COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Methanolysis of acyl–Pd(II) complexes relevant to CO/ethene coupling reactions†

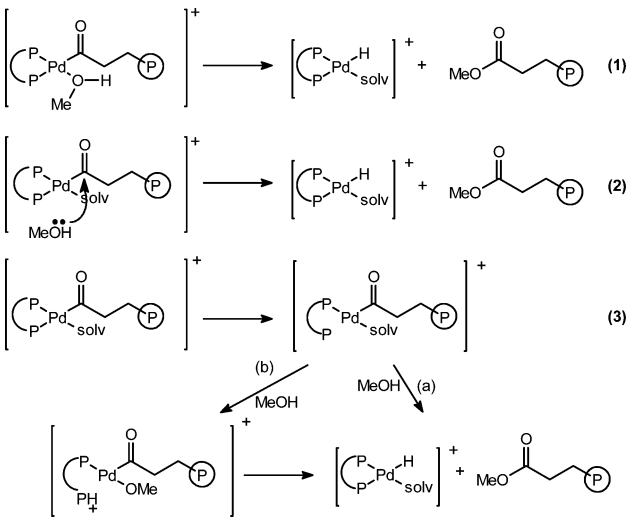
Jianke Liu, Brian T. Heaton, Jonathan A. Iggo* and Robin Whyman

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, P. O. Box 147, Liverpool, UK L69 7ZD. E-mail: iggo@liv.ac.uk; Fax: 44 151 794 3588; Tel: 44 151 794 3538

Received (in Cambridge, Uk) 10th February 2004, Accepted 2nd April 2004
First published as an Advance Article on the web 28th April 2004

Alcoholysis of acyl–Pd(II) complexes relevant to palladium catalysed CO/ethene coupling reactions such as polyketone synthesis/alkoxycarbonylation reactions is shown, in a highly active catalyst system, to proceed *via* coordination of methanol to the Pd centre prior to nucleophilic attack at the acyl carbon.

The propagation steps in the copolymerisation of CO with alkenes and in alkoxycarbonylation of alkenes catalysed by cationic Pd diphosphine complexes[1] have been extensively studied and are now well understood.[2–9] The termination steps of the reaction, however, have been little studied with most information derived from an analysis of the end groups of the polymer chain.[10] Notable exceptions to this are the recent studies by van Leeuwen and Zuideveld,[11] Bianchini,[3] and ourselves[9] that have succeeded in identifying some or all of the intermediates involved in chain transfer by alcoholysis of the acyl and alkyl intermediates. As a consequence several conflicting reaction pathways have been proposed for the alcoholysis of the acyl intermediate (Scheme 1, eqn. (1)–(3)). Thus, van Leeuwen observed that methanolysis is effectively suppressed by diphosphine ligands that adopt a *trans* geometry at Pd and concluded that methanolysis of the acyl must be by *intra*-molecular attack of *cis* coordinated CH_3OH on the acyl carbon, eqn. (1).[11] Similarly, Bianchini notes that methanolysis of the acetyl intermediate [Pd(dppomf)(C(O)CH_3)]OTs, (dppomf = $(C_5Me_4PPh_2)_2Fe$) requires a change in hapticity of the ligand from η^3-*P,P,Fe* (*trans* Ps) to η^2-*P,P* (*cis* Ps) to provide a free coordination site for CH_3OH *cis* to the acyl and may therefore be rate limiting in that reaction.[12] In a later paper however, Bianchini proposes direct *inter*-molecular attack of CH_3OH at the acyl carbon, eqn. (2), based on the observation that methanolysis of [Pd(dppomf)(C(O)CH_3)]OTs is fast whereas the cation is unreactive toward ethene,[3] methanolysis thus appears not to require a vacant coordination site at Pd. Cole-Hamilton has drawn attention to a third possibility in which decoordination of one arm of the phosphine occurs, eqn. (3).[13,14] Methanol can then enter the vacant site and attack the acyl carbon directly, eqn. (3a), or protonate the free phosphine centre to generate a methoxy ligand on Pd, eqn. (3b). Elimination of ester and transfer of the proton from phosphorus to Pd with recoordination of the phosphine completes the methanolysis process. As part of our continuing studies in this area[8,9] we have been investigating the mechanistic pathways available to the prototypical catalyst system Pd/dibpp (dibpp = $(Bu^t_2P)_2C_3H_6$).[15]

