Rhodium(I) complexes of unsymmetrical diphosphines: efficient and stable methanol carbonylation catalysts†

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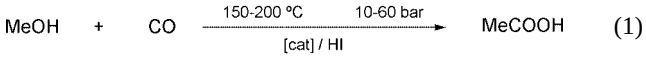
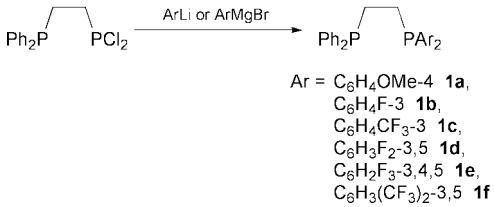
Rhodium complexes of unsymmetrical diphosphines of the type $Ph_2PCH_2CH_2PAr_2$ are catalysts for the carbonylation of methanol; several features of the catalysis are reminiscent of iridium carbonylation catalysts.

Methanol carbonylation (eqn. (1)) is one of the most successful industrial applications of homogeneous catalysis and is currently carried out on a scale of several million tonnes per annum.[1] The rhodium–iodide catalysed process gives acetic acid in better than 99% selectivity and the mechanism has been thoroughly reviewed by Maitlis *et al.*[2] The new *Cativa* process uses an iridium–iodide catalyst and offers many advantages over the rhodium system.[3] The conditions shown in eqn. (1) limit the use of phosphine modified catalysts because of the potential problem of quaternisation of the ligand.[1] Thus, while the rhodium complexes of P,O-, P,N- and P,S-donor ligands have all been reported[4–8] to be methanol carbonylation catalysts, either the conditions used were not the industrial conditions of eqn. (1) and therefore the process would not be viable,[4–6] or the catalysts were found to be unstable.[7,8] Here we report that rhodium complexes of unsymmetrical ethylene diphosphine ligands are more efficient catalysts than their symmetrical dppe analogues for methanol carbonylation and longer-lived than any previously reported ligand-modified catalysts under the harsh conditions of eqn. (1).[9]



(1)

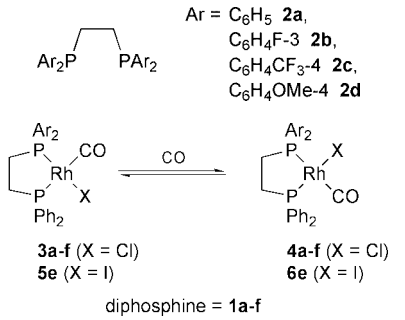
The diphosphines **1a–f**, some of which are known,[10,11] were made according to eqn. (2) and fully characterised. The



(2)

catalysts were prepared by addition of diphosphines **1a–f** or **2a–d** to $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in methanol [eqn. (3)]. Under these conditions the complexes **3a–f** and **4a–f** are formed in approximately 1 : 1 ratio in each case; these isomeric mixtures have been isolated and fully characterised. Similarly the iodo analogues **5e** and **6e** have been prepared and characterised as a 1 : 1 mixture.

The carbonylation catalysis was carried out under the conditions given in eqn. (1) and the results are presented in Table 1.† In each case the conversion of methanol was greater than 98% and the selectivity for acetic acid was greater than 99%; the rates for the diphos systems (entries 1–11) were all lower than the commercial $[RhI_2(CO)_2]^-$ catalyst. The following observations suggest that the catalyst is a diphosphine–



(3)

rhodium complex throughout and not $[RhI_2(CO)_2]^-$. IR spectra obtained *in situ* during catalysis with ligand **1e** showed the absence of the intense ν(CO) bands for $[RhI_2(CO)_2]^-$ at 2059 and 1988 cm^{-1}. At the end of the catalysis, when the solution cooled, a homogeneous orange solution or red crystalline precipitate was present and ^{31}P NMR and IR spectra showed the presence of a mixture of diphosphine rhodium(III) carbonyl complexes (^1J(RhP) *ca.* 100 Hz, ν(CO) *ca.* 2090 cm^{-1}). The product *fac*-$[RhI_3(CO)$(**1b**)$]$ **7** was isolated from the reaction mixture using the catalyst derived from **1b** and the crystal structure of its pentane solvate was determined (see Fig. 1). The octahedral geometry at the rhodium(III) centre is somewhat distorted (iodine atoms I(1) and I(2) lie 0.140 and 0.184 Å respectively from the RhP_2 plane). The carbonyl ligand lies *cis* to the diphosphine phosphorus atoms, which show identical Rh–P bond lengths, any difference in the values being masked by the disorder.‡ The rate of catalysis is constant throughout a run and, after all the methanol was consumed, a second aliquot of methanol was injected and the rate was the same as in the first run. This final observation not only confirms the integrity of the

