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Synthesis and reactivity of palladium hydrido-solvento complexes, including a key intermediate in the catalytic methoxycarbonylation of ethene to methyl propanoate

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The sequence of reaction steps and the role of each reactant, required for the transformation of the Pd(0) precursor [Pd(d^{t}bpx)(dba)] [d^{t}bpx = 1,2-$(CH_2PBu^t_2)_2C_6H_4$; dba = *trans*,*trans*-$(PhCH{=}CH)_2CO$], **1**, into [Pd(d^{t}bpx)H(MeOH)]$^+$, **2a**, the active Pd(II)-hydride catalyst for the methoxycarbonylation of ethene to methylpropanoate, have been delineated using a combination of spectroscopic and crystallographic methods. The preparation and characterisation of a variety of related complexes are described including some unusual examples involving bidentate sulfonate complexes and mono-cationic and neutral palladium hydride complexes. X-Ray crystal structures have been determined for [Pd(d^{t}bpx)(η^2-O_2)], **3**, [Pd(d^{t}bpx)(η^2-BQ)] (BQ = benzoquinone), **4**, [Pd(dcpx)(dbaH)]$^+$ [dcpx = 1,2-$(CH_2PCy_2)_2C_6H_4$], **7**, and [Pd(d^{t}bpx)(η^2-$MeSO_3$)]$^+$, **9b**.

Introduction

Palladium complexes are widely used in catalysis,[1] examples include the Heck reaction,[2] the Wacker process[3] and the alkoxycarbonylation of alkenes.[4] In several of these catalytic processes, palladium-hydrides have been claimed to be involved as key intermediates in the catalytic cycle.[5] Nevertheless, it has always been difficult to unambiguously prove their presence under catalytic conditions. Moreover, palladium-hydrides are usually quite reactive and unstable species, especially in the presence of labile ligands, such as weakly coordinating solvent molecules.[6] We have recently reported the synthesis and characterisation of [Pd(d^{t}bpx)H(MeOH)]$^+$ [d^{t}bpx = 1,2-$(CH_2PBu^t_2)_2C_6H_4$],[7] a rare example of a stable Pd(II)-hydride containing both a chelating diphosphine ligand and a coordinated solvent molecule. This complex is a key intermediate in the catalytic system based on [Pd(d^{t}bpx)(dba)] [dba = *trans*,*trans*-$(PhCH{=}CH)_2CO$], **1**, and $MeSO_3H$ used by Lucite International for the highly selective methoxycarbonylation of ethene to give methylpropanoate (MP),[8] a reaction which we have clearly shown to proceed *via* a hydride catalytic cycle.[7] Circumstantial evidence for the involvement of a Pd–H species in the catalytic methoxycarbonylation of ethene to MP has also been reported by Toniolo *et al.*[9] for a related precursor system containing a monodentate phosphine $[Pd(PPh_3)_2(\eta^1\text{-}OTs)_2]/PPh_3/TsOH$ (Ts = *p*-toluenesulfonate), although in this case spectroscopic studies aimed at the identification and structural elucidation of the catalytic intermediates were not carried out. Herein, we report a detailed study on the genesis, stability and reactivity of [Pd(d^{t}bpx)H(MeOH)]$^+$, **2a**, and related complexes.

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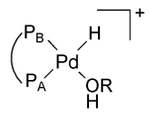
Results and discussion

Synthesis of [Pd(d^{t}bpx)H(MeOH)][TfO], 2a[TfO]

The hydride complex [Pd(d^{t}bpx)H(MeOH)][TfO], **2a**[TfO], can be obtained easily by mixing [Pd(d^{t}bpx)(dba)], **1**, TfOH (2–5 equivalents) and benzoquinone (BQ, 1 equivalent) in MeOH. Analogous compounds [Pd(d^{t}bpx)H(solv)]$^+$ (solv = EtOH, **2b**; ^{n}PrOH, **2c**; ^{i}PrOH, **2d**), containing other primary or secondary alcohols coordinated to the metal, can be obtained in a similar manner, using the appropriate alcohol as solvent instead of MeOH. All these complexes have been characterised in solution by NMR spectroscopy (see Table 1). The NMR data clearly show the presence of two *cis*-P atoms and a hydride ligand *trans* to the lower frequency resonance (P_A). The fact that the NMR data and in particular the chemical shift of P_B are clearly

Table 1 $^{31}P\{^1H\}$ NMR data for [Pd(d^{t}bpx)H(ROH)]$^+$ in ROH at 293 K unless otherwise stated



ROH	δP_A	δP_B	$^2J(P_A–P_B)$/Hz
MeOH, **2a**[a]	25.8	77.5	17.0
EtOH, **2b**	23.9	73.9	17.3
^{n}PrOH, **2c**	24.4	74.1	17.0
^{i}PrOH, **2d**	24.4	72.9	18.8
MeOH, **2a**[b]	21.8	75.5	16.1
^{n}PrOH, **2c**[b]	19.4	68.5	br

[a] Supplementary NMR data: $\delta(H) = -10.0$, $^2J(P_A–H) = 181$ Hz, $^2J(P_B–H) = 22.0$ Hz. [b] At 193 K.

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solvent-dependent suggests that a solvent molecule occupies the fourth coordination site.

The formation of the hydrides **2a**–**d** from **1** requires the co-presence of an acid, a primary or secondary alcohol and an oxidant which can be either oxygen or BQ. Alternatively, the oxidant can be incorporated into the starting Pd(0)-complex. Thus, [Pd(d^{t}bpx)(η^2-O_2)], **3**, and [Pd(d^{t}bpx)(η^2-BQ)], **4**, react with a primary or secondary alcohol in the presence of TfOH to give **2a**–**d**. This contrasts with the reaction of **1** with TfOH in the absence of any oxidant; this latter reaction results in the formation of [Pd(d^{t}bpx)(dbaH)]$^+$, **5**, which has been characterised by VT NMR spectroscopy. For **5**, there is the possibility of a large number of conformers and the $^{31}P\{^1H\}$ NMR spectrum of **5** in MeOH at 193 K consists of four sets of doublets [δP = 38.5 (d, J = 48.0 Hz), 43.6 (d, J = 48.0 Hz), 59.3 (d, J = 48.0 Hz), 65.3 (d, J = 48.0 Hz)] due to the presence of two of the possible conformers; with increasing temperature, coalescence occurs and at 353 K the spectrum consists of two time-averaged doublets [δP = 41.2 (d, J = 48.0 Hz) 62.3 (d, J = 48.0 Hz)] due to the rapid inter-conversion of the two conformers, which differ only in the relative orientation of the d^{t}bpx and dbaH ligands. Consistent with this assumption, the NMR spectra do not change significantly on replacing TfO^- with TsO^-, $MeSO_3^-$ or BF_4^- or on changing the solvent (*e.g.* MeOH, THF, CH_2Cl_2); thus, a direct interaction between the anion or the solvent and the metal does not seem to be involved.

Attempts to obtain suitable crystals of **5** for X-ray diffraction were unsuccessful, but protonation of the analogous complex [Pd(dcpx)(dba)] [dcpx = 1,2-$(CH_2PCy_2)_2C_6H_4$], **6**, results in the formation of [Pd(dcpx)(dbaH)]$^+$, **7**, which has been fully characterised in the solid state as the adduct [Pd(dcpx)(dbaH)]-[$MeSO_3$][$MeSO_3$H][THF]$_2$ (see Fig. 1); this structure represents

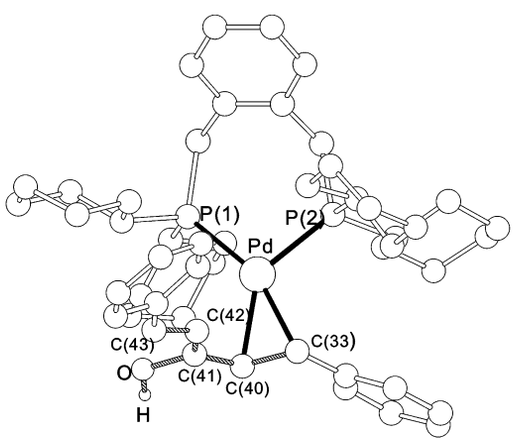


Fig. 1 Molecular structure of [Pd(dcpx)(dbaH)]$^+$, **7**, with key atoms labelled (all H atoms, apart from the C=O ··· H on the dba ligand, have been omitted).