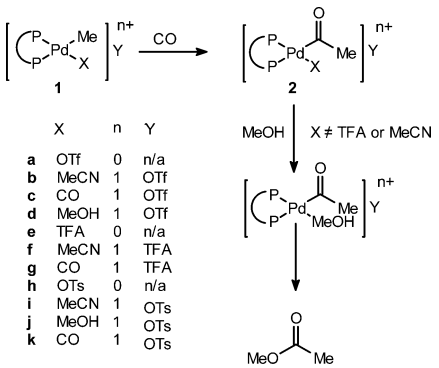


Scheme 1 Proposed pathways for the methanolysis of Pd–acyl complexes.

In this paper, we report the effects of solvent, counter-ion and occupancy of the fourth site on (i) the species present in solutions of the acyl intermediate [Pd(dibpp)(C(O)CH_3)L]$^{n+}$ (n = 0 or 1; L = counter-ion, solvent, or ligand) and (ii) on the methanolysis reaction, which suggest that coordination of CH_3OH to the Pd centre is an essential prerequisite to methanolysis of the Pd–acyl bond.

The $^{31}P\{^1H\}$ NMR spectrum of [Pd(dibpp)(CH_3)(OTf)] (OTf = $CF_3SO_3^-$) **1a**‡ displays two broad singlets at 293 K which resolve into a pair of doublets at 193 K. The exchange process is attributed to coordination–decoordination of the triflate anion, rather than to phosphine dissociation, since the temperature dependence of the spectrum is suppressed by any group capable of binding more strongly than OTf to the Pd centre, *e.g.* **1b–e,h**, Scheme 2, the $^{31}P\{^1H\}$ NMR spectra of which show well resolved pairs of doublets at 293 K.

The acyl complex [Pd(dibpp)(C(O)CH_3)(CO)]$^+$ **2c** is formed quantitatively when excess CO is bubbled through a CH_2Cl_2 solution **1a**, whereas a mixture of [Pd(dibpp)(C(O)CH_3)L]$^{n+}$ (n = 0, L = OTs; n = 1, L = CO) **2h,k** is formed from the tosylate complex **1h**. Finally, bubbling CO through a CH_2Cl_2 solution of **1e** gives **2e** exclusively, the acyl carbonyl species **2g** is not seen. Bubbling CO through a CH_2Cl_2/CH_3CN (9 : 1) solution of **1b** gives **2b** and through a CH_2Cl_2/CH_3CN (9 : 1) solution of the mixture **1e** and **1f** gives a mixture containing both [Pd(dibpp)(C(O)CH_3)TFA] **2e** and [Pd(dibpp)(C(O)CH_3)(CH_3CN)]TFA **2f**. Addition of 1 equivalent of CH_3CN to a CH_2Cl_2 solution containing **2h,k** results in complete displacement of the tosylate anion or CO by CH_3CN.



	X	n	Y
a	OTf	0	n/a
b	MeCN	1	OTf
c	CO	1	OTf
d	MeOH	1	OTf
e	TFA	0	n/a
f	MeCN	1	TFA
g	CO	1	TFA
h	OTs	0	n/a
i	MeCN	1	OTs
j	MeOH	1	OTs
k	CO	1	OTs

Scheme 2 Methanolysis of Pd(dibpp)acyl complexes. Methanolysis does not occur in the presence of coordinating ligands such as TFA or MeCN.

