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N-Heterocyclic carbene coated metal nanoparticles†

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***N*-Heterocyclic carbene coated Au and Pd nanoparticles have been prepared by a ligand exchange reaction; although carbenes quantitatively displaced the thioether and phosphine ligands from the nanoparticle surface, the resultant nanoparticles spontaneously leached metal complexes and aggregated in solution.**

Ionic liquid-stabilised metal nanoparticles attract much attention[1] thanks to their promising catalytic properties and the potential applications of ionic liquids as alternative solvents. However, the stabilisation mode of nanoparticles prepared by the reduction of metal salts in ionic liquids remains unclear. A recent SERS study suggested that imidazolium cations adsorb parallel to the Au nanoparticle surface, achieving electrosteric stabilization.[2] On the other hand, the formation of at least transient *N*-heterocyclic carbenes (NHCs) from ionic liquids during the preparation of Ir(0) nanoparticles was demonstrated by ^{2}H NMR spectroscopy,[3] and ionic liquids were proposed as catalyst poisons for metal nanoparticles.[4] It therefore seems feasible that metal nanoparticles prepared in ionic liquids might be coated with NHCs.

Catalytic reactions of noble metal complexes are often accompanied by the formation of metal nanoparticles. In fact, in many cases, it is debatable whether the catalytically-active species are metal complexes or nanoparticles.[5] For instance, the catalytic properties of metal nanoparticles (Au, Pd) in hydrogenation, alcohol oxidation and alkene epoxidation are well documented.[6,7] Some Pd-catalysed, enantioselective C–C bond-forming reactions were also convincingly demonstrated to involve nanoparticle catalysis.[8] Pd nanoparticles prepared in ionic liquids have shown excellent catalytic activity in Suzuki reactions.[9] Nanoparticle catalysis has many advantages, mainly associated with the feasibility of simple separation and recycling, and hence the development of nanoparticle-based catalysts that reproduce the catalytic properties of metal complexes is desirable.

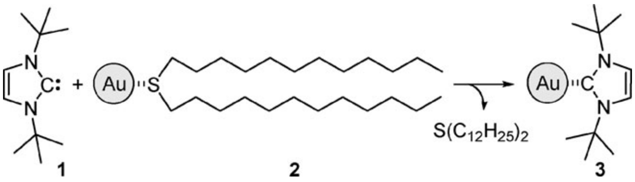
The stabilisation of nanoparticles by NHCs is thus an intriguing possibility. Since the isolation of the first NHC by Arduengo *et al.* in 1991,[10] they have become valuable donor ligands in transition metal-mediated catalysis and organocatalysis, *e.g.* C–H activation, and C–C, C–H, C–N and C–O bond formation.[11] The presence of nitrogen atoms in NHCs makes them much more stable than ordinary carbenes; however they form strong σ-bonds to metals *via* the carbene lone pair, which makes them resistant to degradation at high temperatures, unlike their 'rival' phosphine ligands.[11–13] Due to the lack of back-bonding in metal complex formation, interesting activities have been observed at metal centres.[11,12] In Au and Pd catalysis, NHCs have been shown to be versatile and 'tuneable' ligands that can change a mechanistic pathway or increase the selectivity of the electrophilic metal atom through simple modifications to substituents.[14] If NHC-protected nanoparticles can be prepared, one would expect them to possess similar catalytic properties.

In order to test the stability of NHC-protected nanoparticles, we have explored new methods for their synthesis. Even sterically-shielded NHCs are highly water- and air-sensitive, and are unlikely to survive the reducing conditions required for nanoparticle preparation.[15] Although reduction of an Ag(I)–NHC complex with $NaBH_4$ led to the formation of Ag nanoparticles, they were most likely stabilised by imidazolium groups.[16] Hence the best (and most unambiguous) way of introducing an NHC into the nanoparticle shell is by ligand exchange with nanoparticles protected by a sacrificial labile ligand. Once attached to the metal surface, the NHC ligands are expected to have sufficient stability to allow handling in air.

