Ethene insertion into a palladium–acetyl bond: crystal structure of [Pd(CH_2CH_2COMe)($NC_5H_4CO_2Me$-2)(PPh_3)]BF_4, a novel reaction intermediate from the insertion process

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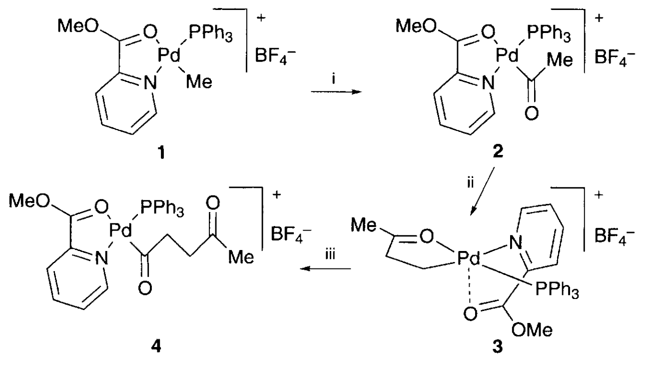
From the catalytic conversion of CO and ethene to polyketone with [Pd(Me)($NC_5H_4CO_2Me$-2)- (PPh_3)]BF_4 1, the reaction of ethene with [Pd(COMe)($NC_5H_4CO_2Me$-2)(PPh_3)]BF_4 2 yields a rare example of an isolable product from the insertion of an unstrained alkene into a Pd–acyl bond, and the crystal structure of [Pd(CH_2CH_2COMe)($NC_5H_4CO_2Me$-2)(PPh_3)]BF_4 3 showing a novel square-pyramidal intermediate with a weakly interacting oxygen in the apical position.

The study of the migratory insertion of carbon monoxide and alkenes into Pd–alkyl and Pd–acyl bonds is important for understanding the Pd^{II}-catalysed copolymerisation reaction of carbon monoxide and alkenes. The insertion reaction of carbon monoxide into a Pd–alkyl bond has been widely studied and occurs readily for many Pd^{II}–alkyl complexes.[1] Recent work on the insertion of alkenes into Pd–acyl complexes has shown that products are usually only observed when using a strained or bulky alkene.[1–10] In general for unstrained (flexible) alkene inserted complexes the availability of a β hydrogen provides an easy pathway for decomposition. The only other example of an isolable product from the insertion of ethene into a Pd–acyl bond was recently described by Rix and Brookhart;[11] no crystal structure was reported.

To study the individual steps involved in the copolymerisation of carbon monoxide and ethene, consecutive additions of each were made to a solution of the catalyst complex **1**,[12] to give complexes **2**, **3** and **4** in quantitative yield (Scheme 1). This catalyst has low activity,† but is relatively stable in solution at room temperature.

Complexes **1**–**4** have been fully characterised by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy.‡ X-ray structures have been obtained for complexes **1** and **3**§ (Fig. 1). In the solid state, complex **3** is remarkably stable, and may be handled in air. The stability of complex **3** is due in part to the intramolecular coordination of the alkyl carbonyl oxygen to palladium.[1–6,8,11] However, this may not be the only factor as the positioning of other ligands may play a role (*vide infra*).



Scheme 1 *Reagents and conditions*: i, CO (*ca.* 10 min), 20 °C; ii, CH_2CH_2 (*ca.* 3 h), 20 °C; iii, CO (*ca.* 2 h), 20 °C

Complex **3** is unique in that all other isolated alkene insertion products have either strongly chelating N,N,[1,3–6,11] P,P[9] ligands or solely monodentate PPh_3.[8] Unlike these systems in which the reaction with carbon monoxide and alkenes is thought to proceed *via* dissociation of a coordinated anion or solvent molecule, it is suspected that for some complexes with N,O,[12–15] P,O[16,17] and P,S[16] ligands the mechanism involves hemilability of the bidentate ligand with a dangling or weakly interacting donor. The latter possibility is confirmed by the crystal structure of **3**, which shows the oxygen donor of the N,O ligand in an apical position perpendicular to the palladium coordination plane (Fig. 1). The Pd–O(21) distance of 2.78(1) Å is very long implying a weak interaction [*e.g.* the Pd–O bond length of complex **1** is 2.180(7) Å]. However, the distance is similar to the long contacts observed for the few examples of five-coordinate palladium complexes containing a weakly bonding oxygen (carbonyl) in the fifth position.[18,19] That the interaction of apical oxygen is weak is confirmed by IR spectroscopy [complex **3**, ν(C=O) = 1733 cm^{-1}; in **1**, **2** and **4** (Scheme 1) ν(C=O) = 1670–1672 cm^{-1}; in free $NC_5H_4CO_2Me$-2, ν(C=O) = 1726 cm^{-1}]. The oxygen is well positioned to act as an incoming ligand in the next step of the copolymerisation reaction (complex **3**→**4**). Spectroscopic