one of the many possible conformers and, at low temperatures, the NMR spectra show the presence of three conformers (see Experimental). The difference in the number of observed conformers in the low temperature spectrum of **5** and **7** probably stems from the different rigidities of the Bu^t- and Cy-groups in **5** and **7** respectively and for **7** there is no coalescence, only broadening, of all these resonances up to room temperature. Selected bond lengths and angles for **7** are given in Table 2. Palladium, the two phosphorus and the two coordinated carbon atoms are almost coplanar; as a result of protonating the oxygen atom in the dba ligand, the C–O bond in **7** is longer than in **6** (1.348 Å *vs.* 1.244 Å).[10]

Finally, **2a**–**d** can also be obtained by dissolving [Pd(d^{t}bpx)-(η^1-OTf)$_2$], **8a**, in a primary or secondary alcohol. This confirms that the presence of both the acid and an oxidant in the previous two synthetic routes (see Scheme 1) is required

Table 2 Selected bond lengths (Å) and angles (°) for [Pd(dcpx)-(dbaH)]$^+$, **7**

Pd–P2	2.305(13)	C40–C41	1.406(7)
Pd–P1	2.353(13)	C41–C42	1.448(7)
Pd–C33	2.158(5)	C44–C43	1.342(7)
Pd–C40	2.213(5)	C41–O1	1.348(6)
C33–C40	1.426(7)	O1–H	0.819(16)
P2–Pd–P1	101.04(5)	P2–Pd–C40	119.90(13)
P2–Pd–C33	100.58(13)	C33–C40–C41	123.4(5)
P2–Pd–C40	138.18(13)	C40–C41–C42	123.7(4)
C33–Pd–C40	38.07(18)	C41–C42–C43	124.9 (5)
P1–Pd–C33	157.93(14)		

Table 3 Selected bond lengths (Å) and angles (°)

a) [Pd(d^{t}bpx)(η^2-O_2)], **3**			
Pd–O(1)	2.0130(16)	Pd–O(2)	2.0187(16)
Pd–P(1)	2.2694(6)	Pd–P(2)	2.2865(6)
O(1)–O(2)	1.443(3)		
O(1)–Pd–O(2)	41.95(7)	P(1)–Pd–P(2)	102.50(2)
b) [Pd(d^{t}bpx)(η^2-BQ)], **4**			
Pd–C(1)	2.179(7)	Pd–C(2)	2.187(7)
Pd–P(1)	2.356(2)	Pd–P(2)	2.364(2)
C(1)–C(2)	1.425(10)	C(4)–C(5)	1.343(11)
C(6)–O(1)	1.241(9)	C(3)–O(2)	1.271(9)
C(1)–Pd–C(2)	38.1(3)	P(1)–Pd–P(2)	104.53(7)

to transform the starting Pd(0)-complex into an appropriate Pd(II)-precursor of the hydride.

Crystal structures of [Pd(d^{t}bpx)(η^2-O_2)], 3, and [Pd(d^{t}bpx)(η^2-BQ)], 4

[Pd(d^{t}bpx)(η^2-O_2)], **3**, and [Pd(d^{t}bpx)(η^2-BQ)], **4**, can be obtained easily by displacement of dba from [Pd(d^{t}bpx)(dba)], **1**, in the presence of an excess of O_2 and BQ, respectively. Crystals suitable for X-ray analysis have been obtained in both cases. Selected bond lengths and angles are given in Table 3. Both contain palladium in a distorted square planar coordination geometry if the O_2 and benzoquinone (BQ) ligands are considered to occupy two coordination sites, or trigonal planar if they each occupy only one site (Figs. 2 and 3). The structure

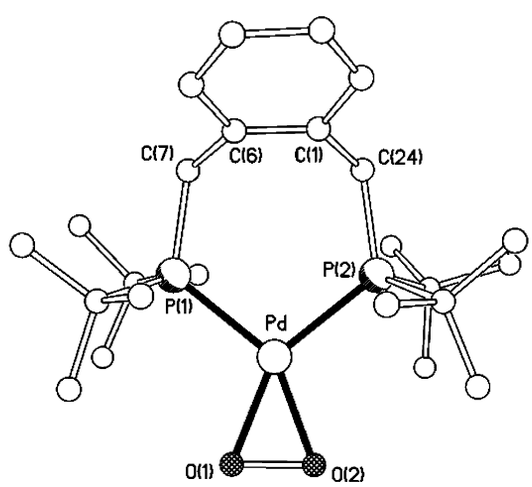
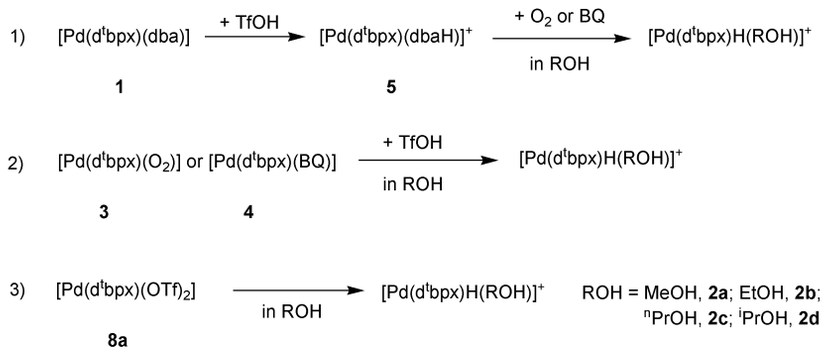


Fig. 2 Molecular structure of [Pd(d^{t}bpx)(η^2-O_2)], **3**, without H atoms and with key atoms labelled.

of **3** (Fig. 2) contains an η^2-O_2; there is a small twist (4.7°) between the PdO_2 and PdP_2 planes and a dihedral angle of 122.2° between the C_6H_4-plane in the diphosphine ligand and the PdP_2 plane. The O–O distance of 1.443(3) Å differs somewhat from that (1.372 Å) observed in the only other previously



Scheme 1

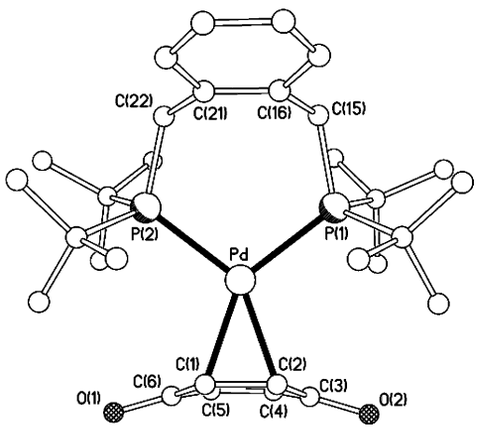


Fig. 3 Molecular structure of [Pd(d^{t}bpx)(η^2-BQ)], **4**, without H atoms and with key atoms labelled.

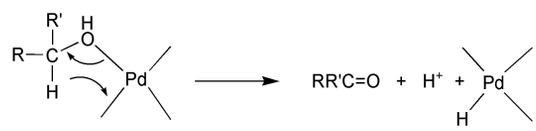
reported palladium diphosphine complex containing dioxygen.[11] However, there is considerable variation in the O–O distance in related complexes of platinum,[12] which reflects a flexible electronic behaviour of the dioxygen ligand that may be considered to be O_2, O_2^-, O_2^{2-}, or of some intermediate character. In complex **4** (Fig. 3) one C=C bond of the BQ ligand is η^2-coordinated to palladium. This bond is significantly longer than the uncoordinated C=C bond [1.404(4) *vs.* 1.378(4) Å]. The BQ ligand is bowed, with the two C=O bonds inclined away from the palladium atom, making angles of 15.9 and 16.1° with the mean plane of the six-membered ring of carbon atoms. The ligand has a dihedral angle of 95.4° to the PdC_2 coordination triangle, in keeping with the η^2-coordination of an alkene. A similar arrangement has been found in other BQ complexes of palladium and platinum.[13] There is a small twist (9.3°) between the PdC_2 and PdP_2 planes. The dihedral angle (121.4°) of the aromatic C_6H_4-linking unit in the diphosphine ligand and the coordination plane of the ligand is in the region generally observed for complexes containing either this ligand or related ligands containing different substituents on the phosphorus atoms.[14]

Solvent effects on the synthesis of [Pd(d^{t}bpx)H(solv)][TfO]

The choice of solvent is very important in the formation of the Pd–H species. Thus, the three different syntheses reported in Scheme 1 are only effective when a primary or secondary alcohol (*e.g.* MeOH, EtOH, ^{n}PrOH, ^{i}PrOH) is employed; no hydride is observed when either a tertiary alcohol (*e.g.* ^{t}BuOH) or non-alcoholic solvents (*e.g.* THF, CH_2Cl_2, CH_3CN, EtCN, MP, acetone) are used. The sole exception is CF_3CH_2OH which, although a primary alcohol, does not yield a detectable hydride.