Bis-*tert*-butylimidazol-2-ylidene (**1**) (Scheme 1) was synthesised by the deprotonation of the corresponding imidazolium salt by KO^{t}Bu.[17] This ligand was then reacted with the Au nanoparticles protected by thioether, **2**.[18] Thioethers weakly bind to Au nanoparticles, and the nanoparticles are only stable in the presence of excess thioether (attempts to purify the nanoparticles by gel permeation chromatography led to irreversible aggregation). Hence, we postulated that a more strongly binding molecule, such as carbene **1**, would readily displace the thioether ligand.

Carbene synthesis and ligand exchange were carried out under inert atmosphere conditions in a dry box (O_2 and H_2O levels < 0.5 ppm) due to the moisture sensitive nature of the NHC ligand. However, subsequent steps were carried out in air.

After the addition of carbene **1** to thioether-protected nanoparticles **2** in benzene, the nanoparticles completely



Scheme 1 Synthesis of NHC-protected Au nanoparticles.

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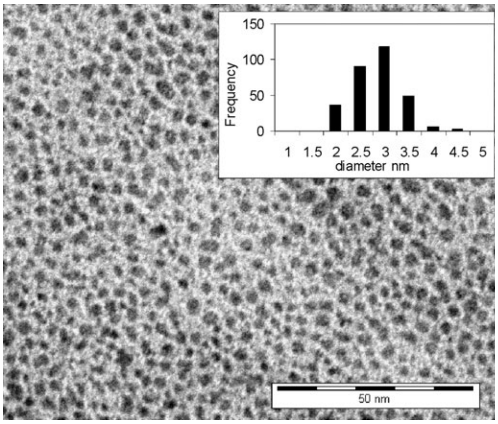

Fig. 1 TEM image and size distribution histogram (inset) of **3**.

precipitated from solution after *ca.* 12 h. A similar result was obtained in toluene, but benzene was chosen to enable the monitoring of small scale reactions by ^{1}H NMR. The precipitate was only soluble in polar solvents (DMSO and CH_3CN). The precipitated nanoparticles were washed with benzene to remove excess ligands, and characterised by TEM, TGA and XPS analyses (see the ESI†). TEM data (Fig. 1) showed nearly spherical NHC-coated nanoparticles **3** with an average diameter *ca.* 2.6 ± 0.5 nm, the same as for thioether-coated nanoparticles **2**. A thermal MS analysis of nanoparticles **3** showed the loss of ligand **1** (m/z 181) at 230 °C as compared to the precursor particles **2**, which showed the loss of the thioether at 219 °C.

XPS confirmed that ligand exchange had gone to completion, as a strong sulfur peak in the spectrum of thioether-coated nanoparticles **2** was not observed for carbene-protected nanoparticles **3** (Fig. 2a). Instead, a clear nitrogen 1s peak (absent in thioether-protected particles **2**) was observed after ligand exchange (Fig. 2b). A comparison of the relative XPS intensities gave the Au : N ratio as 2.5 : 1. This is consistent with the TGA data (loss of *ca.* 35 wt% upon heating), atomic absorption spectroscopy, which showed the presence of 66% Au, and elemental analysis data. Taking into account the average particle size determined from the TEM data (Fig. 1), the overall nanoparticle composition was estimated to be $Au_{840}\mathbf{1}_{340}$, which is comparable with the elemental compositions of similar ligand-protected Au nanoparticles.

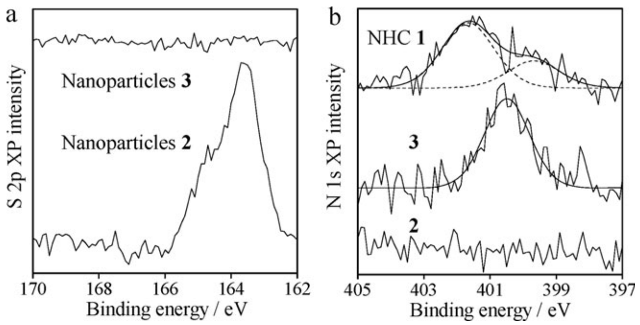

Fig. 2 XPS data: (a) S 2p peak of nanoparticles **2** and **3**, and (b) N 1s peak of ligand **1** and nanoparticles **3**.

