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Insertion of O_2 into a Pd(I)–Pd(I) dimer and subsequent C–O bond formation by activation of a C–H bond

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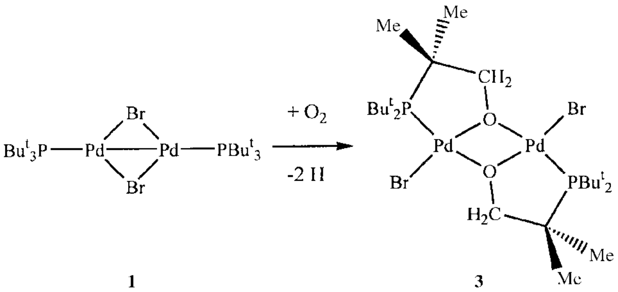
The reaction between O_2 and the dimer $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ leads to the formation of the novel dimeric compound $[\overline{Pd(\mu\text{-}OCH_2\{CMe_2\}P}Bu^t_2)Br]_2$ by coordination of O_2 to the original palladium dimer and further formation of two C–O bonds by intramolecular activation of C–H bonds.

The study of transition metal dioxygen complexes has attracted substantial interest as these types of compounds are involved in the metabolism of O_2 in living organisms.[1,2] These bioinorganic natural systems have inspired chemists to search for synthetic analogues which can be used as industrial catalysts for the oxidation of C–H and C–C bonds.[3] It is believed that, in both the biological and synthetic systems, coordinated species such as O_2^-, O_2^{2-}, HO^-, RO^- and O^{2-} play important roles in the transfer of oxygen to the organic substrates.[4] This belief has led to extensive studies on the synthesis and reactivity of transition metal dioxygen complexes. Owing to their direct relevance to biological systems, nickel,[5] cobalt,[6] copper[7] and iron[8] mono- and bi-nuclear species have been those most extensively studied. By contrast, palladium dioxygen metals have received far less attention even though they have been implicated in various catalytic processes.[9]

During the past few years we have investigated extensively the reactivity of the dimers $[Pd_2(\mu\text{-}X)_2(PBu^t_3)_2]$ (X = Br, **1**; X = I, **2**).[10] These compounds contain two palladium(I) centres and have been demonstrated to react with a wide range of small molecules such as CO, CNR, H_2 and alkynes.[11] While studying these reactions, it was observed that dimer **1** exhibited a high reactivity towards aerial oxygen. The possibility of an oxidative addition of O_2 into this dimeric species, stimulated us to undertake a systematic study of the reaction between these dimers and oxygen. Here we report our preliminary results on the reaction of O_2 with the palladium dimer $[Pd_2(\mu\text{-}Br)_2(PBu^t_3)_2]$ (Scheme 1).



Scheme 1 The reaction between **1** and O_2 leads to the formation of a novel dimeric species in which new Pd–O and C–O bonds are formed. In this process an intramolecular C–H activation occurs.

Crystallographic evidence has demonstrated that in this reaction three transformations occur: coordination of O_2 and cleavage of an O=O bond, intramolecular activation of a C–H bond and formation of new C–O bonds.

When a solution of **1** in dry and deoxygenated benzene was reacted with aerial oxygen, the original dark green colour of the solution changed to orange after few seconds. The $^{31}P\{^1H\}$ NMR spectrum of this mixture showed a singlet at δ 108.0 (*cf.* δ 87.5 for the starting material) suggesting the presence of a single product. The solvent from this mixture was then evaporated under reduced pressure and the remaining dark orange material was analysed spectroscopically† and structurally‡ demonstrating it to be the novel dimer $[\overline{Pd(\mu\text{-}OCH_2\{CMe_2\}P}Bu^t_2)Br]_2$ **3** (Scheme 1). The ^1H NMR spectrum of this new compound showed three doublets in the range δ 1.4–1.7 with an integration ration of 1 : 3 : 9. The doublet integrating for 9 protons corresponds to the Bu^t groups in the PBu^t_3 while the other two doublets correspond to a CMe_2 and a CH_2 group, suggesting cyclometallation of the phosphine. This type of intramolecular rearrangement is well established for PBu^t_3 and the NMR spectra of the resulting compounds are well documented.[12] Signals at high field were not observed suggesting that O–H groups are not present in the new compound **3**. This was also verified by IR spectroscopy which did not show any O–H stretches. Elemental analyses were also consistent with the formulation of **3**.

The unambiguous nature of compound **3** was established by an X-ray crystallographic study. Single crystals were obtained by layering a benzene solution of the dimer with hexane.

