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Facile hydrogen-transfer reduction of multiple bonds by formic acid catalysed with a Pd-561 giant cluster

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A palladium-561 giant cluster/HCOOH hydrogen-transfer reduction system has been found to be efficient for the liquid-phase hydrogenation of aromatic and aliphatic compounds with $N=O$, $C\equiv N$, $C=O$ and $C=C$ bonds under mild conditions; the reduction of nitriles is accompanied by metathesis of amines under unusually mild conditions.

Catalytic transfer reduction of specific functional groups (*e.g.*, $N=O$, $C=C$, $C=O$) is a promising method for addition of hydrogen to organic compounds using platinum metal complexes and hydrogen donors, such as cyclohexene, isopropanol, ascorbic or formic acid, instead of H_2.[1–3] Unlike the majority of substrates, nitriles are fairly resistant to hydrogen-transfer reduction.[1,2] The $C\equiv N$ group is also known to need more drastic conditions than other functional groups for hydrogenation by H_2 with both heterogeneous and homogeneous catalysts.[1,4,5]

In this work, nitriles were found to be readily hydrogenated in the presence of palladium giant cluster of idealized formula $Pd_{561}phen_{60}(OAc)_{180}$ **1**[6] when using formic acid as the hydrogen donor (Table 1).[†]

As seen from Table 1, acetonitrile is readily reduced at 20 °C by formic acid to afford triethylamine and diethylamine according to reactions (1) and (2).

$$2MeC\equiv N + 4HCOOH \longrightarrow Et_2NH + 4CO_2 + NH_3 \qquad (1)$$

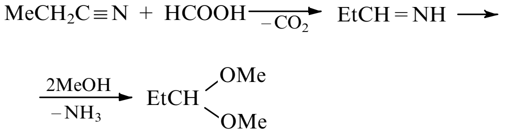
$$3MeC\equiv N + 6HCOOH \longrightarrow Et_3N + 6CO_2 + 2NH_3 \qquad (2)$$

Ethylamine was not detected in appreciable amounts. Similar mixtures of tertiary and secondary amines have been obtained upon hydrogenation of propionitrile and valeronitrile by H_2 (4–100 atm, 20 °C) on Pd/C and Pt/C heterogeneous catalysts.[1]

The hydrogen-transfer reduction of acrylonitrile by HCOOH catalysed with cluster **1** in a methanol solution produced primary amine in 30% yield (Table 1). In this case, the $C=C$ bond was first hydrogenated to form propionitrile followed by its hydrogenation to *n*-propylamine, reaction (3).

$$CH_2=CHC\equiv N + HCOOH \xrightarrow[-CO_2]{} MeCH_2C\equiv N \longrightarrow \xrightarrow[-2CO_2]{2HCOOH} PrNH_2 \qquad (3)$$

Secondary and tertiary amines were also obtained from acrylonitrile, along with dimethoxypropanal whose formation can be explained by methanolysis of the intermediate imine:



$$MeCH_2C\equiv N + HCOOH \xrightarrow[-CO_2]{} EtCH=NH \longrightarrow \xrightarrow[-NH_3]{2MeOH} EtCH(OMe)_2 \qquad (4)$$

Hydrogenation of benzonitrile by HCOOH resulted in the formation of primary and secondary benzylamines; no tertiary amine was found, while toluene constituted about a half of the reaction products irrespective of the reaction media (methanol or neat benzonitrile) (Table 1). In this case, hydrogenolysis of the intermediate imine seems to be more preferable than its methanolysis.

No reduction of nitriles by HCOOH or formate ions was observed under mild conditions with Pd-black [prepared from $Pd(OAc)_2$ and HCOONa] as a catalyst.

