High Turnover Catalysis at Bimetallic Sites of the Hydration of Nitriles to Carboxamides Co-catalysed by Acid. Highly Specific Hydration of Acrylonitrile to Acrylamide

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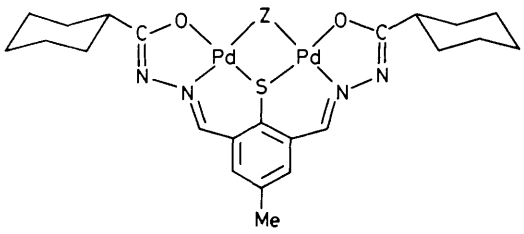
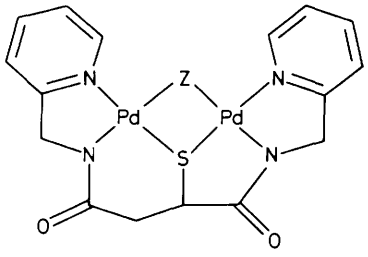
$LPd_2(MeCONH)$ and $L^*Pd_2(MeCONH)$, where L and L* are the binucleating ligands in (**1**) and (**2**), respectively, both catalyse hydration of acetonitrile, the acid dependence of which indicates a bimetallic pathway involving concerted action by the two metals and $L^*Pd_2(CH_2CHCONH)$ catalyses specific hydration of acrylonitrile to acrylamide.

There is currently much interest in the use of small groups of metal centres as catalytic sites. We report here the high turnover catalysis of the hydration of nitriles to carboxamides by di-palladium(II) complexes of thiolate-hinged binucleating ligands. Evidence below supports a genuine bimetallic pathway in which the two metal centres act in concert.

The binucleating ligands used here are those in complexes (**1**) and (**2**), represented by $LPd_2(Z)$ and $L^*Pd_2(Z)$ respectively. Earlier work shows that a wide variety of 3-, 2-, and 1-atom bridges (Z) can be incorporated at these Pd_2 sites.[1,2] Two separate species can also be accommodated, one bonded to each metal centre.[3] These observations point to the



(1)

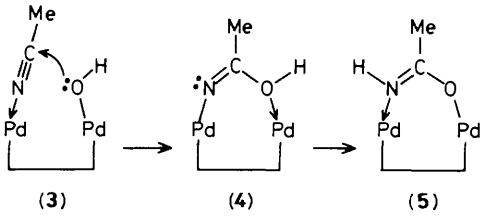


(2)

possibility, which may be widely applicable, of bond formation between the initially separate species to form a new bridge. An example of this type of process, *viz.* (**3**) → (**5**) (Scheme 1), has been described.[4] We report here a catalytic cycle, Scheme 2 (E = L or L*), with turnovers in excess of 4000 moles, in which the process (**3**)→(**5**) constitutes one step [Scheme 2, step (a)]. The ^{1}H n.m.r. spectrum of $LPd_2(OH)$[4] with $MeCONH_2$ (5 equiv.) in $CDCl_3$ at 25 °C shows essentially complete conversion to $LPd_2(MeCONH)$ within 50 min. This indicates that step (b) is a reversible equilibrium lying in favour of $EPd_2(MeCONH)$ in the absence of acid. ^{1}H N.m.r. spectroscopy also shows that in the presence of HBF_4 (1 equiv.), free acetamide is released quantitatively from the bridging site within the time required to make the measurement (25 °C, [$^2H_6$]dimethyl sulphoxide).

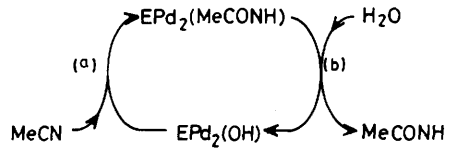
Catalytic hydrations [catalysts introduced as $EPd_2(MeCONH)$] were conducted in homogeneous solution in refluxing H_2O–MeCN mixtures (2:5 v/v) [with tetrahydrofuran (THF) or cyclopentanone co-solvent for the LPd_2 catalyst]. Maximum achievable catalyst concentrations were *ca.* 6 × 10^{-4} M. Acetamide production was monitored by g.l.c. The reactions were co-catalysed by acid (Figure 1). Parallel reactions without Pd_2 catalysts produced a negligible amount of acetamide. Analysis for NH_3 indicated negligible secondary hydrolysis of acetamide. The rate of hydration catalysed by $LPd_2(MeCONH)$ (THF co-solvent) was reduced by *ca.* 80% in the presence of added OH^- (1 equiv.). Degradation of L* by OH^- precluded similar studies with $L^*Pd_2(MeCONH)$. Rates of acetamide production, with and without acid, decreased with time, very much more so with $LPd_2(MeCONH)$. This fall-off did not arise from catalyst decomposition (catalysts could be recovered), but rather from inhibition by the acetamide produced, as a consequence of the reversibility of step (b).