Table 1 Methanol carbonylation data†

Entry	Ligand	Rate[a]	$CH_3CH_2CO_2H$[b]
1	**1a**	2.0	6
2	**1b**	5.0	45
3	**1c**	5.6	50
4	**1d**	8.5	79
5	**1e**	7.6	54
6	**1f**	2.9	31
7	**1b** + Ru[c]	13.7	188
8	**2a**	1.9	4
9	**2b**	2.0	13
10	**2c**	2.3	20
11	**2d**	1.7	12
12[d]	—	18.5	276

[a] At 10% conversion, in mol l^{-1} h^{-1} with estimated errors of 5–10%. [b] Concentration in ppm. [c] $[RuI_2(CO)_4]$ (0.576 g, 1.23 mmol) added to the catalyst mixture. [d] Catalyst is $[RhI_2(CO)_2]^-$.

† Electronic supplementary information (ESI) available: typical experimental procedure for catalysis. See http://www.rsc.org/suppdata/cc/b0/b002802i/

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catalyst but also shows its longevity is greater than any previous rhodium–phosphine catalyst under these conditions[7] since it shows that all the diphosphine catalysts undergo over 500 turnovers without noticable diminution of activity.

In the following respects, the rhodium–diphosphine catalysts resemble the iridium *Cativa* catalysts. The main inefficiencies in traditional rhodium-catalysed methanol carbonylation are the water gas shift reaction and the formation of by-products such as MeCHO, EtI and $CH_3CH_2CO_2H$; this problem is much reduced with the iridium catalysts.[3] The amount of propionic acid reported in Table 1 for the diphosphine catalysts (entries 1–10) is significantly less than with $[RhI_2(CO)_2]^-$ as catalyst under these conditions (entry 12). ^{31}P NMR studies in CH_2Cl_2 show that oxidative addition of MeI to **5e**/**6e** is very rapid. The greater nucleophilicity of [RhI(CO)(diphosphine)] complexes[12] than $[RhI_2(CO)_2]^-$ may partly explain the similarities between the rhodium–diphosphine and the iridium catalysts.

Since the iridium catalysts are promoted by iodide-abstracting ruthenium complexes,[3] we investigated whether $[RuI_2(CO)_4]$ would also promote the rhodium catalyst from diphosphine **1b**; by comparing entries 7 and 2 in Table 1, it is clear that the addition of the Ru complex has more than doubled the rate.

From the data in Table 1, it can be deduced that the influence of the phosphorus substituents is complicated. The rate data are plotted in Fig. 2 as a function of the Hammett constants for the aryl substituents. The plot shows that increasing the electron-withdrawing power of the substituents on the aryl rings in the unsymmetrical diphosphines generally increases the catalyst activity up to a point, beyond which the rate decreases. The significance of the maximum in the curve might be interpreted in terms of a balance of σ-donor and π-acceptor qualities being required to optimise the rate. However entries 4 and 9 in Table 1 are with ligands **1d** and **2b** which would be expected to have similar overall donor/acceptor properties by virtue of the same number of *meta*-fluoro substituents and yet they show very different catalytic performance. In fact, all of the symmetrical diphosphines **2a**–**d** yield catalysts of similarly low activity (entries 8–11). Thus the *asymmetry* of the diphosphine is apparently crucial. Casey *et al.*[10] have shown that unsymmetrical diphosphines are superior to the symmetrical analogues for hydroformylation catalysis and associated this with a preference of the better σ-donor for the axial site in the trigonal bipyramidal intermediates. It is notable that P,O-, P,N- and P,S-donor ligands used previously[4–8] for methanol carbonylation are all unsymmetrical with one strong and one medium or weak donor. For the best one ($Ph_2PCH_2CH_2P(S)Ph_2$), Baker *et al.*[7] showed that only one isomer (with the S-donor *trans* to CO) is formed in the reaction of $[Rh_2I_2(CO)_4]$ with the ligand. By contrast, we find no such diastereoselectivity in the reaction of diphosphines **1a**–**f** with $[Rh_2X_2(CO)_4]$ (X = Cl or I). In the presence of CO, ^{31}P NMR spectroscopy shows that the diastereoisomers **3**/**4** and **5**/**6** interconvert rapidly (eqn. (3) and thus the *ca.* 1 : 1 mixtures observed represent the thermodynamic proportions. Hence there is little difference in the stability of the [RhI(CO)(diphos)] precursors under ambient conditions in CH_2Cl_2 but it is possible that under the radically different conditions of the catalysis, one of the isomers is preferred or one is significantly more reactive.

