Pd cluster catalysis: a review of reactions under anaerobic conditions†

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Discussed in this review are the mechanisms of redox and non-redox catalytic reactions (alkene isomerization, hydrogenation and hydrogen-transfer reduction of multiple bonds, reactions of CO and alkynes) that proceed under anaerobic conditions in the presence of di- and polynuclear palladium complexes with the Pd—Pd bonds.

Palladium clusters are well-known as efficient catalysts for oxidation reactions with molecular dioxygen as an oxidant.[1–4] Meanwhile, a variety of reactions not involving O_2 molecules, mediated by Pd clusters and polynuclear complexes, have been found and investigated over a period since the late 1960s.

In this paper some reactions catalyzed by palladium complexes with Pd—Pd bonds and which occur under anaerobic conditions, for example double bond isomerization, carbonylation reactions and reduction of multiple bonds, are surveyed. As a rule, in the systems under question mononuclear palladium complexes were originally believed to be the catalytically active species. A point of our special interest was to follow in each case how mechanistic investigations revealed cluster complexes to be the actual species responsible for catalysis.

1 Isomerization of alkenes

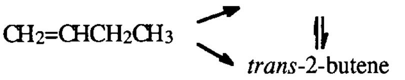
Some of the early evidence for palladium compounds with a Pd—Pd bond goes back to the studies of the Pd-catalyzed isomerization of alkenes[5–10] that have been performed prior to establishing the structural chemistry of palladium clusters.[11–16.]

1.1 Catalysis in the Pd^{II}–Pd^{I} system

Although the C=C bond isomerization of alkenes is conventionally a matter of catalysis by Brønsted or Lewis acids,[17] Pd-catalyzed alkene isomerization has been found to occur during the oxidation of *n*-butenes by Pd^{II} complexes.[5,6] The oxidation of 1-butene by $PdCl_4^{2-}$ in aqueous solution affords methyl ethyl ketone and Pd^0:

$$CH_2{=}CHC_2H_5 + PdCl_4^{2-} + H_2O \rightarrow CH_3C(O)C_2H_5 + Pd^0 + 2H^+ + 4Cl^- \quad (1)$$

In the course of reaction (1), 1-butene was also converted to the isomeric 2-butenes:



(2)

Reaction (2) can also be started from pure *cis*- or *trans*-2-butene, and in all the cases the reaction system reaches a thermodynamic equilibrium in which the mixture contains 2.8% of 1-butene, 74% of *trans*-2-butene and 23.2% of *cis*-2-butene at 298 K.[5]

It was found that under conditions where reaction (1) was suppressed, for example at high acidity and concentration of Cl^- ions, the isomerization did not occur. The isomerization reaction (2) was also absent on contacting *n*-butenes with water-free $PdCl_2$ in thoroughly dried aprotic solvents.[5–7]

Alkyl substituents at the double bond, which hamper alkene oxidation *via* reaction (1), also slow down the isomerization. However, addition of the more rapidly oxidizable 1-alkenes initiated the isomerization of 2- and 3-alkenes,[10] suggesting that 1-alkenes undergoing reactions (1) and (2) generate some active species responsible for the isomerization of both α- and inner alkenes.

Kinetic studies pointed to an interrelation between reactions (1) and (2). The rate of 1-butene oxidation, $-d[1-C_4H_8]/dt$, obeys the following kinetic equation:[18]

$$-\frac{d[1-C_4H_8]}{dt} = k_I\,\frac{[PdCl_4^{2-}][1-C_4H_8]}{[Cl^-]^2[H_3O^+]} + k_{II}\,\frac{[PdCl_4^{2-}]^2[1-C_4H_8]}{[Cl^-]^3[H_3O^+]} \quad (3)$$

The kinetics of the 1-butene isomerization is as follows:[7]

$$-\frac{d[1-C_4H_8]}{dt} = k_{isom}\,\frac{[PdCl_4^{2-}][C_4H_8]_\Sigma}{[Cl^-]^3[H_3O^+]}\,[1-C_4H_8] \quad (4)$$

Comparison of kinetic eqn. (4) with the second term of eqn. (3) points to their similarity. Additional support for this similarity comes from the investigation of kinetic isotope effects (KIE).[6,18] Nearly the same values of the solvent KIE for the alkene oxidation and isomerization reactions were found on going from H_2O to D_2O solutions: $k_{II(oxid)}(H_2O)/k_{II(oxid)}(D_2O) = 4.08 \pm 0.1$[18] and $k_{isom}(H_2O)/k_{isom}(D_2O) = 3.9 \pm 0.1$.[6] The above results suggested that the active sites of the isomerization are generated in the course of the reduction of Pd^{II}.

If the isomerization were catalyzed by palladium(II) complexes, then weak oxidants such as *p*-benzoquinone would not affect the process. In fact, the introduction of *p*-benzoquinone, H_2O_2 or Cu^{2+} halides into a reaction solution at the beginning or during the course of an experiment resulted in cessation of the isomerization, whereas no effect on the oxidation reaction was observed.[5,7,18] The cessation period for the isomerization terminated just after the oxidant had been consumed. An analogous effect of the oxidants was observed in the isomerization of 1-hexene.[7]

The above-mentioned facts indicated that the alkene isomerization is coupled with reaction (1) and that the actual isomerization catalyst is a reduced palladium species that can be readily oxidized by the oxidants mentioned. However, the freshly precipitated Pd metal, which was washed out of palladium chloride residues, did not cause alkene isomerization at

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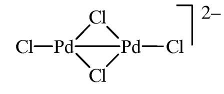
† Non-SI units employed: 1 atm ≈ 101 kPa.

0.1 MPa and 300 K;[5–10] moreover, the addition of large quantities of Pd black (0.1 g mL^{-1}) actually retarded the isomerization. This suggested that some species containing Pd atoms in oxidation state between 0 and +2 are responsible for the alkene isomerization. Examination of the kinetic data led to the conclusion that the isomerization is caused by at least a binuclear Pd complex in a 1+ oxidation state, such as complex **1**,[5,8] which can be formed *via* the second route [the second term of eqn. (4)] of the reduction of palladium(II).



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This is in line with all available data on the isomerization of alkenes catalyzed by Pd compounds. Furthermore, the Pd^I compound $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$, which has been shown by X-ray data to possess a Pd—Pd bond,[19] has been found to catalyze the isomerization of butenes efficiently:[20] 1-butene ⇌ *cis*-, *trans*-2-butene. Another piece of evidence for the catalysis by polynuclear Pd^I complexes has come from the study of 1-butene isomerization in a DMF solution of oligomeric Pd^I chlorocarbonyl $[Pd(CO)Cl]_n$.[21] The reaction was inhibited by *p*-benzoquinone, which oxidized Pd^I to Pd^{II}; however, the isomerization restarted due to Pd^I regeneration just after complete consumption of *p*-benzoquinone.[21]

It appears from the above-mentioned data that the reaction under question bears similarities to a chain reaction. The reduction of $PdCl_4{}^{2-}$ with 1-butene to form the isomerization-active species can be considered as a *chain initiation*:

$$1\text{-}C_4H_8 + 2\ PdCl_4{}^{4-} + H_2O \rightarrow Pd_2Cl_4{}^{2-} + CH_3COC_2H_5 + 2\ H^+ + 4\ Cl^- \quad (5)$$

Chain propagation consists of π-complex formation between Pd^I and 1-butene [eqn. (6)], its transformation to the Pd^I–2-butene complex [eqn. (7)] and subsequent replacement of 1-butene for the coordinated 2-butene [eqn. (8)]:

$$Pd_2Cl_4{}^{2-} + 1\text{-}C_4H_8 \rightleftharpoons 1\text{-}C_4H_8Pd_2Cl_4{}^{2-} \quad (6)$$

$$1\text{-}C_4H_8Pd_2Cl_4{}^{2-} \rightleftharpoons 2\text{-}C_4H_8Pd_2Cl_4{}^{2-} \quad (7)$$

$$2\text{-}C_4H_8Pd_2Cl_4{}^{2-} + 1\text{-}C_4H_8 \rightleftharpoons 1\text{-}C_4H_8Pd_2Cl_4{}^{2-} + 2\text{-}C_4H_8 \quad (8)$$