This analysis‡ confirmed that **3** is the dimeric species $[\overline{Pd(\mu\text{-}OCH_2\{CMe_2\}P}Bu^t_2)Br]_2$ (Fig. 1) which results from the incorporation of aerial O_2 into the original complex **1**. The molecule **3** has non-crystallographic C_2 symmetry about an axis normal to, and passing through the centre of, the Pd_2O_2 ring. This central four-membered ring is folded 52° out of plane about the O··O vector; the non-bonded Pd··Pd and O··O distances are 2.911(1) and 2.566(6) Å. The two five-membered chelate rings both have envelope conformations, with Pd(1)P(1)C(1)O(1) and Pd(2)P(2)C(3)O(2) being planar to within *ca.* 0.04 and 0.08 Å, respectively, and with C(2) and C(4) lying 0.68 and 0.70 Å out of their respective planes with consequent axial/equatorial dispositions of their methyl sub-

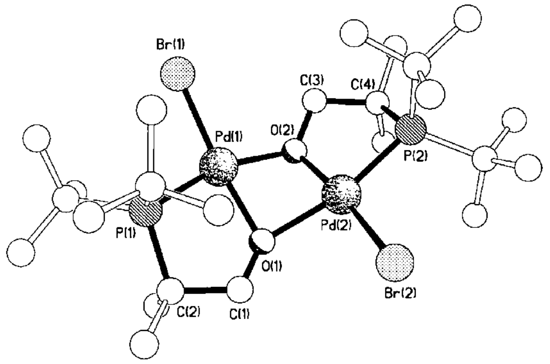


Fig. 1 The molecular structure of **3**. Selected bond lengths (Å) and angles (°): Pd(1)–O(1) 2.001(5), Pd(1)–O(2) 2.125(5), Pd(1)–P(1) 2.226(2), Pd(1)–Br(1) 2.4242(9), Pd(2)–O(1) 2.126(5), Pd(2)–O(2) 2.015(5), Pd(2)–P(2) 2.223(2), Pd(2)–Br(2) 2.4152(9), O(1)–C(1) 1.413(8), O(2)–C(3) 1.408(8), O(1)–Pd(1)–O(2) 76.9(2), O(1)–Pd(1)–P(1) 85.95(14), O(2)–Pd(2)–O(1) 76.6(2), O(2)–Pd(2)–P(2) 87.05(14), C(1)–O(1)–Pd(1) 119.1(4), C(1)–O(1)–Pd(2) 127.6(4), Pd(1)–O(1)–Pd(2) 89.7(2), C(3)–O(2)–Pd(2) 117.0(4), C(3)–O(2)–Pd(1) 127.0(5), Pd(2)–O(2)–Pd(1) 89.3(2).

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stituents. The geometry at each oxygen centre is distinctly pyramidal with both O(1) and O(2) lying *ca.* 0.5 Å out of the plane of their substituents. The coordination at each palladium centre is distorted square planar with *cis* angles in the range 76.9(2)–101.53(5)° and 76.6(2)–100.01(5)° at Pd(1) and Pd(2), respectively, the acute angle in each case being associated with the central Pd_2O_2 ring. The Pd–O–Pd bridges are both asymmetric, with the Pd–O bonds *trans* to bromine [2.001(5) and 2.015(5) Å] being *ca.* 0.1 Å shorter than those *trans* to phosphorus [2.125(5) and 2.126(5) Å]. These distances are comparable to those observed in the few reported examples of Pd_2O_2 rings.[13] In these literature examples the non-bonded Pd··Pd separation is in all cases longer than that we observe in **3**.

A remarkable aspect of the structure of **3** is the formation of two C–O bonds by intramolecular C–H activation of one of the Bu^t groups of each phosphine. This leads to the formation of two five-membered chelate rings, which explains the presence of the three doublets observed in the ^1H NMR spectrum of **3** and is also consistent with the singlet present at δ 108.0 in the $^{31}P\{^1H\}$ NMR spectrum.

Careful inspection of the sample from which the crystals of **3** were taken indicated the presence of very few crystals of both a different colour and morphology (the number of these crystals was negligible compared to the amount of crystals of **3**). X-Ray crystallographic analysis of one of these crystals‡ showed that the structure of this second product is the dimeric species with formula $[\overline{\mathrm{Pd}(\mathrm{Bu}_2{}^t\mathrm{PCMe}_2\mathrm{CH}_2})(\mu\text{-Br})]_2$ **4**. This complex is isomorphous with the already reported chloride analogue having a planar central Pd_2Br_2 ring and folded $PdPC_2$ rings (Fig. 2).[12]

