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Synthesis, X-ray characterisation and reactions of a trigonal planar palladium(0) carbonyl complex, (tbpx)PdCO

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The novel complex (tbpx)PdCO (1), the first example of a structurally characterised sixteen electron, trigonal planar palladium(0) carbonyl complex, was prepared, characterised by NMR spectroscopy and X-ray crystallography, and some unusual aspects of its reactivity were studied.

Lucite International has recently announced a new two-stage process for the synthesis of methyl methacrylate. The intermediate methyl propanoate is synthesised from ethene and CO in methanol using complexes of the type $[(\mathrm{tbpx})\mathrm{PdH}]^+$ (tbpx = 1,2-$(\mathrm{CH_2PBu^t{}_2})_2\mathrm{C_6H_4}$).[1] Deuterium labelling studies have provided evidence for a hydride rather than a carbomethoxide mechanism.[2] The palladium catalysed syntheses of low molecular weight oxygenates[3] or copolymers[4] from olefins and CO have recently been reviewed. We now report some unusual chemical reactions of complexes containing the (tbpx)Pd fragment.

The title compound was synthesised by reaction of the previously reported $(\mathrm{tbpx})\mathrm{PdCl_2}$[5] with ethanol in the presence of CO and triethylamine, or with sodium methoxide in the presence of CO gas. The anticipated carboalkoxide product, (tbpx)PdCl[C(O)OR],[6,7] was not detected. This is an unusual reactivity as palladium carbonyl complexes are known to be susceptible to nucleophilic attack by alkoxides.[7,8a]

The complex **1** was isolated as yellow crystals and displays an IR ν_{CO} band at 1959 $\mathrm{cm^{-1}}$ which is typical of terminal carbonyls. This is unusual, as many palladium(0) carbonyl phosphine complexes prefer μ-bridging modes,[8b] and is most likely due to steric effects of the ligand. The ^{1}H and ^{31}P NMR spectra display no unusual features.† The complex **1** is soluble in alcohols and aromatics; in chloroform it rapidly converts to the dichloride (identified by its ^{31}P NMR chemical shift).[5] Attempts to convert **1** to the solvento-hydride[5] $[(\mathrm{tbpx})\mathrm{PdH(CH_3OH)}]^+$ simply by treatment with trifluoromethanesulfonic acid in methanol failed. Addition of benzoquinone to the complex **1** resulted in rapid evolution of gas with a concomitant change of colour to orange, and ^{31}P NMR spectroscopy showed that the previously reported benzoquinone complex had formed.[9] Addition of one equivalent of acid to this mixture to generate the solvento-hydride[5] immediately changed the colour of the solution to yellow, as expected. Surprisingly, and despite repeated attempts, we were not able to detect the hydride $[(\mathrm{tbpx})\mathrm{PdH(CH_3OH)}]^+$ by NMR spectroscopy as rapid decomposition occurred. Work is in progress to explain this apparent discrepancy.

1 reacted rapidly with trimethylphosphine, and the reaction was investigated by ^{31}P NMR spectroscopy. Addition of approximately one equivalent of trimethylphosphine to a deuterated benzene solution of **1** in an NMR tube did not result in the evolution of gas. A slight colour change was observed, and the ^{31}P NMR spectrum showed a resonance for the starting complex, another assigned to the free bidentate ligand (δ 24.3 ppm) and a broad peak at *ca.* −40 ppm. Addition of a further equivalent of $\mathrm{PMe_3}$ changed the relative intensity of the peaks, and addition of two further equivalents did not significantly affect the ^{31}P NMR spectrum. Addition of a large excess (>20 equivalents) of trimethylphosphine resulted in the peak for the starting complex disappearing and the broad peak shifting from −40 ppm to around −60 ppm. A low temperature ^{31}P NMR experiment confirmed that a dynamic exchange process was occurring, because at −30 °C the broad peak at −60 ppm disappeared and was replaced by a singlet at −61.3 ppm, assigned to free trimethylphosphine, and a broad singlet at −32.7 ppm.[10] Given that no evolution of gas was detected at any stage, an infrared spectrum of this sample was taken to confirm the presence of bound CO, and showed broad peaks consistent with bridging carbonyl groups at 1873, 1859, 1803 and 1735 $\mathrm{cm^{-1}}$. A further broad peak which we tentatively assigned to a terminal carbonyl was found at 1942 $\mathrm{cm^{-1}}$. Thus, it seems reasonable to conclude that $\mathrm{PMe_3}$ displaced the tbpx ligand to yield a palladium trimethylphosphine carbonyl cluster. $\mathrm{Pd_4(CO)_5(PEt_3)_4}$ displays ν_{CO} bands at 1980, 1875, 1845, 1788 and 1755 $\mathrm{cm^{-1}}$.[11] The similarity of the spectrum of this cluster to that we have obtained leads us to the tentative assignment of the latter as $\mathrm{Pd_4(CO)_5(PMe_3)_4}$. We cannot rule out higher nuclearity clusters at this stage but our data do not coincide with the published data on this subject.[12] The many infrared bands, the NMR data, and the different timescales of the two techniques strongly suggest that the coordinated ligands are highly fluxional and that the coordinated and uncoordinated phosphines are in dynamic equilibrium.