† Electronic supplementary information (ESI) available: experimental details and representative $^{31}P\{^1H\}$ NMR spectra. See http://www.rsc.org/suppdata/cc/b4/b402275k/

DOI: 10.1039/b402275k

To summarize, only trifluoacetate anion competes effectively with MeCN for the fourth coordination site and does so even in the presence of a large excess of CH_3CN. The CH_3OH containing cations are only obtained in the absence of CH_3CN. These results indicate that the affinity for the Pd centre of the various anions is TFA > OTs > OTf, as might be expected, and, perhaps surprisingly, that CH_3CN has a higher affinity for the Pd centre than CO which has a slightly greater affinity for Pd than OTs, *i.e.* the affinities of these ligands for the Pd(dibpp) centre is in the order, TFA > CH_3CN > CO > OTs > CH_3OH > OTf. The equilibrium position will, of course, be influenced by the relative concentrations of the species competing for the fourth site. The IR stretching vibration of the carbonyl ligand in **2c** occurs at 2123 cm^{-1} in accord with the report of Drent.[16] However, the relatively weak affinity of CO for Pd in these complexes has not previously been recognized, and has implications for related Pd catalysed carbonylation reactions.

The preparation and characterization of the series of complexes **2b–k** allows us to probe directly, for a highly active catalytic system, the effect of blocking of the fourth coordination site on the methanolysis reaction, Scheme 2.§[11,12] Rapid reaction is seen on addition of excess (10% v/v) CH_3OH at 243 K to CH_2Cl_2 solutions of the acyl complexes, however no reaction is seen in CH_2Cl_2/CH_3CN (9 : 1) solutions in which CH_3CN occupies the fourth site, **2b**, **2f** or **2i**.¶ The reaction of **2e** with CH_3OH in both CH_2Cl_2 and CH_2Cl_2/CH_3CN mixtures requires further comment. No reaction is observed at 243 K on addition of 1–10 equivalents of CH_3OH to a CH_2Cl_2 solution of **2e** even on standing overnight. However, addition of (10% v/v) MeOH to a CH_2Cl_2 solution of **2e** in the presence of ^{13}CO‖ results in immediate formation of the Pd acyl carbonyl complex **2g**, observed *in situ* by $^{31}P\{^1H\}$ NMR, followed by methanolysis to give methyl acetate. These observations can be explained as follows: in the presence of near stoichiometric amounts of CH_3OH, TFA is not dissociated and effectively blocks the fourth coordination site on Pd to incoming CH_3OH, however, in the presence of a large excess of CH_3OH, dissociation of the anion is aided by its solvation by methanol. The first formed solvento cation (which cannot be directly observed) is trapped by the excess CO present in the solution to give **2g**. Methanolysis of **2g** then occurs. Support for this interpretation comes from the observation that addition of (10% v/v) CH_3OH to a mixture of **2e** and **2f** in CH_2Cl_2/CH_3CN (9 : 1) (*vide supra*) results in complete conversion of **2e** to **2f** (which is resistant to methanolysis).

We conclude that, in this system, methanolysis proceeds *via* coordination of CH_3OH to Pd, followed by *intra*-molecular nucleophilic attack on the acyl carbon and the pathway is not affected by the acid used, *i.e.* methanolysis occurs *via* the mechanism shown in eqn. (1) or (3).** We cannot conclusively distinguish between mechanisms (1) and (3), however we note that there is no evidence in our $^{31}P\{^1H\}$ NMR spectra[9] to suggest that decoordination/recoordination of the diphosphine ligand occurs on the NMR timescale. The situation with regard to [Pd(dppomf-)(C(O)Me)]OTs is complicated by the presence of an intra-molecular Fe→Pd bond which reasonably accounts for the observed reactivity of that system.

The financial support of EPSRC, grant GR/R37685, is gratefully acknowledged.

Notes and references

‡ See ref 8 for a general procedure for the preparation of solutions of the complexes **1a–k** and **2a–k** and details of the NMR instrumentation.†

§ Effects due to variation of *e.g.* the diphosphine ligand are excluded.

¶ Decarbonylation reactions dominate on warming to 293 K.

‖ Excess ^{13}CO was added to drive the reaction **1e** → **2e** to completion.

