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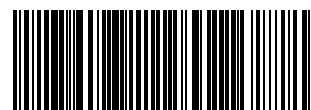
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Nanometallic chemistry: deciphering nanoparticle catalysis from the
perspective of organometallic chemistry and homogeneous catalysis

Nanometallic chemistry: deciphering nanoparticle catalysis from the perspective of organometallic chemistry and homogeneous catalysis

Ning Yan,*[a] Yuan Yuan[b] and Paul J. Dyson*[b]

Nanoparticle (NP) catalysis is traditionally viewed as a sub-section of heterogeneous catalysis. However, certain properties of NP catalysts, especially NPs dispersed in solvents, indicate that there could be benefits from viewing them from the perspective of homogeneous catalysis. By applying the fundamental approaches and concepts routinely used in homogeneous catalysis to NP catalysts it should be possible to rationally design new nanocatalysts with superior properties to those currently in use.

Background

A feature that unites all areas of catalysis is the trade-off between catalyst stability and catalyst activity. The most active catalysts tend to be the least stable and consequently the most active catalysts are seldom used as they do not give acceptable total turnover numbers. The origin of the problem is readily traced to the fact that vacant coordination sites (substrate binding sites) must be generated on the catalysts, whether it is a single metal atom or ion, a small cluster of metal atoms, a metal surface of nano-dimensions or a bulk metallic material.

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Such binding sites are intrinsically unstable – for a single metal atom/ion they are blocked by coordination of suitable ligands (sometimes a donor solvent) or protected by a bulky ligand and at the other extreme bulk metal surfaces are usually protected by an oxide surface that needs to be removed by a thermal treatment to generate the active (and unstable) catalyst. Gold catalysts are an exception due to the inertness of this metal and various methods have been described to remove coatings on supported nanogold catalysts.[1] To view a catalyst only in terms of activity–stability is, however, a gross oversimplification and once a catalyst is in an activated state then further structural and mechanistic details are vital in order to understand how the catalyst works and, with this knowledge, rational improvements should be possible. Moreover, in addition to reaction rate and catalyst stability, selectivity is a parameter of immense importance and developing catalysts that provide a single product in quantitative yield, or

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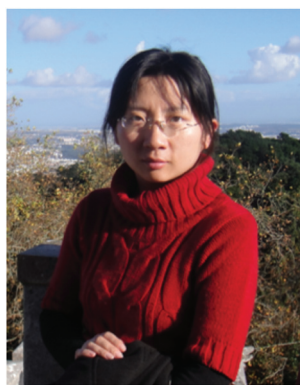
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aspiring as closely as possible to this goal, often dominates over simply obtaining high rates of conversion and high turn-over numbers.

In homogeneous catalysis the mechanistic details of a large number of catalytic processes have been delineated from a combination of *in situ* spectroscopic studies and the application of theoretical methods to provide complete catalytic cycles. With knowledge of the intermediate species and the rate determining step superior catalysts can be, at least in principle, developed. The design of new, homogeneous catalysts generally involves the manipulation of the ligands around the metal center, *via* the modulation of the steric and electronic effects of the ligand, and the application of multidentate and chiral ligands that impart specific geometric and topological constraints.[2–7] Using such an approach reaction rates may be increased, unwanted side products can be eliminated, and enantioselective transformations have become routine.

In contrast to homogeneous catalysts the intricate mechanistic details of nanoparticle (NP) catalysts are often less well developed. Demonstrating that the actual catalyst is a NP as opposed to a homogeneous catalyst derived from the NP often constitutes a mechanism.[8,9] A plethora of elegant studies that reveal how substrates interact with metal surfaces[10–16] and the preferential types of reactions that occur at specific sites on metal surfaces[17–21] should not be overlooked as they provide crucial information that illuminates the process of rational design. A representative example of this latter type of study concerns tetrahedral Rh NPs whose exposed facet is (111) planes that are 6-times more active than spherical NPs and over 100-fold more active than Rh immobilized on activated carbon.[22] Further examples on the size and shape control of NPs for reaction selectivity in catalysis are provided in recent reviews.[21,23] Nevertheless, the routinely used *in situ* spectroscopic methods that provide so much detailed information on homogeneous catalyst mechanisms cannot be easily applied to NP catalysts. The techniques widely applied for studying NP catalysis include transmission electron microscopy (TEM) and a variety of X-ray based techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy. TEM is still challenging as an *in situ* tool and XRD, XPS and XAS are unable to provide information specifically from the catalytically active sites, but instead provide averaged information of both catalytic relevant and irrelevant species. Although there has been considerable progress in recent years,[24] these limitations, relative to homogeneous catalysis, illustrate the challenge of delineating reaction mechanisms on NP catalysts.

NP stability *versus* activity

The kinetic instability of NPs has a profound impact on nanocatalysis as high stability is crucial for industrial processes that must be sufficiently robust to be economically viable. Stabilizers are used to enhance NP stability; indeed the use of stabilizers tends to be a prerequisite for solvent-dispersed NPs for any application. Various types of stabilizers have been explored, ranging from small molecules to macromolecular systems and there are parallels between NP stabilizers and ligands employed in homogeneous catalysis, *i.e.* NP stabilizers often coordinate to the surface metal atoms *via* donor atoms, and like ligands, provide both electronic and steric stabilization.[25]

