COMMUNICATION

Importance of co-donor field strength in the preparation of tetradentate α-diimine nickel hydrosilylation catalysts†

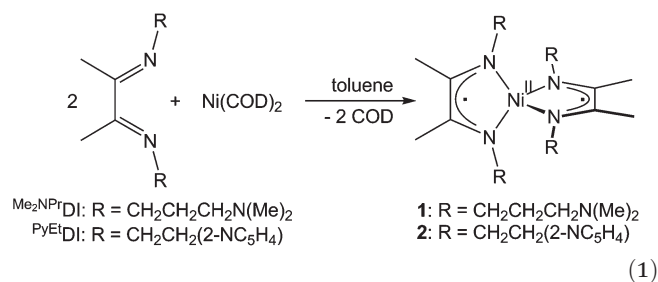Tyler M. Porter,[a] Gabriel B. Hall,[b] Thomas L. Groy[a] and Ryan J. Trovitch*[a]

Although bis(α-diimine)Ni complexes were prepared when amine-substituted chelates were added to Ni(COD)$_2$, the incorporation of strong-field phosphine donors allowed the isolation of (κ^4-*N,N,P,P*-DI)Ni hydrosilylation catalysts. The crystallographic investigation of two different (κ^4-*N,N,P,P*-DI)Ni compounds revealed that the geometry about nickel influences the observed degree of α-diimine reduction.

Redox-active ligands, which assist first-row transition metal catalysis by mediating reversible intramolecular electron transfer, have continued to gain in popularity.[1,2] The coordination chemistry of 1,4-diaza-1,3-butadiene (α-diimine or DI) ligands has been particularly well-investigated[3] as they are structurally simple, easy to prepare, and highly modular non-innocent chelates.[4,5] While these characteristics have enabled the design of several (DI)Ni α-olefin polymerization catalysts,[6,7] selectivity for polymerization over oligomerization has been strongly linked to the incorporation of sterically demanding DI imine substituents.[6,8] Although the inclusion of bulky substituents has remained a guiding force in the development of redox-active ligand-supported catalysts,[1,2] it is believed that integrating secondary donors into the chelate framework may offer the same benefits that steric bulk provides while potentially facilitating the stabilization of high-energy intermediates.[9]

Following this methodology, low-valent nickel complexes featuring a κ^4-DI ligand were targeted so their ability to mediate catalytic transformations, including hydrosilylation,[10,11] could be investigated. Knowing that ^{Me_2NPr}DI (eqn (1), left) is capable of κ^4-coordination to iron,[12] this chelate was prepared using a slightly modified procedure and a stoichiometric quantity was added to Ni(COD)$_2$. Analysis of the resulting red solution by ^{1}H NMR spectroscopy revealed only partial conversion to a new compound featuring an upfield shifted resonance at −0.73 ppm, indicative of bis(ligand) complex formation.[4,13,14] Adding 2 equivalents of ^{Me_2NPr}DI to Ni(COD)$_2$ allowed for the isolation and full characterization of (κ^2-*N,N*-^{Me_2NPr}DI)$_2$Ni (**1**, eqn (1)).

^{Me_2NPr}DI: R = CH$_2$CH$_2$CH$_2$N(Me)$_2$
^{PyEt}DI: R = CH$_2$CH$_2$(2-NC$_5$H$_4$)

1: R = CH$_2$CH$_2$CH$_2$N(Me)$_2$
2: R = CH$_2$CH$_2$(2-NC$_5$H$_4$)

$$(1)$$

Because the dimethylamino groups of ^{Me_2NPr}DI did not allow for κ^4-DI ligation, a formal Ni(0) complex supported by ^{PyEt}DI (eqn (1), left) was sought. This ligand has been reported to bind Cu(II) in a tetradentate fashion[15] and the glyoxal-derived variant of this chelate has been found to adopt κ^4-coordination to Ni(II).[16] Although ^{PyEt}DI has not been previously isolated, this ligand was prepared following the condensation of 2,3-butanedione with 2 equivalents of 2-(2-aminoethyl)-pyridine in a sealed reaction vessel at 100 °C. Unfortunately, adding a single equivalent of ^{PyEt}DI to Ni(COD)$_2$ also resulted in limited formation of the respective bis(ligand) complex, (κ^2-*N,N*-^{PyEt}DI)$_2$Ni (**2**, eqn (1)), as judged by ^{1}H and ^{13}C NMR spectroscopy. As with **1**, complex **2** was prepared following the direct addition of two ^{PyEt}DI equivalents to Ni(COD)$_2$. Furthermore, the bidentate coordination of each ^{PyEt}DI moiety was confirmed by single crystal X-ray diffraction (Fig. 1).