Nitrile hydration is known to be catalysed by mononuclear hydroxo-platinum(II) complexes in strongly basic solution, the C–O bond forming step involving nucleophilic attack by free, unco-ordinated hydroxide upon the co-ordinated nitrile.[5] The above evidence for the Pd_2 catalysts, in particular the co-catalysis by acid and the inhibition by hydroxide, clearly excludes a similar mechanism in which free OH^- attacks a nitrile co-ordinated to one Pd atom with no participation by its neighbour. The evidence is, however, entirely consistent with



(3) (4) (5)

Scheme 1



Scheme 2

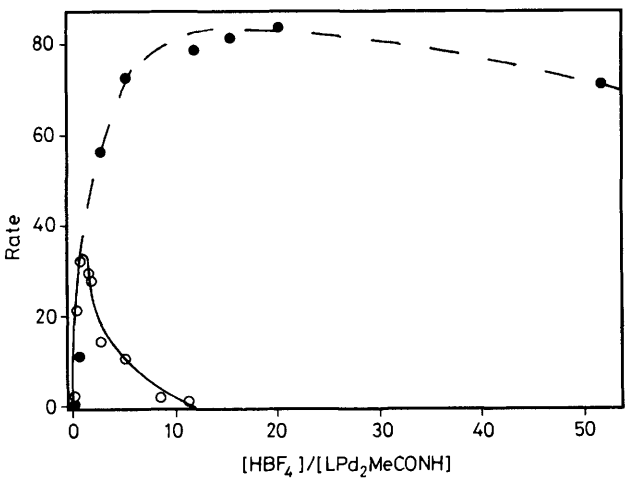


Figure 1. Dependence of initial rates of acetamide production upon relative concentration of HBF_4 (mol equiv.). Rate in mol $MeCONH_2$ mol^{-1} $EPd_2(MeCONH)$ h^{-1}; ●, $LPd_2(MeCONH)$ (4.6 × 10^{-4} M), MeCN–H_2O–THF (5:2:1 v/v). 76 °C; ○, $L^*Pd_2(MeCONH)$ (5.0 × 10^{-4} M), MeCN–H_2O (5:2 v/v), 76 °C.

the bimetallic mechanism in which the nucleophile is co-ordinated OH^- as in (**3**) → (**5**); step (a) is expected to be very slow at high acid concentration when the concentration of the hydroxo intermediate is negligible and step (b) to be very slow at low acid concentration because protonation of the bridging $MeCONH^-$ is required for its release; only at intermediate acid concentrations do both steps proceed at significant rates, leading to the maxima in the rate *vs.* [H^+] plots. Co-ordination of OH^- greatly reduces its basicity, allowing it to exist in sufficient concentration for the overall cycle to proceed, even in solutions acidic enough to accelerate the amide-releasing step (b). The fact that the nucleophilicity of OH^- as well as its basicity is reduced by co-ordination is offset by the highly favourable steric arrangement in the binuclear system.

Hydration of acrylonitrile catalysed by Pt–OH complexes is generally very indiscriminate giving mixtures of acrylamide (often a minor product) and products of attack at the alkene such as $HOCH_2CH_2CN$, $O(CH_2CH_2CN)_2$ and $CH_2{=}C(CN)CH_2CH_2CN$.[5] By contrast, acrylonitrile hydration catalysed by $L^*Pd_2(CH_2CHCONH)$[2] yields acrylamide very cleanly with no detectable amounts (capillary g.l.c.) of the above products. This reaction also is co-catalysed by acid.

The specificity of this reaction provides further support for the bimetallic pathway *via* a highly organised intermediate analogous to (**3**).

These results demonstrate for the first time that the following three basic requirements for catalysis of condensation processes at bimetallic sites can be met: (i), the site is able to accommodate two separate potential reactants in close proximity; (ii), bond formation between the two can occur; and (iii), the newly formed bridging species can be released so that the cycle can be repeated. This example provides encouragement that other processes catalysed by metal pairs await discovery.

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