Catalytic stability and activity are generally counterproductive and the more stable the NPs the lower the catalytic activity and this dichotomy has been demonstrated numerous times. For example, Ir NPs coated with amines or phosphines, which are relatively strong ligands, are catalytically inactive whereas Ir NPs protected with ammonium or phosphonium salts, which do not formally coordinate to the metal surface, are highly active hydrogenation catalysts and yet also highly unstable.[26] Similar trends have been observed with Rh NP[27] and comparisons of various dendrimer and polymer stabilizers also show that the most catalytic active NPs are the least stable.[28]

The first elemental step of a reaction catalyzed by a NP depends upon the reaction in question, however, it is usually considered to correspond to the adsorption of a substrate (or substrates) onto the particle surface, and for hydrogen, following the formation of hydrides (even into deeper layers within the NP).[29–31] As a consequence of this process within the catalytic cycle the availability of reactive surface metal atoms is crucial and dynamic interactions (migration or dissociation to generate coordinately unsaturated surface atoms) between the NP stabilizer and NP surface are a prerequisite, see Scheme 1 for the proposed mechanism applicable to solvent dispersed NPs in the hydrogenation of a model substrate. As such, stabilizers that form strong or even irreversible interactions, typically coordination (covalent) bonds that occupy a large number of surface atoms, result in poor catalysis. It is therefore imperative to strike a balance between catalytic activity and stability which can only be achieved by careful control of the NP surface–stabilizer interactions, *i.e.* covalent, steric and electrostatic interactions.[32] There is a direct comparison with ligands that bind to single metal centers in a homogeneous

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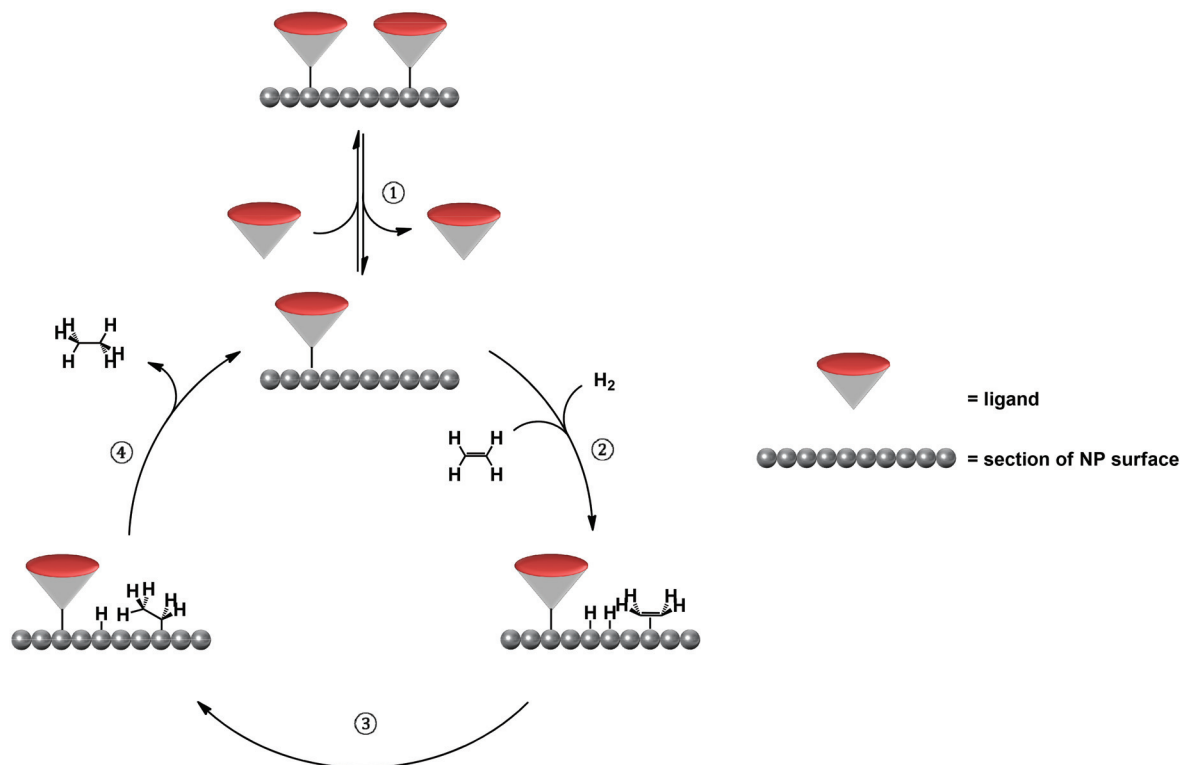
Scheme 1 Plausible steps for catalytic hydrogenation using stabilizer-coated dispersed NPs (with ethylene as a model substrate). (1) Ligand (stabilizer) dissociation from the NP pre-catalyst to afford the active catalyst species. (2) Oxidative addition of hydrogen and association of ethylene, note that is unclear in which order these reactions take place and that the resulting hydrides and ethylene ligands can migrate over the surface and adopt different multicenter bonding modes. (3) Migratory insertion to afford an alkyl bound to the NP surface. (4) Reductive elimination to afford the product, ethane, simultaneously regenerating the active NP catalyst.

catalyst, as ligands coordinate to the metal *via* lone pairs or π-bonds, or can offer steric protection *via* the presence of bulky substituents, and can be neutral or charged, with all components influencing ligand exchange kinetics.