The geometry about the metal centre in **2** is best described as a distorted tetrahedron, having an acute dihedral angle between the two 5-membered chelate planes of 74.8°. Notably, this complex features elongated N(1)–C(2) and N(2)–C(3) bond distances of 1.344(3) and 1.341(3) Å, respectively, along with a

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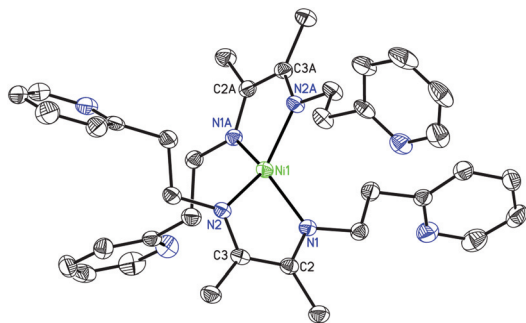
Fig. 1 The solid state structure of **2** at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Relevant bond distances and angles are provided throughout the text and in Table S2 of the ESI.†

significantly shortened C(2)–C(3) distance of 1.416(4) Å. Based on prior crystallographic studies,[4,5] the α-diimine bond distances determined for **2** strongly suggest that each ligand is singly reduced and that the electronic structure of this complex is best described as having a high-spin Ni(II) centre ($S_{Ni} = 1$) that is antiferromagnetically coupled to each ligand based radical. Additional evidence that **2** possesses this electronic structure was obtained by cyclic voltammetry, as two one-electron oxidation waves were observed at $E^1_{1/2} = -0.84$ and $E^2_{1/2} = -0.56$ V (*vs.* Fc$^+$/Fc, Fig. S21 of the ESI†). These potentials directly correlate to those previously described for a related alkyl-substituted (DI)$_2$Ni complex featuring two monoanionic DI ligands ($E^1_{1/2} = -0.82$ and $E^2_{1/2} = -0.53$ V relative to Fc$^+$/Fc in THF).[5]

Although κ^4-DI coordination to Ni(0) could not be achieved when amines were built into the chelate framework, it was hypothesized that the incorporation of strong-field co-donors would more effectively compete for metal-based electron density through backbonding, therefore preventing bis(ligand) complex formation. For this reason, DI ligands featuring phosphinoalkyl imine substituents were pursued. Since the optimal carbon-chain length for tetradentate DI coordination was unclear, chelates featuring either ethylene (^{Ph_2PEt}DI, eqn (2)) or propylene (^{Ph_2PPr}DI, eqn (2)) bridges to diphenylphosphine substituents were synthesized in a similar fashion to ^{PyEt}DI (see ESI† for experimental details). Whereas an alternate preparation of ^{Ph_2PEt}DI has been previously reported,[17] literature discussion of ^{Ph_2PPr}DI has remained limited.[18]

The stoichiometric addition of ^{Ph_2PEt}DI to Ni(COD)$_2$ in benzene-d_6 resulted in an immediate colour change from yellow to a dark green solution. Analysis by ^{1}H NMR spectroscopy revealed the complete disappearance of Ni(COD)$_2$ and the formation of a complex featuring a single DI backbone methyl resonance that was split into a well-defined triplet (1.95 ppm, 4.3 Hz). This resonance collapsed into a singlet upon ^{31}P decoupling (Fig. S13 of the ESI†) and ^{31}P NMR spectroscopy further confirmed that the newly formed compound, (κ^4-*N,N,P,P*-^{Ph_2PEt}DI)Ni (**3**, eqn (2)), possesses a single phosphorous environment (56.36 ppm). In contrast, adding a single equivalent of ^{Ph_2PPr}DI to Ni(COD)$_2$ resulted in an instantaneous colour change from yellow to a dark red solution.

