Difference in the Reactivities of H- and Me-Substituted Dinucleating Bis(iminopyridine) Ligands with Nickel(0)

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Supporting Information

ABSTRACT: The reactivity of dinucleating bis-(iminopyridine) ligands bearing H (L1, (N,N′)-1,1′-(1,4-phenylene)bis(N-(pyridin-2-ylmethylene)methanamine)) or Me substituents (L2, (N,N′)-1,1′-(1,4-phenylene)bis(N-(1-(pyridin-2-yl)ethylidene)methanamine)) on the imine carbon atom with Ni(COD)2 (COD = 1,5-cyclooctadiene) has been investigated. Treatment of L1 with 2 equiv of Ni(COD)2 forms dinuclear Ni2(L1)(COD)2, whereas the reaction of L2 with 2 equiv of Ni(COD)2 leads to Ni2(L2)2, along with 1 equiv of Ni(COD)2. The compounds were characterized by 1H and 13C NMR spectroscopy, mass spectrometry, and elemental analysis; the structure of Ni2(L2)2 was determined by XRD. Ni2(L2)2 exists as syn and anti stereoisomers in the solid state and in solution. DFT calculations suggest Ni(I) for both Ni2(L1)(COD)2 and Ni2(L2)2, with the radical anion localized on one iminopyridine fragment in Ni2(L1)(COD)2 and delocalized over two iminopyridine fragments in Ni2(L2)2. Both Ni2(L1)(COD)2 and Ni2(L2)2 undergo a reaction with excess diphenylacetylene, forming diphenylacetylene complexes. However, whereas Ni2(L1)(diphenylacetylene)2 decomposes upon removal of the excess diphenylacetylene, Ni2(L2)2 demonstrates a reversible disassembly/assembly sequence upon the addition/removal of diphenylacetylene.

Redox-noninnocent1 ligands play an active role in redox transformations mediated by a metal–ligand system.2 Delineation of the factors that control the reactivity of the redox-active ligand systems is important for their application in catalysis.3 Iminopyridines have been recently demonstrated to possess noninnocent ligand character,4,5 closely related to that of the much studied α-diimines,6 bis(imino)pyridines,7 and bipyridines.8 The majority of the iminopyridine systems investigated so far had an H substituent on the imine carbon atom.4,5,9−12 Herein, we demonstrate that the nature of the substituent can have a profound impact on the reactivity of these ligands with reduced metal centers.

We are targeting dinucleating redox-active ligand platforms for cooperative dinuclear and multinuclear catalysis. As our first goal, we aim to develop the chemistry of the dinucleating bis(iminopyridine) ligands, depicted in Figure 1, that are capable of binding reduced metal centers. As part of the ligand design, we decided to investigate two different substituents attached to the imine carbon atom: H (L1) and Me (L2). L1 and L2 are flexible ligands, enabling syn and anti relative orientations of the iminopyridine chelating units. L1 has been previously shown to form both dinuclear complexes13 and metallosupramolecular systems,14 depending on the reaction conditions; L2 has not been synthesized before. L1 and L2 were obtained by condensation of 1,4-xylylenediamine with carboxypyridine (L1) or acetylpyridine (L2) and were isolated as crystalline solids from MeOH, in 81% (L1) and 76% (L2) yields.

Next, we targeted dinuclear Ni species. Treatment of 2 equiv of Ni(COD)2 with L1 forms blue-violet 1a, isolated in 57% yield (Figure 2). The 1H NMR spectrum of 1a is consistent with the expected Ni2(L1)(COD)2 formulation. Most characteristically, COD signals are observed at 3.8, 2.7, and 1.7 ppm, supporting its rigid binding to the metal 6g,k,15 (Figure S5, Supporting Information). Furthermore, the asymmetric nature of the iminopyridine ligand leads to two sets of signals for the alkene CCH (around 3.8 ppm) and for one of the methylene (2.7 ppm) protons. The 13C NMR is consistent with these observations (Figure S6), displaying two sets of CCH (82.8 and 81.9 ppm) and CCH2 (31.4, 31.3 ppm) signals. The methylene (NCCH2Ph) protons of the ligand backbone appear as a sharp singlet (5.26 ppm), consistent with a flexible behavior of 1a. Further support for the formation of 1a was obtained by mass spectrometry. The compound displays limited stability under vacuum or in solution for prolonged

Figure 1. Syn and anti conformations of the bis(iminopyridine) ligands L1 and L2.
periods of time, forming an insoluble brown material. As a result, our multiple attempts to obtain its crystal structure proved unsuccessful.