There is a direct parallel to classical heterogeneous catalysis, in which the surface reaction is characterized by either the Eley–Rideal or Langmuir–Hinshelwood mechanisms, which may also be applied to solvent dispersed NPs. For reactions involving two substrates, the Eley–Rideal mechanism corresponds to a reaction in which only one of the substrates adsorbs to the catalyst surface and the other reacts directly with it from the gas or solution phase, whereas in the Langmuir–Hinshelwood mechanism, both reactants are adsorbed on the catalyst surface. Alkene hydrogenation with Ir NP catalysts obey the Langmuir–Hinshelwood mechanism,[33] as do deoxygenation reactions catalyzed by polyvinylpyrrolidone (PVP) stabilized Pt NPs.[34] The direct transfer of classical surface reaction kinetics to NP systems provides useful information concerning the nature of the catalyst (heterogeneous *versus* homogeneous) and, to some extent, the reaction mechanism. However, NP catalysis in the solution phase must undergo a stabilizer dissociation step prior to substrate absorption. Indeed, adding more PVP reduces the reaction rate of the deoxygenation reaction mentioned above, suggesting that the stabilizer competes with the substrate for the same surface sites, and implying that a stabilizer dissociation step should be included in the kinetic model.

NP aggregation and fragmentation

Poorly stabilized NPs tend to be more active as their reactive surfaces are more readily exposed. However, they are also less stable and are more prone to aggregate into larger metallic species or fragment into monometallic (homogenous) units that are presumably stabilized by the solvent or NP stabilizer. NP aggregates tend to be less active catalysts as their surface areas, *i.e.* reactive areas, are reduced. And for many reactions, *e.g.* arene hydrogenation,[35] NPs are more active than their mononuclear counterparts due to multicenter bond activation and electronic effects induced by the surrounding metal atoms. However, NPs also appear to act as reservoirs of homogenous monometallic catalysts generated *in situ*, following reaction with a substrate, and consequently completely switching the reaction mechanism. There has been much debate concerning the nature of the active catalytic species in C–C coupling reactions including Heck,[36–41] Ullmann,[42] and Suzuki[43,44] couplings catalyzed by Pd NPs,[45,46] with evidence to suggest that the NP is essentially a source of Pd(II) species formed from the oxidative addition of the arylhalide substrate
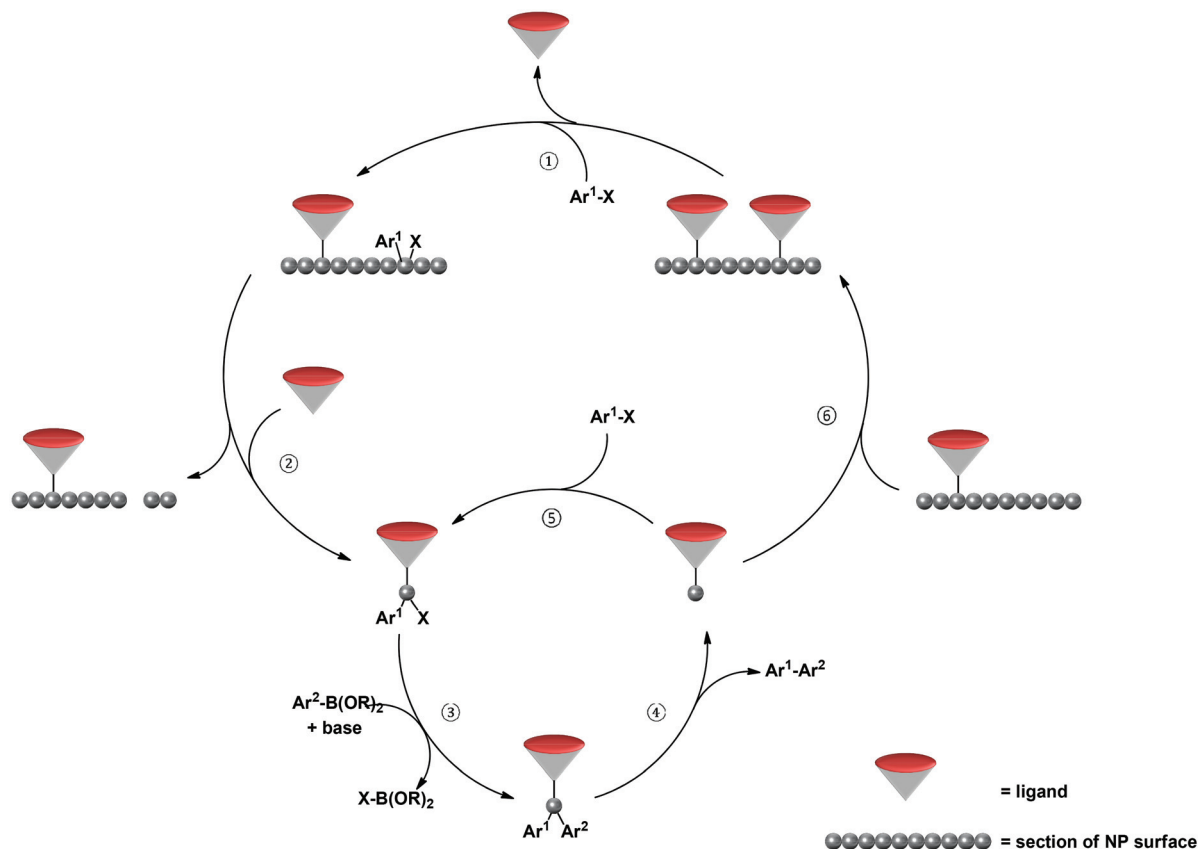
Scheme 2 Generic catalytic cycle showing the interplay between NPs and the active Pd(II) catalyst for C–C cross coupling reactions. (1) Ligand (stabilizer) dissociation providing access of the substrate to the NP surface following by oxidative addition of the aryl-halide substrate. (2) Release of the Pd(II) ion and formation of an active catalyst following further reaction with the ligand stabilizer. (3) Transmetallation. (4) Reductive elimination of the product to afford a Pd(0) species. (5) Oxidative addition of the aryl-halide substrate to regenerate the active Pd(II) catalyst. (6) Reformation of the NP pre-catalyst. Note that the trigonal intermediate shown is a representation of the active catalyst species and should not be considered as the actual geometry which is presumably square planar and could be formed from a chelating ligand stabilizer, reaction with two monodentate ligands or a combination of ligand and solvent.

