COMMUNICATION

ChemComm
www.rsc.org/chemcomm

The effect of mechanistic pathway on activity in the Pd and Pt catalysed methoxycarbonylation of ethene

Joanna Wolowska,[a] Graham R. Eastham,[b] Brian T. Heaton,*[a] Jonathan A. Iggo,*[a] Chacko Jacob[a] and Robin Whyman*[a]

[a] *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*

[b] *Lucite International, PO Box 90, Wilton, Middlesborough, Cleveland, UK TS90 8JE*

Received (in Cambridge, UK) 30th August 2002, Accepted 8th October 2002

First published as an Advance Article on the web 24th October 2002

All the intermediates involved in the platinum catalysed methoxycarbonylation of ethene have been characterised by *in situ* NMR; the low activity of platinum catalysts in this reaction is shown to be due to trapping of the active intermediates by carbon monoxide at *every* step in the catalytic cycle and to the ready reversibility of the product forming reactions.

Lucite International has recently announced a new process for the manufacture of methyl methacrylate *via* the Pd catalysed methoxycarbonylation of ethene to methyl propanoate (MEP).[1] The catalyst used is capable of converting ethene, CO and MeOH to methyl propanoate at a rate of 50 000 mol of product per mol of catalyst per hour with a selectivity of 99.98%.[1,2] We have shown, *via* characterisation of all the intermediates, that this reaction follows a hydride catalytic cycle,[3] a result that has recently been confirmed by isotope scrambling experiments.[4]

The catalytic performance of analogous Pt complexes is poor, with rates typically four orders of magnitude lower. In order to understand if there is an intrinsic limitation associated with the 3rd row metal catalyst,[5] (unlike the situation with, for example, halide-promoted Rh and Ir catalysts for methanol carbonylation),[6] we have undertaken a detailed mechanistic NMR investigation of the Pt system. Elucidation of all the intermediates involved in the Pt cycle has revealed some unexpected differences between the chemistry of the Pd and Pt systems, particularly the ready reversibility of the alkyl migration step on Pt, which has allowed us to propose an explanation for the low activity of the Pt catalyst in this reaction.

Pt(L–L)(dba) **1** {L–L = 1,2-$(CH_2PBu^t_2)_2C_6H_4$} reacts in MeOH with CF_3SO_3H in the presence of O_2 or BQ (benzoquinone) to give a new complex, characterised by ^1H and ^{31}P NMR spectroscopy as the metal hydride complex [Pt(L–L)H(MeOH)][CF_3SO_3] **2**. Thus, the $^{31}P\{^1H\}$ NMR spectrum of **2** at room temperature, Table 1, shows two main resonances each showing Pt satellites. The resonance at 34.0 ppm shows a further doublet splitting in the absence of ^1H decoupling. The proton NMR spectrum of **2** shows a doublet of doublets (with Pt satellites) at −7.3 ppm [$^2J(P_{trans}\text{-}H) = 176$ Hz, $^2J(P_{cis}\text{-}H) = 18$ Hz, $^1J(\text{Pt-H}) = 805$ Hz], values of δ and J typical of a hydride ligand *trans* to phosphorus, in agreement with the proposed formulation of **2**. As in the case of Pd,[7] the hydride is formed *via*[Pt(L–L)(dbaH)][CF_3SO_3] **3**, Table 1.

On bubbling ethene through a methanol solution of **2** for *ca.* 30 min at 193 K, quantitative conversion to [Pt(L–L)(CH_2CH_3)][CF_3SO_3] **4** occurs. **4** has been characterised by comparison of its $^{31}P\{^1H\}$ NMR data with those reported in literature.[8]As for the Pd analogue,[7] δ_P *cis* to C_α is insensitive to solvent and the values of ^1J(CH) are in the range for sp^3 carbon, Table 1, indicating the ethyl ligand in **4** forms a β-agostic interaction with the metal centre. This contrasts with Pt(ethyl) complexes of other diphosphine ligands reported by Scrivanti *et al.* that do not contain such an interaction.[9]