Investigation of the isolated product by multinuclear NMR spectroscopy confirmed the formation of (κ^4-*N,N,P,P*-^{Ph_2PPr}DI)Ni (**4**, eqn (2)), which also exhibits a single ^{31}P resonance at 39.03 ppm. Although both the ^{1}H and {^{31}P}^{1}H NMR spectra recorded for **4** featured 6 methylene resonances, the ^{1}H NMR resonances found for **3** collapsed into two multiplets upon ^{31}P decoupling, suggesting that **3** possesses ligand arms that are equivalent from top to bottom in benzene-d_6 solution at 23 °C.

$$(2)$$
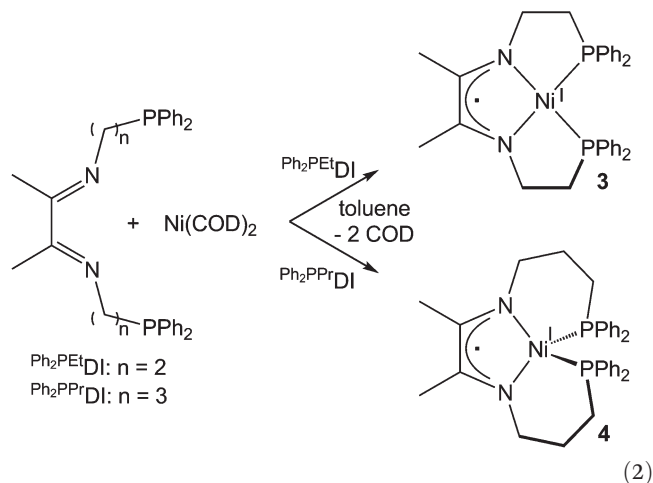
The different colours observed for **3** (green) and **4** (red) in solution prompted the investigation of each complex by UV-visible spectroscopy. Although both complexes exhibited a spectrum dominated by charge transfer bands (Fig. S20 of the ESI†), the transitions observed for **3** [420 nm ($\varepsilon = 5600$ M^{-1} cm^{-1}) and 714 nm ($\varepsilon = 5000$ M^{-1} cm^{-1})] were higher in energy than the same bands observed for **4** [498 nm ($\varepsilon = 11\,800$ M^{-1} cm^{-1}) and 780 nm ($\varepsilon = 1000$ M^{-1} cm^{-1})]. Notably, the MLCT band associated with backbonding into the phosphine donors of **3** was found to have a much higher extinction coefficient than the same transition observed for **4**, suggesting that geometric differences might be influencing the relative degree of overlap between the Ni(3d) orbitals and the P(σ*) and DI(π*) orbitals of the chelate.