to a surface Pd atom.[47–50] Many of the different homogenous catalysts used for C–C coupling reactions transform under the reactions conditions to form a highly conserved active catalyst, *i.e.* PdL_2 (L is usually a phosphine or other two electron donor ligand), which is probably very similar to that generated from NPs – especially those protected by ligand-based stabilizers such as phosphines or generated in strong donor solvents. Scheme 2 shows a tentative catalytic cycle indicating the interplay between the NPs and the active catalytic species. The first step in the process also involves the formation of a vacant coordination site that enables oxidative addition of the substrate to take place. It is not unreasonable to assume that with NPs coated by ligand stabilizers, dissociation of the ligand generates the reactive Pd(0) center on the surface of the NP, and following oxidative addition of the substrate the resulting Pd(II) ion can react with the ligand in solution stabilizing the active catalyst. Thus, the ligand has a dual role and the stabilizer properties are therefore crucial even though the active catalyst does not correspond to intact NPs. In the presence of macromolecular stabilizers the solvent may serve this function and in this respect superior activities are found for NPs stabilized in donor solvents relative to non-donor solvents.[51–53]

Strong donor solvents such as DMSO and DMF are often the preferred solvents for coupling reactions and, likewise, ionic liquids (ILs) functionalized with donor groups tend to be superior to simple ILs in cross coupling reactions.[54–57]

Stabilizer design

The application of ligands (frequently used in coordination chemistry and homogeneous catalysis) in NP catalysis, provides a relatively facile way to manipulate the properties of the NPs (see below). The application of macromolecular stabilizers (that may also coordinate to the NP surface) is, however, much more widespread and PVP is one of the most widely used polymers for stabilizing NP with high catalytic activities. PVP combines weakly coordinating N- and O-functionalities with steric protection (see Fig. 1). In general, NPs will have a higher stability if the PVP to metal ratio is high, but usually at the expense of the catalytic activity.[58] At constant PVP : metal ratios, the higher the molecular weight the higher the stability of the NPs, but again with reduced activities.[59] These differences in activity and stability can be attributed to the reasons given
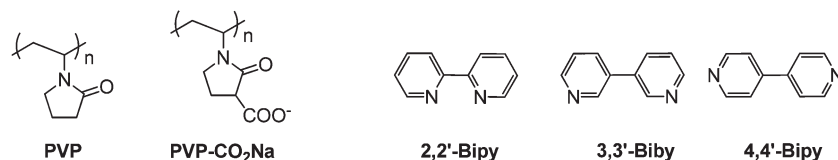
Fig. 1 Examples of polymers and ligands used to stabilize NPs in catalytic reactions.
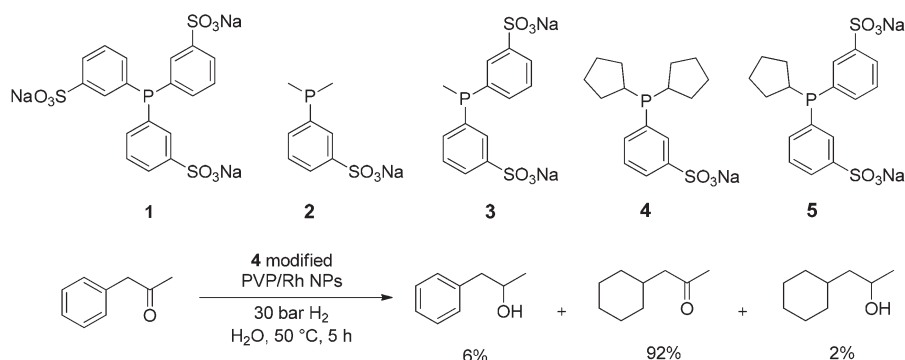
Scheme 3 Chemoselective hydrogenation of phenylacetone by PVP-stabilized Rh NPs improved by the presence of water soluble phosphine ligands.

above, *i.e.* the prerequisite generation of vacant substrate binding sites *via* the (partial) dissociation of the stabilizer. To obtain stabilizers that are superior to PVP, *i.e.* providing NP catalysts of comparable or even superior activity, while simultaneously endowing higher stability and recyclability (since the stability of solvent-dispersed nanocatalysts remains a challenge), the strength and type of interactions between the NP surface and the stabilizer must be fine-tuned. The introduction of carboxylate groups into the PVP structure was shown to enhance NP stability *via* the ability of the carboxylate group to weakly coordinate to the metal surface and additional electrostatic stabilization *via* the formation of a protective electronic double layer.[60] Rh NPs protected by this modified polymer (see Fig. 1) exhibit superior thermal and catalytic stability to PVP coated NPs.

Much remains to be learnt about how to rationally modify PVP-type stabilizers and the delineation of further mechanistic insights should facilitate the design process. Nevertheless, many interesting systems have been reported, *e.g.* the development of pH[61] and thermally[62,63] induced phase-switchable systems. In addition to macromolecular stabilizers, small molecules (ligands) such as thiols,[64–67] amines,[68] pyridines,[69] and phosphines,[70–72] have also been used to stabilize NPs. Since these types of ligands are frequently encountered in homogeneous catalysis, especially phosphines, their electronic and steric effects have been established and related to catalytic activity, a feature that could prove useful in nanocatalysis.