Inspection of the N 1s shift in the XPS spectrum of carbene **1** (Fig. 2b) confirmed the poor stability of free carbene **1**, as evidenced by the presence of two peaks at 401.6 and 399.6 eV (the latter was attributed to the amide functionality resulting from ring-opening of carbene **1**).[15] Importantly, the NHC-protected Au nanoparticles did not show this shoulder, which confirms the higher stability of the nanoparticle-coordinated carbene. It is interesting to note that the N 1s binding energy in nanoparticles **3** (400.3 eV) is lower than in the free carbene.

The analytical data unequivocally demonstrates that the ligand exchange reaction of NHC **1** with nanoparticles **2** gave target carbene-protected nanoparticles **3**. The carbene-coated nanoparticles could be stored for prolonged periods (*e.g.*, months) in solid form at −4 °C without any change to their UV spectrum or solubility. However, nanoparticle solutions (in DMSO, CH_3CN or CH_2Cl_2) were only stable for a limited period of time (*ca.* 12 h). Prolonged storage led to a colour change from red/brown to purple and the formation of a precipitate. The precipitate was only soluble in DMSO but nanoparticles precipitated again from the solution obtained over several hours, leading to a completely insoluble black mass of irreversibly-aggregated nanoparticles. Nanoparticles **3** were also soluble in ionic liquids (*e.g.*, butyl-3-methylimidazolium chloride), but storage of the solution over *ca.* 12 h resulted in the formation of the same precipitate. The poor stability of the nanoparticle solutions was not caused by the oxidation or hydrolysis of the ligand as the same behaviour was observed for nanoparticles stored under dry/anaerobic conditions in a dry box. An MS analysis of the mother liquor after nanoparticle degradation (Fig. 3) clearly showed the presence of NHC–Au–X complexes (X = Br, Cl), a bis[NHC–Au–NHC]$^+$ complex and ligand **1**.

These data unambiguously show that the poor stability of the carbene-protected Au nanoparticles is due to the loss of NHC–Au complexes from the nanoparticle surface into

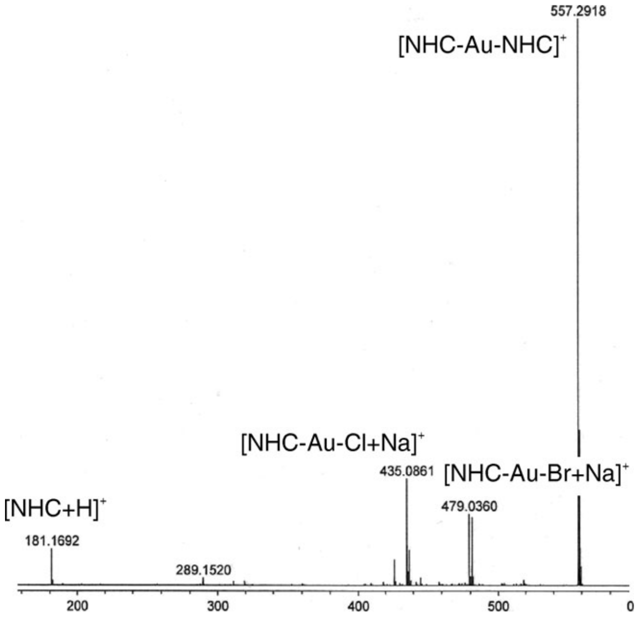

Fig. 3 An ESI-MS of a solution after degradation of nanoparticles **3**.

solution. This was further confirmed by NMR spectroscopy. Due to the rigidity of the molecule, the tumbling of the Au nanoparticle-attached carbene was severely restricted, leading to the broadening of all NMR signals beyond detection. However we observed weak but sharp proton signals in the ^{1}H NMR spectrum of purified nanoparticles **3** that grew during nanoparticle ageing/degradation. These NMR signals were assignable to NHC–Au complexes, confirming their spontaneous desorption from the nanoparticle surface.