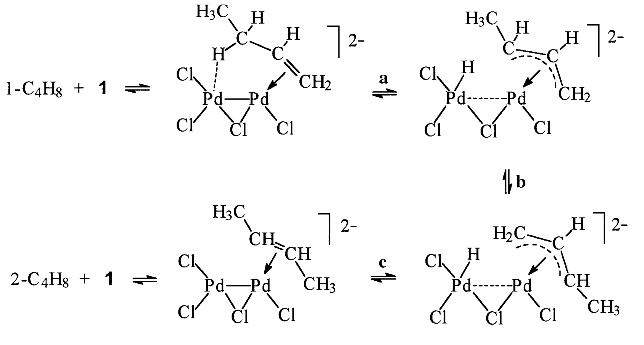
Decomposition of the Pd^I complexes and/or (more probably) Pd^I π-complexes giving rise to inactive Pd metal [eqn. (9)] can be considered as the *chain termination step*:

$$C_4H_8Pd_2Cl_4{}^{2-} \rightarrow C_4H_8PdCl_3{}^- + Pd_{solid} + Cl^- \quad (9)$$

The scheme consisting of eqn. (5)–(9) is in line with the available kinetic data.[7,18] A kinetic analysis shows that complex **1** can perform 10 to 100 turnovers of the isomerization during its lifetime.

The reaction is not accompanied by H/D exchange between alkenes and solvent in a D_2O solution,[6,22–24] suggesting that the isomerization reaction is an inner-sphere process. The isomerization of the isotope-labeled hexenes leads to a 1,3-shift of H atoms,[25] as shown in Scheme 1. In this scheme, the Pd atoms of the dimeric complex exercise different functions. One Pd atom interacts with the alkene double bond and, due to its acceptor ability, facilitates the splitting of the C—H bond in position 3 of the alkene molecule. The other Pd atom captures the H atom and transfers it from C_3 to C_1.

A key step in Scheme 1 is the oxidative insertion of an alkene molecule into the Pd—Pd bond (step **a**; the dashed line denotes a weak Pd—Pd interaction sustained by the bridging groups). The complex containing both the coordinated hydride ion and π-allyl ligand is formed at this stage. Rotation of the π-allyl group around the metal–metal axis (step **b**) and a follow-up transfer of the hydride ion to the C_1 atom of the coordinated allyl ligand (step **c**) results in the formation of a π-complex containing 2-butene instead of 1-butene.



Scheme 1

The mechanism of the alkene isomerization shown in Scheme 1 suggests a reversible hydrogen abstraction from the alkene molecule to form the intermediate π-allyl complex. An alternative mechanism, which incorporates a metal σ-alkyl intermediate *via* reversible addition and elimination of metal hydride to the alkene molecule, has also been proposed.[10,22,26,27] Such a mechanism requires the participation of Pd hydrido complexes. It is difficult to distinguish between these mechanisms based on the available experimental data. Nevertheless, recent studies with giant Pd clusters have brought important information about the reaction mechanism.

1.2 Cluster-catalyzed isomerization

1.2.1 Giant palladium clusters. One of the common preparation procedures for the synthesis of noble metal clusters is the reduction of the metal complexes in their higher oxidation states, for instance Pd^{II}, in the presence of 'soft' bases as ligands, such as L = PR_3, 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy).[28,29] On reducing $Pd(OAc)_2$ by H_2 (1 atm, 20 °C) with small amounts of L = phen or bpy in an AcOH solution (containing $\frac{1}{2}$ mole of phen per Pd atom), an X-ray amorphous substance **2** was obtained:[1,30,31]

$$4n\ Pd_3(OAc)_6 + 3n\ L + 15n\ H_2 \rightarrow 3[Pd_4L(OAc)_2H_4]_n, \quad n \approx 100 \quad (10)$$

2

Based on the TEM, SAXS, EXAFS, MAS ^1H NMR and elemental analysis data, this substance has been formulated as a polymeric hydrido complex whose molecules are built of $\cdots\{[(Pd_4LH_3)H(Pd_4LH_3)H]^{4+}(OAc^-)_4\}\cdots$ chains curled into balls of 20 ± 4 Å mean diameter.[1,31]

Hydrido complex **2** is unstable in air, losing the hydride ligands on exposure to O_2 and transforming into a new high molecular weight substance with the experimental formula $Pd_{570\pm30}phen_{63\pm3}(OAc)_{190\pm10}$ (**3**). Based on the HREM, electron diffraction, STM, NMR and EXAFS data, together with the elemental analysis data, the measurements of molecular mass and magnetic susceptibility, the molecule of **3** has been approximated, in an extension of the Chini concept of 'magic numbers',[32] by the idealized formula $Pd_{561}phen_{60}(OAc)_{180}$.[1,30] A molecule of **3** consists of a positively charged metal core of ≈25 Å in diameter, containing ≈570 ± 30 densely-packed Pd atoms (*i.e.*, 1 + 12 + 42 + 92 + 162 + 252 = 561 Pd atoms in an idealized five-shell icosahedron- or cuboctahedron-shaped core), ≈60 phen ligands and ≈180 outer-spheric OAc^- anions, the latter counterbalancing the positive charge (+180) of the metal core. The average formal charge of Pd atoms in the molecule of cluster **3** is $\approx +\frac{1}{3}$ (*i.e.*, the total charge of the metal core, +180, divided by the total number of Pd atoms, 561, is equal to +0.32).

These data are in line with the results of Schmid and coworkers, who obtained by a slightly varied preparation procedure the Pd-561 giant cluster formulated as $Pd_{561}phen_{38}O_{\approx 200}$.[33] The outer-spheric coordination of OAc^- ligands in cluster **3** is in line with the ease of their replacement by other anions. For example, complete substitution of the OAc^- anions accompanied by some hydrolysis, was observed on treatment of an aqueous solution of **3** with KPF_6 to form the cluster of idealized formula $Pd_{561}L_{60}O_{60}(PF_6)_{60}$ (**4**, L = phen):

$$\underset{\mathbf{3}}{Pd_{561}L_{60}(OAc)_{180}} + 60\ PF_6^- + 60\ H_2O \rightarrow \underset{\mathbf{4}}{Pd_{561}L_{60}O_{60}(PF_6)_{60}} + 120\ AcOH + 60\ OAc^- \quad (11)$$

The structure of cluster **4** has been determined by the same techniques as those used for cluster **3**.[1,31]

1.2.2 Isomerization by Group VIII metal clusters. Recently, the isomerization of allyl alcohol to propanal, which in fact is a 1,3-migration of the C=C bond:

$$CH_2{=}CHCH_2OH \rightarrow CH_3CH{=}CHOH \rightarrow CH_3CH_2CH{=}O \quad (12)$$

has been found to be efficiently catalyzed by the giant cluster $Pd_{570\pm30}phen_{63\pm3}(OAc)_{190\pm10}$, **3**, [idealized formula $Pd_{561}phen_{60}(OAc)_{180}$] in a MeCN solution at room temperature under Ar.[34] Cluster **3**, consisting of Pd atoms in a low oxidation state ($\approx\frac{1}{3}$, see above) and containing no hydride ligands, seems, therefore, to function as the active species in a π-allyl mechanism, like that shown in Scheme 1. It is also unlikely that mononuclear Pd^{II} complexes participate, because of their known capability to convert allyl alcohol into either acrolein, which is its normal oxidation product, or to stable π-allyl complexes,[35,36] none of which were formed in this case. In this case, participation of Pd metal was also ruled out, because Pd black has been shown not to catalyze the double bond isomerization.[34,36]

