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Research paper

Coordination and electronic characteristics of a nitrogen heterocycle pincer ligand

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ABSTRACT

The Fe(II) coordination chemistry of *bis*(pyrazole-3-yl)pyridine ligands with both proton or methyl substituents on pyrazole nitrogen are investigated, including the willingness of the ligand to undergo redox change. Protons on the pyrazole nitrogen promote intermolecular hydrogen bonding and lead to redox irreversibility; N methylation of those nitrogens eliminates those intermolecular interactions and leads to reversible outer-sphere reducibility. The resulting anion radical of the N-methylated ligand has more spin in the pyridine moiety than in the pyrazolyl pincer ligand arms, but also detectably delocalized into the electron withdrawing pyrazolyl pincer ligand arms; EPR and density functional calculations assist in characterizing the ligand radical anion, as its potassium complex.

1. Introduction

We are attracted to ligands which connect two identical redox active heterocycles to a central linker to create a redox active pincer ligand. Perhaps the best known pincer with these characteristics is that which links two *ortho* phenylenediamine rings via a central amide bridge, and such chemistry has been actively studied [1] (**A**, Scheme 1). We are interested in a pincer with rings which are more difficult to reduce, for their resulting higher reducing power, and thus considered pyrazoles. Pyrazoles are heterocycles which combine a monoazabutadiene fragment with an electron donating amine functionality (**B** and **C**, Scheme 1). These have been explored as pincer arms simply for *mer* tridentate character [2–6], but never with an eye towards their redox activity. The connectivity between pyrazole and pyridine can have large impact on inter-ring communication, and connection via pyrazole nitrogen (pyrazol-1-yl, **B**) has been much more investigated than the carbon-connected pyrazol-3-yl isomer (**C**, Scheme 1) which we study here [7,8]. We describe here the characteristics of several iron complexes of this pyrazol-3-yl type **C**, both with and without reactive proton functionality on the pyrazole ring (substituent R), as a first step towards probing this ligand class' redox activity [9,10].

2. Results

2.1. Ligand electronic character

L^R (Scheme 2; superscript indicates substituent on each pyrazole **amine** nitrogen) is comprised of two heterocycles: pyridine and pyrazole. Is pyrazole an electron donating or an electron withdrawing substituent on pyridine? It is valuable to dissect nitrogen donor ligands into two functionalities according to whether they are high oxidation state (imine $R_2C{=}NR'$) or low oxidation state (amine R_2NH). Pyrazole has, as ring elements, an electron-withdrawing imine, an electron-donating amine, and a vinyl component. The net outcome of these competing oxidized and reduced nitrogen contributors, conjugated via the vinyl component, leaves uncertain whether a pyrazole acts as an electron rich- or electron poor-substituent. To better understand which part of L^R should accept the electron upon reduction, we performed a computational study of the electron affinities of some nitrogen heterocycles. The CBS-QB3 model [11,12] yields reliable electron affinities (to within ~1 kcal/mol), the energy change upon removing an electron from the anionic species. For pyridine (Scheme 3) excellent agreement with experiment is seen (−0.61 eV calculated vs. −0.62 eV experimental) [13].

Based on these agreements and the average electron affinity error of ~1 kcal mol^{-1} benchmarked by Petersson and co-workers [11,12], we felt confident interpreting these results. As seen in Scheme 3, the electron affinity of all of the heterocycles is negative,

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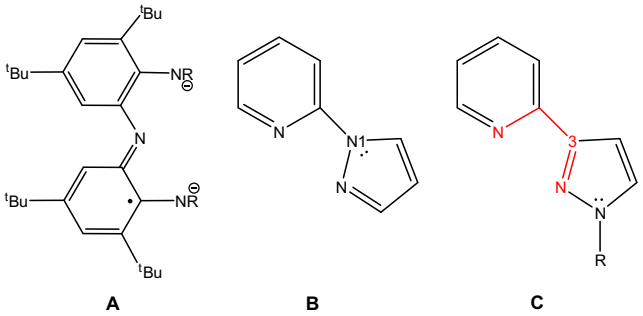
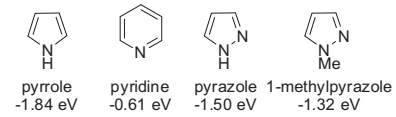


Scheme 1. Redox active pincer ligands.

which indicates that in the gas phase, electron addition is thermodynamically unfavored. Both pyrazole and N-methyl pyrazole are more negative (less favorable) than that of pyridine, so this would anticipate that reduction of the L^R pincer ligand would take place more in the pyridine portion. This conclusion is reinforced by an independent evaluation: the LUMO and LUMO + 1 of a truncated L^{Me} pincer (Fig. 1) are localized on pyridine while the LUMO + 2 and LUMO + 3, which are higher in energy by ~1 eV (consistent with the calculated electron affinity difference), are localized on the pyrazole rings. The truncated computational model for L^{Me} is simplified with a methyl group instead of a *t*-butyl groups at the 5-position of the pyrazole. LUMO + 1 has greater C(pyridyl)–C(pyrazolyl) *bonding* character, and reduction thus strengthens this bond. This will have the effect of increasing diazabutadiene delocalization as these orbitals become populated upon reduction.