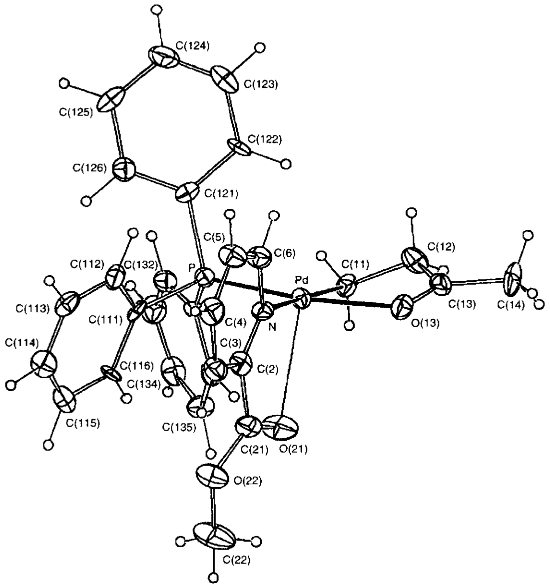


Fig. 1 Crystal structure of the cation of **3**; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radius of 0.1 Å. Selected bond lengths (Å) and angles (°); Pd–P 2.215(6), Pd–N 2.19(1), Pd–C(11) 2.00(1), Pd–O(13) 2.16(2), Pd–O(21) 2.78(1), C(13)–O(13) 1.23(2); P–Pd–N 97.3(5), P–Pd–C(11) 89.5(6), P–Pd–O(13) 169.5(3), N–Pd–C(11) 172.9(8), N–Pd–O(13) 91.6(6), C(11)–Pd–O(13) 81.4(7).

evidence[‡] confirms that on addition of further carbon monoxide to intermediate **3**, the re-association of the N,O chelate occurs to yield complex **4**, an analogue of **2**.[20] Other bond lengths and angles for complex **3** are typical of similar norbornene and norbornadiene inserted complexes.[1,8] The complex exists only as the thermodynamically favoured isomer having PPh_3 and the alkyl group *cis* to each other, indicating isomerisation as well as ethene insertion has occurred in the conversion of **2** into **3**.

Significantly, theoretical modelling of the carbon monoxide insertion and isomerisation mechanism in complexes containing N,O ligands has suggested the involvement of square-pyramidal intermediates having a very long, weak bond to the ligand in the apical position.[13,21] The intermediate $[PdMe(CO)(PH_3)(HN{=}CHCH{=}O)]^+$ was calculated to have an apical Pd–O distance of 2.82 Å.[21] Five-coordinate species were found to offer a novel low-energy pathway for isomerisation,[13] which occurs during the catalytic copolymerisation reaction discussed here. The structure of **3** provides clear experimental evidence that isomerisation *via* the theoretically proposed five-coordinate intermediate is a feasible pathway.

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Footnotes

[†] Complex **1** (0.1 mmol) in 40 ml CH_2Cl_2 at 20 °C; $p(CO)$ = 20 bar; $p(CH_2CH_2)$ = 20 bar; produces *ca.* 0.2 g polyketone after 1 h.

[‡] For data relating to complexes **1** and **2** see ref. 12. Complex **3**: Anal. Calc. for $C_{29}H_{29}O_3BF_4NPPd$: C, 52.48; H, 4.40; N, 2.11. Found: C, 52.71; H, 4.18; N, 2.14%. Selected IR and NMR data: IR (CH_2Cl_2): $\nu(C{=}O)$ 1733 (CO_2Me), 1637 cm^{-1} ($PdCH_2CH_2COMe$). ^1H NMR (300 MHz, $CDCl_3$): δ 3.17 (t, 2 H, *J* 6.0 Hz, $PdCH_2CH_2$), 2.41 (s, 3 H, $COCH_3$), 1.72 (dt, 2 H, *J* 6.0, 2.7 Hz, $PdCH_2CH_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 232.4 (*C*OMe), 164.2 (*C*O_2Me), 51.0 ($PdCH_2CH_2$), 27.8 ($COCH_3$), 23.0 ($PdCH_2$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 36.2. Complex **4**: selected IR and NMR data: IR (CH_2Cl_2): $\nu(C{=}O)$ 1715 (PdCO and COMe), 1670 cm^{-1} (CO_2Me). ^1H NMR (300 MHz, $CDCl_3$): δ 2.86 (t, 2 H, *J* 4.8 Hz, CH_2CH_2COMe), 2.18 (t, 2 H, *J* 4.8 Hz, $PdCOCH_2CH_2$), 2.07 (s, 3 H, $COCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.0 (PdCO), 206.8 (*C*OMe), 171.2 (*C*O_2Me), 44.0 (d, *J* 24 Hz, PdCO*C*H), 37.9 (CH_2COMe), 29.6 ($PdCOCH_3$). ^{31}P NMR (121 MHz, $CDCl_3$): δ 24.7.

[§] *Crystal data* for **3**: crystals suitable for X-ray diffraction were obtained from a $CDCl_3$–diethyl ether solution at 0 °C. $C_{29}H_{29}BF_4NO_3PPd{\cdot}CDCl_3$, M = 784.1, monoclinic, space group $P\bar{2}_1/c$, a = 21.721(6), b = 7.695(4), c = 24.091(5) Å, β = 123.91(2)°, U = 3342 Å^3, D_c (Z = 4) = 1.56 g cm^{-3}. 2206 Independent 'observed' [$I > 3\sigma(I)$] absorption-corrected diffractometer data (μ_{Mo} = 9.0 cm^{-1}, λ = 0.71073 Å, $2\theta_{max}$ 50°, specimen: 0.07 × 0.52 × 0.28 mm, $a^*_{min.max}$ = 1.06, 1.34) refined by full-matrix least squares (anisotropic thermal parameter forms for non-hydrogen atoms; n_v = 397) to conventional R on $|F|$ 0.068, R_w (statistical weights) being 0.061. The cation is well defined but thermal motion of BF_4^- and $CDCl_3$ entities was very high; site occupancy of the latter was set at unity after trial refinement. The crystal decomposed by *ca.* 15% during data collection. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/116.

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