It is important to note that during the synthesis of [Pd(d^{t}bpx)H(^{i}PrOH)]$^+$, **2d**, the formation of acetone has been detected *via* IR and ^{13}C NMR spectroscopy. The alcohol acts as a reactant in the hydride formation [see eqn. (1)] and this explains why the choice of solvent is so important.

It seems likely that the hydride is formed *via* β-hydride elimination from a molecule of alcohol coordinated to the metal (see Scheme 2) resulting in oxidation of the alcohol to



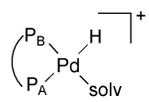
Scheme 2

either an aldehyde or a ketone. The reason that no hydride is formed in CF_3CH_2OH is probably related to the presence of the very strongly electron withdrawing trifluoromethyl group which makes it more difficult to oxidise. It is interesting to note that it is also possible to obtain a hydride complex even in a mixture of THF/H_2O. In this case, the hydride is formed by oxidation of water [eqn. (2)]; gas evolution (*i.e.* O_2) is observed during this reaction.

The hydride cannot be formed directly in non-alcoholic solvents. Nevertheless, it is still possible to obtain hydride complexes in such solvents by, for example, dissolution of **8a** in MeOH, followed by removal of MeOH *in vacuo* and dissolution of the residue in the solvent. New complexes, [Pd(d^{t}bpx)H(solv)]$^+$ (solv = THF, **2f**; CH_3CN, **2g**; EtCN, **2h**; MP, **2i**), have been obtained in this way and characterised by NMR spectroscopy (see Table 4); the chemical shift of P_B is once again found to be strongly solvent dependent, consistent with solvent coordination.

When the direct syntheses reported in Scheme 1 are undertaken in a dry non-alcoholic solvent, the product is either [Pd(d^{t}bpx)(η^2-TfO)]$^+$, **9a**, or [Pd(d^{t}bpx)(solv)$_2$]$^{2+}$ (solv = CH_3CN, **10a**; EtCN, **10b**; MP, **10c**), depending on the reaction conditions. The ^{31}P{^{1}H} NMR spectrum of **9a** (see below for its full

Table 4 ^{31}P{^{1}H} NMR data for [Pd(d^{t}bpx)H(solv)]$^+$ in different solvents at 293 K unless otherwise stated



Solvent	δP_A	δP_B	$^2J(P_A–P_B)$/Hz
THF, **2f**[a]	21.3	69.7	18.3
CH_3CN, **2g**[b]	23.9	68.8	19.8
EtCN, **2h**[c]	23.0	69.4	19.6
MP, **2i**[d]	24.3	72.7	18.6
THF, **2f**[e]	21.6	72.8	18.1
EtCN, **2h**[e]	21.1	67.1	19.8

[a] δ(H) = −12.4, $^2J(P_A–H)$ = 184 Hz, $^2J(P_B–H)$ = 28.3 Hz. [b] δ(H) = −9.1, $^2J(P_A–H)$ = 185 Hz, $^2J(P_B–H)$ = 21.6 Hz. [c] $^2J(P_A–H)$ = 189 Hz. [d] $^2J(P_A–H)$ = 183 Hz. [e] At 193 K.

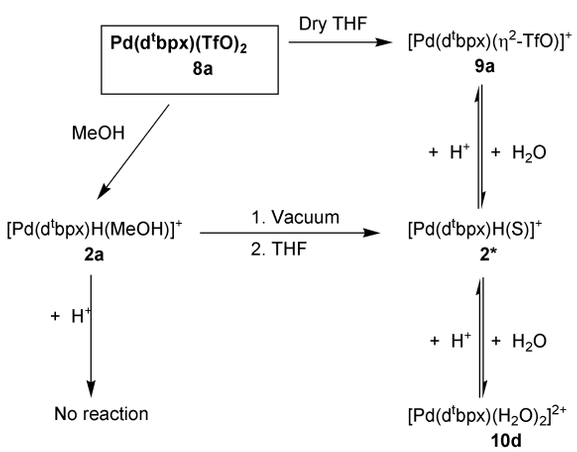
$$[Pd(d^tbpx)(\eta^1\text{-}OTf)_2] + 2CH_3CH(OH)CH_3 \rightarrow [Pd(d^tbpx)H(^iPrOH)]^+ + CH_3C(O)CH_3 + TfOH + TfO^- \quad (1)$$
8a **2d**

$$[Pd(d^tbpx)(\eta^1\text{-}OTf)_2] + 2H_2O \rightarrow [Pd(d^tbpx)H(H_2O)]^+ + 0.5O_2 + TfOH + TfO^- \quad (2)$$
8a **2e**

$$[Pd(d^tbpx)(\eta^1\text{-}OTf)_2] + MP \rightleftharpoons [Pd(d^tbpx)(\eta^2\text{-}OTf)]^+ \rightleftharpoons [Pd(d^tbpx)(MP)_2]^{2+} + 2TfO^- \quad (3)$$
8a **9a** **10c**

characterisation) in THF consists of a singlet at 80 ppm, whereas, in contrast, dissolution of **8a** in CH_3CN or EtCN gives a species with a ^{31}P resonance at 58 ppm. Since the resonances associated with **9a** and **10** are very different and, because of the high coordination ability of nitriles, it is reasonable to conclude that the species present in CH_3CN and EtCN are **10a** and **10b**, respectively.

Further information on the formation of the hydride and its stability can be obtained using mixtures of THF/H_2O and MP/MeOH. **8a** dissolves partially in dry THF to give **9a**. As described above, the hydride **2f** can be obtained in THF by synthesising **2a** in MeOH in the absence of free acid, evaporating the solution to dryness *in vacuo* and dissolving the residue in THF. It is also possible to obtain a hydride in THF by careful addition of water to a THF solution of **9a**. The complex so formed is $[Pd(d^tbpx)H(H_2O)]^+$, **2e** (for its spectroscopic characterisation see below); once formed, **2e** further reacts with water to give $[Pd(d^tbpx)(H_2O)_2]^{2+}$, **10d** (see Scheme 3). All of these

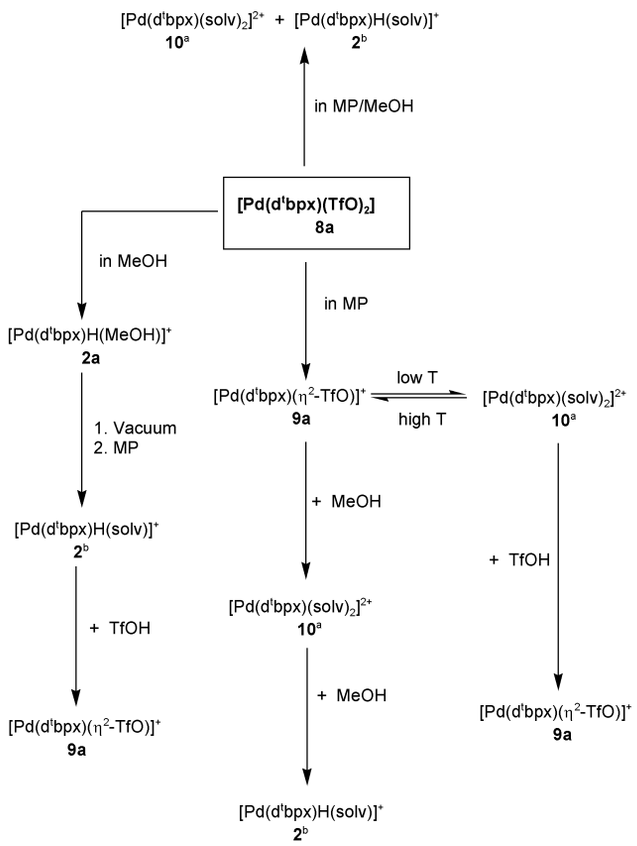


* S = THF, **2f**; H_2O, **2e**

Scheme 3

reactions can be partially reversed by addition of TfOH. It is sufficient to add 6–7 equivalents of acid to a THF solution of the hydride in order to convert it almost completely into **9a**; gas evolution (probably H_2) is observed during this reaction. This last step can be reversed by addition of water. Hence, there is a three-component, two-equilibria system in THF, involving **9a**, the hydrides $[Pd(d^tbpx)H(solv)]^+$ (solv = THF, **2f**; H_2O, **2e**) and **10d**. The predominant species in solution is dependent on the ratio of acid to water. The only limitation to the complete reversibility of the system is the low solubility of these complexes when excess water is used.