1 is air sensitive and slowly degrades in solution even under a nitrogen atmosphere; however, single crystals of this material can be obtained by slow, low temperature crystallisation from ethanol under an atmosphere of CO gas. An X-ray structural investigation substantiated the unusual geometry of this complex (Fig. 1). It is worth pointing out that the palladium centre is planar and that formally it is a sixteen-electron species. The P–Pd–P bite angle is around 107° in **1** compared to *ca.* 104° for

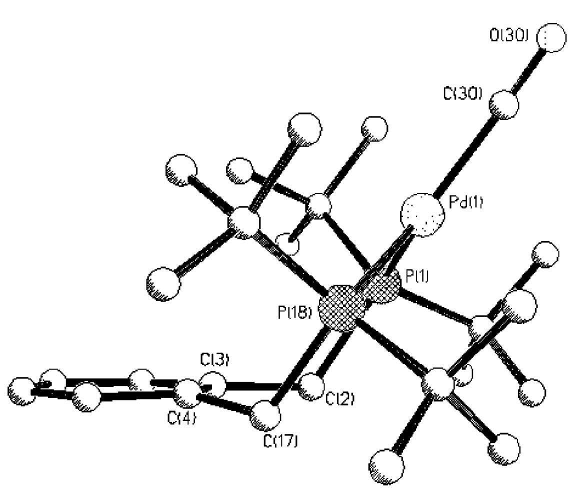

Fig. 1 Molecular structure of **1** showing the geometry of the palladium centre and of the ligand.‡ Hydrogen atoms omitted for clarity and key atoms labelled. Selected bond lengths (Å) and angles (°) Pd–P(1) 2.3446(16), Pd–P(18) 2.3551(15), Pd–C(30) 1.872(7), C(30)–O(30) 1.126(8), P(1)–Pd–P(18) 107.26(6), P(18)–Pd–C(30) 130.1(2), P(1)–Pd–C(30) 122.7(2), P(18)–C(17)–C(4) 120.5(4) P(1)–C(2)–C(3) 119.8(4).

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the analogous dba complex, presumably due to the lesser steric hindrance of the carbonyl compared to dba.[1] Other related complexes such as the benzoquinone complex and the dioxygen analogue show similar or smaller P–Pd–P angles (104.5° and 102.5° respectively).[9] The Pd–P bond lengths (2.3446(16) and 2.3551(16) Å for **1**) can be compared to the lengths of the corresponding bonds in the benzoquinone (2.356(2) and 2.364(2) Å) and dioxygen analogue (2.2694(6) and 2.2865(6) Å).[9]

In conclusion, we have synthesised and structurally characterised the first planar three-coordinated palladium(0) carbonyl complex. The carbonyl group can be displaced by benzoquinone, and **1** will react with chloroform to yield the corresponding dichloride. Perhaps surprisingly, the bidentate ditertiary phosphine ligand tbpx appears to be displaced from **1** by trimethylphosphine, whilst the labile carbonyl group is retained, to yield a highly fluxional cluster tentatively formulated as $Pd_4(CO)_5(PMe_3)_4$.

Notes and references

† ^{31}P NMR (CD_3OD, 121 MHz) δ 50.6 ppm; ^{1}H NMR (CD_3OD, 300 MHz) δ 1.4 (d, 36H, ^{t}Bu), 3.6 (m, 4H, CH_2), 7.1 (m, 2H, C_6H_4), 7.4 (m, 2H, C_6H_4) ppm.

‡ *Crystallographic data for* **1**: Rigaku Mercury diffractometer with graphite-monochromated Mo–Kα radiation (λ = 0.71073 Å), 293K. $C_{25}H_{44}OP_2Pd$, M = 528.94, monoclinic, space group $P2(1)/n$, a = 11.837(3), b = 16.063(4), c = 14.731(3)) Å β = 93.358(7) °, U = 2796.0(11) Å^3, Z = 4, D_c = 1.257 Mg m^{-3}, μ = 0.791 mm^{-1}, $F(000)$ = 1112. Of 10203 measured data, 4392 were unique (R_{int} = 0.0347) and 3478 observed ($I > 2\sigma(I)$]) to give R_1 = 0.0590 and wR_2 = 0.1335. CCDC 211529. See http://www.rsc.org/suppdata/cc/b3/b305854a/ for crystallographic data in .cif format.

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