More evidence for isomerization catalysis by cluster complexes has been given by several structurally determined clusters of the Group VIII metals (*e.g.*, tri- and tetra-nuclear Fe, Ru, Os, Co clusters), which have been found to catalyze alkene isomerization.[37–41] For instance, 1-pentene was isomerized in the presence of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in an inert atmosphere, apparently indicating the participation of unstable π-allyl intermediates.[37,38] Nevertheless, some examples of clusters with M—H bonds are also known. $Ru_4H_4(CO)_{12}$ is more active than $Ru_3(CO)_{12}$ in 1-pentene isomerization[40] and $Co_3(CO)_6(PBu_3)_3$ has been found to conduct isomerization only under an H_2 pressure of 60 atm,[41] implying the participation of hydride complexes in the reaction mechanism.[42]

It is noteworthy that, unlike the isomerization of allyl alcohol, 1-butene was not isomerized with a measurable rate in the presence of the giant palladium cluster **3**.[1,34] Meanwhile, the alkene isomerization was found to proceed readily in the presence of the hydrido complex **2**.[1] Cluster **2** is also catalytically active in the dimerization of lower alkenes, converting ethylene to an equilibrium mixture of *n*-butenes and propylene to the isomeric *n*-hexenes. Both the dimerization and isomerization are inhibited by O_2, which transforms cluster **2** to the less active giant cluster **3**.[1]

2 Reduction of multiple bonds

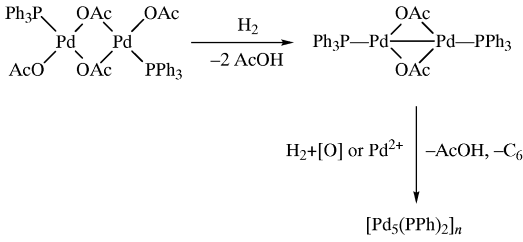
Hydrogenation of multiple bonds is one of the best known applications of Pd complexes in homogeneous catalysis.[43–45] The ability of palladium(II) complexes to catalyze the reduction processes by molecular hydrogen has been known since the early work,[46] where ferric chloride was found to be reduced by H_2 in solutions of palladium chloride. Palladium(II) salts and mononuclear complexes were commonly used as catalyst precursors for various hydrogen reactions.[44,45] However, for many of these catalytic systems the nature of the molecular species that are responsible for the catalytic activity is still unclear.

The major application of Pd clusters in catalysis is in hydrogenation reactions.[3,33,42,47,48] In the majority of cases, the reactions studied involve dihydrogen as a reducing agent. Meanwhile, some other reductants (2-propanol, formic acid, cyclohexene, *etc.*) can be used as a source of hydrogen atoms in the hydrogen-transfer reduction reactions.[49,50]

2.1 Hydrogenation with H_2

As a rule, when palladium(II) mononuclear complexes are used as catalyst precursors for the catalysis of hydrogenation reactions, some auxiliary ligands, for instance, soft bases like phosphines, phen, bpy or CO, are necessary to stabilize such a catalyst. Since the catalyzed reaction occurs in the H_2 atmosphere, the low-valent Pd complexes of a cluster nature can be expected to form under these conditions.[3,47,51,52]

Phosphines, particularly PPh_3, are most commonly used both for the synthesis of noble metal clusters and as the auxiliary ligands in catalytic systems for hydrogenation.[44,45] A variety of low and high molecular weight Pd complexes can be formed under the action of H_2 on Pd^{II} complexes, depending on the nature of the acido ligand, the solvent and the phosphine-to-Pd ratio.[3,51–53] For instance, the absorption of H_2 with $[Ph_3PPd(OAc)_2]_2$ in CH_2Cl_2 solution results in the formation of the polymeric low-valent Pd complex **5**, $n \approx 4$:[28,52]



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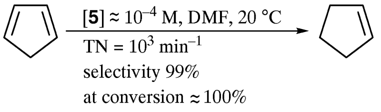
Complex **5** is formed reproducibly only if the gas phase contains small amounts (0.1–0.5%) of O_2, or if a small amount (≈1–2 mol per mol Pd) of a peroxide or $Pd(OAc)_2$ is added. This complex is apparently the actual species that is responsible for the efficient catalysis of the hydrogenation of various organic substances (Table 1).[51]

Cluster **5** is rather poorly soluble in organic solvents. No data concerning its structure are available. The complex does not absorb dihydrogen. However, in the presence of unsaturated substrates and cluster **5**, a fast H_2 absorption occurs with reduction of alkenes to alkanes and very selective formation of alkenes from alkynes or dienes. In a DMF solution, cluster **5** showed high activity and selectivity in the hydrogenation of alkynes, alkenes, and dienes (see Table 1), for example:



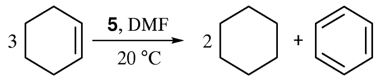
The high activity of the catalyst remains unchanged even after 7×10^4 mol of C_5H_6 per mol Pd have been reacted.

Table 1 Hydrogenation of organic compounds with H_2 in solutions of cluster **5** (20 °C, 1 atm, DMF solution)

Class of compound	Substrate	Reaction product	Catalytic activity[a]
Alkynes	Phenylacetylene	Styrene	120
Dienes	1,3-Pentadiene	2-Pentene	1000
Alkenes	1-Pentene	Pentane	100
	2-Pentene	Pentane	100
Aldehydes	Salicylaldehyde	Salicyl alcohol	2
Nitro compounds	Nitrobenzene	Aniline	5
Nitroso compounds	α-Nitroso-β-naphtol	α-Amino-β-naphtol	10
Quinones	*p*-Benzoquinone	Hydroquinone	5
Azo compounds	Azobenzene	Hydrazobenzene	2
Schiff bases	2-Oxybenzylidine-4-methoxyphenylamine	2-Oxybenzyl-4-methoxyphenylamine	2

[a] TN/(mol H_2) (mol Pd) min^{-1}

Cyclohexene undergoes disproportionation to benzene and cyclohexane in a DMF solution of cluster **5**:



Kinetic studies of the hydrogenations catalyzed by cluster **5**[53,47,51–53] indicated that it can undergo dissociation in a DMF solution:

$$\underset{\mathbf{5}}{[Pd_5(PPh)_2]_4} \rightleftharpoons 4\underset{\mathbf{5a}}{[(Pd_5(PPh)_2]} \quad (16)$$

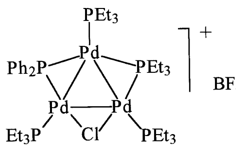
A complex between an alkyne or diene molecule S and cluster **5a** is formed in the first step:

$$\mathbf{5a} + S \rightleftharpoons \mathbf{5a} \cdot S \quad (17)$$

followed by reaction of the complex with H_2:

$$\mathbf{5a} \cdot S + H_2 \rightarrow \mathbf{5a} + \text{hydrogenation products} \quad (18)$$

Elimination of benzene due to the dephenylation of phosphine ligands attached to the Group VIII metal atom under the action of reductants (*e.g.*, sodium amalgam, H_2, HCOOH) is a general occurrence.[28a,b] For instance, a high-nuclearity substance formulated as $[(Pd_3P)_8PPh_3]_n$, along with benzene, are obtained on reducing $Pd(acac)_2$ with H_2 in solutions containing PPh_3.[52] A series of cationic trinuclear clusters $[Pd_3(PPh_2)_2(PR_3)_3X]^+BF_4^-$ (R = Ph, Et; X = Cl, Br, SCF_3) were synthesized and the crystal structure of the cluster $[Pd_3(PPh_2)_2(PEt_3)_3Cl]^+BF_4^-$ (**6**) has been determined by X-ray diffraction.[55]



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Hydrogenolysis of the P—C bond to form an alkane and a PR_2 ligand also occurred when Pd^{2+} trialkylphosphine (*e.g.*, PBu_3) complexes were treated with H_2.[52] In the case of a hydrogen-transfer reduction (see below), mononuclear Pd and Pt complexes readily lose the aryl or alkyl groups of the phosphine ligands. Reduction of $[Ph_3PPt(OAc)_2]_2$ with formic acid resulted in further dephenylation to form the PhP ligand;[28,56]

$$\begin{aligned}[Ph_3PPt(OAc)_2]_2 &\xrightarrow[-AcOH]{HCOOH} [Ph_3PPt(OCOH)_2]_2 \\ &\xrightarrow[-CO_2]{} [Ph_3PPtH_2]_n \\ &\xrightarrow[-C_6H_6]{} [Ph_2PPt]_n \\ &\xrightarrow[-C_6H_6]{} [PhPPt]_m \quad (19)\end{aligned}$$