Formic acid, and especially formate anion, are expected to serve as donors of hydride ions,[5] readily forming Pd–H hydride groups at the surface of the cluster metal core. In this context, hydrogen-transfer reduction mediated by Pd giant clusters seems to be close in its mechanism to hydrogenation by H_2 catalysed by heterogeneous Pd catalysts, whose active phase consists of small Pd metal particles supported on an inert carrier. In fact, cluster **1** displayed high catalytic activity in the hydrogen-transfer reduction of various aromatic compounds.

As seen from Table 1, nitrobenzene, nitrosobenzene and phenylhydroxylamine were readily reduced by HCOOH to form aniline in quantitative yields in solutions containing cluster **1** (TOF ≈ 3000 at 20 °C). Hydrogenation of the $C=O$ and $C=C$ bonds attached to the phenyl ring was performed in this catalytic system as readily as that of N-containing functional groups in aromatic compounds.

It is noteworthy that the substrate molecules with both highly-polar ($N=O$, $C=O$) and low-polar ($C=C$, NH–OH)

Table 1 Hydrogen-transfer reduction of organic compounds by formic acid catalysed by cluster **1**.[a]

Substrate	Substrate conversion (%)	Products (yield, % mol on substrate converted)	TOF[b]
$MeC\equiv N$	3	Et_2NH (20) Et_3N (80)	1480
$CH_2=CHC\equiv N$ [c]	100	$PrNH_2$ (30) Pr_2NH (10) Pr_3N (45) $EtCH(OMe)_2$ (15)	600
$PhC\equiv N$	3.5	$PhCH_2NH_2$ (40) $(PhCH_2)_2NH$ (55) PhMe (55)	2200
$PhNO_2$ [d]	100	$PhNH_2$ (100)	3160
$PhN=O$ [d]	100	$PhNH_2$ (100)	3030
PhNHOH [d]	100	$PhNH_2$ (100)	2970
$PhC(Me)=O$ [d]	90	PhCH(OH)Me (65) PhEt (35)	2500
$PhCH=O$ [d]	100	PhMe (50) $PhCH(OMe)_2$ (50)	1530
$PhCH=CH_2$ [d]	100	PhEt (100)	2840

[a] [**1**] = 2.5 g dm^{-3} (3.1×10^{-5} mol dm^{-3}), $T = 20$ °C, argon atmosphere, substrate : HCOOH = 1 : 2, time of reaction 5 h.
[b] TOF = turnover frequency : mole of substrate converted per one hour by mole of cluster **1**. [c] 0.15 mol dm^{-3} solution in MeOH, time of reaction 24 h. [d] [substrate]$_0$ = 0.2 mol dm^{-3} in MeOH solution; time of reaction 2 h.

[†] Cluster **1** was prepapred by the method described in ref. 6. In a typical experiment, 25 mg of cluster **1** in 10 ml of solvent (a neat substrate or 0.2 mol dm^{-3} solution in MeOH) and formic acid (substrate : HCOOH = 1 : 2) was stirred under Ar during 5 h at 20 °C. The reaction products were identified by GC-MS; their concentrations were measured by GLC.

functional groups are subjected almost equally to hydrogen-transfer reduction with the cluster **1**–HCOOH catalytic system. These facts imply that virtual H^- ion is not in fact involved in the reaction mechanism.

Joint transfer reduction of the substrates in pairs is also of interest. Our experiments showed that the product composition of the hydrogenation of nitrobenzene by HCOOH in a MeCN solution containing cluster **1** depended on the duration of the reaction. After 5 h of reaction time, the main reaction product was *N*-ethylaniline; the rest was aniline (8%) and *N,N*-diethylaniline (2%). When reaction time increased to 24 h, the reaction produced no aniline, only 5% of *N*-ethylaniline and 95% of *N,N*-diethylaniline. Note that in both cases nitrobenzene was completely converted.

