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Evidence for Ligand Non-innocence in a Formally Ruthenium(I) Hydride Complex

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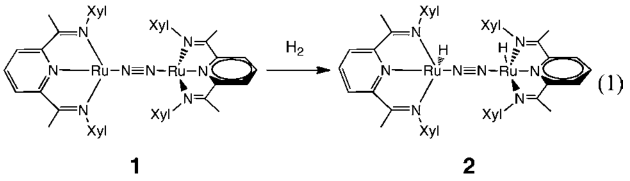
Late transition metal complexes of 2,6-bis(imino)pyridyl ligands initially garnered attention as effective catalysts for olefin polymerization and other reactions.[1] More recently, however, there has been an increased effort to elucidate the "non-innocent" character of this remarkably versatile class of multidentate ligands, and there is clear evidence that $[N_3^R]$ ligands ($[N_3^R]$ = 2,6-(RN=CMe)$_2$C$_5$H$_3$N) can serve as acceptors for a variable number of electrons.[2] In certain cases, low-valent $[N_3^R]$M complexes are best described by canonical forms representing full transfer of one or more electrons from the metal to relatively remote ligand orbitals, e.g. $[N_3^R]^-/M^+$ or $[N_3^R]^{2-}/M^{2+}$. Several groups have shown that surprisingly complex electronic structures and magnetic behavior can result in these formally low-valent complexes.[3] In some instances, such metal-to-ligand charge transfer character in the ground-state is manifest as ligand-centered chemical reactivity.[4] In many other cases, however, the reaction chemistry remains metal-centered and is not appreciably different from what one would predict on the basis of the formal oxidation state.

Our group has previously described the highly reactive, formally zerovalent ruthenium complex, $\{[N_3^{Xyl}]Ru\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**1**), where $[N_3^{Xyl}]$ = 2,6-(XylN=CMe)$_2$C$_5$H$_3$N and Xyl = 2,6-xylyl.[5] Unlike many first-row transition metal complexes of non-innocent ligands that exhibit magnetic properties resulting from interaction of high-spin metal centers with ligand radicals, **1** is diamagnetic in solution and the solid state. In addition, the reactivity of **1** reported previously points to nothing more complicated than a *formally* Ru(0) center with a neutral [N$_3$] ligand.[5,6] It was noted, however, that the unusual and temperature *independent* shift of the imine methyl groups in the ^{1}H NMR spectrum of **1** may reflect possible ligand non-innocence.[5] We now report the synthesis and properties of a binuclear, formally Ru(I) dinitrogen-bridged hydride species, $\{[N_3]Ru(H)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**2**), and evidence for the role of ligand non-innocence in the stability and properties of this complex.

Treatment of **1** with excess dihydrogen (~4 atm) in ether or aliphatic solvents at ambient temperature leads to the rapid formation of **2**, isolated as a purple crystalline solid (77%, eq 1). Compound **2** appears to be the first formally Ru(I) hydride complex to have been isolated and structurally characterized. Many paramagnetic hydride complexes are unstable, although several odd-electron complexes of other metals bearing terminal[7] and bridging[8] hydride ligands have been structurally characterized.



1 **2**

The ^{1}H NMR spectrum of **2** exhibits isotropically shifted resonances between δ 2 to 20, consistent with an open-shell electronic structure. The low symmetry of **2** evident by ^{1}H NMR is consistent with a binuclear structure in solution, e.g. four different resonances are observed for the eight xylyl methyl groups (C_2 symmetry overall, C_1 local symmetry at each Ru), whereas only two xylyl methyl environments would be expected for a mononuclear [N$_3$]Ru(H)(N$_2$) structure (C_s symmetry at Ru). Resonances for the hydride ligand, *p*-pyridine CH and imine methyl groups are not observed in the ^{1}H spectrum, presumably due to paramagnetic broadening; furthermore, no signals were observed in the ^{13}C spectrum. Although the metal hydride in **2** is not directly observed by NMR, it is strongly implied by the significant shift of the ligand proton resonances in **2-*d*$_2$**, which is rapidly formed from **1** and D$_2$. Ligand shifts of $\Delta\delta \approx 0.2$ are appreciably larger than seen in isotopically substituted diamagnetic molecules,[9] but would be consistent with an Ru−H(D) on a paramagnetic metal center. Theopold and co-workers coined the term PIECS (paramagnetic isotope effect on chemical shift) for the phenomenon.[10] In addition, the IR spectrum of **2** exhibits an Ru−H stretch at 2003 cm^{-1} which is not observed in **2-*d*$_2$**.