Two intermediates can be observed in the reaction of **4** with ^{13}CO by carrying out the reaction in CH_2Cl_2 at 193 K, followed by warming to 293 K; these have been characterised as [Pt(L–L)(C_2H_5)(^{13}CO)]$^+$ **5** and [Pt(L–L)(^{13}C(O)Et)(^{13}CO)]$^+$ **6**, by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy, Table 1, Fig. 1. **6** is only formed on warming the solution to room temperature in the presence of excess CO. Thus, at 193 K only the resonances due to [Pt(L–L)(C_2H_5)(^{13}CO)]$^+$ **5** are seen in the $^{13}C\{^1H\}$ NMR spectrum, Fig. 1a; these disappear on warming to 293 K to be replaced by two doublets of doublets showing Pt satellites at 173.2 ppm in the carbonyl and at 223.9 ppm in the acyl region, Fig. 1b. This transformation is *reversible*, cooling the solution of **6** to 193 K results in reformation of **5**. On prolonged standing of this solution at low temperature, the resonances of **5** decrease slightly in intensity and resonances due to a new complex **7** and

Table 1 NMR spectroscopic data for the complexes in MeOH at 293 K, unless stated otherwise

Compound	δ ^{31}P (ppm)/J(Hz)	δ ^{13}C (ppm)/J(Hz)	δ ^1H (ppm)/J(Hz)
[Pt(L–L)H(MeOH)][CF_3SO_3] **2**	$P_A = 46.2$, $^1J(\text{Pt-}P_A) = 4312$ $P_B = 34.6$, $^1J(\text{Pt-}P_B) = 2095$ $^2J(P_A\text{-}P_B) = 6$		$H = -7.3$, $^1J(\text{Pt-H}) = 805$ $^2J(P_A\text{-H}) = 18$, $^2J(P_B\text{-H}) = 176$
[Pt(L–L)(dbaH)][CF_3SO_3] **3**^{a}	$P_A = 53.0$, $^1J(\text{Pt-}P_A) = 4733$ $P_B = 40.8$, $^1J(\text{Pt-}P_B) = 2965$ $P'_A = 57.7$, $^1J(\text{Pt-}P'_A) = 4700$ $P'_B = 35.5$, $^1J(\text{Pt-}P'_B) = 2994$		
[Pt(L–L)(CH_2CH_3)][CF_3SO_3] **4**	$P_A = 52.5$, $^1J(\text{Pt-}P_A) = 5108$ $P_B = 37.0$, $^1J(\text{Pt-}P_B) = 2759$		
[Pt(L–L)(C_2H_5)(^{13}CO)][CF_3SO_3] **5**^{ab}	$P_A = 29.4$, $^1J(\text{Pt-}P_A) = 1531$ $P_B = 16.4$, $^1J(\text{Pt-}P_B) = 3259$ $^2J(P_A\text{-}P_B) = 24$	$CO = 179.8$, $^1J(\text{Pt-CO}) = 1416$ $^2J(P_A\text{-CO}) = 10$, $^2J(P_B\text{-CO}) = 126$ $C_\alpha = 4.0$, $^2J(P_B\text{-}C_\alpha) = 54$, $C_\beta = 18.3$	$^1J(C_\alpha\text{-H}) = 130$ $^1J(C_\beta\text{-H}) = 126$
[Pt(L–L)(C(O)Et)(CO)][CF_3SO_3] **6**^{b}	$P_A = 23.0$, $^1J(\text{Pt-}P_A) = 3616$ $P_B = 23.1$, $^1J(\text{Pt-}P_A) = 1397$ $^2J(P_A\text{-}P_B) = 26$	$CO = 173.2$, $^1J(\text{Pt-CO}) = 1487$ $C(O) = 224.0$, $^1J(\text{Pt-C(O)}) = 514$ $^2J(P_A\text{-CO}) = 93$, $^2J(P_B\text{-C(O)}) = 69$	
[Pt(L–L)H(CO)][CF_3SO_3] **7**	$P_A = 42.2$, $^1J(\text{Pt-}P_A) = 2985$ $P_B = 33.2$, $^1J(\text{Pt-}P_A) = 2011$ $^2J(P_A\text{-}P_B) = 19$	$CO = 179.3$, $^1J(\text{Pt-CO}) = 1299$ $^2J(P_A\text{-CO}) = 113$, $^2J(P_B\text{-CO}) = 8$	$H = -4.2$, $^1J(\text{Pt-H}) = 740$ $^2J(P_A\text{-H}) = 15$, $^2J(P_B\text{-H}) = 145$

^{a} NMR data at 193 K. ^{b} Recorded in CH_2Cl_2.