These data suggest that under catalysis with Pd giant cluster, a redistribution of alkyl groups occurred; this is referred to in organic chemistry as a metathesis of alkylamines.[7] In order to check this suggestion, dimethylamine was kept for 5 h in a MeCN solution containing cluster **1** and HCOOH. In contrast to the reduction of neat MeCN (see Table 1), only 10% of triethylamine and 5% of diethylamine were obtained, while dimethylethylamine composed 85% of the reaction products:

$$\mathrm{MeCN} + \mathrm{Me_2NH} \longrightarrow \underset{85\%}{\mathrm{EtNMe_2}} + \underset{5\%}{\mathrm{Et_2NH}} + \underset{10\%}{\mathrm{Et_3N}} \qquad (5)$$

Additional support for this suggestion came from experiments with joint reduction of the other pairs in methanol and MeCN solutions, where radical-exchanged amines were obtained along with the normal hydrogenation products [see, *e.g.*, reactions (6) and (7)].

$$\mathrm{PhNO_2} + \mathrm{MeCN} \longrightarrow \underset{8\%}{\mathrm{PhNH_2}} + \underset{90\%}{\mathrm{PhNHEt}} + \underset{2\%}{\mathrm{PhNEt_2}} \qquad (6)$$

$$\mathrm{PhCN} + \mathrm{Me_2NH} \longrightarrow \underset{45\%}{\mathrm{PhMe}} + \underset{40\%}{\mathrm{PhCH_2NH_2}} + \underset{10\%}{\mathrm{(PhCH_2)_2NH}} + \underset{5\%}{\mathrm{PhCH_2NMe_2}} \qquad (7)$$

Based on these data, some speculations concerning the mechanism of the giant Pd cluster-catalysed reductions by formic acid can be proposed. The first function of the cluster catalyst seems to be to abstract H atoms from the HCOOH molecule, forming Pd–H moieties at the surface of its metal core. It is still unclear which of the H atoms of the HCOOH molecule is involved in this reaction. Methyl formate was proved to be incapable of reducing all the substrates mentioned in the presence of cluster **1**. When using tetrabutylammonium formate as a reducing agent instead of formic acid, the hydrogenation proceeded *ca.* 20–30 times slower compared to the reaction with participation of formic acid. Meanwhile, the rate of hydrogenation by formic acid substantially accelerated, up to 10 times, in the presence of 30–50% of alkylammonium formates (Figure 1). These facts evidence that both formic acid and formate anion can participate in the hydrogen-transfer reduction.

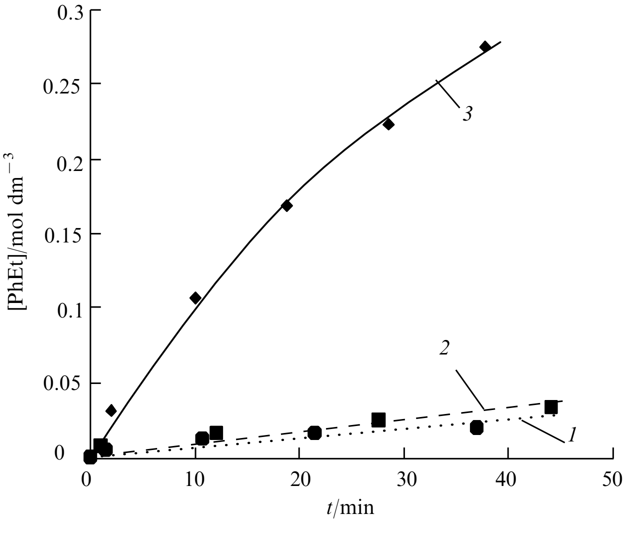
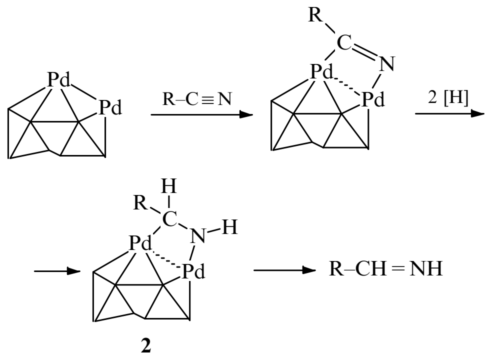