The behaviour in MP is quite similar to that found in THF. The reaction of **1** with TfOH and BQ (or O_2) in MP results in the formation of **9a**, which reacts with MeOH to give $[Pd(d^tbpx)(MeOH)_2]^{2+}$, **10e**. Further addition of MeOH results in the formation of the hydride. This result is important because it demonstrates that **10e** is a precursor in the hydride formation. Presumably, activation of MeOH occurs *via* coordination to the metal followed by an intramolecular redox process to give the Pd–H species, **2a** (see Scheme 4).



[a] solv = MeOH, **10e**; MP, **10c**
[b] solv = MeOH, **2a**; MP, **2i**

Scheme 4

Dissolution of **8a** in pure MP results in the formation of **9a** ($\delta P = 81$); on cooling to 193 K, **10c** ($\delta P = 52$) is formed. Hence, an equilibrium sandwiched between these two species exists in solution [eqn. (3)], the exact position of which depends on both the temperature and the amount of acid present.

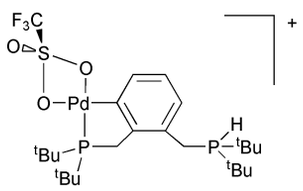
A hydride species may also be obtained in MP by synthesising **2a** in MeOH in the absence of free acid, evaporating the solvent *in vacuo* and dissolution of the residue in MP. Similar to the behaviour in THF, the stability of the hydride decreases on addition of TfOH. In all cases, **9a** forms slowly in the absence of acid, suggesting that the presence of the hydride in pure MP is more likely a consequence of kinetic rather than thermodynamic factors. Interestingly, dissolution of **8a** in MP/MeOH results in the formation of a mixture of **10e** and **2a**, their relative amounts depending on the MP/MeOH ratio. **9a** is the only species present at room temperature in pure MP. On addition of MeOH, **10e** is first formed, followed by the appearance of the hydride; in a MeOH rich solution, the hydride is the predominant species present.

Reactivity of [Pd(d^tbpx)H(MeOH)][TfO], 2a[TfO], towards oxidants

Palladium hydrides are usually very air sensitive.[6] Nevertheless, **2a** can be obtained by bubbling O_2 for *ca.* 20 minutes through a

solution of **1** in MeOH at room temperature in the presence of TfOH. This reaction is very clean, giving **2a** as the only product, and no further reaction occurs even on bubbling O_2 for a further hour.

As reported above, it is also possible to obtain **2a** by addition of BQ to a solution of **1** in MeOH in the presence of TfOH. The reaction goes to completion in a few minutes, and the best results have been obtained using 1–7 moles of BQ per mole of palladium; **2a** is the only product formed under these conditions and is in direct contrast to Toniolo's results[9] on analogous reactions involving palladium complexes containing PPh_3. NMR measurements on solutions of **2**, containing > 1 but < 7 equivalents of BQ per Pd show the presence of free BQ, which does not appear to be involved in any dynamic exchange, but in the presence of additional BQ a second species, which has two singlets at 42.4 and 105.6 ppm in the $^{31}P\{^1H\}$ NMR spectrum, starts to appear. The resonance at lower frequency is split into a doublet [^1J(P–H) = 460 Hz] in the ^{31}P spectrum. This species can be formulated as $[Pd\{\eta^2\text{-}PBu^t_2CH_2C_6H_3CH_2PHBu^t_2\}(\eta^2\text{-}TfO)]^+$ (see Scheme 5), **11**, by analogy with the NMR



11

Scheme 5

data of a closely related compound, *i.e.* $[Pd\{\eta^2\text{-}PBu^t_2CH_2\text{-}C_6H_2(OCH_3)CH_2PBu^t_2\}(\mu\text{-}Br)]_2$, **12**, which was characterised by ^{31}P NMR (105 ppm, s) and X-ray diffraction.[15] The complete conversion of **2a** into **11** requires *ca.* 50 equivalents of BQ per equivalent of palladium.

Metalation of the phosphine ligand is not an unusual reaction in palladium chemistry, particularly for palladium-hydrides.[16–18] Nevertheless, it is quite unusual to observe such a reaction that is promoted by an oxidant such as BQ; previous reports have suggested that quinones react with palladium-hydride complexes in MeOH to form Pd–OMe compounds.[9,19]

Substitution reactions

Complex **2a** is a very useful starting material for the preparation of other palladium-hydride complexes *via* substitution of the coordinated MeOH with other ligands. We have already examined the replacement of MeOH by other solvent molecules to give **2b**–**i**. The aquo-hydrido complex **2e** can be obtained in MeOH by addition of an excess of water, or in THF using traces of water. Moreover, **2a** reacts in MeOH with $[Me_4N]X$ (X = Cl, Br, I) to give $[Pd(d^tbpx)HX]$ (X = Cl, **2j**; Br, **2k**; I, **2l**). In the same way, $[Pd(d^tbpx)H(py)]^+$ (py = pyridine), **2m**, $[Pd(d^tbpx)H(PPh_3)]^+$, **2n**, and $[Pd(d^tbpx)H(PPh_2H)]^+$, **2o**, can be obtained by addition of py, PPh_3 and PPh_2H, respectively, to a solution of **2a** in MeOH. Finally, addition of ^{12}CO or ^{13}CO to **2a** at 198 K results in the formation of $[Pd(d^tbpx)H(CO)]^+$, **2p**, and $[Pd(d^tbpx)H(^{13}CO)]^+$, **2q**, respectively. All these compounds have been characterised spectroscopically by multinuclear NMR measurements (see Table 5); none show any exchange process in the range 173–293 K.

The formation of the apparently closely related complexes **2a**–**q** occurs with quite different stoichiometries of reagents. Thus, the formation of **2a**–**d** and **2f**–**i** requires the use of a solvent which coordinates to the metal as a ligand. The formation of **2a**–**d** occurs either in the presence or in the absence of acid, whereas **2f**–**i** is formed only in the absence of acid; in the presence of acid, **9a** (in THF and MP) and **10a**–**b** (CH_3CN and EtCN) are formed respectively. The formation of **2e** in THF requires the addition of a few equivalents of water, the exact amount depending on the amount of free acid present. Further addition of water results in the formation of **10d**. This should be compared with the same reaction in MeOH, which requires the addition of a large excess of water to give **2e** and, in contrast to the reaction in THF, no further reaction has been observed. Complexes **2j**–**l** have been obtained always as a mixture together with $[Pd(d^tbpx)X_2]$ (X = Cl, **13a**; Br, **13b**; I, **13c**). The formation of **2n**–**o** requires the addition of exactly one equivalent of the phosphine, whereas 5–10 equivalents of py have been used for the synthesis of **2m**. Further addition of py results in the formation of $[Pd(d^tbpx)(py)_2]^{2+}$, **10f**. The NMR data for all these dicationic and neutral palladium-complexes are reported in Table 6. The formation of such complexes, formally, involves displacement of hydride by a neutral or anionic ligand (*i.e.* H_2O, Py, Cl^-, Br^-, I^-) followed by further reaction with a proton to give H_2. Related reactions have been reported for other palladium-hydride complexes. For instance, $[Pd(PEt_3)_2HCl]$[20] reacts progressively with KCN in MeOH to give $[Pd(PEt_3)_2H(CN)]$ (one equivalent of KCN) and then $[Pd(PEt_3)_2(CN)_2]$ (two equivalents of KCN) together with H_2 evolution; in this case, it was proposed that the proton originates from methanol [eqn. (4)].