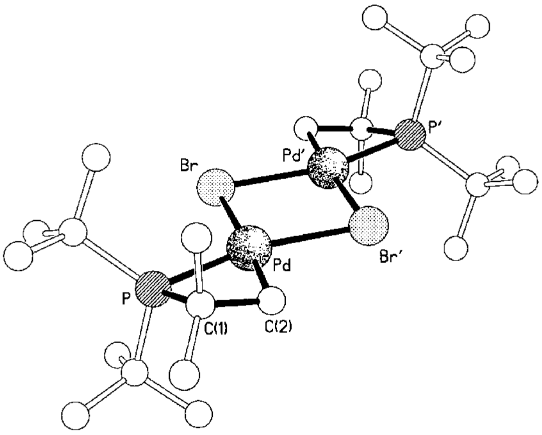

Fig. 2 The molecular structure of **4**. Selected bond lengths (Å) and angles (°): Pd–C(2) 2.048(8), Pd–P 2.215(2), Pd–Br′ 2.5497(11), Pd–Br 2.5922(12), P–Pd–C(2) 69.6(2), Br–Pd–Br′ 88.30(4), Pd–Br–Pd′ 91.70(4). There is a 25° out of plane fold about the P··C(2) vector in the $PdPC_2$ ring.

Interestingly when the oxygenation reaction was attempted with the analogous iodo-dimer $[Pd_2(\mu\text{-}I)_2(PBu^t{}_3)_2]$, no reaction was observed. As we have reported previously, dimer **1** tends to be much more reactive than **2** towards small molecules such as CO, H_2, CNR and alkynes.[11] In the present investigation, this difference in reactivity has once again been observed.

The results presented here have demonstrated the ability of a Pd(I) dimer to react with aerial oxygen. In this process, three transformations seem to be taking place: *(i)* coordination of an O_2 molecule and cleavage on an O=O bond, *(ii)* intramolecular activation of two C–H bonds and *(iii)* formation of two new C–O bonds. To our knowledge, this is the first example of a palladium compound in which such a process has been demonstrated by crystallographic characterisation. The mechanistic aspects of this reaction are yet to be studied. For example an important question that remains to be answered is whether the two oxygen atoms come from the same O_2 molecule or from two different ones. Also important will be to establish the exact mechanism by which the reaction occurs and the fate of the two hydrogen atoms lost in the activation of the C–H bond. Experiments are currently in progress to attempt to provide answers to these questions.

Notes and references

† *Spectroscopic data* for **3**: ^1H-NMR (C_6D_6): δ 1.63 [9H, d, $C(CH_3)_3$], 1.58 [3H, d, $C(CH_3)_2$], 1.50 (1H, d, CH_2). $^{31}P\{^1H\}$ NMR $\{(CD_3)_2CO\}$: δ 108.0 (s). Elemental analysis. Calc. for $C_{24}H_{52}O_2P_2Br_2Pd_2$: C, 35.6; H, 6.7. Found: C, 35.9; H, 6.8%.

‡ *Crystal data*: for **3**: $C_{24}H_{52}O_2P_2Br_2Pd_2$, M = 807.2, monoclinic, space group $P2_1/c$ (no. 14), a = 15.668(1), b = 14.187(1), c = 15.099(1) Å, β = 113.44(1)°, V = 3079.1(3) Å^3, Z = 4, D_c = 1.741 g cm^{-3}, μ(Cu-Kα) = 135.8 cm^{-1}, $F(000)$ = 1616, T = 293 K; pale orange platy rhombs, 0.37 × 0.23 × 0.05 mm, Siemens P4/PC diffractometer, graphite-monochromated Cu-Kα radiation, ω-scans, 4568 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give R_1 = 0.043, wR_2 = 0.103 for 3890 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 120°$] and 290 parameters.

For **4**: $C_{24}H_{52}P_2Br_2Pd_2$, M = 775.2, monoclinic, space group $P2_1/c$ (no. 14), a = 7.788(3), b = 15.368(5), c = 13.557(3) Å, β = 105.40(2)°, V = 1564.3(8) Å^3, Z = 2 (the complex has crystallographic C_i symmetry), D_c = 1.646 g cm^{-3}, μ(Mo-Kα) = 38.2 cm^{-1}, $F(000)$ = 776, T = 293 K; orange prisms, 0.27 × 0.13 × 0.05 mm, Siemens P4/PC diffractometer, graphite-monochromated Mo-Kα radiation, ω-scans, 2753 independent reflections. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 to give R_1 = 0.048, wR_2 = 0.089 for 1796 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 136 parameters.

CCDC 182/1713. See http://www.rsc.org/suppdata/cc/b0/b004537n/ for crystallographic files in .cif format.

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