In heterogeneous catalysis ligands tend to be used as additives or poisons to modify various catalytic parameters, such as chemoselectivity, by influencing the preferential coordination – and hence activation – of specific functionalities of the substrate. This approach, termed selective poisoning, has

been transferred to dispersed NP catalysts. Water-soluble phosphine ligands with different steric and electronic properties (Scheme 3) were added to PVP stabilized Rh NPs and the activity of the resulting NPs were evaluated in the aqueous phase hydrogenation of phenylacetone.[73] In the presence of the ligands the aromatic ring was selectively reduced in preference to the carbonyl group with a chemoselectivity exceeding 90%. The high chemoselectivity was attributed to the modification of the NP surface (site blocking) due to the coordination of the phosphine ligands to sites that favor binding the carbonyl group over the aromatic ring preventing approach of the C=O group. Moreover the higher hydrophobicity of ligand **4** (compared to the others), that gave the highest selectivity, could also hinder the approach of the polar ketone functionality to the NP surface.

A similar study on Ru NPs in THF explored the role of different mono and bis-phosphine ligands in the hydrogenation of *o*-methylanisole (Scheme 4).[74] The nature of the phosphine strongly influences the catalytic activity. NPs protected by triarylphosphine ligands are inactive or, at best, display very poorly activities, whereas the complete hydrogenation of *o*-methylanisole takes place when the NPs are coated with dialkylarylphosphines. Notably, trialkylphosphine coated NPs are less active than dialkylarylphosphine coated NPs which makes it difficult to rationalize the role of steric and electronic effects of the ligands. The aryl substituents could potentially interact with the surface of the NPs blocking access of the active catalytic sites to the substrate. In addition, the alkylphosphines are stronger donor ligands than the triarylphosphines, pushing electron density onto the NP surface to favor π-back bonding with the substrate, thereby facilitating substrate binding and oxidative addition of H_2 (although these steps are
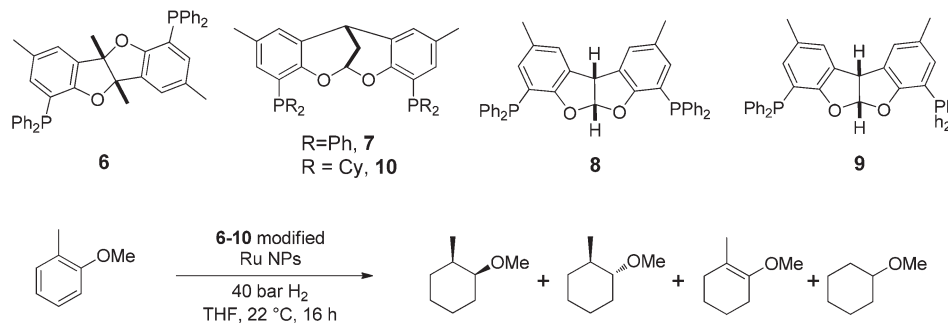
Scheme 4 Hydrogenation of o-methylanisole using ligand modified Ru NPs.

unlikely to be the rate determining in the catalytic cycle). However, neither of these explanations satisfactorily account for the lower activity of the trialkylphosphines although their high air and moisture could be relevant.

Another study involving Ru NPs immobilized in [bmim][Tf$_2$N], prepared in the presence of varying amounts of octylamine, shows that as the octylamine : Ru ratio increases from 0 to 0.2 the activity increases, and then at higher ratios the activity dramatically decreases.[75,76] Two factors are suggested to be responsible for these observations. First, increasing the amount of amine enhances the electron density at the metal surface influencing substrate binding (see above). Second, at higher octylamine levels steric hindrance ultimately impedes substrate absorption on the NP surface inhibiting the reaction rate. Since the partially hydrogenated product, p-menthene, decreases considerably as the octylamine concentration increases, a hydrophobicity effect has also been proposed, i.e. the affinity of the hydrophobic ligand at the NP surface discourages the p-menthene (which is also hydrophobic) from diffusing into the more polar IL phase thus favoring further hydrogenation.

Based on the above mentioned ideas hemilabile bipyridine-based nanoparticle stabilizers that enhance both reactivity and stability were developed. Rh NPs coated with a series of sterically similar bipy-based ligands with varying electronic parameters, i.e. bipy with COOMe, Cl, Me, t-Butyl, MeO or NH$_2$ substituents at the 4,4′ position, were evaluated for catalytic activity in the hydrogenation of toluene. The Rh NPs coated by the most electron-poor stabilizers, viz. CO$_2$Me-bipy and Cl-bipy, are the most catalytically active (see Fig. 2). Since the rate determining step in the proposed catalytic cycle for the hydrogenation of an arene ring corresponds to the addition of the first molecule of hydrogen to the arene, breaking the aromaticity of the ring to form a diene,[77] dissociation of the ligand stabilizer is a prerequisite to catalysis. Consequently, it is not surprising that the most electron-poor stabilizers, i.e. those that bind most weakly to the NP surface, dissociate most readily to give the most active catalysts, but at the same time they also afford the least stable NPs (apparent from the re-cycling experiments).