$$[Pd(PEt_3)_2HCl] + 2KCN + MeOH \longrightarrow [Pd(PEt_3)_2(CN)_2] + H_2 + KCl + KOMe \quad (4)$$

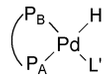
The effect of the acid on hydride formation

It has been shown that the reaction of **1** in MeOH with BQ and TfOH results in the formation of $[Pd(d^tbpx)H(MeOH)]^+$, **2a**. The choice of the acid is of paramount importance in determining the course of this reaction. When an acid containing a strongly coordinating anion (*e.g.* HCl and CF_3CO_2H) is used, $[Pd(d^tbpx)Cl_2]$, **13a**, and $[Pd(d^tbpx)(O(O)CCF_3)_2]$, **13d**, are formed. However, when the reaction of **1** in MeOH is carried out in the presence of an acid containing a very weakly coordinating anion (*e.g.* HBF_4), the hydride **2a** is formed. The analogous reactions of $MeSO_3H$ and TsOH are quite different, since neither **2a**, nor $[Pd(d^tbpx)(\eta^1\text{-}MeSO_3)_2]$, **8b**, nor $[Pd(d^tbpx)(\eta^1\text{-}TsO)_2]$, **8c**, are formed; instead, the species $[Pd(d^tbpx)(\eta^2\text{-}MeSO_3)]^+$, **9b**, and $[Pd(d^tbpx)(\eta^2\text{-}TsO)]^+$, **9c**, which are analogous to **9a**, have been identified. Both these compounds are structurally related to **9a**, but their chemistry is different. In fact, **9a** can be observed only in non-polar or weakly polar solvents (*i.e.* THF, MP, CH_2Cl_2), whereas **9b** and **9c** are stable in all the solvents studied (*i.e.* THF, MP, CH_2Cl_2, MeOH, acetone); partial dissociation is only observed in CH_3CN.

Diffusion of n-hexane into THF solutions containing any of **9a**–**c** in each case gave crystals but, unfortunately, only the X-ray data of **9b** are of sufficiently good quality and show the formation of $[Pd(d^tbpx)(\eta^2\text{-}MeSO_3)][MeSO_3][MeSO_3H]$ (see Fig. 4). Selected bond lengths and angles for **9b** are given in Table 7. The anion is actually a dimer due to the interaction of the methanesulfonate anion with a molecule of methanesulfonic acid *via* a hydrogen bond. The cation is nearly square-planar, and it is worthwhile noting that the two phosphorus, palladium, both oxygens coordinated to the metal and the sulfur atoms are approximately co-planar. The bond angles deviate from ideal square-planar geometry: the P1–Pd–P2 angle is 100.59(6)°, whereas O1–Pd–O2 is 65.7(1)°. The resulting local symmetry around the metal centre is nearly C_{2v} and the benzene ring of d^tbpx and the methyl group of $MeSO_3^-$ adopt a pseudo-*trans* configuration with respect to the square planar ligand geometry around palladium.

To the best of our knowledge, the structure of a palladium complex containing a chelating sulfonate anion has not been

Table 5 NMR data for $[Pd(d^tbpx)HL']^{n+}$ ($n = 0$ or 1) in MeOH at 293 K unless otherwise stated



L′	δP_A	δP_B	δH	$^2J(P_AP_B)$/Hz	$^2J(P_AH)$/Hz	$^2J(P_BH)$/Hz
MeOH, **2a**	23.9	75.7	−10.0	16.0	181	22.0
H_2O, **2e**	22.4	72.9	–[a]	br	190	–[a]
H_2O, **2e**[b]	23.1	71.7	–[a]	18.3	186	–[a]
Cl^-, **2j**	20.0	67.2	−10.4	21.6	180.7	28.4
Br^-, **2k**	21.6	67.6	−9.7[c]	21.4[d]	203	26.2[c]
I^-, **2l**	21.0	63.5	−9.3[d]	21.2	182	38.0[d]
py, **2m**	23.3	66.6	−9.4	18.4	182	17.1
PPh_3, **2n**[e]	35.0	60.0	−8.1	27.1	160	23 or 11[f]
PPh_2H, **2o**[g]	32.9	59.2	−6.4	26.4	168.0	Not resolved
CO, **2p**[h]	30.7	60.3	−5.3	21.6	167.4	15.8

[a] ^1H not recorded. [b] in THF at 293 K. [c] in THF at 193 K. [d] In MeOH at 193 K. [e] Supplementary NMR data: $\delta(PPh_3) = 11$, $^2J(PPh_3–P_B) = 330$ Hz, $^2J(PPh_3–P_A) = 26.3$ Hz, $^2J(PPh_3–H) = 23$ or 11 Hz. [f] Impossible to distinguish between the two values due to *cis*-^2J(P–H). [g] Supplementary NMR data: $\delta(PPh_2H) = 5.4$, $\delta(PPh_2H) = 6.6$, $^2J(PPh_2H–P_B) = 327.0$ Hz, $^2J(PPh_2H–P_A) = 33.1$ Hz, $^1J(PPh_2H–H) = 315.0$ Hz. [h] In MeOH at 293 K. Supplementary NMR data for $[Pd(d^tbpx)H(^{13}CO)]^+$, **2q**: $\delta(CO) = 183.3$, $^2J(P_b–C) = 102$ Hz.

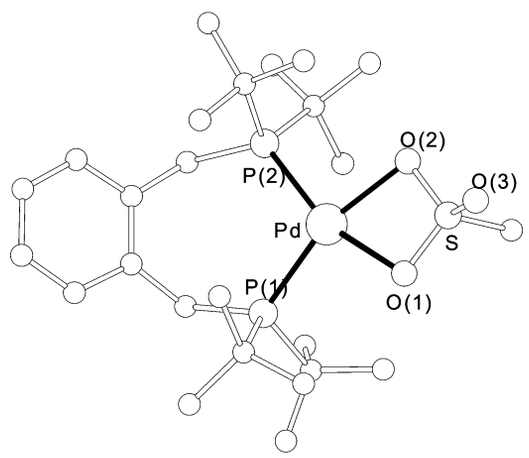


Fig. 4 Molecular structure of $[Pd(d^tbpx)(\eta^2\text{-}MeSO_3)]^+$, **9b**, without H atoms and with key atoms labelled.

reported previously, and examples with other metals are also very rare.[21,22] The coordination of RSO_3^- as a monodentate ligand is more common. As examples, it is worthwhile noting $[Pd(dppp)(H_2O)(\eta^1\text{-}TsO)]^+$,[23] **14a**, and $[Pd(dppp)(H_2O)(\eta^1\text{-}TfO)]^+$,[24] **14b**. In both cases, the Pd–O bond for the sulfonate anion is shorter than in **9b** [2.152(3) Å for **14a** and 2.159(3) Å for **14b** compared to an average value of 2.180 Å for **9b**].

The ^{31}P NMR spectrum at room temperature of all three compounds **9a**–**c** always consists of a singlet which is shifted to higher frequency (*i.e. ca.* 78 ppm for **9a** and *ca.* 70 ppm for **9b**,**c**; the exact shift depends on the solvent) with respect to the dicationic species, $[Pd(d^tbpx)(solv)_2]^{2+}$ (see Table 6). The different behaviour of **9a** compared to **9b**,**c** is probably due to the fact that the coordination of TfO^- is weaker than either $MeSO_3^-$ or TsO^-; thus, TfO^- readily dissociates in polar solvents giving $[Pd(d^tbpx)(solv)_2]^{2+}$, which then further reacts to give a hydride complex in the presence of an alcohol. Dissociation of $MeSO_3^-$ and TsO^-, and hence, the formation of the hydride **2a** in the presence of $MeSO_3H$ or TsOH, requires more forcing conditions; in fact, only partial dissociation is observed even in a polar solvent such as CH_3CN. Thus, reaction of **9b** or **9c** in MeOH with 6–10 equivalents of pyridine results in the nearly complete formation of **2m**. Pyridine is a strong ligand and, therefore, it can coordinate to the metal, forcing the sulfonate anion to pass from η^2- to η^1-coordination. The loss of the additional stabilisation *via* the chelate effect allows ready replacement of RSO_3^- by MeOH, which is activated on coordination to the metal, thus allowing hydride formation.

