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The carbonylation of methyl iodide and methanol to methyl acetate catalysed by palladium and platinum iodides

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Palladium(II) salts catalyse the carbonylation of methyl iodide in methanol to methyl acetate (5 atm CO, 140 °C) in the presence of a large excess of iodide, even without amine or phosphine co-ligands; platinum(II) salts show similar reactions but are a little less effective.

The substantial current interest in reactions catalysed by palladium–phosphine or palladium–amine[1,2] complexes prompts us to disclose new data on methanol carbonylation catalysts. We find that palladium(II), in the presence of an excess of iodide, catalyses the carbonylation of methyl iodide in methanol to methyl acetate at 5 atm CO, 140 °C. Under these conditions phosphine or amine co-ligands are not required.

The BP–Monsanto process for making acetic acid, methyl acetate, and/or acetic anhydride from methanol relies in its key (organometallic) steps on the carbonylation of methyl iodide catalysed by a rhodium and iodide system.[3] The *Cativa* process recently developed by BP Chemicals uses a closely related but more effective system based on a promoted iridium/iodide catalyst.[4,5] A number of other catalyst systems have been examined,[6] but because of the economic importance of the process, the search for new catalysts continues.

Although various carbonylation reactions involving palladium complexes have been described, they generally require co-ligands such as amines or phosphines.[7] If they are not present, the process is quickly deactivated with the formation of (inactive) palladium metal.

A palladium catalysed carbonylation of methyl iodide would be expected to comprise a cycle with individual steps similar to those found for rhodium and iridium, and since palladium complexes generally undergo carbonylation, migratory insertion and reductive elimination very easily, the slow rate determining step in the methyl iodide carbonylation cycle is probably the oxidative addition. In rhodium and iridium chemistry this step is enhanced by a more nucleophilic metal centre,[8] which can be achieved for example, by increasing the electron density at the metal with basic ligands. This could account for the reported use of ligands such as bipy in the palladium catalysed carbonylations.

We first investigated methyl iodide carbonylation using chelate N-ligands (‘N–N’), including bipyridyl and the very convenient Ar-BIAN ligands [bis(arylimino)acenaphthenes, derived from acenaphthenequinone and an aromatic primary amine, $ArNH_2$, Ar = phenyl, 4-tolyl, *etc.*] which can easily be ‘tuned’ by changes in the aryl substituents.[2] Reactions related to methanol carbonylation have also been modelled on palladium complexes, for example,[2]

$$[\mathrm{Pd(tmeda)(Me)(OR)}] + \mathrm{CO}\ (1\ \mathrm{atm},\ 25\,^{\circ}\mathrm{C}) \xrightarrow{\mathrm{Me_2CO}} \mathrm{MeCO_2R} + \mathrm{Pd^0}\ [\mathrm{tmeda} = \mathrm{Me_2NCH_2CH_2NMe_2};\ \mathrm{R} = \mathrm{Ph,\ CH(CF_3)_2}]$$

but we found no catalytic turnover (< 1 in 16 h) on carbonylating the chelate-iodomethyl complexes, [Pd(‘N–N’)(Me)(I)] in neat methanol.

However, catalytic reactions occurred in the presence of methyl iodide (Table 1). The complexes [Pd(4-Tol-BIAN)(Me)(I)], and [Pd(bipy)(Me)(I)], $[Pd(PPh_3)_2Cl_2]$ all gave turnovers in the range 10–20/16 h; the Ar-BIAN ligands were slightly better than bipy, and both were comparable to triphenylphosphine.

Substantial further improvements were achieved on addition of 40–100 equiv. per palladium of either a base or an ionic iodide.† Under our operating conditions the highest turnovers (*ca.* 110/16 h) were found using $[Pd(PPh_3)_2Cl_2]$ and Bu_4NI as additive. Slightly lower turnovers were obtained for other additives such as triethylamine, LiI, and other quaternary ammonium iodides. Higher amounts of a given iodide led to higher turnovers. Addition of small amounts of water (100–500 equiv./Pd) led to decreased turnovers but did not quench the reaction. Separate investigations showed that the role of amines was to generate the quaternary ammonium iodides by reaction with MeI.

When the solution containing $[Pd(PPh_3)_2Cl_2]$ and Bu_4NI was examined by ^{31}P NMR spectroscopy at the end of a catalytic reaction, there was no sign of PPh_3 coordinated to palladium. The only signal (δ 22.2) that could be detected was due to $[PPh_3Me]I$.