DOI: 10.1039/b208450c

This journal is © The Royal Society of Chemistry 2002

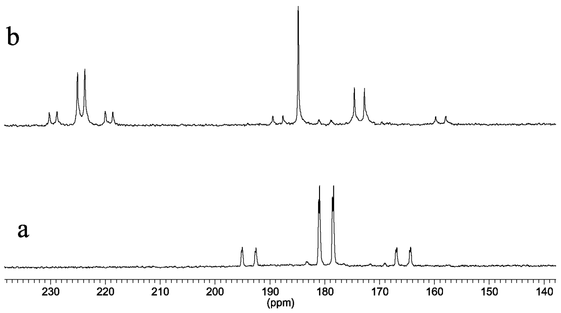


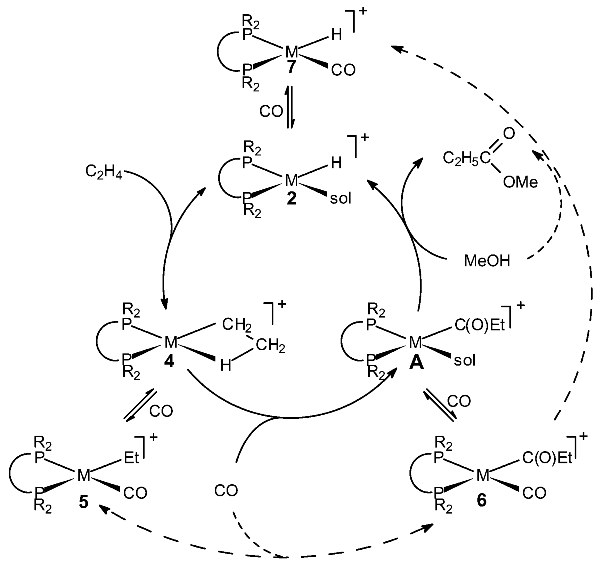
Fig. 1 $^{13}C\{^1H\}$ NMR spectra in CH_2Cl_2 of **5** at 193 K (a) and **6** at 293 K (b).

ethene, but *not* MEP, appear. **7** has been characterised by $^{31}P\{^1H\}$, ^{31}P, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopies as [Pt(L–L)H(CO)][CF_3SO_3]. The stability of **7** contrasts sharply with that of the Pd analogue which has a lifetime of only a few minutes at 223 K whereas solutions of **7** appear to be indefinitely stable at 293 K.

The formation of a stable carbonyl–ethyl complex **5** and the absence of alkyl migration at 193 K to give the acyl complex is in marked contrast with the reactivity pattern observed in the Pd system in which addition of CO to the ethyl complex results in immediate formation of a solvento–acyl complex **A** even at the lowest temperatures studied. A carbonyl–ethyl complex must be involved, at least as a transition state, in the Pd cycle but has not been conclusively identified; that the carbonyl acyl is readily detected as an intermediate in the Pt system indicates stabilization with respect to alkyl migration, of the ethyl intermediate **4** as the ethyl–carbonyl complex **5** occurs only in the Pt system. The ready reversibility of the reaction **5** ↔ **6** on Pt when compared with Pd is surprising; that the Pt ethyl–carbonyl complex only converts to the acyl complex on warming the solution to 293 K implies that the formation of **6** from **5** is an endothermic process. Steric congestion around the metal centre will be greater for Pd in which the acyl complex is formed at 193 K and one equivalent of CO is consumed in the reaction sequence **5** → **6** thus it seems unlikely that entropic factors are responsible for the difference in the positions of the Pd and Pt equilibria. We conclude that the position of the equilibrium is controlled by an enthalpic preference of the Pt centre for an ethyl rather than an acyl ligand.

