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# Synthesis and reactivity of a conveniently prepared two-coordinate bis(amido) nickel(II) complex†

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**A strictly two-coordinate nickel(II) bis(amido) complex has been prepared and its reactivity towards a variety of small molecules is described. Ni[N(SiMe$_3$)(DIPP)]$_2$ reacts with DMAP and acetonitrile to form T-shaped three-coordinate complexes, and preliminary results show that Ni[N(SiMe$_3$)(DIPP)]$_2$ is a catalyst for the hydrosilation of olefins with secondary silanes at ambient temperature.**

Two-coordinate metal complexes are a relatively small class of compounds with unusual structural, electronic, and chemical properties.[1] The low coordination number and inherently electron deficient nature of these compounds suggest that they should display a rich reaction chemistry associated with activations and conversions of a wide array of substrates. However, chemical reactions of two-coordinate complexes have not been extensively investigated. Low-coordinate complexes have been shown to mediate interesting chemical transformations such as nitrene- and phosphinidine-group transfer to ethylene,[2] and the activation of small molecules such as $N_2O$.[3] Two-coordinate compounds have also been shown to activate $CO_2$.[4] Most importantly, two-coordinate bis(amido) M[N(SiMe$_3$)$_2$]$_2$ complexes of first row metals have found wide utility as convenient starting materials for inorganic and organometallic compounds.[5] Metal bis(amido) complexes are also used as precursors in nanoparticle synthesis.[6] In these laboratories, the recent discovery that Fe[N(SiMe$_3$)$_2$]$_2$ is a catalyst precursor for the efficient hydrosilation of organic carbonyl compounds[7] prompted further investigations of the reaction chemistry of two-coordinate amido complexes of the first row metals.

While two-coordinate, bis(amido) complexes of iron, cobalt, and manganese are well known,[8] related nickel(II) complexes have only recently been reported.[9] One such compound, Ni{HN[2,6-(2,6-diisopropylphenyl)]}$_2$, may be described as pseudo-four-coordinate, in that the solid-state structure contains two additional close contacts between the nickel center and aryl groups of the amido ligand.[9a] Herein we report the synthesis and characterization of a strictly two-coordinate nickel(II) bis(amido) complex, its reactivity towards small molecules and preliminary results on its activity as a catalyst in the hydrosilation of olefins.

Compound **1** was synthesized by reaction of Ni(DME)Br$_2$ with 1.9 equiv of Li[N(SiMe$_3$)(2,6-iPr$_2$C$_6$H$_3$)] in benzene over 6 h at ambient temperature. Workup of the reaction mixture afforded dark purple crystals of **1** from hexanes in 86% yield.† The X-ray structure of **1** (Fig. 1) reveals a perfectly linear structure, with a crystallographically imposed 180° N–Ni–N bond angle. The 1.7987(11) Å Ni–N bond length is the shortest Ni–N(amido) distance yet observed. For comparison, related compounds bearing bulky terphenyl groups, synthesized by Cui and Power, possess Ni–N bond lengths of 1.818(3) and 1.8284(15) Å, respectively.[9a,b] The two amido ligands adopt an eclipsed configuration whereby both substituents on the two trigonal planar nitrogen atoms occupy the same plane. This is in contrast to the staggered, allene-like structure adopted by the similar iron compound Fe[N(SiMe$_3$)$_2$]$_2$ in its monomeric state.[8] The eclipsed conformation is also adopted by the Ni(II) bis(amido) complexes of Cui and Power and appears to be the most stable, even in the absence of secondary interactions between the metal and pendent aryl groups on the ligand. The $^1$H NMR spectrum exhibits strongly paramagnetic shifts that are assigned by integration (see Supporting Information†). The magnetic moment of 2.67 $\mu_B$, determined by Evans' method,[10] is consistent with two unpaired electrons per nickel.

Compound **1** reacts with the nitrogen donor compounds *p*-dimethylaminopyridine (DMAP) and acetonitrile to produce

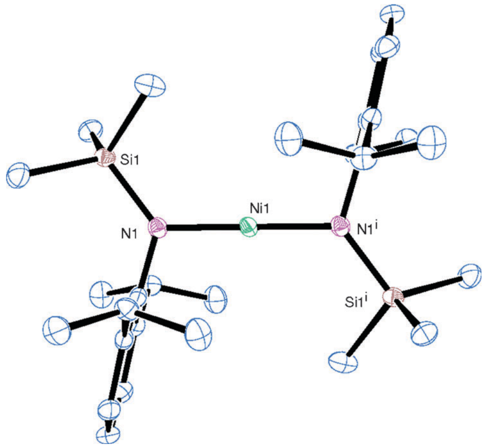

**Fig. 1** ORTEP diagram of **1**. Thermal ellipsoids shown at 50% probability. Bond lengths (Å) and angles (deg): Ni–N = 1.7987(11); N–Ni–N = 180.00(8).