2.2. Ligand synthesis and characterization

Ligand synthesis used conventional pyrazole methodology, which involves cyclization of a 1,3-diketone with hydrazine (Scheme 2) [2,6]. The ^1H NMR spectrum of L^H in $CDCl_3$ shows all expected CH signals, and indicates twofold symmetry, consistent with equivalent pyrazole arms of the pincer form. The NH protons are not observed, apparently due to a dynamic process: the proton equilibrating between the two inequivalent pyrazole nitrogens in a given ring. Given the evidence (see below) for hydrogen bonding, it was thought that the NH exchange process might be suppressed in



Scheme 3. Electron affinities of five- and six-membered nitrogen-containing heterocycles calculated at the CBS-QB3 level of theory.

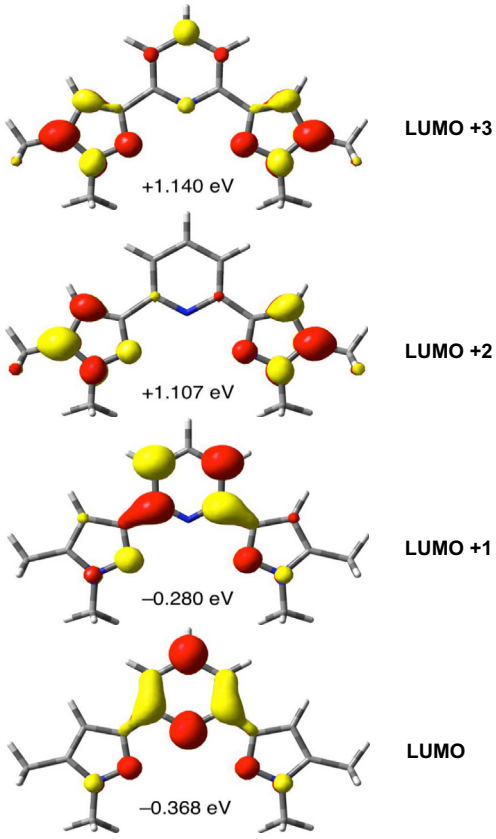
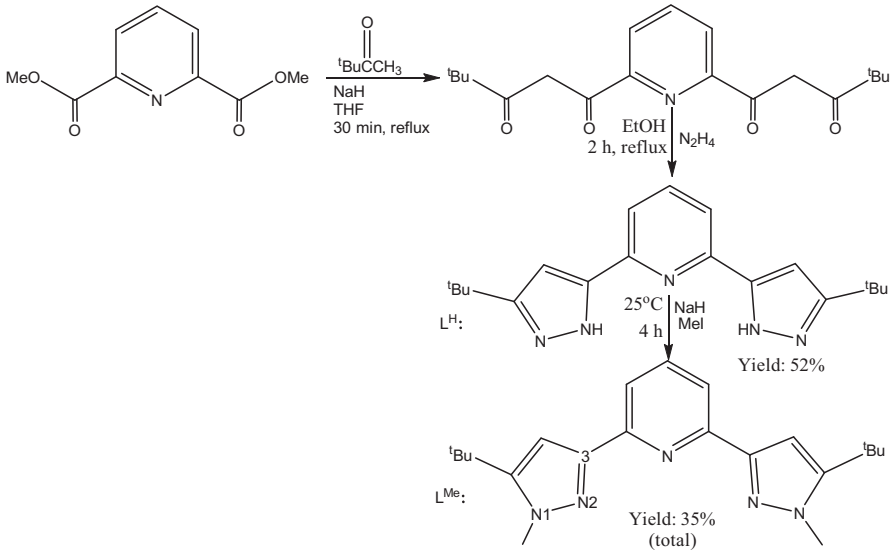


Fig. 1. Lowest unoccupied orbitals in L^{Me} at the geometry of a complex (see below).



Scheme 2. Route to ligand synthesis and alkylation.