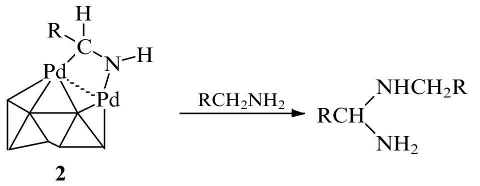
Figure 1 Curves of accumulation of ethylbenzene in the course of hydrogen-transfer reduction of styrene by formic acid and its mixtures with Et_3N: *1*, HCOOH; *2*, HCOOH:Et_3N = 1:1.5; *3*, HCOOH:Et_3N = 1.5:1. {[**1**] = 2.5 g dm^{-3} (3.1×10^{-5} mol dm^{-3}), *T* = 20 °C, argon atmosphere, $[\mathrm{HCOOH}]_0$ = 0.5 mol dm^{-3}}.



Scheme 1

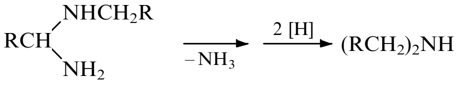
The second function of the giant Pd cluster seems to activate the C≡N, N=O and C=O bonds *via* oxidative addition of a substrate across the Pd–Pd bond. In the case of nitrile molecule the H atoms transfer to the coordinated substrate molecule should give rise to the coordinated aldimine molecule as shown in Scheme 1.

The subsequent transfer of two H atoms to intermediate **2** should give a primary amine. However, in the presence of free amine in the reaction solution intermediate **2** can undergo nucleophilic attack by the amine molecule to give rise to an elusive geminal diamine:



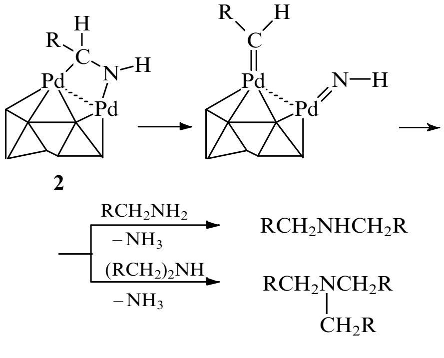
(8)

Elimination of the NH_3 molecule from the diamine and reduction of Schiff's base formed affords a secondary amine:



$$\mathrm{RCH}\begin{matrix}\mathrm{NHCH_2R}\\ \mathrm{NH_2}\end{matrix} \xrightarrow[-\mathrm{NH_3}]{} \xrightarrow{2\,[\mathrm{H}]} \mathrm{(RCH_2)_2NH} \qquad (9)$$

Repetition of this route with the coordinated aldimine and secondary amine should give a tertiary amine. Another mechanism assumes the intermediate formation of coordinated carbene species as shown in Scheme 2.



Scheme 2

Insertion of the intermediately-formed carbene species into the N–H bond of the primary amine is expected to afford a secondary amine, and analogous reaction with the secondary amine should give a tertiary amine.

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References

1 P. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, 1979.

2 R. A. W. Johnstone, A. H. Wilby and I. D. Entwistle, *Chem. Rev.*, 1985, **85**, 129.

3 G. Zassinovich and G. Mestroni, *Chem. Rev.*, 1992, **92**, 1051.

4 C. de Bellefon and P. Fouilloux, *Catal. Rev.-Sci. Eng.*, 1994, **36**, 459.

5 J. Volf and J. Pasek, *Stud. Surf. Sci. Catal.*, ed. L. Cerveny, Elsevier, Amsterdam, 1986, vol. 27, p. 105.

6 M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolarov, I. I. Moiseev, D. I. Kochubey, V. A. Likholobov, A. L. Chuvilin and K. I. Zamaraev, *J. Mol. Catal.*, 1989, **53**, 315.

7 J. March, *Advanced Organic Chemistry. Reactions Mechanism and Structure,* J. Wiley & Sons, New York, 1992.

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