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three-coordinate, nearly T-shaped complexes $\mathrm{Ni[N(SiMe_3)(DIPP)]_2(DMAP)}$ (**2**) and $\mathrm{Ni[N(SiMe_3)(DIPP)]_2(MeCN)}$ (**3**), respectively (Fig. 2). Reaction of **1** with 1 equivalent of DMAP in pentane for 20 min at ambient temperature, and subsequent evaporation of the solvent results in quantitative formation of the analytically pure compound **2**. Recrystallization from pentane afforded **2** as red crystals in 89% yield.

The structures of both **2** and **3** exhibit significant distortions from an ideal trigonal planar geometry. The N–Ni–N bond angles in these compounds are 155.07(7)° and 161.26(6)°, respectively, resulting in a nearly T-shaped coordination geometry (Fig. 3). Interestingly, despite the added steric hindrance, the eclipsed geometry of the two amido substituents in compound **1** is almost entirely conserved in both **2** and **3**. Furthermore, the plane occupied by the substituents of both amido ligands contains the ligand field, which would seem to maximize steric interactions between the three ligands on the metal center and their substituents.

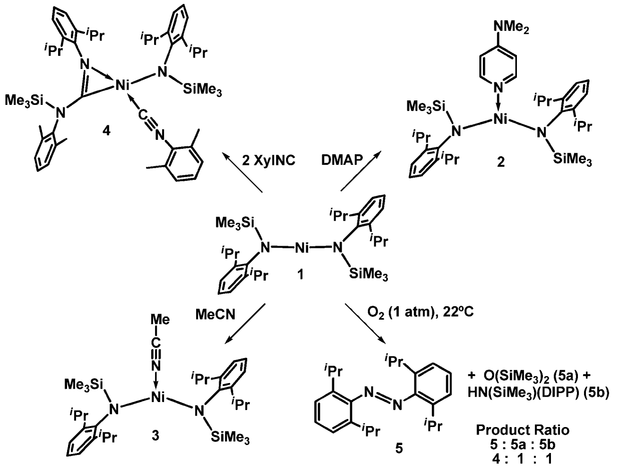


**Fig. 2** Reactions of $\mathrm{Ni[N(SiMe_3)(DIPP)]_2}$ (**1**).

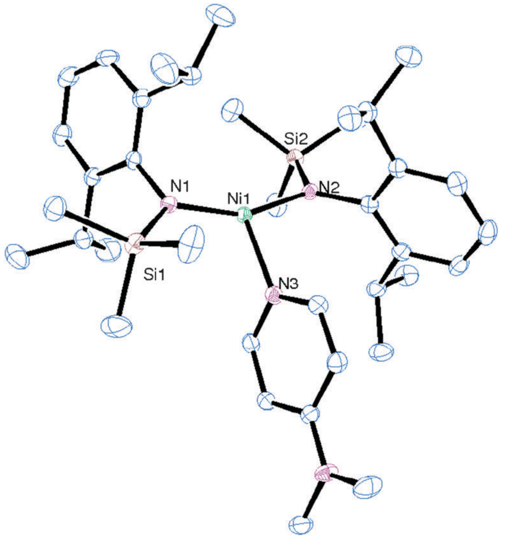


**Fig. 3** ORTEP diagram of **2**. Thermal ellipsoids shown at 50% probability. Bond lengths (Å) and angles (deg): Ni–N1 = 1.8614(15); Ni–N2 = 1.8717(15); Ni–N3 = 2.0187(16); N1–Ni–N2 = 155.07(7); N1–Ni1–N3 = 103.71(6); N2–Ni1–N3 = 100.47(6).

Reaction of compound **1** with 2 equivalents of 2,6-dimethylphenylisocyanide in benzene at ambient temperature over 30 min resulted in formation of the diamagnetic insertion product **4** in 96% yield, as determined by NMR spectroscopy (Fig. 4). Reaction of **1** with 1 equivalent of 2,6-dimethylphenylisocyanide resulted in formation of 0.5 equivalents of **4** and unreacted starting material. Interestingly, the product arises from insertion of an isonitrile into an Ni–N bond, accompanied by cleavage of a Ni–Si bond *via* 1,3-migration of the trimethylsilyl group from the amido nitrogen to a nitrogen atom originating from the isonitrile reactant (Scheme 1). The diamagnetic nature of **4** suggests that the structure is best regarded as a distorted, square planar Ni(II) d$^8$ species. The coordinated C–N bond distance is 1.278(2) Å, which is slightly longer than expected for a C=N double bond, but somewhat shorter than similar, less sterically crowded ligands in related insertion products of zirconium (1.299–1.315 Å).[11] While there is significant double bond character between the carbon and nitrogen bound to the metal center, the π-system of that bond is oriented perpendicular to the plane formed by the carbon, nitrogen and nickel atoms, resulting in no interaction between the π-system and the metal center. Rather, the ligand is a bidentate XL-type donor, and isoelectronic with an acyl group.