Taking into account the high affinity of NHCs for Au, the poor stability of nanoparticles **3** is surprising. In order to verify if the limited stability of the NHC-protected nanoparticles is specific to Au, we used a similar approach to prepare Pd nanoparticles stabilised by ligand **1**. Trioctylphosphine-protected Pd nanoparticles were prepared by ageing $Pd(OAc)_2$ in the presence of trioctylphosphine at 300 °C for 3 d.[19] The nanoparticles were characterised by TEM (average size was *ca.* 3 nm, see the ESI†) and elemental analysis. The trioctylphosphine-coated nanoparticles were then reacted with carbene **1** in a dry box. Ligand exchange resulted in the formation of a precipitate that would only dissolve in polar solvents. The precipitated nanoparticles were purified by washing with benzene. Interestingly, these nanoparticles showed a very similar behaviour to the Au nanoparticles. The NHC-protected Pd nanoparticles aggregated irreversibly within 15 h when kept in solution. An ESI-MS analysis of the mother liquor after nanoparticle aggregation showed peaks for both the NHC and $[\text{NHC–Pd}]^+$ complex (see the ESI†). It appears therefore that the poor stability of NHC-coated nanoparticles is a common property of both Pd and Au examples.

Although the formation of Au–carbene complexes during degradation of NHC-protected nanoparticles is surprising, the formation of Au(I) species has previously been reported for several ligand exchange reactions of Au nanoparticles. For instance, the ligand exchange of thiol-protected nanoparticles with triphenylphosphine is accompanied by the formation of Au(I) thiolates.[20] Similarly, the reaction of thiols with triphenylphosphine-protected nanoparticles leads to the formation of PPh_3AuCl and polyphosphine–Au complexes.[21] Since these ligand exchange reactions are likely to be dissociative (*e.g.*, beginning with a rate-determining dissociation of a Au(I) complex from the nanoparticle surface), their mechanism could be similar to the degradation of NHC-coated nanoparticles. It is worth noting that while thiol-protected Au nanoparticles are very stable, triphenylphosphine-protected Au nanoparticles irreversibly aggregate in solution, albeit on a longer timescale than the NHC-coated particles described here.

Recent crystal structures of thiol-protected Au nanoparticles revealed that they are best described as Au cores surrounded by Au thiolates.[22] The core atoms have a high coordination number and form regular polyhedra. On the other hand, the Au atoms associated with ligands have much lower coordination numbers and presumably have weaker bonds with the core. This is consistent with the crystal structure of triphenylphosphine-protected Au nanoparticles.[23] Similarly, nanoparticles **3** can perhaps be thought of as Au particles protected by a Au–NHC complex. This would explain the dissociation of the complexes from the nanoparticle surface, driven by their high stability and the steric demands of ligand **1**.

In conclusion, NHC-protected Au and Pd nanoparticles have been prepared and characterised. Intriguingly, these nanoparticles have a limited stability in solution. A spontaneous irreversible aggregation of nanoparticles leads to the formation of NHC–metal complexes that is presumably driven by steric factors. These observations suggest that NHC-coated nanoparticles will leach mononuclear NHC–metal species in catalytic processes (*e.g.* cross-couplings).

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Experimental section

Under an inert atmosphere, nanoparticles **2** (30 mg) were dissolved in benzene (5 mL), and a 200-fold excess of bis(1,3-*tert*-butyl)imidazol-2-ylidene (**1**) (0.11 mmol) was added as a solid portion. The particles were left to precipitate overnight without stirring. They were then centrifuged (4000 rpm, 3 min), washed with benzene (3 × 5 mL) and dried under vacuum.

The synthesis of carbene **1**, nanoparticles **2** and the full characterisation details of nanoparticles **3** are given in the ESI.†

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