** Under catalytic conditions, where methanol is the solvent and excess CO is present, mass action will ensure that methanol competes effectively with the anion or CO for the fourth coordination site allowing the methanolysis reaction to proceed. Thus, addition of 10% CH_3OH to a CH_2Cl_2 solution of **2c** and CO at 243 K, results in progressive formation of the Pd–acyl–(CH_3OH) complex **2d** and formation of methyl acetate (detected by $^{13}C\{^1H\}$ NMR).

$^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for **1a–k** *and* **2a–k**: P *trans* to CH_3 or $C(O)CH_3$ given first; coupling to P_{trans} is given first; *J* in Hz. [a] Recorded in CH_2Cl_2 [b] Recorded in CH_2Cl_2/CH_3CN (9 : 1) [c] Recorded in CH_2Cl_2/CH_3OH (9 : 1): **1a** [Pd(dibpp)$CH_3(CF_3SO_3)$] [a] δ_P 18.8 d, −16.6 d (J_{PP} = 41); **1b** [Pd(dibpp)$CH_3(CH_3CN)][CF_3SO_3]$ [b] δ_P 11.0 d, −15.6 d (J_{PP} = 41); **1c** [Pd(dibpp)$CH_3(CO)][CF_3SO_3]$ [a] δ_P −0.5 d, −12.3 d (J_{PP} = 47), δ_C 181.6 dd (J_{PC} = 114, 16); **1d** [Pd(dibpp)$CH_3(CH_3OH)][CF_3SO_3]$ [c] δ_P 18.8 d, −14.2 d (J_{PP} = 41); **1e** [Pd(dibpp)$CH_3(CF_3CO_2)$] [a] δ_P 12.7 d, −11.4 d (J_{PP} = 41); **1f** [Pd(dibpp)$CH_3(CH_3CN)][CF_3CO_2]$ [b] δ_P 10.8 d, −15.6 d (J_{PP} = 41); **1g** [Pd(dibpp)$CH_3(CO)][CF_3CO_2]$ [a] δ_P −0.8 d, −13.5 d (J_{PP} = 48), δ_C 181.6 dd (J_{PC} = 114, 16); **1h** [Pd(dibpp)$CH_3(CH_3C_6H_4SO_3)$] [a] δ_P 17.2 d, −12.2 d (J_{PP} = 42); **1i** [Pd(dibpp)$CH_3(CH_3CN)][CH_3C_6H_4SO_3]$ δ_P 11.1 d, −15.7 d (J_{PP} = 42); **1j** [Pd(dibpp)$CH_3(CH_3OH)][CH_3C_6H_4SO_3]$ [c] δ_P 18.9 d, −14.3 d (J_{PP} = 42); **1k** [Pd(dibpp)$CH_3(CO)][CH_3C_6H_4SO_3]$ [a] δ_P −0.6 d, −13.4 d (J_{PP} = 47), δ_C 181.7 dd (J_{PC} = 114,16); **2b** [Pd(dibpp)–$(C(O)CH_3)(CH_3CN)][CF_3SO_3]$ [b] δ_P 5.4 d, − 19.6 (J_{PP} = 70), δ_C 242.6 dd (J_{PC} = 112, 10); **2c** [Pd(dibpp)$(C(O)CH_3)(CO)][CF_3SO_3]$ [a] δ_P −6.7 d, −19.2 d (J_{PP} = 73), δ_C 235.2 dd (J_{PC} = 88, 5); 176.9 dd (J_{PC} = 80, 20); **2d** [Pd(dibpp)$(C(O)CH_3)(CH_3OH)][CF_3SO_3]$ [c] δ_P 13.4 d, −19.1 d (J_{PP} = 66), δ_C 243 dd (J_{PC} = 116, 12); **2e** [Pd(dibpp)$(C(O)CH_3)(CF_3CO_2)$] [a] δ_P 10.0 d, −15.8 d (J_{PP} = 67), δ_C 247.8 dd (J_{PC} = 125, 10); **2f** [Pd(dibpp)$(C(O)CH_3)(CH_3CN)][CF_3CO_2]$ [b] δ_P 4.9 d, −19.7 d (J_{PP} = 70), δ_C 242.8 dd (J_{PC} = 112, 10); **2g** [Pd(dibpp)$(C(O)CH_3)(CO)][CF_3CO_2]$ [c] δ_P −6.1 d, −18.5 d (J_{PP} = 73), δ_C 234.7 dd (J_{PC} = 88,6); 176.9 dd (J_{PC} = 79,20); **2h** [Pd(dibpp)$(C(O)CH_3)(CH_3C_6H_4SO_3)$] [a] δ_P 12.5 d, −16.6 d (J_{PP} = 70), δ_C 244.6 dd (J_{PC} = 122,12); **2i** [Pd(dibpp)$(C(O)CH_3)(CH_3CN)]$ $[CH_3C_6H_4SO_3]$ [b] δ_P 4.9 d, −19.7 d (J_{PP} = 70), δ_C 242.6 dd (J_{PC} = 113,10); **2j** [Pd(dibpp)$(C(O)CH_3)(CH_3OH)][CH_3C_6H_4SO_3]$ [c] δ_P 13.4 d, −19.2 d (J_{PP} = 66), δ_C 245.5 dd (J_{PC} = 117, 12); **2k** [Pd(dibpp)$(C(O)CH_3)(CO)]$ $[CH_3C_6H_4SO_3]$ [a] δ_P −6.8 d, −18.6 d (J_{PP} = 73), δ_C 235.5 dd (J_{PC} = 88, 5); 176.9 dd(J_{PC} = 80, 20).