The X-ray crystal structure of **2** confirms a binuclear, dinitrogen-bridged structure. As illustrated in Figure 1, the solid-state structure of **2** consists of two square pyramidal centers bridged by an essentially linear dinitrogen ligand (RuNN = 177.3(4)°), with the hydride ligands located *trans* to the vacant coordination sites. The two [N$_3$]Ru planes are perpendicular. Elongation of the imine C−N bond and contraction of the C$_{pyr}$−C$_{imine}$ bonds have been attributed to delocalization of metal-based electron density onto primarily ligand-based orbitals The imine C−N distances (1.333(5), 1.334(6) Å) are slightly shorter, and the C$_{pyr}$−C$_{imine}$ distances (1.445(6), 1.433(7) Å) are longer than in **1**, suggesting that the ligand in **2** is somewhat less reduced. The N−N distance of the bridging N$_2$ ligand is also shorter in **2** (1.132(6) Å) than **1** (1.161(5) Å), again consistent with a less electron-rich metal in the former.

Linear plots of the ^{1}H chemical shifts of **2** versus 1/*T* confirm Curie−Weiss behavior[11] (Supporting Information), and the solution magnetic moment of 3.50 μ_B per $\{[N_3]Ru(H)\}_2(N_2)$ (Evans Method[12]) corresponds to one unpaired electron per [N$_3$]Ru(H) unit. Although clearly paramagnetic in solution, **2** was found to be *diamagnetic* in the solid state between 2.4 to 130.0 K.[13] The origin of this inconsistency between solid and solution states is found in the crystal structure of **2**. As shown in Figure 2, there are close intermolecular contacts between neighboring molecules of **2**. In an arrangement reminiscent of aromatic ring "π-stacking", Ru-pyridine units of two molecules are positioned parallel and head-to-tail, offset such that each metal is 3.29 Å from the para carbon of the adjacent pyridine.

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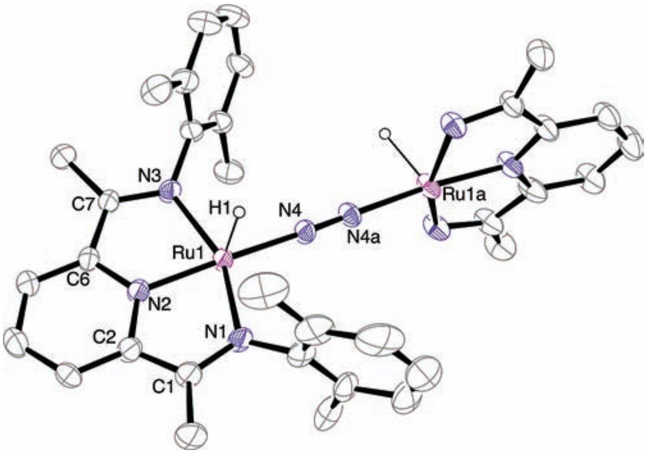

Figure 1. ORTEP drawing of complex **2** (30% probability ellipsoids). Ligand hydrogen atoms and xylyl groups on the $[N_3]Ru(1a)$ unit are omitted for clarity. Selected bond lengths (Å): Ru1−N4, 1.953(3); N1−C1, 1.333(5); N3−C7, 1.334(6); C1−C2, 1.445(6); C6−C6, 1.433(7); N4−N4a, 1.132(6).

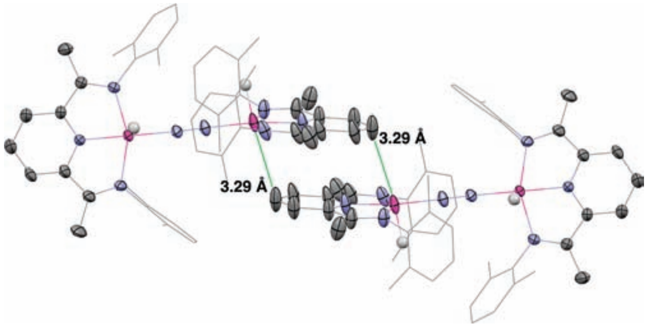

Figure 2. Crystal structure of **2** highlighting one set of intermolecular Ru−pyridine contacts. The $Ru-C_{para}$ contacts are 3.29 Å, and the distance between the mean pyridine planes is 3.26 Å.