Unlike platinum, treatment of the palladium complex $[Ph_3PPd(OAc)_2]_2$ with formic acid leads to the formation of a polyhydride complex $[Pd_2(PPh_2)H_x]_n$ and the binuclear phenyl derivative of palladium $[Pd(Ph)(\mu\text{-}O_2PPh_2)(PPh_3)]_2$ with a Ph—Pd bond and phosphonate bridges, whose structure has been established by X-ray diffraction.[57]

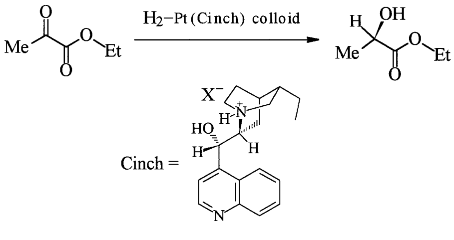
Recently, a colloid-like giant nickel cluster enveloped by a ligand shell consisting of PhP groups was obtained by reducing a nickel complex containing PPh_3.[58]

It follows from the aforementioned literature that hydrogenations using Pd or Pt phosphine complexes are often complicated by destructive hydrogenolysis of phosphine ligands and that the nature of the catalytically active species is rather complicated.

A somewhat clearer picture is available in the case of palladium catalysts containing heteroaromatics like phen or bpy as the auxiliary ligands. For instance, the reduction of $Pd(OAc)_2$ by H_2 in the presence of phen was found to form the polymeric hydrido complex $[Pd_4(phen)(OAc)_2H_4]_{\approx 100}$ (**4**, see *section 1.2.1* above), which exhibited catalytic activity in the hydrogenation of unsaturated substrates (*e.g.*, alkenes, quinones) in acetic acid solution under mild conditions (20 °C, 0.1 MPa).[1,59]

Clusters **4** and **3** are soluble in acetic acid and some organic solvents and can be used as homogeneous catalysts. In contrast, analogs of the giant cluster **3** containing bigger metal cores ($Pd_{1415}(phen)_{60}O_{\approx 1100}$ and $Pd_{2057}(phen)_{84}O_{\approx 1600}$)[33,60] and somewhat varied heteroaromatics as ligands (phen, 3-*n*-butyl-1,10-phenanthroline, 3-*n*-heptyl-1,10-phenanthroline, 2,9-di(2-methylbutyl)-1,10-phenanthroline and (−)-cinchonidine) are insoluble but can be used as efficient heterogeneous catalysts for the hydrogenation of unsaturated organic compounds when supported on TiO_2.[58,61]

The giant clusters mentioned above closely approximate colloidal palladium, serving as a model of a colloidal state of noble metals.[2,31,33,48] One of the recent applications of quasi-homogeneous catalytic systems based on noble metal colloids can be exemplified by the highly efficient enantioselective hydrogenation of ethyl pyruvate in the presence of the Pt colloid protected with chiral molecules of dihydrocinchonidine:[62]



This catalytic system provided an optical yield of 81.3% with a turnover frequency of 35.8 s^{-1}. The catalyst used in this work seems to be a giant platinum cluster with dihydrocinchonidine ligands coordinated at the surface of its metal core as colloid-protective groups.[62]

2.2 Hydrogen-transfer reduction

Hydrogen-transfer reduction allows one to hydrogenate multiple bonds (*e.g.*, N=O, C=C, C=O) without using H_2 as a source of hydrogen atoms. Isopropanol, cyclohexene, ascorbic and formic acid are commonly used as hydrogen donors.[44,49,50] Among these reactions, hydrogenation of carbon–nitrogen multiple bonds is of special interest for Pd cluster catalysis. For instance, heterogeneous catalysts such as Raney nickel or Raney cobalt are commonly used for hydrogenation of nitriles and normally the C≡N group needs more drastic conditions than other functional groups with both heterogeneous and homogeneous catalysts.[45,63,64]

Recently, the giant cluster **3** has been found to provide high catalytic activity under ambient conditions in the hydrogen-transfer reduction of nitriles using formic acid as the hydrogen donor.[65] As seen in Table 2, acetonitrile is readily reduced at 20 °C by formic acid to afford triethylamine and diethylamine according to:

$$2\,MeC{\equiv}N + 4\,HCOOH \rightarrow Et_2NH + 4\,CO_2 + NH_3 \quad (21)$$

$$3\,MeC{\equiv}N + 6\,HCOOH \rightarrow Et_3N + 6\,CO_2 + 2\,NH_3 \quad (22)$$

Ethylamine was not found in any detectable amount. Similar mixtures of tertiary and secondary amines were obtained on the hydrogenation of propionitrile and valeronitrile by H_2 (4–100 atm, 20 °C) on Pd–C and Pt–C heterogeneous catalysts.[45]

The hydrogen-transfer reduction of acrylonitrile by HCOOH catalyzed with cluster **3** in a methanol solution produced primary amine in 30% yield (Table 2). In this case, the C=C bond was first hydrogenated to form propionitrile, followed by its hydrogenation to *n*-propylamine:

$$CH_2{=}CHC{\equiv}N + HCOOH \xrightarrow[-CO_2]{} Et{-}C{\equiv}N \xrightarrow[-2\,CO_2]{2\,HCOOH} n\text{-}PrNH_2 \quad (23)$$

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

$$Et{-}C{\equiv}N + HCOOH \xrightarrow[-CO_2]{} Et{-}CH{=}NH \xrightarrow[-NH_3]{2\,MeOH} EtCH(OMe)_2 \quad (24)$$

Hydrogenation of benzonitrile by HCOOH resulted in the formation of primary and secondary benzylamines; no tertiary amine was found, while toluene constituted about half of the reaction products (Table 2). In this case, hydrogenolysis of the intermediate imine seems to be preferable to 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 anions,[64] readily forming Pd—H hydride groups at the surface of the cluster metal core. In this context, the hydrogen-transfer reductions mediated by Pd giant clusters seem to be mechanistically related to hydrogenations with H_2 catalyzed by supported Pd catalysts, whose active phase consists of Pd metal particles. In fact, cluster **3** displayed high catalytic activity in the hydrogen-transfer reduction of various aromatic compounds (Table 3).[65]

As seen in Table 3, nitrobenzene, nitrosobenzene and phenylhydroxylamine are readily reduced by HCOOH to form aniline in quantitative yields in solutions of cluster **3** (TOF ≈ 3000 h^{-1} at 20 °C). The C=O and C=C bonds attached to the phenyl ring are hydrogenated in this catalytic system as readily as that of the N-containing functional groups in aromatic compounds.