Table 6 ^{31}P NMR data for $[Pd(d^tbpx)X_2]^{n+}$ ($n = 2$ or 0) at 293 K unless otherwise stated

X	n	Solvent	δP
CH_3CN, **10a**	2	CH_3CN	57.3
EtCN, **10b**	2	EtCN	58.1
MP, **10c**	2	MP[a]	51.9
H_2O, **10d**	2	THF	53.8
MeOH, **10e**	2	MP/MeOH (4 : 1)	60.0
py, **10f**	2	MeOH	48.7
Cl^-, **13a**	0	MeOH	39.3
Br^-, **13b**	0	MeOH[a]	42.9
I^-, **13c**	0	THF	40.0

[a] At 193 K.

Table 7 Selected bond lengths (Å) and angles (°) for $[Pd(d^tbpx)(\eta^2\text{-}MeSO_3)]^+$, **9b**

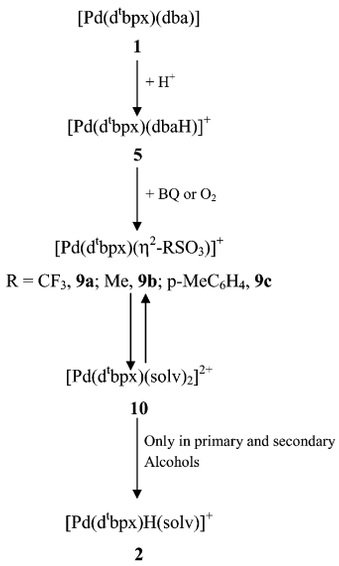
Pd–P2	2.267(2)	Pd–P1	2.274(2)
Pd–O2	2.172(4)	Pd–O1	2.188(4)
P1–Pd–P2	100.59(6)	P1–Pd–O2	163.2(1)
O1–Pd–O2	65.7(1)	O1–Pd–P2	161.0(1)
P2–Pd–O2	95.8(1)	P1–Pd–O1	98.2(1)

Water can be used instead of pyridine, but in this case a large excess is required, probably because water is a weaker ligand than pyridine. Finally, the hydride **2a** can be partially formed by thermal activation of **9b**,**c**. Thus, heating **9b** or **9c** in MeOH to reflux under nitrogen for *ca.* 1 h results in partial formation of the hydride. This result is very important, since it demonstrates that the hydride can be formed in the presence of $MeSO_3H$ at the temperatures required for industrial operation.

Conclusions

This paper reports the synthesis of a wide range of Pd(II)-hydride complexes containing the d^tbpx ligand and a neutral or anionic ligand in the fourth coordination site. In particular, it has been demonstrated that the special diphosphine used in this study can stabilise the hydride even in the presence of weakly coordinating ligands (*e.g.* ROH, THF, MP, H_2O). To the best of our knowledge, no other examples of such complexes have been reported to date; only a few Pd(II)-hydrides containing a diphosphine ligand have been fully characterised,[25–28] and all of them contain a strongly coordinating ligand in the fourth coordination site (*eg.* PR_3, SnR_3^-).

The formation of the hydride **2a** from **1** is not a simple,



Scheme 6

single stage reaction; instead, it involves four sequential steps (Scheme 6). The first reaction involves protonation of **1** to give $[Pd(d^tbpx)(dbaH)]^+$, **5**, which is readily oxidised by O_2 or BQ to give $[Pd(d^tbpx)(\eta^2\text{-}RSO_3)]^+$ (R = CF_3, **9a**; Me, **9b**; *p*-MeC_6H_4, **9c**). The oxidation is very fast at high temperature and, under the industrial operating conditions, traces of O_2 are sufficient to induce this step. The third step involves the displacement of the coordinated RSO_3^- anion and formation of $[Pd(d^tbpx)(solv)_2]^{2+}$. This reaction is an equilibrium and its exact position depends on both the nature of the R-group in the anion and the solvent used. Polar solvents favour the formation of $[Pd(d^tbpx)(solv)_2]^{2+}$, whereas basic R-groups shift the equilibrium towards the formation of $[Pd(d^tbpx)(\eta^2\text{-}RSO_3)]^+$. The final step in the hydride formation is a redox process involving the solvent (Scheme 2). This reaction is irreversible and involves β-hydride elimination from a primary or secondary alcohol coordinated to the metal; only in such solvents is the hydride formed. Thus, MeOH fulfils at least three different roles in the catalytic process for the methoxycarbonylation of ethene to methylpropanoate:

1. it is a reagent in the formation of MP;
2. it is directly involved in the formation of the palladium-hydride $[Pd(d^tbpx)H(MeOH)]^+$, **2a**, which is one of the key catalytic intermediates involved in the methoxycarbonylation of ethene;
3. it stabilises the hydride, probably *via* solvation of the ionic species present in solution and, in particular, H^+. For example, **2f** reacts in THF with H^+ to give **6** and H_2, whereas no reaction is observed in MeOH.

The stability of all the hydrides herein reported is very surprising, especially in the case of the hydrido-solvento complexes **2a**–**e**. For instance, **2a** can be stored in MeOH at room temperature for 2–3 days before decomposition occurs; it has been studied in solution at 353 K, even though under these conditions it decomposes in less than 20 minutes. In the presence of $MeSO_3H$ instead of TfOH, hydride formation is less facile, but at the same time **9b** is stable at 353 K for hours. This difference in stability may account for the preference for $MeSO_3H$ in the catalytic process.

Finally, $[Pd(d^tbpx)H(CO)]^+$ is very unstable even at low temperature, indicating that addition of CO accelerates hydride decomposition. We have shown elsewhere[7] that **2a** reacts with ethene to give $[\overline{Pd(d^tbpx)(CH_2CH_3)}]^+$, one of the intermediates in the catalytic cycle, and the efficiency of the catalytic system is dependent upon the competition between the reaction of **2a** with ethene and CO.

Experimental

General

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and carefully dried solvents. ^{13}C-enriched samples were prepared using standard high vacuum line techniques. All NMR measurements were performed on Bruker AMX200 and AMX400 instruments using commercial probes. The chemical shifts were referenced to external H_3PO_4 (85% in D_2O) for phosphorus, and to internal TMS for carbon and proton. ^1H NMR spectra of metal hydrides dissolved in non-deuterated solvents were recorded using $^1H/^{31}P$ correlations measured *via* zero and double quantum coherences.[29] High temperature NMR measurements were recorded using a 10 mm sapphire tube. All chemicals were used as received from Aldrich Chemical Co., except $[Pd(d^tbpx)(dba)]$, **1**,[8] [Pd(dcpx)(dba)], **6**,[8] and $[Pd(d^tbpx)(\eta^1\text{-}OTf)_2]$, **8a**,[30] which were prepared by published methods. ^{13}CO (99.8%) was purchased from Isotec Inc. Many of the compounds reported below have not been isolated because of their instability and/or because on attempted crystallisation, only oils were obtained. Nevertheless, NMR measurements and detailed isotopic labelling experiments, allow all of these compounds to be formulated unambiguously.

Syntheses

$[Pd(d^tbpx)H(MeOH)][TfO]$, 2a[TfO]. Different synthetic routes are possible.

(a) From [Pd(dᵗbpx)(dba)], 1, and oxygen. To a solution of $[Pd(d^tbpx)(dba)]$ (100 mg, 0.136 mmol) in MeOH (2 ml), TfOH (60.5 μl, 0.680 mmol) was added with a micropipette. Oxygen was bubbled through the solution for *ca.* 20 min when the colour of the solution changed from deep-red to orange–yellow, and the reaction was monitored by NMR spectroscopy until completion.

(b) From [Pd(dᵗbpx)(dba)], 1, and BQ. $[Pd(d^tbpx)(dba)]$ (100 mg, 0.136 mmol) and BQ (29.4 mg, 0.272 mmol) were mixed as solids and degassed under vacuum. The solids were partially dissolved in MeOH (2 ml) followed by addition of TfOH (60.5 μl, 0.680 mmol); NMR measurements showed that **2a**[TfO] was formed in a few minutes.