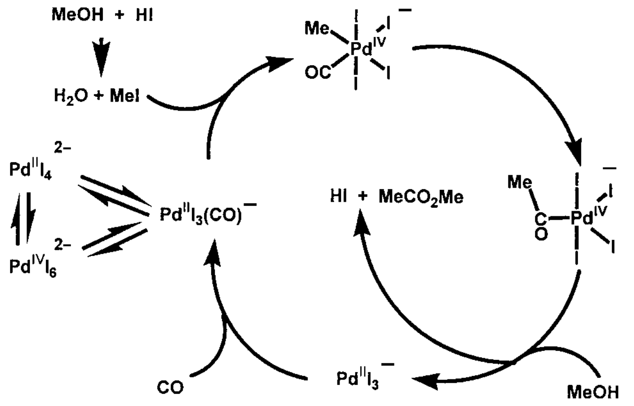
Thus the PPh_3 has become detached during the catalysis. To examine whether the ligand plays an important role, we investigated the catalytic behaviour of simple salts of palladium without any amine or phosphine co-ligands. Palladium iodide proved to be an effective catalyst by itself in the presence of excess iodide (but with no other stabilising ligand), giving a typical turnover of *ca.* 75/16 h.

A rather parallel reactivity sequence was provided by platinum. Again here $[PtI_4]^{2-}$ (formed *in situ*) was effective (turnover *ca.* 70/16 h), as were phosphine and amine complexes $[PtL_2Cl_2]$ [L_2 = $(PPh_3)_2$ > 4-Tol-BIAN ≈ bipy, ≈ $\{P(C_6H_{11})_3\}_2$].‡ Again, ^{31}P NMR examination of the catalyst solution using $[Pt(PPh_3)_2Cl_2]$ at the end of the reaction showed

Table 1 Carbonylation of methyl iodide and methanol to methyl acetate promoted by palladium or platinum complexes and anionic iodide[a]

Catalyst	Iodide additive/mmol	Turnover
[Pd(4-Tol-BIAN)(Me)(I)][b]	—	< 1
[Pd(4-Tol-BIAN)(Me)(I)][c]	—	10 ± 2
[Pd(4-Tol-BIAN)(Me)(I)]	—	20 ± 5
$[PdCl_2(PPh_3)_2]$	—	9 ± 2
$[PdCl_2(PPh_3)_2]$	Bu_4NI (0.4) or $(C_5H_{11})_4NI$ (0.4)	110 ± 5
$[PdCl_2(PPh_3)_2]$	LiI (1) or Et_3N (1)	95 ± 10
$[PdCl_2(PPh_3)_2]$	Bu_4NI (0.4) + water (100–500)	60 ± 5
$[PdCl_4]^{2-}$	Bu_4NI (0.5) or LiI (1)	80 ± 5
$[PdI_2]$	LiI (1)	70 ± 5
$[PtCl_2(PPh_3)_2]$	—	9 ± 2
$[PtCl_2(PPh_3)_2]$	Bu_4NI (0.4)	30 ± 5
$[PtI_4]^{2-}$	Bu_4NI (0.5) or LiI (1)	65 ± 5
$[Ni(NO_3)_2]$	Bu_4NI (0.5) or LiI (1)	15 ± 5
$[NiCl_2(PPh_3)_2]$	Bu_4NI (0.4)	15 ± 5

[a] *Conditions*: catalyst (0.01 mmol), methyl iodide (6 mmol, except where indicated) and iodide (as specified), and methanol (50 mmol) in Fisher–Porter tubes operating at a pressure of 5 atm CO, 140 °C, for 16 h. Analysis of the product (methyl acetate) was by GC (PE 8700; 10 m supel-Q-plot column, FID). Total turnover = number of equivalents of methyl acetate produced per equivalent of catalyst. [b] As *a* above but without any methyl iodide. [c] As for *a* above but with 0.6 mmol methyl iodide.



Scheme 1 A possible catalytic cycle for methanol carbonylation based on Pd^{II}/Pd^{IV}.

the presence of only $[PPh_3Me]I$ (δ 22.2). When K_2PtCl_4 + MeOH + MeI + Bu_4NI + CO (5 atm/16 h/140 °C) was used as the catalyst system, a $\nu(CO)$ 2063 cm^{-1} was observed in the IR spectrum of the residue once the volatiles had been removed. This is precisely the wavenumber quoted by Calderazzo and coworkers for $[Pt(CO)I_3]^-$,[9] and suggests that this species is involved in our catalytic cycle. No metal carbonyl was detected at the end of our palladium catalysed reactions, but Calderazzo and coworkers noted that $[Pd(CO)I_3]^-$ readily lost all its CO when the pressure was removed, and thus it is not surprising that we did not observe it.

Palladium catalysed methanol carbonylation, in the presence of very large amounts of specific promoters, such as sulfolane, and preferably an amine (*e.g.* 2,2′-bipyridyl) has been described in patents by van Leeuwen (Shell).[10] Those methanol carbonylation reactions required both quite severe conditions (for example, 182 °C/110 bar CO) and the addition of promoters such as bipyridyl; methanol carbonylation in the absence of such promoters was not claimed and platinum salts were specifically excluded from the Shell patents.

There do not appear to have been any reports of platinum catalysed carbonylations to methyl acetate, though the carbonylation of methanol to methyl formate has been noted,[6] and Kozitsyna and Moiseev reported that an unusual diphenylphosphido–platinum species in the presence of BF_3 did catalyse the carbonylation of methyl acetate to acetic anhydride.[11]

Nickel in the presence of iodide has long been known to catalyse methanol carbonylation, but only under drastic conditions (200–300 atm/230–350 °C).[12] We have tried nickel catalysts under our conditions and find activity but at quite a low level in the presence of 50–100 equiv. of iodide.