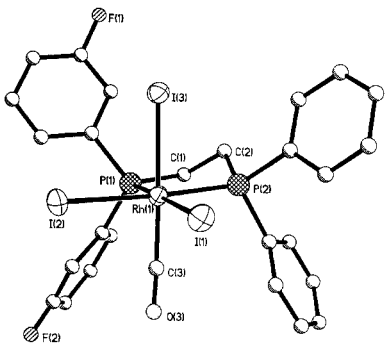

Fig. 1 The molecular structure of **7** showing one of the two orientations of the *meta*-C_6H_4F groups. Important molecular dimensions include: bond lengths (Å) Rh(1)–C(3) 1.885(6), Rh(1)–P(1) 2.335(2), Rh(1)–P(2) 2.3370(15), Rh(1)–I(1) 2.7337(7), Rh(1)–I(2) 2.7296(7), Rh(1)–I(3) 2.6869(6); bond angle (°) P(1)–Rh(1)–P(2) 86.03(6).

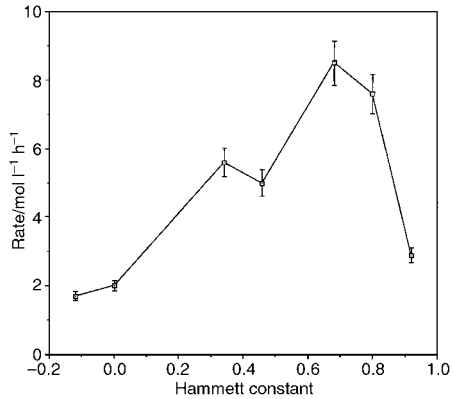

Fig. 2 Plot of the rate of methanol carbonylation (from Table 1) as a function of the Hammett substituent constant, σ for the Ar substituents in the ligands $Ph_2PCH_2CH_2PAr_2$. The error bars represent a 7.5% error in the rate measurement.

In conclusion we have established that unsymmetrical diphosphine–rhodium complexes are very active and selective catalysts for methanol carbonylation under industrially significant conditions and these catalysts have several features in common with the iridium *Cativa* catalysts.

We thank BP Chemicals and the EPSRC for financial support.

Notes and references

‡ *Crystal structure analysis* of $[Rh(CO)I_3[Ph_2P(C_2H_4)P(3\text{-}C_6H_4F)_2]\cdot 0.5C_5H_{12}$, **7**·$0.5C_5H_{12}$. *Crystal data*: $C_{29.5}H_{22}F_2I_3OP_2Rh$, M = 976.02, orthorhombic, space group *Pbca* (no. 61), a = 18.850(3), b = 15.338(4), c = 20.992(4)Å, T = 173 K, U = 6069(6) Å^3, Z = 8, μ = 3.755 mm^{-1}, 6885 unique data, $R1$ = 0.038. The fluorine atoms are disordered occupying one *meta* site on each of the four aryl rings equally as a consequence of the enantiomers of **7** crystallising at the same site in the unit cell. CCDC 182/1645. See http://www.rsc.org/suppdata/cc/b0/b002802i/ for crystallographic files in .cif format.

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