Moreover, the molecular structures of **3** and **4** were determined by single crystal X-ray diffraction (Fig. 2).[19] The geometry about the Ni centre in **3** can be described as distorted square planar, as the acute dihedral angle between the planes defined by Ni(1)–N(1)–C(2)–C(3)–N(2) and Ni(1)–P(1)–P(2) is only 32.5°. In contrast, the geometry about the Ni centre in **4** is best defined as distorted tetrahedral; the same dihedral angle for this complex is 56.3°. While this observation confirms that the ethylene-bridged donor arms of **3** restrict this complex from achieving approximate tetrahedral coordination about Ni, this characteristic also appears to influence the relative degree of DI reduction observed between the two complexes. The N(1)–C(2) and N(2)–C(3) bond distances in **4** were determined to be 1.340(3) and 1.341(3) Å, respectively, while the C(2)–C(3) distance was found to be shortened to 1.414(3) Å. These bond lengths are statistically indistinguishable from the same distances in **2** and strongly indicate[4,5] that the electronic
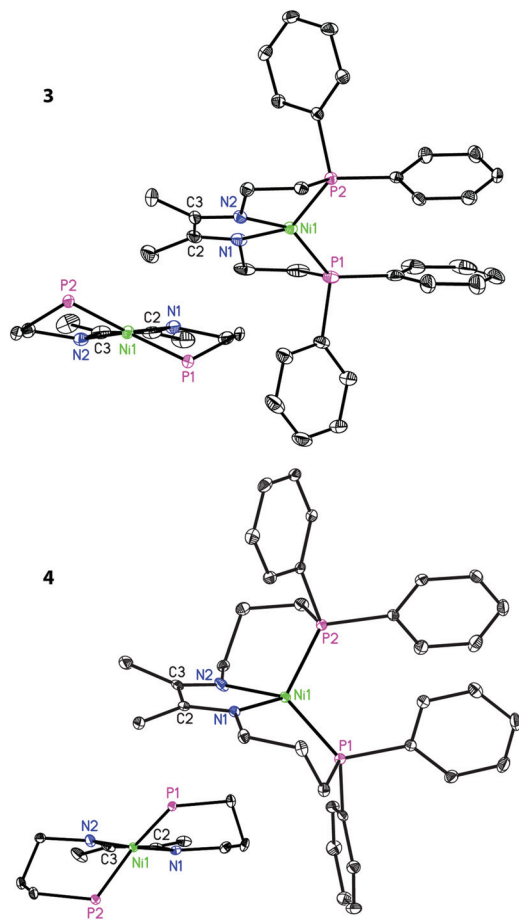
Fig. 2 The molecular structure of **3** (top) and **4** (bottom) at 30% probability ellipsoids. Hydrogen atoms are omitted for clarity and the aryl groups were removed to generate the core representations shown at the bottom left of each structure. Relevant bond distances and angles are provided throughout the text and in Tables S3 and S4 of the ESI.†

structure of **4** is best described as having a Ni(ɪ) centre that is antiferromagnetically coupled to a DI radical monoanion.

In contrast, complex **3** features N(1)–C(2) and N(2)–C(3) bond lengths of 1.360(4) and 1.373(3) Å, respectively, which are longer than the imine distances determined for **2** and **4**. Concurrently, the C(2)–C(3) bond distance of 1.388(4) Å established for **3** is shortened by approximately 0.027 Å relative to **2** and **4**, indicating a greater degree of DI ligand reduction. Although the metrical parameters associated with the imine bonds in **3** are consistent with those determined for other complexes featuring a doubly reduced α-diimine ligand,[20] the C(2)–C(3) bond distance of 1.388(4) Å is longer than one might expect to observe for this level of chelate reduction (1.36–1.37 Å).[4,5] Further crystallographic evidence that the Ni centre in **3** may possess a higher physical oxidation state than **4** is also observed upon inspection of the Ni–N bond distances. The Ni(1)–N(1) and Ni(1)–N(2) distances of 1.896(2) and 1.885(2) Å, respectively, for **3** are shorter than the bond lengths of 1.9369(17) and 1.9250(18) Å found for **4**.

Complimentary methods to probe the electronic structure of **3** and **4** have also been utilized. The redox properties of

each complex were investigated using cyclic voltammetry, and upon scanning from negative to positive potentials, **3** and **4** exhibited fully reversible one electron oxidation waves at $E^1_{1/2} = -0.54$ V and -0.46 V (relative to Fc$^+$/Fc in acetonitrile), respectively. Additionally, **4** was found to exhibit a significantly broadened, yet reversible, oxidation at $E^2_{1/2} = 0.21$ V while the cyclic voltammogram of **3** featured a partially reversible (scan rate = 50 mV s^{-1}) and irregularly shaped oxidation at $E^2_{1/2} = -0.13$ V. While this 0.30 V difference in $E^2_{1/2}$ values is significant, the CV data collected for **3** and **4** is otherwise analogous (Fig. S22 of the ESI†), suggesting these complexes may possess the same electronic structure (as proposed in eqn (2)). It should be appreciated that as tetradentate complexes of this type approach their square planar geometric limit, the energy of the highest lying Ni d-orbital will increase, boosting the likelihood that the ligand LUMO (π*) will become doubly populated. A complete DFT investigation of **3** and **4** is underway, which may more accurately address the question of when (at what dihedral angle) the redox-active DI core of the chelate becomes a true dianion. Neither **3** nor **4** was found to exhibit an X-band EPR signal in frozen toluene solution at 130 K or 140 K, respectively.