(c) From [Pd(dᵗbpx)(η²-O₂)], 3. To a suspension of $[Pd(d^tbpx)(\eta^2\text{-}O_2)]$ (72.5 mg, 0.136 mmol) in MeOH (2 ml), TfOH (60.5 μl, 0.680 mmol) was added whereupon the product was formed in a few minutes.

(d) From [Pd(dᵗbpx)(η²-BQ)], 4. The method was the same as in (c) using $[Pd(d^tbpx)(\eta^2\text{-}BQ)]$ instead of $[Pd(d^tbpx)(\eta^2\text{-}O_2)]$.

(e) From [Pd(dᵗbpx)(η¹-OTf)₂], 8a. $[Pd(d^tbpx)(\eta^1\text{-}OTf)_2]$ (100 mg, 0.125 mmol) was dissolved in MeOH (2 ml) and the hydride **2a**[TfO] was formed immediately. $^{31}P\{^1H\}$ NMR (MeOH, 293 K): δ 25.8 (d, *J* 17 Hz), 77.5 (d, *J* 17 Hz). ^{31}P NMR (MeOH, 293 K): δ 25.8 (d, *J* 179.4 Hz), 77.5 (br). ^1H NMR (MeOH, 293 K): δ −10.0 (dd, *J* 179.7 and 14.3 Hz).

$[Pd(d^tbpx)H(ROH)][TfO]$ (ROH = EtOH, 2b[TfO]; ^{n}PrOH, 2c[TfO]; ^{i}PrOH, 2d[TfO]). The same methods used for **2a**[TfO] can be adopted, using EtOH, ^{n}PrOH or ^{i}PrOH instead of MeOH. The ^{31}P NMR data are summarised in Table 1.

$[Pd(d^tbpx)H(H_2O)][TfO]$, 2e[TfO]. *(a) Synthesis in MeOH.* To a solution of $[Pd(d^tbpx)(dba)]$ (100 mg, 0.136 mmol) in MeOH (2 ml), BQ (14.7 mg, 0.136 mmol) and TfOH (100 μl, 0.680 mmol) were added, followed by the slow addition of H_2O and the reaction monitored by ^{31}P NMR spectroscopy. After addition of 2 ml of H_2O, the starting complex **2a** was completely converted into **2e**. $^{31}P\{^1H\}$ NMR (MeOH, 293 K): δ 22.4 (br), 72.9 (br). ^{31}P NMR (MeOH, 293 K): δ 22.4 (d, *J* 190 Hz), 72.9 (br).

(b) Synthesis in THF. A solution of $[Pd(d^tbpx)H(THF)]^+$ (0.136 mmol) in THF (2 ml) was prepared as described above, followed by addition of H_2O (5.00 μl, 0.278 mmol); further addition of water resulted in the formation of $[Pd(d^tbpx)(H_2O)_2]^{2+}$. $^{31}P\{^1H\}$ NMR (THF, 293 K): δ 23.1 (d, *J* 18.3 Hz), 71.7 (br d, *J* 18.3 Hz). ^{31}P NMR (THF, 293 K): δ 23.1 (d, *J* 186 Hz), 71.7 (br).

[Pd(d^{t}bpx)H(solv)][TfO] (solv = THF, 2f[TfO]; CH_3CN, 2g[TfO]; EtCN, 2h[TfO]; MP, 2i[TfO]). A solution of [Pd(d^{t}bpx)H(MeOH)][TfO] (0.136 mmol) in MeOH (2 ml) was prepared as described above. The solvent was removed under vacuum and the residue re-dissolved in the appropriate solvent (2 ml). The product was then analysed using NMR spectroscopy. The best route for the preparation of **2a**[TfO] started from **8a**. The ^{31}P NMR data are summarised in Table 4.

[Pd(d^{t}bpx)HX] (X = Cl, 2j; Br, 2k; I, 2l). $[NMe_4]X$ (X = Cl, Br, I) was added slowly as a solid to a solution of [Pd(d^{t}bpx)H(MeOH)][TfO] in MeOH (2 ml), until all the starting material had completely reacted as shown by NMR spectroscopy. The final products were not very soluble in MeOH. Hence, some of the NMR data have been collected in THF, after evaporation of the solvent *in vacuo* and dissolution of the residue in THF. The ^1H NMR spectrum of [Pd(d^{t}bpx)HI] has been recorded at 193 K, because the compound is not very stable at room temperature. In all the reactions, $[Pd(d^tbpx)X_2]$ was formed as a by-product. ^{31}P NMR data are summarised in Table 5.

[Pd(d^{t}bpx)H(py)][TfO], 2m[TfO]. BQ (14.7 mg, 0.136 mmol) and TfOH (100 μl, 0.680 mmol) were added to a solution of [Pd(d^{t}bpx)(dba)] (100 mg, 0.136 mmol) in MeOH (2 ml), followed by the slow addition of pyridine (52.4 μl, 0.653 mmol). It is preferable to add the pyridine very slowly and to monitor the progress of the reaction by NMR, in order to avoid the formation of $[Pd(d^tbpx)(py)_2]^{2+}$. $^{31}P\{^1H\}$ NMR (MeOH, 293 K): δ 23.3 (d, *J* 18.4 Hz), 66.6 (d, *J* 18.4 Hz). ^{31}P NMR (MeOH, 293 K): δ 23.3 (d, *J* 182 Hz), 66.6 (br). ^1H NMR (MeOH, 293 K): δ −9.4 (dd, *J* 17.1 and 182 Hz).

[Pd(d^{t}bpx)H(PPh_3)][TfO], 2n[TfO]. Solid PPh_3 (28.5 mg, 0.102 mmol) was added to a solution of **2a**[TfO] (0.102 mmol) in MeOH (2 ml), prepared as described above. All the solid dissolved and the solution slightly changed colour from brown–orange to orange–red. The formation of **2n**[TfO] was detected through multinuclear NMR measurements. $^{31}P\{^1H\}$ NMR (MeOH, 293 K): δ 11.0 (dd, *J* 330 and 26.3 Hz), 35.0 (t, *J* 27.1 Hz), 60.0 (dd, 330 and 26.3 Hz). ^{31}P NMR (MeOH, 293 K): δ 11.0 (d, *J* 330 Hz), 35.0 (d, *J* 160 Hz), 60.0 (d, *J* 330 Hz). ^1H NMR (MeOH, 293 K): δ −8.1 (ddd, *J* 160, 23 and 11 Hz).

[Pd(d^{t}bpx)H(PPh_2H)][TfO], 2o[TfO]. The method was the same as for **2n**[TfO] using PPh_2H instead of PPh_3. The NMR data are summarised in Table 5.

[Pd(d^{t}bpx)H(CO)][TfO], 2p. A solution of [Pd(d^{t}bpx)H(MeOH)][TfO] (0.136 mmol) in MeOH (2 ml) was prepared as described above in an NMR tube and cooled in a dry ice/acetone bath, followed by addition of *ca.* one equivalent of CO and the solution was shaken at low temperature. After 30 minutes, the NMR tube was directly transferred from the low temperature bath to the pre-cooled NMR probe and analysed by multinuclear NMR spectroscopy. The analogous compound $[Pd(d^tbpx)H(^{13}CO)]^+$, **2q**, was prepared in a similar way, using ^{13}CO instead of ^{12}CO. The NMR data are reported in Table 5.

[Pd(d^{t}bpx)(η^2-O_2)], 3. Oxygen was bubbled through a solution of [Pd(d^{t}bpx)(dba)] (1.02 g, 1.39 mmol) in THF (30 ml) for *ca.* 30 minutes. The reaction was stopped when full conversion of the starting material into $[Pd(d^tbpx)(\eta^2\text{-}O_2)]$ had occurred as shown by NMR analysis. The product was isolated as an orange solid after addition of pentane. Crystals suitable for X-ray analysis were obtained after recrystallisation from THF/pentane. Yield: 480 mg (67%). Found: C, 54.57; H, 8.64. $C_{24}H_{44}O_2P_2Pd$ requires: C, 54.04; H. 8.26%. $^{31}P\{^1H\}$ NMR (toluene, 293 K): δ 60.1 (s).

