1h)–O(1m) 179.0(1), P(3)–Pd(2)–P(4) 107.05(5).

Quinone and hydroquinone complexes with palladium and PPh$_3$ with known structures are required for the identification of palladium complexes formed in reaction (1). The aim of this work was to synthesise new Pd^0 complexes with PPh$_3$, *p*-benzoquinone and hydroquinone, to characterise them by X-ray diffraction analysis and to examine their catalytic activity in reaction (1).

According to ^{31}P NMR spectra, several complexes were formed in the reaction of PdL$_4$ (L is PPh$_3$) with *p*-benzoquinone in a CHCl$_3$ (CDCl$_3$) solution. We failed to prepare single crystals of complexes in this system. However, in attempts to synthesise a Pd^0 complex with hydroquinone, a compound with the L$_2$PdQ unit was formed, probably, because of slow oxidation of hydroquinone with oxygen of the air. Red crystals of compound **1** with the composition [Pd(PPh$_3$)$_2$Q]$_2$H$_2$Q·MeOH (0.049 mmol, 48% yield) were formed in the reaction of hydroquinone (0.909 mmol) with Pd(PPh$_3$)$_4$ (0.104 mmol) in methanol (2 ml) at room temperature in air for 12 h. Figure 1 demonstrates the structure of complex **1**.†

This complex consists of two Pd(PPh$_3$)$_2$Q moieties hydrogen-bonded to a hydroquinone molecule. A palladium atom, two phosphorus atoms and two carbon atoms at the palladium-coordinated double bond of the quinone lie in the same plane. Two double bonds of the quinone are arranged in another plane, which is almost perpendicular to the above plane. The quinone molecule is non-planar, and the carbonyl groups are out of the plane on the opposite side of palladium. Complex **1** is a solvate complex, one methanol solvate molecule is connected by hydrogen bond to the oxygen atom of a quinone. Complex **1** is the

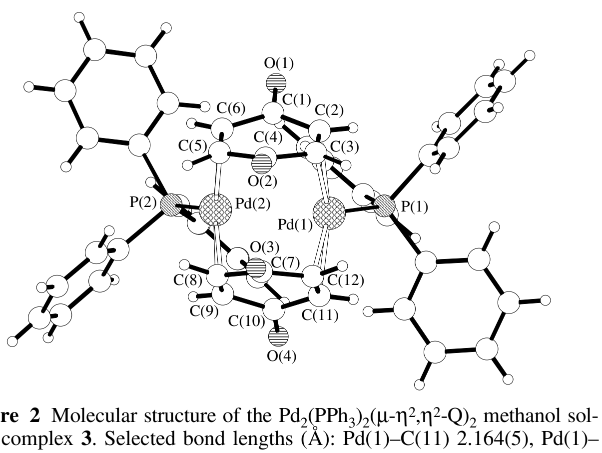


Figure 2 Molecular structure of the Pd$_2$(PPh$_3$)$_2$(μ-η^2,η^2-Q)$_2$ methanol solvate complex **3**. Selected bond lengths (Å): Pd(1)–C(11) 2.164(5), Pd(1)–C(2) 2.181(5), Pd(1)–C(3) 2.213(5), Pd(1)–C(12) 2.210(5), Pd(1)–P(1) 2.360(1), Pd(1)–Pd(2) 2.975(1), C(2)–C(3) 1.386(7); selected bond angles (°): P(2)–Pd(2)–Pd(1) 124.61(4).

---

† *Crystal data for complex* **1**: C$_{45.5}$H$_{39}$O$_{3.5}$P$_2$Pd, M = 810.11, triclinic, a = 12.670(3), b = 18.711(4) and c = 19.220(4) Å, α = 62.39(3), β = 71.88(3), γ = 78.94(3)°, V = 3831.2(15) Å^3, T = 293(2) K, space group $P\bar{1}$ (no. 2), Z = 4, μ(MoKα) = 0.886 mm^{-1}, 14065 reflections measured on a CAD-4 diffractometer, 6791 unique [$R_{(\mathrm{int})}$ = 0.0126] were used in all calculations. The final $R^{(F2)}$ = 0.0243 (all data).