To overcome this dichotomy a hemilabile bis-bipyridine ligand was designed that exhibits superior activity and stability
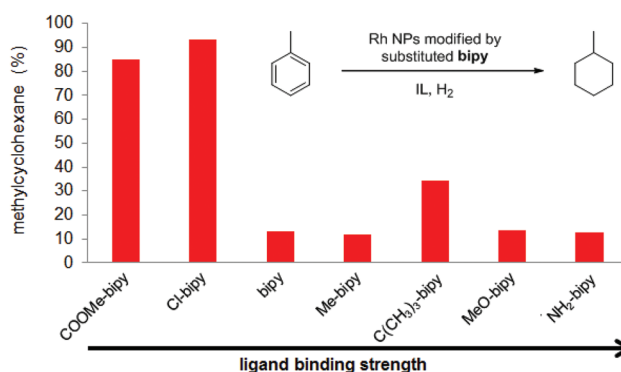

Fig. 2 Rh NPs catalysed hydrogenation of toluene as a function of the stabilizer (Rh : stabilizer ratio = 2).

relative to the 4,4′-derivatised bipyridine ligands. The proposed role of the hemilabile ligand is illustrated in Fig. 3, suggesting that the bis-bipyridine ligand is less prone to complete dissociation from the NP surface, thus increasing the stability of the NP core.

Other ligands that have been used in nanocatalysis to impart specific effects on the reaction, in particular asymmetric reactions employing NPs coated with chiral ligands.[78] The hydrogenation of α-ketoesters, e.g. ethyl pyruvate, has been widely studied using cinchona alkaloid-type ligands (Scheme 5) and enantiomeric excesses (ee's) of up to 98% have been obtained with Pt NP pre-catalysts.[79,80] To maintain high conversions and ee's further aliquots of the chiral ligands must be added during the reaction, apparently due to the depletion of the ligands from the surface of the NP. This requirement, however, also implies that chiral homogeneous complexes that correspond to the active catalytic species are formed in situ.

Numerous examples of asymmetric hydrogenation and hydrogen transfer using NPs coated with chiral ligands have been reported.[81–83] It has been proposed that low selectivities, in comparison to related mononuclear systems, could be due to dynamic behavior of the ligands at the NP surface rather than the formation of molecular catalysts.[84] However, further studies are required to delineate the nature of the active catalyst, and in terms of ligand design, until further mechanistic
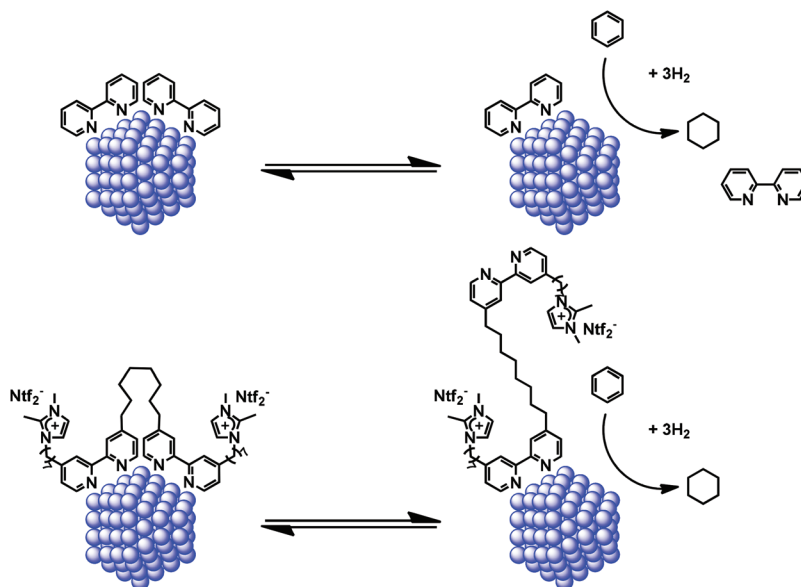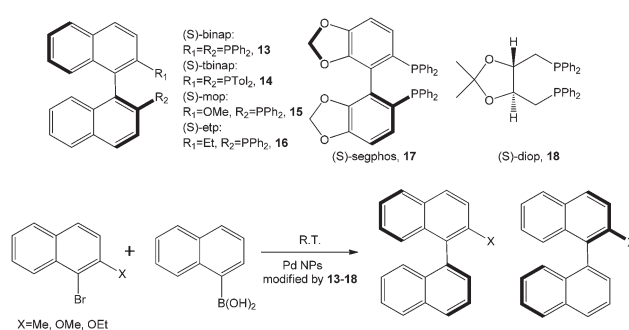
Fig. 3 The proposed role played by bipyridine (top) and a hemilabile bis-bipyridine with a C_8 spacer group (bottom) in NP catalyzed hydrogenation of benzene accounting for the higher stability of the latter.
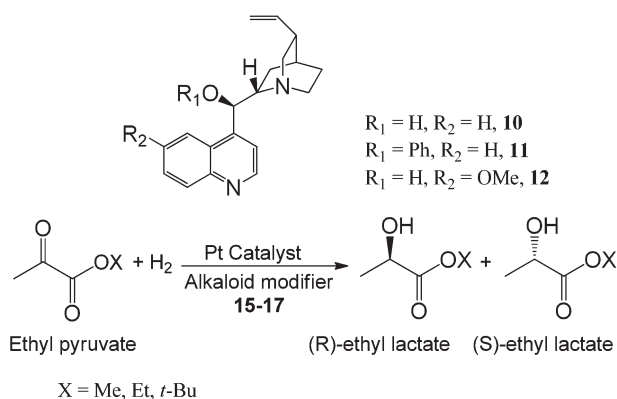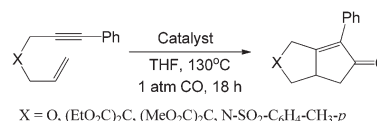

Scheme 5 Enantioselective hydrogenation of pyruvates using an alkaloid-modified Pt NPs.