Having studied the electronic structure of two different (κ^4-DI)Ni complexes, we sought to determine if either complex was capable of mediating the hydrosilylation of unsaturated organic substrates. Fortunately, in spite of their geometric differences, both **3** and **4** were found to catalyse the hydrosilylation of cyclohexanone, diisopropyl ketone, and phenylacetylene (Table 1). Using an equimolar quantity of PhSiH$_3$

Table 1 The hydrosilylation of unsaturated substrates using **3** or **4**

Entry	Cat.	Substrate	Products (Ratio)	Conv.[a] (%)
1	3	cyclohexanone	PhSiH(OCy)$_2$ PhSiH$_2$(OCy) (20 : 1)	93
2	4	cyclohexanone	PhSiH$_2$(OCy) PhSiH(OCy)$_2$ (2 : 1)	>99
3	3	diisopropyl ketone	PhSiH(OCH(^{i}Pr)$_2$)$_2$ PhSiH$_2$(OCH(^{i}Pr)$_2$) (11 : 1)	>99
4	4	diisopropyl ketone	PhSiH(OCH(^{i}Pr)$_2$)$_2$ PhSiH$_2$(OCH(^{i}Pr)$_2$) (1 : 1)	>99
5	3	Ph———H	trans-(Ph)HC=CH(SiH$_2$Ph)[b]	>99
6	4	Ph———H	trans-(Ph)HC=CH(SiH$_2$Ph)[b]	>99

[a] Conversion determined by NMR spectroscopy at 24 h. [b] Major product.

and 5 mol% of either **3** or **4**, the near complete hydrosilylation of each substrate was observed after 24 h at ambient temperature. Efforts to optimize the performance of these catalysts, while determining their substrate scope and functional group tolerance, are underway.

Notes and references

1 O. R. Luca and R. H. Crabtree, *Chem. Soc. Rev.*, 2013, **42**, 1440.
2 P. J. Chirik and K. Wieghardt, *Science*, 2010, **327**, 794.
3 G. Van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151.
4 M. M. Khusniyarov, K. Harms, O. Burghaus and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2006, 2985.
5 N. Muresan, K. Chlopek, T. Weyhermüller, F. Nesse and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 5327.
6 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
7 C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664.
8 S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65.
9 H. Ben-Daat, G. B. Hall, T. L. Groy and R. J. Trovitch, *Eur. J. Inorg. Chem.*, 2013, 4430–4442.
10 S. Chakraborty, J. A. Krause and H. Guan, *Organometallics*, 2009, **28**, 582, and references therein.
11 S. Chakraborty and H. Guan, *Dalton Trans.*, 2010, **39**, 7427.
12 N. J. Hardman, X. Fang, B. L. Scott, R. J. Wright, R. L. Martin and G. J. Kubas, *Inorg. Chem.*, 2005, **44**, 8306.
13 M. Svoboda and H. tom Dieck, *Z. Naturforsch., B: Chem. Sci.*, 1981, **36**, 814.
14 H. tom Dieck, M. Svoboda and T. Greiser, *Z. Naturforsch., B: Chem. Sci.*, 1981, **36**, 823.
15 M. L. P. Santos, I. A. Bagatin, E. M. Pereira and A. M. D. C. Ferreira, *J. Chem. Soc., Dalton Trans.*, 2001, 838.
16 A. Kriza, L. Pricop, A. Meghea and N. Stanica, *J. Indian Chem. Soc.*, 2001, **78**, 448.
17 T. D. DuBois, *Inorg. Chem.*, 1972, **11**, 718.
18 J. W. Corr, *The synthesis of a series of ligands containing nitrogen and phosphorus or arsenic donor atoms within the same moiety. An investigation of the donor properties of these ligands toward certain transition metals*, Dissertation, University of North Carolina, Chapel Hill, 1967.
19 The needle of **3** analyzed by X-ray diffraction appeared red in colour.
20 T. Spaniel, H. Görls and J. Scholz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1862.