This Ru−C separation is longer than in η^6-arene ruthenium complexes (average D(Ru−C) = 2.21 Å,)[14] but much closer than van der Waals contacts. Furthermore, the plane−plane separation between the mean pyridine rings is ~3.26 Å, considerably closer than the ~3.4 Å separation seen in organic π-stacks.[15] A search of the Cambridge Structural Database[14] revealed a single previous instance of intermolecular M···pyridine stacking in bis(imino)pyridyl transition metal complexes, the crystal structure of $[N_3^{DiP}]Mn(CH_3)$ (DiP = 2,6-$(iPr)_2C_6H_3$). Although not noted in the original report by Gambarotta and co-workers, this complex exhibits a ~3.35 Å separation between Mn−pyridine units of neighboring molecules.[16] The magnetic susceptibility of the manganese complex was reported as 4.82 μ_B; it is likely this complex will exhibit a discrepancy between solid- and solution-state magnetic properties similar to that seen for **2**.

The electronic structure of $[N_3^{Me}]Ru(H)N_2$ (**2-mod**), a model for the Ru(I) hydride complex (**2**), was investigated computationally at the B3LYP[17] level of theory employing the 6-31G(d,p)[18] basis set for nonruthenium atoms and the SDD[19] basis set for ruthenium. Mononuclear model hydride complex **2-mod** consists of a single open shell $[N_3]Ru(H)(N_2)$ unit with methyl groups on the imine nitrogen atoms. The optimized geometry is in good agreement with the solid state structure; all calculated N−Ru, C═N, and $C_{ortho}-C_{imine}$ bond lengths are within 0.02 Å of the experimental values, except for N−N distance in the N_2 ligand, which is terminal in the model, but bridging in **2**.

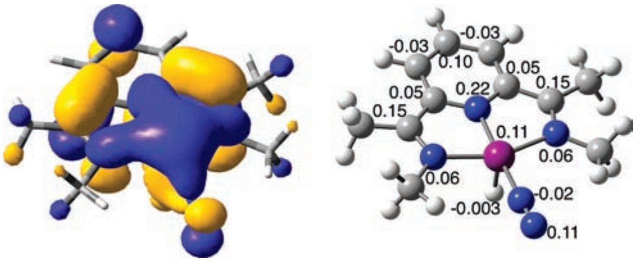

Figure 3. Calculated molecular orbital surface plot for the SOMO of **2-mod** (left). Mulliken spin densities are indicated for selected atoms (right).

The calculated molecular orbitals are consistent with a large contribution of the $Ru(II)/[N_3]^{1-}$ formalism. The SOMO of **2-mod** is substantially delocalized onto the $[N_3]$ ligand (73%), with only 19% on the metal, and 8% on the N_2 ligand, and is antibonding with respect to the imine C═N bond and bonding between $C_{ortho}-C_{imine}$ (Figure 2.) The SOMO exhibits some density at the pyridine para-carbon, but has nodes at the meta-positions; this may explain why the meta, but not para, pyridine protons are observed in the (paramagnetically shifted) ^1H NMR spectrum. Some delocalization of unpaired spin density on the imine methyl groups may also explain the absence of the C_{imine}-methyls from the NMR spectrum. Although not a perfect measure of spin delocalization, the Mulliken spin densities (Figure 3) indicate substantially lower unpaired electron density on ruthenium (0.11) than on the pyridine and imine atoms of the $[N_3]$ ligand (>0.8).

DFT calculations were also performed for dinitrogen-bridged, binuclear complexes, both with methyl groups as a model ($\{[N_3^{Me}]Ru(H)\}_2(N_2)$), and the full xylyl-substituted **2**. These results will be discussed in detail in a subsequent report, but the optimized geometrical parameters, molecular orbital descriptions, and distribution of spin density are not qualitatively different from those for **2-mod**; interaction of the unpaired spins on the two perpendicular $[N_3]Ru$ fragments via the dinitrogen bridge appears to be very modest.