Scheme 6 Asymmetric Suzuki–Miyaura coupling reactions of naphthyl halides catalyzed by chiral Pd NP pre-catalysts at room temperature.

Scheme 7 Intramolecular Pauson–Khand reaction catalyzed by immobilized Co–Rh NPs.

insights are delineated the same approaches as those used in homogenous chiral catalysis could prove valuable.

Chiral ligands have also been used in C–C coupling reactions catalyzed by NP pre-catalysts. The catalytic activity and enantioselectivity of Pd NPs coated with chiral phosphines were found to vary considerably in room-temperature asymmetric Suzuki–Miyaura cross coupling reactions (Scheme 6).[85] At a low catalyst loadings (0.1%), Pd NPs stabilized by **13** exhibited the highest activity (96%) and enantioselectivity (69% ee). By analogy to homogeneous catalysis it was proposed that the dihedral angle of the backbone axes of aryl bis-phosphine ligands plays a significant role on the enantioselectivity of the reaction. Application of a stronger base resulted in an increase the reaction rate and also significantly enhanced the enantioselectivity. These effects are also consistent with the formation of catalytic palladium(II) bis-phosphine species.

A highly active bimetallic Co–Rh nanocatalyst immobilized on charcoal, and decorated with a chiral bis-phosphine ligand, provides ee's of up to 87% in the Pauson–Khand reaction (Scheme 7). While this reaction is usually attributed to homogeneous catalytic species, which cannot be completely excluded here, mercury poisoning experiments indicated that the active catalyst could involve NPs.[86] The addition of mercury completely eliminated catalysis suggesting the critical role of Co–Rh NPs in catalysis. Mercury poisoning is a key test used to ascertain the role of NP catalysis.[87–89]

Solvent stabilizers

The role of solvent in influencing the properties of NPs should not be overlooked and in this context some of the most impressive examples of nanocatalysis dispersed in solvents correspond to ionic liquid (IL) dispersed systems in which the NP acts as the catalysts or serves as a catalyst reservoir affording mononuclear catalytic species.[90] ILs are more than just a solvent and they help stabilize the NPs, although it has been shown that additional stabilizers can further enhance the catalytic performance,[91] including both ligands,[92–100] and polymers.[60,101,102] Derivatization of ligands with ionic tags facilitates dispersion and retention of NPs in ILs (Fig. 4). Likewise, ionic PVP derivatives result in the same solubility properties. An IL-like copolymer formed from the copolymerization of the PVP monomer and a vinylimidazolium unit, poly (N-vinyl-2-pyrrolidone)-co-(1-vinyl-3-butylimidazolium chloride) (see Fig. 4) is highly IL soluble and Rh NPs stabilized by this ionic polymer exhibit long lifetimes leading to high turnover numbers in the hydrogenation benzene and other substrates.[102,103]

Ionic polymers can provide more than idealized solubility properties. Following a detailed kinetic analysis of the Pt NP catalyzed oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid, an important reaction in downstream biomass processing, it was shown that a highly electron rich NP surface would enhance catalytic activity. Subsequent manipulation of the nanoparticle surface by the introduction of an ionic polymer stabilizer afforded surface electron-rich Pt nanoparticles that catalyze the transformation under mild conditions in the absence of additives. Thus, the electron donating properties of the polymer can be likened to the application of electron donating ligands, i.e. as the catalytic metal center becomes more electron rich, reactions that involve an oxidation at the metal, such as oxidative addition, become more facile.

Stabilizers can be designed to influence the solubility properties of NPs in the same way that ligands influence the solubility properties of homogeneous catalysts. A classic example in homogenous catalysis is the development of the water soluble ligand, TPPTS, that replaced triphenylphosphine in an aqueous-organic biphasic hydroformylation reaction.[104] It is highly desirable that NPs also have tunable solubilities so that they can be dispersed in specific solvents.[105] Using PVP as an example, PVP-stabilized NPs are essentially confined to water[106] and alcohols,[101,107] due to the insoluble nature of PVP in non-protic solvents. However, the polarity of PVP can be easily modified by the inclusion of alkyl chains allowing Rh NPs protected by them to disperse in a wide range of solvents ranging in polarity from water to hexane.[108]

Chiral ligand modified NPs in ILs have been evaluated at enantioselective catalysts. For example, TPPTS-stabilized Ru NPs modified with the water soluble chiral ligand **22** were evaluated in the catalytic asymmetric hydrogenation of aromatic ketones (Scheme 8).[109] The conversion and selectivity depend on the solubility of the catalyst in the IL and water increases the ee. Interestingly, the reaction does not proceed in the absence of **22**, indicating that the active catalyst could correspond to mononuclear species. Using $RuCl_2(TPPTS)_2$ as the catalyst under the same condition the conversion was considerably lower as a long induction period is needed to
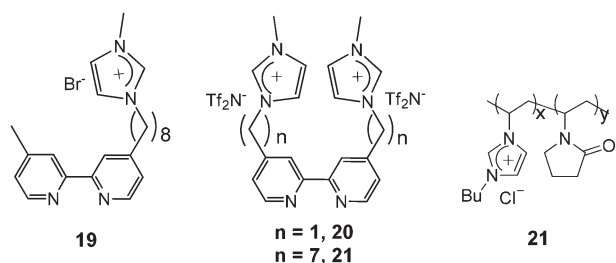

Fig. 4 Examples of ionic ligands and an ionic polymer used to protect Rh NPs.