Table 1 Effect of the initial Pd compound on the characteristics of reaction (1).[a]

Catalyst precursor	R/mol dm^{-3} h^{-1}	t/min	S (%)
$Pd(PPh_3)_2Cl_2$	0.000	120	traces
$Pd(OAc)_2 + 2PPh_3$	0.043	200	58
$Pd(PPh_3)_4$	0.070	127	54
$[Pd(PPh_3)_2Q]_2H_2Q{\cdot}MeOH$ (**1**)	0.080	104	63
$[Pd(PPh_3)Q]_2{\cdot}1.5MeOH$ (**3**) + $2PPh_3$	0.042	184	68
$Pd(dba)_2 + 2PPh_3$	0.031	219	72

[a] The [Q]:[Pd] ratio is 17; S is the selectivity for methylphenylpropiolate; R is the quasi-steady-state rate of formation of methylphenylpropiolate; t is the reaction time.

first complex of this kind. If the above synthesis was performed in a nitrogen atmosphere, the solution exhibited no detectable changes over a long period of time. Yellow crystals of compound **2** with the composition $Pd(PPh_3)_3$ were formed in an insignificant amount after six months. According to X-ray diffraction data, this compound is a new crystalline modification of a previously synthesised complex.[15] The structure of compound **2** will be considered elsewhere.

After the dissolution of complex **1** in acetone, compound **3** of the composition $[Pd(PPh_3)Q]_2{\cdot}1.5MeOH$ was formed in 76% yield on standing for several days at room temperature. According to X-ray diffraction data, compound **3** is a dimer complex containing two $Pd(PPh_3)$ units linked by two *p*-benzoquinone bridging molecules. These bridges are arranged so that both of the double bonds of each *p*-benzoquinone molecule are coordinated to different palladium atoms. Complex **3** is a solvate complex having 1.5 molecules of methanol, which are disordered (Figure 2).‡

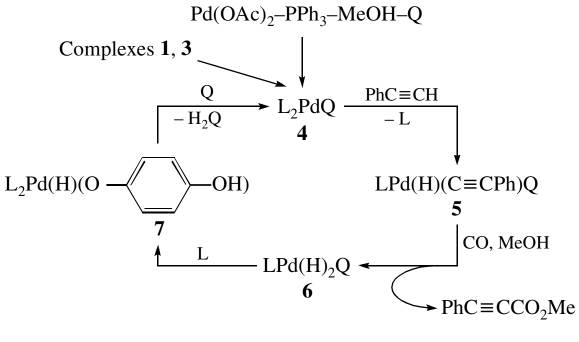
The distance between palladium atoms in complex **3** is 2.975 Å, which is longer than the Pd–Pd bond length in the metal (2.75 Å) and the Pd–Pd distance in the similar complex $Pd_2(\mu\text{-dafo})(\mu\text{-}\eta^2,\eta^2\text{-}Q)_2$ (2.77 Å).[14] In contrast to known palladium complexes with *p*-benzoquinone, complexes **1** and **3** contain a monodentate triphenylphosphine ligand. Complex **3** is formed from complex **1**, which contains a hydroquinone bridge.

A comparison of the ^{1}H, ^{13}C and ^{31}P NMR spectra of the synthesised complexes with the spectra of the $Pd(OAc)_2$–PPh_3–Q and $Pd(PPh_3)_4$–Q systems indicates that complex **1** is formed, along with other palladium complexes and products of the interaction of PPh_3 with *p*-benzoquinone, from $Pd(OAc)_2$ under reaction conditions. Complex **3** is predominant in the $Pd(PPh_3)_4$–Q system. The signals due to these complexes disappeared after the addition of phenylacetylene to the system. It is likely that the conversion of these compounds into reaction intermediates is responsible for this disappearance.

Table 1 compares the catalytic activities of palladium complexes formed *in situ* from $Pd(OAc)_2$ and $Pd(PPh_3)_4$[16] in the oxidative carbonylation of phenylacetylene by reaction (1) with the activities of complexes **1** and **3**. It can be seen that all of the used Pd^0 compounds exhibited commensurable catalytic activities. This fact may indicate that various Pd^0 complexes exhibit similar catalytic activities or various precursors [including $Pd(OAc)_2$] are converted into the same catalytically active complex. It is most likely that a Pd^0 complex with *p*-benzoquinone is catalytically active.

The rate of reaction remained almost unaffected with changes in the pH of the solution (MeCOOH and MeCOONa were added) over the range 5.9–7.7. An increase in the acidity up to pH 0.4 (a CF_3COOH additive) stopped the reaction.