Reactions of bis(silylamido) complexes of Co and Fe with oxygen have been utilized in effective preparations of metal oxide nanoparticles.[6] In this context, the stoichiometric reaction of **1** with dioxygen, which also results in N–Si bond cleavage, was examined. Reaction of **1** under 1 atm of $O_2$ (99.99% pure) produced a mixture of the amine $\mathrm{HN(SiMe_3)(DIPP)}$ and the

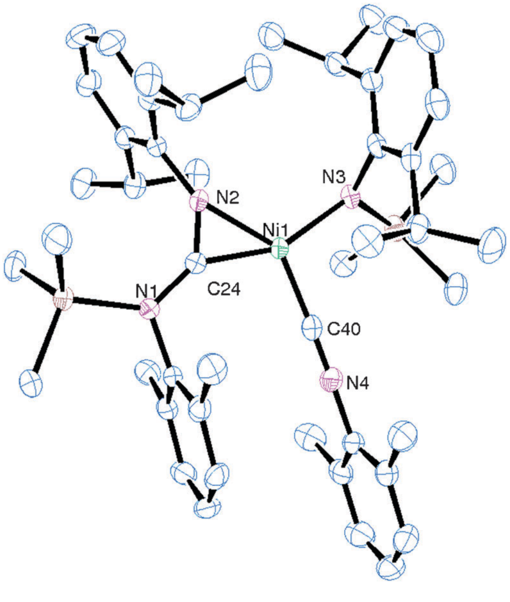
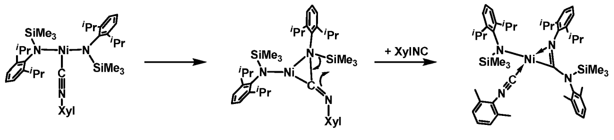


**Fig. 4** ORTEP diagram of **4**. Thermal ellipsoids shown at 50% probability. Bond lengths (Å) and angles (deg): Ni1–N2 = 1.9699(16); Ni1–C24 = 1.8181(19); N2–C24 = 1.278(2); N2–Ni1–C24 = 39.16(7).

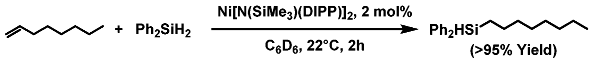


**Scheme 1** Formation of insertion product 4.

diazo compound $(2,6\text{-}iPr_2C_6H_3)_2N_2$ (**5**) in an approximately 4 to 1 molar ratio (by $^1H$ NMR spectroscopy). The diazo compound was characterized by X-ray diffraction, NMR spectroscopy and high-resolution mass spectrometry.

Formation of the diazo compound is accompanied by loss of $-SiMe_3$ groups to form 0.5 equivalent of $(Me_3Si)_2O$ per equivalent of **5** (as determined by $^1H$ and $^{13}C$ NMR spectroscopy) and an insoluble brown powder. This powder has proven difficult to characterize, due to its insolubility in all solvents including 6M HCl. Infrared spectroscopy revealed no notable features and the material was determined to be amorphous by powder XRD. Elemental analysis (CHN) showed that the powder contained carbon, nitrogen and hydrogen in a ratio which closely matches that of a $-N(SiMe_3)(DIPP)$ group (C, 39.08%; H, 6.30%; N, 3.29%) and the observed stoichiometry is consistent with the incorporation of one amido group per Ni into this powder. Reaction of **1** with 1 equivalent of $O_2$ per Ni center resulted in incomplete consumption of the starting material and a mixture of the free amine and **5** as before, but in an approximately 7 to 1 ratio. Presumably, the nitrogen-bound proton of the observed $HN(SiMe_3)(DIPP)$ product arises from the amido moiety which becomes incorporated into the insoluble powder. Further, based on the increase in the production of the amine relative to the diazo product when using sub-stoichiometric amounts of oxygen, it seems likely that the amine is formed initially, and is subsequently oxidized to form the diazo compound **5**. This oxidation may be catalyzed by the transient Ni species remaining from initial reaction with oxygen before formation of the insoluble Ni-containing material occurs.

Given the observed activity of $Fe[N(SiMe_3)_2]_2$ as a catalyst for the hydrosilation of carbonyl compounds,[7] complex **1** has been investigated as a catalyst for the hydrosilation of olefins with secondary silanes. Reaction of **1** with 55 equivalents of 1-octene and 50 equivalents of diphenylsilane in $d_6$-benzene at room temperature over 2 h resulted in formation of the anti-Markovnikov addition product (n-octyl)diphenylsilane in >95% yield with no observed isomerization of the olefin to internal isomers (eqn (1)). Ongoing investigations are addressing the scope, utility and mechanism of this reaction type in various hydrosilations.



(1)

In summary, **1** represents a stable, conveniently prepared bis(amido) complex containing two-coordinate nickel(II). Initial reactivity studies indicate that **1** mediates several interesting chemical transformations. These results should be of use in further investigations of **1** as a precursor to a variety of nickel-based compounds, catalysts and materials.

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