Under conditions where a competitive reduction of the substrates (*e.g.*, $PhNO_2$–MeCN) was expected, the hydrogenation of nitrobenzene by HCOOH in a MeCN solution of cluster **3** over 5 h afforded mainly *N*-ethylaniline, the other products being aniline and *N*,*N*-diethylaniline:

$$PhNO_2 + MeCN \rightarrow \underset{90\%}{PhNHEt} + \underset{8\%}{PhNH_2} + \underset{2\%}{PhNEt_2} \quad (25)$$

When the reaction time was increased to 24 h, the reaction produced no aniline, only 5% of *N*-ethylaniline, and 95% of *N*,*N*-diethylaniline. In all of the experiments no alkylamines were formed until the nitrobenzene had been completely consumed.[65]

These data suggest that under catalysis with Pd giant clusters, the redistribution of alkyl groups occurred, that is, a metathesis of amines.[17] In order to check this suggestion, dimethylamine was maintained for 5 h in the MeCN solution containing cluster **3** and HCOOH. In contrast to the

Table 2 Hydrogen-transfer reduction of nitriles by formic acid catalyzed with cluster **3**[a]

Substrate	Substrate conversion/%	Reaction products	Yield/mol % (based on substrate converted)	TOF[b]
MeC≡N (neat)	3	Et_2NH	20	1480
		Et_3N	80	
$CH_2{=}CHC{\equiv}N$[c]	100	$PrNH_2$	30	600
		Pr_2NH	10	
		Pr_3N	45	
		$CH_3CH_2CH(OMe)_2$	15	
PhC≡N (neat)	3.5	$PhCH_2NH_2$	40	2200
		$(PhCH_2)_2NH$	55	
		$PhCH_3$	55	
PhC≡N[d]	95	$PhCH_2NH_2$	45	1200
		$(PhCH_2)_2NH$	45	
		$PhCH_3$	10	

[a] [3] = 2.5 g L^{-1} (3.1 × 10^{-5} mol L^{-1}), $T = 20$ °C, argon atmosphere, substrate:HCOOH = 1:2, time of reaction 5 h. [b] TOF = turnover frequency (mol of substrate converted per hour by 1 mol of cluster **3**). [c] 0.15 mol L^{-1} solution in MeOH, time of reaction 24 h. [d] 0.19 mol L^{-1} solution in MeOH.

Table 3 Hydrogen-transfer reduction of aromatic compounds by formic acid catalyzed with cluster **3**[a]

Substrate	Substrate conversion/%	Reaction products	Yield/mol % (based on substrate converted)	TOF[b]
$PhNO_2$	100	$PhNH_2$	100	3160
PhNHOH	100	$PhNH_2$	100	2970
PhN=O	100	$PhNH_2$	100	3030
$PhC(CH_3)=O$	90	$PhCH_2(OH)CH_3$	65	2500
		$PhCH_2CH_3$	35	
PhCH=O	100	$PhCH_3$	50	1530
		$PhCH(OMe)_2$	50	
$PhCH=CH_2$	100	$PhCH_2CH_3$	100	2840

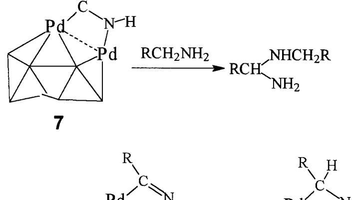
[a] [**3**] = 2.5 g L^{-1} (3.1×10^{-5} mol L^{-1}), $T = 20\,°C$, argon atmosphere, $[substrate]_0 = 0.17 \times 0.20$ mol L^{-1} in MeOH solution; substrate:HCOOH = 1:2, time of reaction 2 h. [b] TOF = turnover frequency (mol of substrate converted per hour by 1 mol of cluster **3**).

reduction of neat MeCN (see Table 2), only 10% of triethylamine and 5% of diethylamine were obtained, while dimethylethylamine composed 85% of the reaction products. Additional support for this suggestion was obtained from experiments on the joint reduction of the $PhCN + Me_2NH$ and $PhCN + PhNH_2$ pairs in methanol solutions. In both substrate pairs, organic-group-exchanged amines were obtained, along with the normal hydrogenation products:

$$PhCN + Me_2NH \xrightarrow{HCOOH/Pd_{561}} \underset{45\%}{PhCH_3} + \underset{40\%}{PhCH_2NH_2} + \underset{10\%}{(PhCH_2)_2NH} + \underset{5\%}{PhCH_2NMe_2} \quad (26)$$

Based on these data, some speculations concerning the mechanism of the giant Pd cluster-catalyzed reductions by formic acid can be envisaged. The first function of the cluster catalyst seems to be abstraction of 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 shown to be incapable of reducing all of the substrates mentioned in the presence of cluster **3**.[65] When tetrabutylammonium formate was used as a reducing agent instead of formic acid, the hydrogenation was 20–30 times slower compared to the reaction with formic acid. Meanwhile, the rate of hydrogenation by formic acid was accelerated by nearly ten times in the presence of 30–50% of alkylammonium formates. These facts suggest that both formic acid and formate anion can participate in the hydrogen-transfer reduction.

The second function of the giant Pd cluster seems to be to activate the C≡N, N=O and C=O bonds *via* the oxidative addition of a substrate across the Pd—Pd bond. In the case of the nitrile molecule, the transfer of hydrogen to the coordinated substrate molecule should give rise to a coordinated aldimine molecule as shown in Scheme 2. The subsequent transfer of two H atoms to the intermediate **7** should give a primary amine. However, in the presence of free amine in the reaction solution intermediate **7** can undergo a nucleophilic attack by the amine, giving rise to an elusive geminal diamine:



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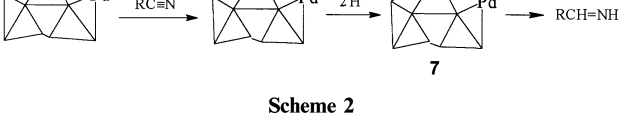
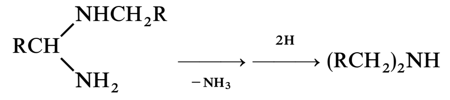


Scheme 2

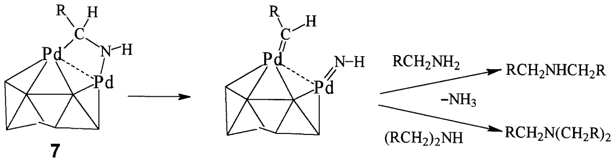
Elimination of the NH_3 molecule from the diamine and reduction of the resultant Schiff's base would afford a secondary amine:



$$RCH\begin{matrix}\diagup NHCH_2R\\ \diagdown NH_2\end{matrix} \xrightarrow[-NH_3]{} \xrightarrow{2H} (RCH_2)_2NH \quad (28)$$

Repetition of this route with the coordinated aldimine and a secondary amine should give a tertiary amine.

An alternative mechanism (Scheme 3) assumes the intermediate formation of a coordinated carbene species. Insertion of the intermediately formed carbene species into the N—H bond of the primary amine is expected to afford the secondary amine, while the analogous reaction with a secondary amine should give a tertiary amine.

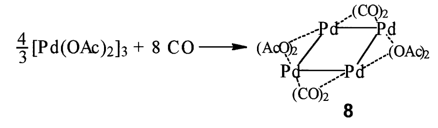


Scheme 3

3 Carbonylation reactions

Palladium-catalyzed reactions with the participation of carbon monoxide are of great industrial importance.[66–68] Among others, carbonylation of nitroaromatics and alkynes attracted our interest as these reactions are still believed to be mediated by mononuclear Pd^{II} complexes (see, for instance, pp. 1072 and 1119 in ref. 68).

Meanwhile, CO is well-known to readily reduce Pd^{II} to form Pd^{I} and Pd^{0} clusters both in neutral and acid media. For example, the tetranuclear cluster **8** with a rectangular Pd_4 metal skeleton was obtained by reaction between Pd^{II} acetate and CO (1 atm, 50 °C) in AcOH solution:[11]



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A number of low-valent Pd clusters containing up to 38 palladium atoms have been synthesized by reactions of Pd^{II} with CO in the presence of soft donor ligands such as phosphines or phen (which are often used as components of catalytic systems for carbonylation reactions[69–75]) and structurally characterized by X-ray diffraction analysis (see, *e.g.*, refs. 11–16).

On the other hand, low-valent Pd complexes could be reoxidized to Pd^{II} by an appropriate oxidant, such as nitrobenzene, when it is present in the reaction system. Therefore, statements that a Pd^{II} mononuclear complex is responsible for the observed catalysis in such carbonylation reactions, without compelling evidence, seem to be rather risky.