DFT calculations were also undertaken to probe whether pyridine stacking in the solid state of **2** is merely a vestige of weak crystal packing forces or a stronger interaction resulting from the observed spin pairing in the solid state. Dimeric model complex **{2-mod}₂** contains two subunits of **2-mod** related by stacking of the pyridyl rings as observed in the crystal structure of the *N*-xylyl derivative. The geometry of **2-mod** was optimized as an unrestricted singlet, resulting in pyridyl $C_{para}-Ru$ distances of 3.042 Å. This somewhat shorter contact than in **2** is consistent with the reduced steric demands of the model. The close contact between the dimer halves is a clear indication of a bonding interaction. The HOMO of **{2-mod}₂** (Figure 4) is clearly the in-phase combination of SOMOs from the two **2-mod** monomers (Figure 3) and is bonding with respect to the $Ru-C_{para}$ and interpyridine C−C interactions. The imine carbon atoms also appear to be involved in bonding between the two planar fragments, which is not unreasonable given the unpaired electron density found on these atoms in the monomer. This process is not merely antiferromagnetic coupling of spins on isolated centers but is more comparable to covalent bond formation from the combination of two radicals. The homolytic cleavage back into radicals in solution does indicate the bond is quite weak but is no more surprising than the equilibrium dimerization of trityl[20a] or $Cp^*Cr(CO)_3$[20b] radicals. One largely superficial difference in the case of **2**, of course, is the delocalization of

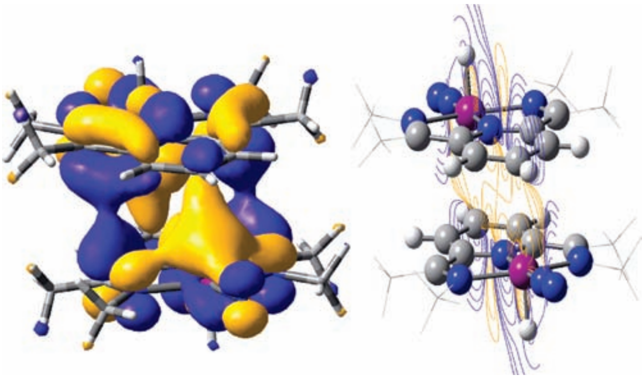

Figure 4. Molecular orbital surface (left) and contour (right) plots of the HOMO of **{2-mod}**$_2$.

the bond over 22 atoms. The "bond enthalpy" of this interaction can be very roughly estimated from the DFT calculations as 3.53 kcal/mol.[21]

Ironically, it is the inherent limitations of most DFT methods that highlight the significance of electron pairing in bonding the two fragments. Commonly employed DFT functionals such as B3LYP grossly underestimate long-range forces; thus, DFT calculations do not generally reproduce attractive "π-stacking" interactions due solely to van der Waals forces. In the absence of additional stabilization, the pyridine/pyridine interaction would be shown as *repulsive* by these DFT methods. Indeed, attempts to optimize the stacked pyridine geometry of **{2-mod}**$_2$ as a triplet (one unpaired electron on each monomer) were unsuccessful, as was optimization of the stacked dimer of (open-shell singlet) **1** subunits.

In conclusion, the DFT calculations and observed dimerization of **2** in the solid state are consistent with substantial delocalization of unpaired e-density from Ru to the $[N_3]$ ligand; i.e. **2** maybe better described as a Ru(II) hydride complex containing a radical anion $[N_3]$ ligand. This higher than "expected" metal oxidation state may also explain why $[N_3]RuH_2$ complexes are not formed under excess hydrogen. There are also potential implications regarding the electronic structure and reactivity of the parent complex, **1**. An analogous Ru(I)/$[N_3]^-$ canonical form for **1** suggests metalloradical character in a formally closed shell complex and raises the possibility that the reaction to produce **2**, with a single hydrogen atom on each metal, could proceed via the type of bimetallic, four-centered transition state previously only observed for odd-electron complexes.[22,23] Experimental and computational results on the structure of **1** and the mechanism of formation of **2** are currently under investigation.

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Supporting Information Available: Details of synthetic procedures, spectroscopic details, X-ray crystallographic data for **2** in CIF format, computational details, and coordinates of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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