1 E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
2 *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, ed. A. Sen, Kluwer Academic Publishers, Dordrecht, 2003.
3 C. Bianchini, A. Meli and W. Oberhauser, *Dalton Trans.*, 2003, 2627.
4 Z. Freixa and P. van Leeuwen, *Dalton Trans.*, 2003, 1890.
5 J. Ledford, C. S. Shultz, D. P. Gates, P. S. White, J. M. DeSimone and M. Brookhart, *Organometallics*, 2001, **20**, 5266.
6 K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara and N. Koga, *J. Am. Chem. Soc.*, 1997, **119**, 12779.
7 C. Bianchini, A. Meli, G. Muller, W. Oberhauser and E. Passaglia, *Organometallics*, 2002, **21**, 4965.
8 J. Liu, B. T. Heaton, J. A. Iggo and R. Whyman, *Angew. Chem. Int. Ed*, 2004, **43**, 90.
9 W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *Organometallics*, 2002, **21**, 1832; W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *J. Chem. Soc., Dalton Trans.*, 2002, 3300; G. R. Eastham, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *Chem. Commun.*, 2000, 609.
10 W. P. Mul, E. Drent, P. J. Jansens, A. H. Kramer and M. H. W. Sonnemans, *J. Am. Chem. Soc.*, 2001, **123**, 5350.
11 P. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523; M. A. Zuideveld, P. C. J. Kamer, P. W. M. N. van Leeuwen, P. A. A. Klusener, H. A. Stil and C. F. Roobeek, *J. Am. Chem. Soc.*, 1998, **120**, 7977.
12 C. Bianchini, A. Meli, W. Oberhauser, P. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal'sin, *Organometallics*, 2003, **22**, 2409.
13 D. J. Cole-Hamilton and R. A. M. Robertson, in *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, ed. A. Sen, Kluwer Academic Publishers, Dordrecht, 2003, Chap. 3.
14 G. R. Eastham, PhD, University of Durham, 1996.
15 R. I. Pugh and E. Drent, in *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*, ed. A. Sen, Kluwer Academic Publishers, Dordrecht, 2003, Chap. 2.
16 W. P. Mul, H. Oosterbeek, G. A. Beitel, G. J. Kramer and E. Drent, *Angew. Chem. Int. Ed.*, 2000, **39**, 1848.