3.1 Carbonylation of nitroaromatics and phenol

Recently, the giant palladium cluster **3** has been shown to catalyse efficiently carbonylation of nitrobenzene. It was found that phenyl isocyanate (PIC) was formed according to reaction (30), in 12% yield, based on the original nitrobenzene, when a slurry of cluster **3** was stirred under CO (100–150 atm) at 150 °C (Table 4).[76]

$$PhNO_2 + 3\ CO \rightarrow PhNCO + 2\ CO_2 \qquad (30)$$

In the same work the oxidative carbonylation of phenol to diphenyl carbonate (DPC) was studied using a giant cluster **5** as a catalyst.[76] Carbonylation of alcohols and phenols to dialkyl and diaryl carbonates can be viewed as a redox reaction.

$$2\ ROH + CO + \tfrac{1}{2}\ O_2 \rightarrow (RO)_2CO + H_2O, \qquad (31)$$

where the CO molecule is oxidized to a carbonate moiety and a hydroxyl-containing substrate loses two H atoms to form H_2O. Patents protecting the performance of reaction (31) in the presence of Cu, Hg or Pd compounds are well-known[77] and palladium catalysts appear to be the most common among these.[67,78–80] Although reaction (31) looks fairly promising, its feasibility is mainly restricted to the synthesis of dimethyl carbonate from methanol and CO[78,79] and the literature concerning the catalysts for the synthesis of diaryl carbonates is mainly limited to patents.[81]

Based on the above-mentioned capability of cluster **3** to catalyse the carbonylation of nitrobenzene, it seemed promising to combine CO oxidation [reaction (31)] and nitroarene reduction [reaction (30)] within a unified Pd-based catalytic system. A giant palladium cluster could be expected to serve as such a catalyst due to both its capability to facilitate the nucleophilic attack of a ROH molecule on CO and its ability to act as an electron reservoir for the reduction of $ArNO_2$.

The average formal charge of palladium atoms in cluster **3** is equal to $\approx +\frac{1}{3}$ (see above, *section 1.2.1*). On the basis of electrostatic considerations (the Gauss theorem), the positive charge of the cluster nucleus is expected to be located largely on the 252 outer-layer Pd atoms of the idealized cluster structure resulting in a $+180/252 \approx +\frac{2}{3}$ formal charge for these metal atoms. Therefore, the outer-layer Pd atoms could be expected to enhance the reactivity of CO toward nucleophilic attack by the ROH molecule.

The experiments showed that oxygen-free CO is not oxidized by contacting giant clusters **3** and **4** at 1–100 atm and 20–90 °C, attesting that $Pd^{2/3+}$ is incapable of CO oxidation.[76] Nevertheless, based on the analogy with the giant cluster-catalysed oxidation of alkenes:[1]

$$C_2H_4 + AcOH + \tfrac{1}{2}\ O_2 \xrightarrow{[Pd_{561}]} CH_2{=}CHOAc + H_2O \qquad (32)$$

co-oxidation of CO and phenol by dioxygen was expected to take place in the presence of cluster **3** or **4**:

$$CO + 2\ PhOH + \tfrac{1}{2}\ O_2 \xrightarrow{[Pd_{561}]} O{=}C(OPh)_2 + H_2O \qquad (33)$$

However, contrary to expectation, no diphenyl carbonate was found in the reaction products (Table 4). Instead, CO_2 was readily formed in the pesence of O_2, when a solution of cluster **3** in neat phenol or a slurry of **3** in THF, CH_2Cl_2 or MeCN solutions of PhOH were contacted with a CO–O_2 (95 : 5 to 90 : 10) gas mixture, even at a pressure of 150 atm and temperatures up to 150 °C:[76]

$$CO + \tfrac{1}{2}O_2 \xrightarrow{[Pd_{561}]} CO_2 \qquad (34)$$

These facts imply that the electrophilicity of Pd atoms in the giant cluster is insufficient to allow the nucleophilic attack of the PhOH molecule to the coordinated CO group. Unlike alkenes, in the case of CO a new reaction route arises that includes the insertion of a CO molecule into the Pd—O bond that is formed on coordination of a O_2 molecule with the giant cluster, as shown in Scheme 4.

When nitrobenzene was used instead of dioxygen in order to suppress this route, diphenyl carbonate was obtained in a solution of cluster **3** in a nitrobenzene–phenol mixed solvent (Table 4). Phenyl isocyanate was found in the reaction products in yields as great as 30 to 50% of that of diphenyl carbonate. The reduction of nitrobenzene in a hydroxyl-containing medium, PhOH, was hardly expected to result in the same products (phenyl isocyanate mainly) as those formed in an aprotic solvent: neat nitrobenzene. Thus, the phenyl ester of phenylcarbamic acid, PhNHCOOPh, diphenylurea, PhNHCONHPh, and aniline, $PhNH_2$, were identified as the products of nitrobenzene reduction in the PhOH solution.

Therefore, the coupling of two processes occurred in the presence of cluster **3**, where Ox was nitrobenzene and Red was phenylisocyanate, aniline, and others.

(1) oxidative carbonylation of phenol:

$$2\ PhOH + CO + Ox \rightarrow (PhO)_2CO + Red \qquad (35)$$

(2) reductive carbonylation and reduction of nitrobenzene:

$$PhNO_2 + CO \rightarrow PhNCO$$

$$(\text{plus } PhNHCOOPh,\ PhNHCONHPh,\ PhNH_2) \qquad (36)$$

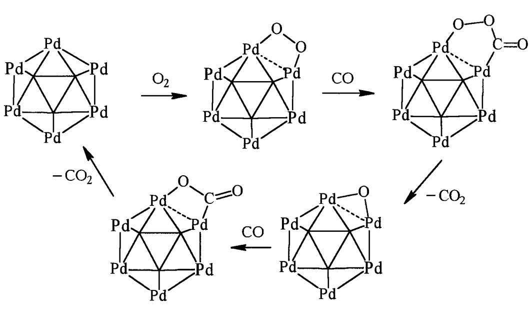
The coupling of reactions (35) and (36) can be understood within the framework of Scheme 5 where the metal core of the $Pd_{\approx 570}$ cluster functions as an electron-transfer mediator.

Unlike giant Pd clusters, Pd blacks were found to be incapable of catalyzing the reactions (35) and (36).‡ No products of phenol carbonylation were found in the presence of Pd

Table 4 Carbonylation reactions catalyzed by cluster **3** in PhOH solutions[a]

p(CO)/ atm	Oxidant, concentration/ mol L^{-1}	[PhOH]/ mol L^{-1}	Yield[b] DPC	PIC
145	O_2 (5 atm)	10.6	0	0
150	$PhNO_2$, 7.5[c]	0	—	67
150	$PhNO_2$, 2.7	7.6	21	60
140	$PhNO_2$, 2.7[c]	7.6	260	120
140	$PhNO_2$, 4.8[c]	5.3	230	135

[a] 150 °C, 3 h reaction time. [b] Mol of products per mol of cluster 3. [c] NMe_4Br (2 mol L^{-1}) was added.



Scheme 4

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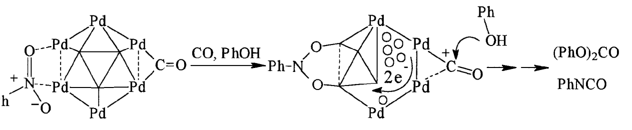
‡ Detailed comparison of the structure and reactivity of giant Pd clusters, Pd colloids and Pd blacks is a special topic that is beyond the scope of this paper.



Scheme 5

black prepared from $PdCl_2$ and $Pd(OAc)_2$ by common procedures.[76]

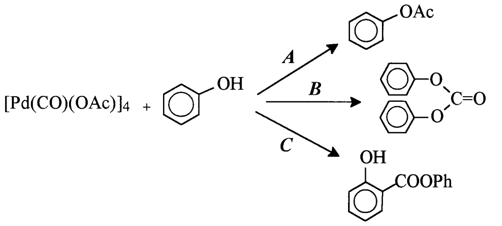
In the catalytic system under study, both reductants (CO and phenol) and oxidant (nitrobenzene) were present. Under these conditions some degradation of the giant cluster to form smaller clusters or even Pd^{II} complexes cannot be ruled out. In this context, the reactivities of possible intermediates, Pd^{II} acetate and the Pd^{I} carbonylacetate cluster **8**, toward CO and phenol were also studied.[76] The experiments showed that Pd^{II} acetate was readily reduced by CO (1 atm) in a phenol solution at 50 °C to afford CO_2 and phenyl acetate, according to reaction (37).

$$Pd(OAc)_2 + CO + PhOH \rightarrow Pd^0 + CO_2 + PhOAc + AcOH \quad (37)$$

No diphenyl carbonate was found in the reaction products.