R = Et, Bu, Octyl, Dodecyl, Hexadecyl

R_1 = H, o-F, o-Cl, o-Br, o-CH$_3$O, p-CF$_3$, p-CH$_3$O, R$_2$ = CH$_3$
R_1 = H, R$_2$ = C$_2$H$_5$
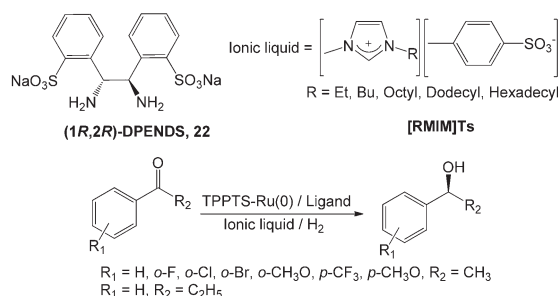
Substrate	TPPTS-stabilized Ru		$RuCl_2(TPPTS)_2$	
	Conversion	ee (%)	Conversion (%)	ee (%)
Acetophenone	100	80.3	50.3	80.3
2'-Bromo-acetophenone	99.6	82.7	9.2	82.9
4'-Methoxy-acetophenone	96.0	76.5	3.6	57.7

Scheme 8 Asymmetric hydrogenation of aromatic ketones catalyzed by Ru NPs in ILs in comparison to RuHCl(TPPTS)₂ (both in the presence of the chiral ligand (1R,2R)-DPENDS).

generate the active species, RuHCl(TPPTS)$_2$. This control experiment indicates that either the Ru NPs are the active catalytic species or that the active catalyst is more easily generated from the NPs and further experiments are required to distinguish between these possibilities.

Concluding remarks and outlook

Enormous progress has been made towards understanding the surface chemistry and catalytic properties of heterogeneous catalysts, including immobilized NPs.[23,110–114] In contrast, dispersed NP catalysts are poorly understood and very few quantitative studies have been reported. While mechanisms determined for heterogeneous catalysts may be transferred to dispersed NP catalysts, albeit with caution, applying principles from homogeneous catalysis could also prove beneficial.

Determining the molecular-level mechanistic steps involved in transformations using nanocatalysts dispersed in solvents is considerably challenging, and in many of the examples described herein it is not always clear if the active catalyst is the NP or a mononuclear species derived from it. Homogenous catalysts may be studied by high resolution spectroscopic techniques such as IR and NMR spectroscopy, often employed *in situ*. Other techniques are required for NPs; *in situ* XAS is a promising technique that can be used to monitor NPs during catalysis, it provides the valent state, and the coordination environment (including coordination number and the bond length) of an element of interest. However, XAS provides averaged information of a certain element, *i.e.* the data could contain information from surface active sites, surface spectator atoms and non-surface atoms, which makes it difficult to obtain a clear picture of the entire catalytic cycle and identify key intermediates.

The gap is closing between dispersed NP and homogenous catalysts. The structures of mononuclear pre-catalysts are often characterized by single crystal X-ray diffraction. Obtaining single crystals of NPs, in contrast, is a considerable challenge, but recent crystal structures of very large clusters, *e.g.* Au$_{102}$-(*p*-mercaptobenzoic acid)$_{44}$[65] (Fig. 5) indicate that barriers between molecular systems and NP systems are starting to diminish.

Despite differences between NP and homogeneous catalysts it is clear that ligand can be used to alter the sterics and electronics of NP surfaces much in the same way they alter the metal center of homogeneous catalysts. With greater mechanistic understanding, the rational manipulation of NPs with ligands and other types of stabilizers should provide a complementary method to the traditional methods used to control NP reactivity such as size and shape and the use of NP alloys in which the polarity differences between the metals lead to catalytic enhancements.[57] Combined, new NP catalysts can be expected that will find uses in highly challenging reactions, such as CO$_2$ fixation and biomass transformations, and the confluence of concepts from heterogeneous catalysis,
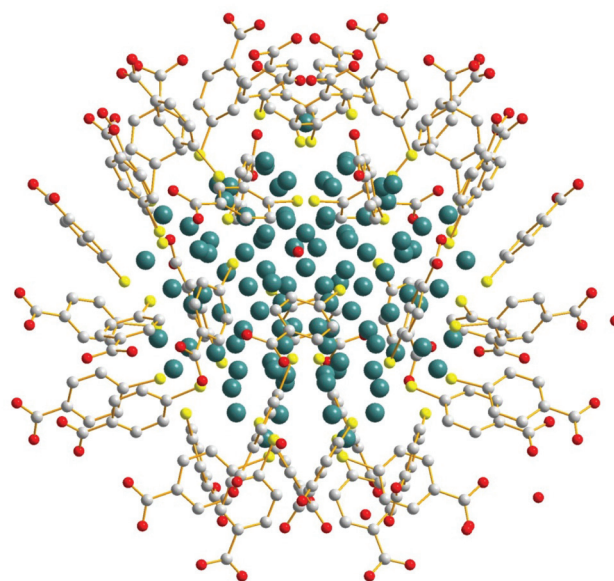
Fig. 5 Sulfur–gold interactions in the surface of the Au$_{102}$(*p*-mercaptobenzoic acid)$_{44}$ cluster/NP. Gold atoms are blue and sulfur atoms are yellow.

homogeneous catalysis and nanoscience should facilitate their rational design.

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