The reaction of \( L^2 \) with 2 equiv of \( \text{Ni(COD)}_2 \) took a different path. Under identical reaction conditions, purple product 2 was formed, along with an equimolar amount of \( \text{Ni(COD)}_2 \). The \( ^1H \) NMR spectrum of 2 in \( \text{CD}_2 \text{Cl}_2 \) at room temperature exhibits two sets of resonances attributable to two different species \( (2b, c) \) in a ca. 2:1 ratio and no signals attributable to \( \text{COD} \) (Figure S7). The imino Me groups gave rise to two peaks at −0.3 and −0.5 ppm. This unusual chemical shift for a Me group is consistent with a Me group in the vicinity of a radical anion,\(^7b\) indicating noninnocent behavior of \( L^2 \) upon coordination to the reduced Ni centers. The presence of two different structural isomers \( (2b, c) \) was confirmed by an X-ray structure determination (Figure 3). Two isomers are present in the asymmetric unit in a 2:1 ratio (nearly identical with the NMR ratio). The prevalent isomer, \( 2b \), features an anti conformation of the chelating iminopyridine units in \( L^2 \), whereas \( 2c \) has a syn conformation of the iminopyridine units. \( L^1 \) has been reported to feature either syn\(^14b\) or a mixture of syn and anti isomers\(^14e\) in supramolecular assemblies. Different isomers have been proposed to be stabilized by noncovalent packing interactions.\(^14\) Herein, we show that discrete, molecular species can display similar isomerism both in solution (\( ^1H \) NMR) and in the solid state. The average imine \( -N \) (1.43 Å) and \( C-N \) (1.33 Å) bonds are similar between the structures and are intermediate between those of singly reduced \( (1.41 \text{ Å} \text{ and } 1.34 \text{ Å}) \) and neutral \( (1.47 \text{ Å} \text{ and } 1.28 \text{ Å}) \) iminopyridine.\(^4d\) Dihedral angles between Ni−N−N−N planes are similar for the anti \( (2b) \) and syn \( (2c) \) structures (51°). We note that a dinculeating \( \text{bis(iminopyridine)} \) ligand with a shorter linker, \( N,N'\text{-bis(6-methyl-2-pyridymethylene)} \text{ethane-1,2-diamine}, \) has been shown to form di-Ni complexes featuring the anti geometry exclusively.\(^16\)

We monitored both transformations by \( ^1H \) NMR spectroscopy in toluene-\( d_8 \) at 23 °C (Supporting Information). For \( L^1 \), only reactants \( (L^1 \text{ and } \text{Ni(COD)}_2) \) and products \( (1a \text{ and } \text{COD}) \) are observed. The formation of \( 1a \) is fast: it is almost complete within several minutes (Figure S22). No traces of the \( 1b \) or \( 1c \) dimer (see below) were detected during the time the reaction was monitored by \( ^1H \) NMR (ca. 6 h). In contrast, the reaction of \( L^2 \) with \( \text{Ni(COD)}_2 \) is slow: signals of free \( L^2 \) were present in the spectrum after ca. 2 h (\( \delta \) 4.59 ppm, Figure S19). Furthermore, signals attributable to \( \text{Ni}_2(L^2)(\text{COD})_2 \) were observed in the reaction of \( L^2 \) with 2 equiv of \( \text{Ni(COD)}_2 \). Initially, \( \text{Ni}_2(L^2)(\text{COD})_2 \) was observed as a predominant product, but as the reaction progressed the concentration of \( \text{Ni}_2(L^2)(\text{COD})_2 \) decreased and the concentration of \( \text{Ni}_2(L^2)_2 \) increased. After 5 h, \( \text{Ni}_2(L^2)(\text{COD})_2 \) constituted <10% of \( \text{Ni}_2(L^2)_2 \) in the reaction mixture. These concentration profiles suggest that \( \text{Ni}_2(L^2)(\text{COD})_2 \) is an intermediate in the formation of \( \text{Ni}_2(L^2)_2 \). (see eq 1).