[Pd(d^{t}bpx)(η^2-BQ)], 4. BQ (1.18 g, 10.94 mmol) was added to a solution of [Pd(d^{t}bpx)(dba)] (8.01 g, 10.94 mmol) in THF (200 ml). The solution turned bright orange after stirring for 1 h. The reaction solution was stirred for a further 16 h during which time no further colour change occurred. The reaction was fine-filtered to remove palladium metal and the solvent removed under reduced pressure to yield a deep orange–red solid. This was washed with cold hexane (−30 °C) followed by cold ether (−30 °C). The washings were discarded and the remaining solid dried under reduced pressure to yield the product as an orange–red powder. Crystals suitable for X-ray analysis were obtained by recrystallisation from THF layered with heptane. Yield: 3.0 g (45%). Found: C, 59.72; H, 8.07%. $C_{30}H_{48}O_2P_2Pd$ requires: C, 59.20; H, 7.89%. $^{31}P\{^1H\}$ NMR (THF, 293 K): δ 51.4 (s).

[Pd(d^{t}bpx)(dbaH)]X (X = $MeSO_3$, 5[$MeSO_3$]; TfO, 5[TfO]; TsO, 5[TsO]; BF_4, 5[BF_4]). The reaction can be carried out in MeOH, THF, MP or CH_2Cl_2 and, usually, one mole of acid per mole of Pd-complex is sufficient for complete reaction. It is very important to avoid the presence of oxygen in order to prevent the oxidation of **5**. To a solution of [Pd(d^{t}bpx)(dba)] (100 mg, 0.136 mmol) in the appropriate solvent (2 ml of MeOH, THF, MP or CH_2Cl_2), 1 equivalent of the acid HX was added from a micropipette (or as a solid in the case of TsOH). The colour of the solution changed from yellow–orange to deep red, with a concomitant change in the NMR spectrum. $^{31}P\{^1H\}$ NMR (MeOH, 193 K): δ 38.5 (d, *J* 48.0 Hz), 43.6 (d, *J* 48.0 Hz), 59.3 (d, *J* 48.0 Hz), 65.3 (d, *J* 48.0 Hz). $^{31}P\{^1H\}$ NMR (MeOH, 353 K): δ 41.2 (d, *J* 48.0 Hz), 62.3 (d, *J* 48.0 Hz).

[Pd(dcpx)(dbaH)][$MeSO_3$], 7[$MeSO_3$]. Addition of $MeSO_3H$ (77.2 μl, 1.19 mmol) to a solution of [Pd(dcpx)(dba)] (200 mg, 0.238 mmol) in THF (5 ml) gave a deep-red solution. This solution was layered with n-hexane (5 ml) and after one week, some red crystals, which X-ray analysis showed to be $[Pd(dcpx)(dbaH)][MeSO_3][MeSO_3H][THF]_2$, were formed. $^{31}P\{^1H\}$ NMR (MeOH, 193 K): δ 7.5 (d, *J* 71.7 Hz), 11.0 (d, *J* 78.6 Hz), 11.8 (d, *J* 70.2 Hz), 21.7 (d, *J* 69.4 Hz), 23.2 (d, *J* 72.5 Hz), 28.9 (d, *J* 79.4 Hz).

[Pd(d^{t}bpx)(η^2-TfO)][TfO], 9a[TfO]. To a solution of [Pd(d^{t}bpx)(dba)] (65.0 mg, 0.088 mmol) in an appropriate solvent (2 ml of THF, CF_3CH_2OH, CH_2Cl_2, MP or acetone), BQ (65.0 mg, 0.583 mmol) and TfOH (39.0 μl, 0.440 mmol) were added; the resulting orange solution of the product was analysed by ^{31}P NMR spectroscopy. The same product was obtained directly by dissolving $[Pd(d^tbpx)(TfO)_2]$ in the same solvents. $^{31}P\{^1H\}$ NMR (THF, 293 K): δ 80.0 (s). $^{31}P\{^1H\}$ NMR (THF, 193 K): 78.7 (s). $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 293 K): δ 77.0 (s).

[Pd(d^{t}bpx)(η^2-$MeSO_3$)][$MeSO_3$], 9b[$MeSO_3$]. $MeSO_3H$ (45.7 μl, 0.680 mmol) was added *via* a micropipette to a solution of [Pd(d^{t}bpx)(dba)] (100 mg, 0.136 mmol) in an appropriate solvent (2 ml of MeOH, THF, MP, CH_2Cl_2 or acetone). Oxygen was then bubbled through the solution for *ca.* 30 minutes, until the colour of the solution turned from deep-red to pale-yellow. At this point, **9b** was the only species detected in solution by NMR. Alternatively, the same product can be obtained by addition of BQ to the deep-red solution. Crystals suitable for X-ray analysis were obtained by layering the THF solution of **9b** with n-hexane. The compound crystallises as [Pd(d^{t}bpx)(η^2-

Table 8 Data collection and refinement details

Complex	[Pd(d^{t}bpx)(η^2-O_2)] **3**	[Pd(d^{t}bp)(η^2-BQ)] **4**	[Pd(dcpx)(dbaH)][Me-SO_3] [$MeSO_3H$][THF]$_2$ **7**	[Pd(d^{t}bpx)(η^2-$MeSO_3$)] [$MeSO_3$][$MeSO_3H$] **9b**
Formula	$C_{24}H_{44}O_2P_2Pd$	$C_{30}H_{48}O_2P_2Pd$	$C_{59}H_{90}O_9P_2PdS_2$	$C_{27}H_{54}O_9P_2PdS_3$
M	532.9	609.0	1175.95	787.27
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	8.9816(5)	8.725(3)	14.422(3)	11.87(2)
b/Å	19.8520(10)	16.465(6)	15.236(3)	15.410(7)
c/Å	14.5897(8)	21.038(8)	15.695(3)	11.168(6)
a/°	90	90	72.45(3)	109.17(4)
β/°	102.199(2)	94.544(7)	85.34(3)	108.21(7)
γ/°	90	90	65.79(2)	72.06(6)
U/Å^3	2542.6(2)	3012.8(19)	2995.6(11)	1784(3)
Z	4	4	2	2
D_c/g cm^{-3}	1.392	1.343	1.304	1.465
μ/mm^{-1}	0.87	0.75	0.423	0.831
Data measured	15908	15281	15324	4940
Unique data	5916	5301	7168	4668
R_{int}	0.034	0.120	0.086	0.017
Parameters	275	334	672	379
R (F, $F^2 > 2\sigma$)	0.031	0.066	0.054	0.040
R_w (F^2, all data)	0.075	0.167	0.140	0.049

$MeSO_3$][$MeSO_3$][$MeSO_3H$]. $^{31}P\{^1H\}$ NMR (MeOH, 293 K): *δ* 70.0 (s).

X-Ray crystallography

Data for complexes [Pd(d^{t}bpx)(η^2-O_2)] and [Pd(d^{t}bpx)(η^2-BQ)] were collected on a Bruker SMART CCD diffractometer at 160 K with Mo-Kα radiation (*λ* = 0.71073 Å) and corrected for absorption; data for [Pd(dcpx)(dbaH)][$MeSO_3$][$MeSO_3H$]-[THF]$_2$ were collected on a STOE-IPDS image plate diffractometer at 233 K using graphite monochromated Mo-Kα radiation (*λ* = 0.71073 Å), whereas data for [Pd(d^{t}bpx)(η^2-$MeSO_3$)][$MeSO_3$][$MeSO_3H$] were collected on a Rigaku AF65 diffractometer at 153 K using graphite monochromated Mo-Kα radiation (*λ* = 0.71069 Å). The structures were solved and refined by standard techniques using Bruker SHELXTL programs.[31] Crystallographic data are listed in Table 8. The crystal of complex [Pd(d^{t}bpx)(BQ)] was a thin plate (0.06 mm) and data were weak, leading to a less precise structure and some residual electron density peaks up to 2.6 e Å^{-3} around the palladium atom.

CCDC reference numbers 162523, 162524, 181821 and 181822.

See http://www.rsc.org/suppdata/dt/b2/b202372p/ for crystallographic data in CIF or other electronic format.

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