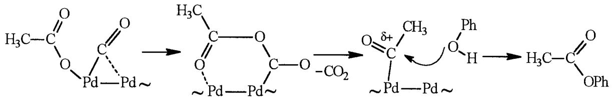
Pd^{I} complexes were also reduced by CO to give CO_2 and Pd^0. Unlike Pd^{II} in this case phenol can be involved in the redox reaction of CO and Pd^{I}. Nevertheless, only traces of diphenyl carbonate, phenyl acetate and phenyl salicylate were found in the products of the reaction between the tetranuclear cluster **8** and phenol at 90 °C under Ar or in an atmosphere of air (Table 5). However, under CO pressure (120–140 atm), and particularly with the addition of NMe_4Br, the yields of diphenyl carbonate, phenyl salicylate and phenyl acetate increased substantially. Diphenyl carbonate was also formed in a fairly good yield (42% based on coordinated CO) as the product of the reaction between polymeric $[Pd(CO)Cl]_n$ and phenol, whereas the other polymeric palladium(I) halide, $[Pd(CO)Br]_n$, yielded much less diphenyl carbonate (Table 5).[76]

Thus, in the reaction of cluster **8** with phenol, three pathways were observed that led to the formation of phenyl acetate, diphenyl carbonate and phenyl salicylate [eqn. (38), routes ***A***, ***B*** and ***C***, respectively]:



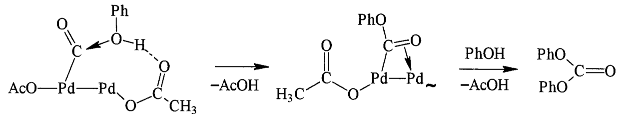
(38)

Esterification of the OAc^- anion *via* reaction (38***A***) seems to be a fairly uncommon reaction. It can be explained by the insertion of CO into the >Pd—OAc bond, forming the unstable intermediate >Pd—C(O)—OAc,[82] which can easily eliminate CO_2 to form a coordinated acetyl ligand. The aryl acetate is formed as a result of attack by a PhOH molecule, according to Scheme 6. Phenyl acetate seems to be formed by carbonylation of $Pd(OAc)_2$ in a similar way, *via* reaction of phenol with the CH_3CO^+ group attached to a Pd^{II} atom.



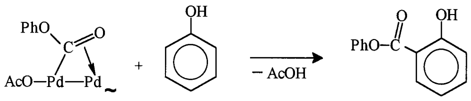
Scheme 6

Formation of diphenyl carbonate *via* reaction (38***B***) can be explained as the result of nucleophilic attack of the PhOH molecule on the CO ligand, according to Scheme 7.



Scheme 7

The third pathway of the reaction between cluster **8** and phenol [reaction (38***C***)], resulting in the formation of salicyl ester, may be considered as evidence for the attack on the aromatic ring of the phenol molecule by the coordinated PhO—C(=O)— group, reaction (39):



(39)

Hence, this study showed that palladium complexes of various oxidation states (2+, 1+, $\frac{2}{3}$+) differ substantially in their reactivity toward the CO plus phenol reagent system. In the case of cluster **8**, the pathway described by Scheme 6 predominates. The reaction includes the insertion of CO into the Pd—OAc bond, followed by CO_2 elimination to form a Pd—acyl complex, whose reaction with phenol gives phenyl acetate. This pathway is also realized in the case of Pd^{II} acetate.

The failure of diphenyl carbonate synthesis in the cluster **3**–CO–PhOH–O_2 aerobic system is apparently due to the low nucleophilicity of the PhOH molecule and the enhanced rate of the CO into Pd—O bond insertion. The use of $PhNO_2$ as an oxidant under anaerobic conditions allows one to avoid this obstacle and to perform the diphenyl carbonate synthesis as an oxidation reaction conjugated with the carbonylation and reduction of $PhNO_2$. The electron transfer from the coordinated CO to the oxidant molecule *via* the metal skeleton of

Table 5 Organic products of the reaction of Pd^{I} carbonyl complexes with phenol

Pd complex	Solvent, T/°C	p/(CO)/ atm	$p(O_2)$/ atm	Yield[a] Ph_2CO_3	PhOAc	PS
8	PhOH–THF, 20–60	0	0[b]	≈0.1	≈0.1	≈0.1 ≈0.1
8	PhOH, 90	0	0.2	≈0.1	≈0.1	≈0.1
8[c]	PhOH, 150	140	0	0.8	7.3	3.2
8[c]	PhOH, 120	120	5	25	46	5.0
$[Pd(CO)Cl]_n$	PhOH, 120	120	0	42	0	0
$[Pd(CO)Br]_n$	PhOH, 120	120	0	0.3	0	0

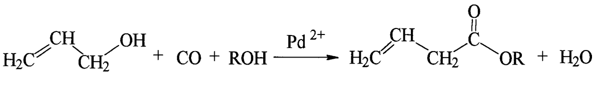
[a] Based on CO coordinated in the Pd^{II} complex (%). [b] Under argon (1 atm). [c] 2 mol L^{-1} of NMe_4Br was added.

a giant cluster (Scheme 5) makes possible the nucleophilic attack of phenol on the coordinated CO molecule to form diphenyl carbonate simultaneously with the reduction of nitrobenzene. In other words, coupled redox reactions can occur on such nanoparticle catalysts.

Hence, the above-mentioned data give evidence that participation of the low-valent Pd clusters in the mechanism of carbonylation of nitrobenzene and phenol is at least no less probable (or is often more probable) than that of the commonly cited mononuclear Pd^{II} complexes.

3.2 Carbonylation of allyl alcohol and propyne

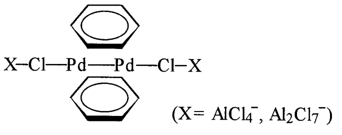
Allyl alcohol and its derivatives are known readily to undergo aryloxy/alkoxycarbonylation in the presence of Pd^{II} complexes, reaction (40).[83,84]



$$H_2C{=}CH{-}CH_2{-}OH + CO + ROH \xrightarrow{Pd^{2+}} H_2C{=}CH{-}CH_2{-}C(=O){-}OR + H_2O \qquad (40)$$

A recent study of the Pd^{II}-catalyzed carbonylation of allyl alcohol in different ROH media (R = Ph, alkyl) showed that phenoxycarbonylation (R = Ph) proceeds more rapidly than the alkoxycarbonylation (*e.g.*, R = Bu).[84] This observation drove the authors[84] to the conclusion that the PhOH molecule is a better nucleophile than BuOH. However, in all other organic reactions phenols are known as rather poor nucleophiles, much less so than simple alcohols. This fact suggests that another explanation should be used to rationalize the observed acceleration of the reaction occurring in the presence of a palladium catalyst.

The ability of the aromatic ring to stabilize the Pd^I—Pd^I moiety is well-known since the discovery of the binuclear complex **9**.[19]



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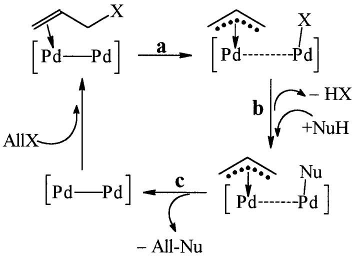
It is quite possible that the analogous $(Pd^I)_2$ complex can be formed in the system under discussion. If so, the increase in the reaction rate in a phenol solution is a result of the ability of PhOH molecules to stabilize the active species responsible for reaction (40), rather than the illusive 'enhanced nucleophilicity' of PhOH.