Reaction of the ethyl complex **4** with *one* equivalent of CO in MeOH at room temperature rapidly gives **7**. When this reaction was repeated in the presence of excess ^{13}CO, a resonance due to MEP was observed in the $^{13}C\{^1H\}$ NMR spectrum in addition to those of **7**. Addition of MeOH at 290 K to a sample of **2** reacted first with $^{13}CH_2{=}CH_2$, then treated with excess ^{13}CO, and subsequently evaporated to dryness (to remove excess carbon monoxide and ethylene), results in quantitative conversion (by ^{31}P NMR) to the carbonyl hydride **7**. In the $^{13}C\{^1H\}$ NMR spectrum, resonances due to MEP *and* $^{13}CH_2{=}CH_2$ are observed in addition to those of **7**. These reactions demonstrate that, in the Pt system, only in the presence of excess CO is there significant forward reaction **4** → **5** → **6** → **7** + MEP *i.e.* **7** is a thermodynamic sink and will form *via* the back reaction **4** → **2** → **7** preferentially to the forward reaction to MEP in the absence of excess CO. This contrasts with the chemistry of the analogous Pd–ethyl complex which gives MEP and [Pd(LL)H(MeOH)]$^+$ on reaction with one equivalent of CO in MeOH and formation of MEP and catalyst degradation products on reaction with excess CO. The quantitative formation of **7** in the reactions above implies that methanolysis probably occurs *via* the carbonyl–acyl complex **6** rather than *via* the solvento–acyl complex **A** as found in the Pd system.

The observed reactivity of the Pt and Pd complexes is summarized in Scheme 1 in terms of the proposed catalytic cycle for the methoxycarbonylation of ethene. The higher affinity of Pt for CO results in the resting states of all the intermediates switching from the solvento adducts in the Pd cycle to the analogous carbonyl complexes in the Pt cycle. It is also noteworthy that in the Pt system the *reverse* reactions in the equilibria hydride ↔ ethyl ↔ acyl are readily accessible; thus we have shown that, in the absence of methanol, the carbonyl hydride **7** is formed from both **5** and **6** presumably by the back reaction, a feature not observed in the Pd system in which the momentum of the reaction appears to be in the forward direction. The carbonyl hydride complex **7** is much less reactive towards ethylene than the solvento hydride and this reaction is probably rate limiting in the Pt system although methanolysis of the carbonyl acyl complex is also slow.[5]



Scheme 1 The Pd and Pt catalysed methoxycarbonylation of ethene, M = Pd (inner cycle dominates) or Pt (complexes in outer cycle dominate).

In summary, we have shown that the Pt catalysed methoxycarbonylation of ethene follows an analogous pathway to the highly active Pd system. However, the formation of stable carbonyl complexes that are thermodynamic sinks for the reaction effectively removes Pt from the catalytic cycle. Coupled with more ready reversiblity of the product forming reactions observed in the Pt system, this, rather than the fact that the reactions of third row transition metals are usually slower than their analogous second row, accounts for the observed low activity of Pt in the methoxycarbonylation of ethene.

We thank Lucite International and the EPSRC for financial support.

Notes and references

1 W. Clegg, G. R. Eastham, M. R. J. Elsegood, R. P. Tooze, X. L. Wang and K. W. Whiston, *Chem. Commun.*, 1999, 1877.
2 E. Drent and P. M. H. Budzelaar, *Chem. Rev.*, 1996, **96**, 663.
3 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; G. R. Eastham, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *Chem. Commun.*, 2000, 609.
4 G. R. Eastham, R. P. Tooze, M. Kilner, D. F. Foster and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2002, 1613.
5 G. N. Il'inich, V. N. Zudin, A. V. Nosov, V. A. Rogov and V. A. Likholobov, *J. Mol. Catal. A: Chem.*, 1995, **101**, 221.
6 P. M. Maitlis, A. Haynes, G. J. Sunley and M. J. Howard, *J. Chem. Soc., Dalton Trans.*, 1996, 2187.
7 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.
8 N. Carr, L. Mole, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, 1992, 2653.
9 A. Scrivanti, C. Botteghi, L. Toniolo and A. Berton, *J. Organomet. Chem.*, 1988, **334**, 261.