\[
\text{L}^2 + 2\text{Ni(COD)}_2 \rightarrow \text{Ni}_2(L^2)(\text{COD})_2 \\
\rightarrow \frac{1}{2}\text{Ni}_2(L^2)_2 + \text{Ni(COD)}_2
\]

Figure 3. Solid-state structure of the anti \( (2b) \) and syn \( (2c) \) stereoisomers of \( 2 \) (50% probability ellipsoids). Hydrogen atoms and solvent molecules were omitted for clarity. The ratio of \( 2b \) to \( 2c \) in the structure is 2:1, as a full molecule of \( 2b \) and a half-molecule of \( 2c \) occupy an asymmetric unit.

Figure 2. Reactivity of \( L^1 \) and \( L^2 \) with \( \text{Ni(COD)}_2 \).
Computed bond lengths of 1.44 and 1.33 Å for the imine C–C and C–N bonds agree well with those observed in the crystal structure. The corresponding orbital analysis for \([\text{Ni}(L^3)]^0\) (Figure 4) shows a Ni d\(_{x^2−y^2}\) radical magnetically coupled to a ligand \(\pi\) radical with an overlap of 0.25, suggesting weak AF coupling. A second orbital has nonunity overlap, though the value is large at 0.86 and both orbitals are dominated by d\(_{\pi}\) character. We therefore assign this as a doubly occupied Ni d\(_{\pi}\) orbital. A Mulliken spin density of 1.1 at Ni further supports assignment as NiI, though the data could be alternatively interpreted as having a fractional oxidation state between NiI and NiII. Wieghardt and co-workers observed similar behavior for a related bis(iminopyridine) complex.4a We also computed the electronic structure for a model of \([\text{Ni}(L^1)(\text{COD})]^0\). The results suggest a Ni I center and a monoanionic iminopyridine ligand, in contrast to the case for the bis(iminopyridine) complex. Additional model complexes with different substituents on the imine carbon show that the electronic structure at Ni and iminopyridine does not qualitatively change for the two bis(iminopyridine) and iminopyridine–COD complexes as a function of the substituent. A full analysis of all species can be found in the Supporting Information.

Thus, we postulated that \(L^2\) in \(\text{Ni}_2(L^2)_2\) will be more labile than \(L^1\) in \(\text{Ni}_2(L^1)(\text{COD})_2\). Our initial reactivity studies have focused on the reactions of \(\text{Ni}_2(L^3)(\text{COD})_2\) and \(\text{Ni}_2(L^2)_2\) with diphenylacetylene as a \(\pi\)-acid model. Treatment of \(\text{Ni}_2(L^3)(\text{COD})_2\) with excess diphenylacetylene (4 equiv) leads to the replacement of COD ligands, forming \(\text{Ni}_2(L^3)(\text{PhCCPh})_2\) (3a). However, removal of the excess diphenylacetylene leads to the formation of an insoluble brown material, precluding the isolation of 3a in a pure form. As no free ligand was detected in the soluble phase, we propose that \(L^1\) remains coordinated to Ni, consistent with its stronger coordination to the metal. In contrast, \(\text{Ni}_2(L^2)_2\) displays reversible binding of diphenylacetylene (Figure 5). Treatment of 2b,c with excess diphenylacetylene (4 equiv) opens the dimer \(\text{Ni}_2(L^2)_2\) to give a mixture of

![Figure 4. Top-down view of isodensity surfaces (0.05 au) for the \([\text{Ni}(L^3)]^0\) corresponding orbitals. \(S_{\alpha\beta}\) is the overlap between the \(\alpha\) and \(\beta\) orbitals and is only listed for nonunity (<0.99) values.](image)

![Figure 5. Reaction of \(\text{Ni}_2(L^2)_2\) with diphenylacetylene.](image)
Organometallics

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