In summary, we have shown that, in the presence of excess iodide, palladium and platinum salts catalyse the carbonylation of methyl iodide in methanol to methyl acetate at 5 atm CO, 14 °C. The reactions taking place are best described by,

$$MeI + MeOH + CO \rightarrow MeCO_2Me + HI$$

followed by,

$$HI + MeOH \rightarrow MeI + H_2O$$

Catalytic cycles involving either M^{II}/M^{IV} or M^0/M^{II} (M = Pd, Pt) seem possible and an example of the former is illustrated in Scheme 1. It may be noted that iodide can stabilise Pd^{IV} as in Cs_2PdI_6.[13]

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Notes and references

† Bromide and chloride were also effective as promoters but less so than iodide.

‡ The ligands do seem to have a (second order) effect on the reaction; for example the tricyclohexylphosphine complexes $[M\{P(C_6H_{11})_3\}_2Cl_2]$ (M = Pd, Pt) are significantly less effective than the corresponding triphenylphosphine complexes. An effect of the counter-cation is also evident. Both these points are currently under investigation.

1 B. L. Shaw, *New J. Chem.*, 1998, 77; B. L. Shaw, S. D. Perera and E. A. Staley, *Chem. Commun.*, 1998, 1361.

2 I. Toth and C. Elsevier, *J. Am. Chem. Soc.*, 1993, **115**, 10 388; G. M. Kapteijn, A. Dervisi, M. J. Verhoef, M. A. F. H. van den Broek, D. M. Grove and G. van Koten, *J. Organomet. Chem.*, 1996, **517**, 123.

3 P. M. Maitlis, A. Haynes, G. J. Sunley and M. J. Howard, *J. Chem. Soc., Dalton Trans.*, 1996, 2187.

4 K. E. Clode, D. J. Watson and C. J. E. Vercauteren (BP Chemicals) EP 616997, priority date, 26/3/93; K. E. Clode, (BP Chemicals) EP 786447, priority date, 26/3/93; C. S. Garland, M. F. Giles and G. J. Sunley (BP Chemicals) EP 643034, priority date, 10/9/93; C. S. Garland, M. F. Giles, A. D. Poole and G. J. Sunley (BP Chemicals) EP 728726, priority date, 21/2/95; M. J. Baker, M. F. Giles, C. S. Garland and G. Rafaletos (BP Chemicals) EP 749948, priority date, 21/6/95; see also, *Chem. Br.*, 1996, 483; M. Howard, *Abstracts, XI International Symposium on Homogeneous Catalysis*, St. Andrews, 1998, p. M2.

5 T. Ghaffar, H. Adams, P. M. Maitlis, G. J. Sunley, M. J. Baker and A. Haynes, *Chem. Commun.*, 1998, 1023.

6 T. W. Dekleva and D. Forster, *Adv. Catal.*, 1986, **34**, 81.

7 See, for example, P. M. Maitlis, *Organic Chemistry of Palladium, Vol. II, Catalytic Reactions*, Academic Press, New York, 1971, p. 18; R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, 1985, p. 341; J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, 1995.

8 D. Forster, *J. Am. Chem. Soc.*, 1975, **97**, 951; C. E. Hickey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1984, 1609; A. Fulford, C. E. Hickey and P. M. Maitlis, *J. Organomet. Chem.*, 1990, **398**, 311; J. Rankin, A. D. Poole, A. C. Benyei and D. J. Cole-Hamilton, *Chem. Commun.*, 1997, 1835.

9 B. P. Andreini, D. Belli Dell'Amico, F. Calderazzo and G. Pelizzi, *J. Organomet. Chem.*, 1988, **354**, 369; B. P. Andreini, D. Belli Dell'Amico, F. Calderazzo, M. G. Venturi, G. Pelizzi and A. Segre, *J. Organomet. Chem.*, 1988, **354**, 357.

10 P. W. N. van Leeuwen (Shell Internationale Research Maatschappij BV) EP 0090443; priority date 30/3/82; P. W. N. van Leeuwen and C. F. Roobeek (Shell Internationale Research Maatschappij BV) EP 0133331; priority date 25/7/83.

11 N. Yu Kozitsyna and I. I. Moiseev, *Kinet. Katal.*, 1990, **31**, 251; 1992, **32**, 975.

12 W. Reppe, H. Kroeper, N. von Kutepow and H. J. Pistor, *Annalen*, 1953, **582**, 72; see also A. A. Kelkar, R. S. Ubale, R. M. Deshpande and R. V. Chaudhari, *J. Catal.*, 1995, **156**, 290.

13 D. Sinram, C. Brendel and B. Krebs, *Inorg. Chim. Acta*, 1982, **64**, L131; see also G. Thiele, K. Brodersen, E. Kruse and B. Holle, *Chem. Ber.*, 1968, **101**, 2771.

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