In summary, the experimental data allowed us to exclude the hypotheses that involved Pd^{II} compounds as active species,[7,16] steps with the participation of protons and with Pd^0 back oxidation by *p*-benzoquinone (the absence of a sufficient concentration of protons) from consideration. The following tentative mechanism can be proposed for reaction (1):



This work was supported in part by the Russian Foundation for Basic Research (grant nos. 98-03-32108, 02-03-06199, 01-03-32883 and 00-03-32578). We are grateful to Yu. A. Ustynyuk and V. M. Nosova for performing NMR experiments.

References

1 I. I. Moiseev, *π-Kompleksy v zhidkofaznom okislenii olefinov* (*π-Complexes in the Liquid-Phase Oxidation of Olefins*), Nauka, Moscow, 1970, p. 111 (in Russian).
2 P. M. Henry, *Palladium-Catalyzed Oxidation of Hydrocarbons*, D. Reidel Publ. Co., Dordrecht, 1980.
3 J. E. Backvall, *Pure Appl. Chem.*, 1992, **64**, 429.
4 (*a*) A. P. Belov, N. G. Satsko and I. I. Moiseev, *Kinet. Katal.*, 1972, **13**, 892 [*Kinet. Catal.* (*Engl. Transl.*), 1972, **13**, 802]; (*b*) A. P. Belov, N. G. Satsko and I. I. Moiseev, *Dokl. Akad. Nauk SSSR*, 1972, **202**, 81 [*Dokl. Chem.* (*Engl. Transl.*), 1972, **202**, 1].
5 H. Grennberg, A. Gogoll and J. E. Backvall, *Organometallics*, 1993, **12**, 1790.
6 (*a*) L. N. Zhir-Lebed' and O. N. Temkin, *Kinet. Katal.*, 1984, **25**, 316 [*Kinet. Catal.* (*Engl. Transl.*), 1984, **25**, 255]; (*b*) L. N. Zhir-Lebed' and O. N. Temkin, *Kinet. Katal.*, 1984, **25**, 325 [*Kinet. Catal.* (*Engl. Transl.*), 1984, **25**, 263].
7 L. G. Bruk and O. N. Temkin, *Inorg. Chim. Acta*, 1998, **280**, 202.
8 C. Amatore, E. Carre, A. Jutand and M. A. M'Barki, *Organometallics*, 1995, **14**, 1818.
9 N. B. Shitova, L. N. Kuznetsova, E. N. Yurchenko, I. A. Ovsyannikova and K. I. Matveev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1453 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22**, 1414).
10 T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet and J. A. Ibers, *J. Organomet. Chem.*, 1974, **65**, 253.
11 M. Hiramatsu, K. Shiozaki, T. Fujinami and S. Sakai, *J. Organomet. Chem.*, 1983, **246**, 203.
12 M. Tschoerner, G. Trabesinger, A. Albinaty and P. S. Pregosin, *Organometallics*, 1997, **16**, 3447.
13 B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia and G. Mestroni, *Organometallics*, 1997, **16**, 5064.
14 R. A. Klein, P. Witte, Ruud van Belzen, J. Fraanje, K. Goubitz, M. Numan, H. Schenk, J. M. Ernsting and C. J. Elsevier, *Eur. J. Inorg. Chem.*, 1998, 319.
15 V. S. Sergienko and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1987, **28**, 103 [*J. Struct. Chem.* (*Engl. Transl.*), 1987, **28**, 548].
16 L. G. Bruk, I. V. Oshanina. V. R. Khabibulin, V. M. Nosova, O. N. Temkin and Y. A. Ustynyuk, *Int. Conf. Organometallic Compounds–The Material of Future Millennium*, Nizhni Novgorod, 2000, p. 20.

Received: 13th March 2002; Com. 02/1903

---

‡ *Crystal data for complex* **3**: $C_{51}H_{47}O_{5.5}P_2Pd_2$, M = 1022.63, monoclinic, a = 35.948(6), b = 12.070(2) and c = 23.214(5) Å, β = 66.84(2)°, V = = 9260.65(3) Å^3, T = 293(2) K, space group $C2/c$ (no. 15), Z = 8, μ(MoKα) = 0.886 mm^{-1}, 8916 reflections measured on a CAD-4 diffractometer, 4257 unique [$R_{(int)}$ = 0.015] were used in all calculations. The final $R^{(F2)}$ = 0.026 (all data).

Atomic coordinates, bond lengths, bond angles and thermal parameters for **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/105.