Within this hypothesis, reaction (40) can be envisaged as consisting of the following steps (see Scheme 8; the ligands coordinated to the Pd—Pd moiety are omitted for simplicity). In step **a** the allylic substrate undergoes an oxidative addition across the Pd—Pd bond. As a result, a π-allyl Pd complex is formed. The dotted line in the formulaes of the intermediate complexes denotes the bridging groups (*e.g.*, PhOH) that keep the two Pd atoms together. An attack of a nucleophile directed to the allyl group (step **b**) leads to the observed reaction product All—Nu and regenerates the original Pd—Pd catalytic species (step **c**).



Scheme 8

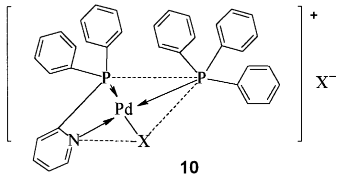
Another version of the mechanism based on the Pd^I—Pd^I catalytic species includes substitution of an X^- anion with the nucleophile anion and subsequent reductive elimination of All—Nu and regeneration of the catalytically active Pd—Pd complex.

One more example of the possible participation of low-valent complexes with a Pd—Pd bond is the highly efficient homogeneous Pd catalysts for the methoxycarbonylation of alkynes to acrylic esters.[74,85,86]

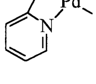
$$Me{-}C{\equiv}CH + CO + MeOH \rightarrow H_2C{=}C(Me)COOMe \qquad (41)$$

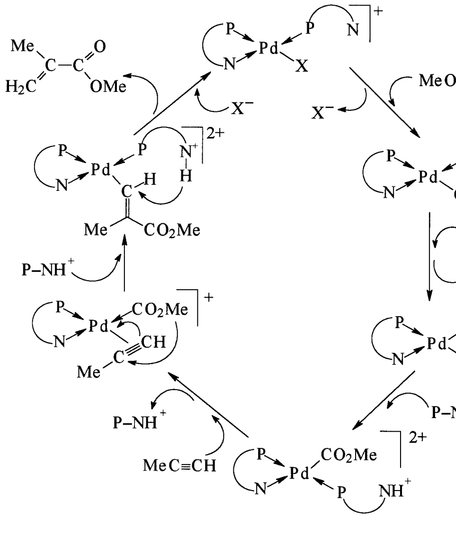
The homogeneous catalytic system is normally prepared from $Pd(OAc)_2$, a phosphine ligand L and an acid HX in a MeOH solution. It was found that the structure of the organic group in the tertiary phosphine ligand has a drastic effect on both the selectivity and activity of the catalytic system. The most efficient catalyst was that containing L = 2-pyridyldiphenylphosphine ($2\text{-}PyPPh_2$) as an auxiliary ligand. On going from $2\text{-}PyPPh_2$ to $3\text{-}PyPPh_2$, $4\text{-}PyPPh_2$ or PPh_3, a dramatic decrease in the catalyst activity and selectivity was observed.[85]

It was believed that the mononuclear Pd^{II} cationic complex **10** is assembled *in situ* and is responsible for the observed performance of the catalytic system.[85] The mechanistic scheme based on complex **10**, one in line with some qualitative observations,[85–87] is given in Scheme 9. This scheme resumes some criticism. First of all, the stated[87] high stability of a little-precedented (*i.e.*, in Pd^{II} chemistry) four-membered chelate cycle seems fairly questionable. Such a coordination does not explain the unusual catalytic activity of the Pd complexes formed in this system. Some additional details of the behavior of the catalytic system (*e.g.*, a minor influence of the Me group when introduced into the 2′ position of the L ligand)[87] cast doubt on any involvement of the mononuclear complex **10** in the reaction mechanism.



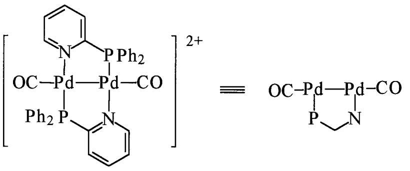
10





Scheme 9

On the other hand, 2-pyridyldiphenylphosphine is a unique ligand for stabilizing binuclear Pd$^{\rm II}$—Pd$^{\rm II}$ complexes owing to its geometry and the disposal of the coordination centers. Due to the known ease of the Pd$^{\rm II}$ to Pd$^{\rm I}$ reduction by CO in polar protic media (see, *e.g.*, ref. 11) it seems to be quite probable that in a CO atmosphere a palladium(I) carbonylphosphine complex of type **11** is first formed in this catalytic system.



11

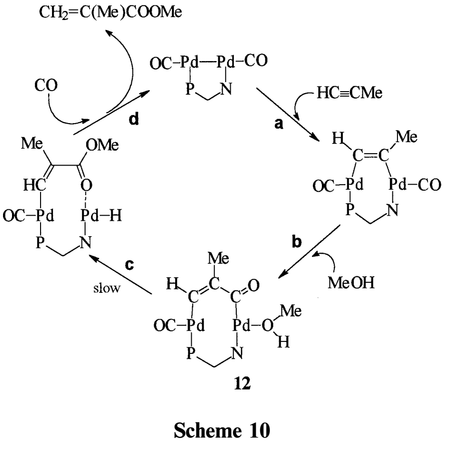
If this is the case, for propyne carbonylation, taking into account the observed first-order kinetics with respect to the MeOH concentration, zero-order with respect to [HX] and the lack of any influence of CO pressure on the reaction rates,[87] one can speculate that this reaction occurs *via* the alternative mechanism shown in Scheme 10.

In this scheme, the alkyne molecule is inserted across the Pd—Pd bond of complex **11** in step **a**. In step **b** the CO ligand inserts into the σ Pd—C bond of the coordinated alkyne molecule. It is noteworthy that the insertion occurs at the C—Me rather than at the C—H bond. This could be due to a specific steric situation in the Pd—C(Me)≡CH group. However, the more probable reason for this effect is that both the Pd—CMe and Pd—CH bonds are polarized with a positive charge on the C atoms. However, the positive charge of the C atom that is bound to the methyl group is expected to be noticeably higher than that of the C atom attached to the H atom. Because of this, the CO insertion is a polarity-controlled process, which produces intermediate **12** containing the —CH=C(Me)—CO— rather than the —CO—CH=C(Me)— group. The slow step **c** is a nucleophilic attack of the MeOH molecule (free or coordinated) onto the Pd—CO bond, followed by the reductive elimination of the vinyl ligand to form the final product and the original catalytically active Pd—Pd complex.

Concluding Remarks

The range of anaerobic reactions that are catalyzed by low-valent palladium complexes with Pd—Pd bonds, or by Pd clusters, is not exhausted by the examples outlined herewith. For instance, the water-soluble tetranuclear Pd cluster with bridging phosphinidene ligands having the composition $Pd_4(\mu^3\text{-PArNa})_2(\mu^3\text{-PPh})_2(H_2O)_8$ ($Ar = C_6H_4\text{-}m\text{-}SO_3^-$) has been found to catalyze the hydration of alkenes, with a ≈100% Markovnikov regioselectivity, in nearly neutral (pH 4) aqueous solution under Ar at 20 °C.[88,89]

The octanuclear heterometallic cluster $Na_2\{Pd_4[CpMo(CO)_3]_4\}$ was found to catalyze dehydration of aliphatic (MeOH, EtOH, *n*-PrOH, Me_3CCH_2OH and arylaliphatic ($PhCH_2OH$, Ph_2CHOH) alcohols in inert atmosphere.[90,91] The data available suggest that the reaction proceeds *via* an uncommon mechanism with intermediacy of carbene species.[92]



Scheme 10

Although giant Pd clusters cannot be classified as strong acids or strong bases, they were found to catalyze some reactions that are conventionally subjected to acid or base catalysis. For example, acetal (ketal) formation from aldehydes (ketones) and alcohols, which is typical of acid catalysis, is efficiently catalyzed by giant clusters **3** and **4** in Ar atmosphere without any added acid catalyst.[1,93]

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