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Radical Ligands

Metal Complexes of Aminyl Radicals

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electronic structure · N ligands · nitrogen · radicals · transition metals

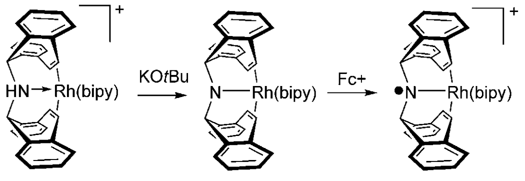
Transition-metal complexes with open-shell configurations typically have their spin density more or less confined to the metal ion: the unpaired electron (or electrons) resides in metal-based d orbitals, and there is minimal delocalization onto the ligands that comprise the inner coordination sphere of the complex. Metal complexes in which an unpaired electron resides on a ligand are relatively rare but are by no means unknown or unimportant. Semiquinone anions[1] and phenoxyls[2] are two examples of well-known radical ligands, both of which are delocalized π radicals which bind to metals through oxygen atoms. Both of these classes of radical ligands have attracted significant attention because of their importance in bioinorganic chemistry and their interesting physical properties.

Radical ligands in which nitrogen atoms are the donors are also known. A variety of radical anion species fall into this group,[3] as do neutral radicals such as verdazyls[4] and thiazyls.[5] In most of these cases the unpaired electron is delocalized over the ligand's conjugated π system, and the radicals enjoy some level of stability even as uncoordinated species: most are persistent in solution and some (e.g. verdazyls and thiazyls) are isolable compounds.

Aminyl radicals ($R_2N^{\bullet}$), perhaps the simplest organic nitrogen-based radicals, are normally very unstable and short-lived species.[6,7] Early claims[8,9] that certain metal complexes could be formulated as metal aminyls (Figure 1 a) proved to be incorrect.[10,11] In these and other cases,[12] the metal aminyl formulation turns out to be of secondary importance, and these species are still best described as the more familiar metal amides (Figure 1 b). Other complexes, in which the evidence for metal aminyl character was more compelling, were not sufficiently stable to be isolated, thereby limiting the studies of these complexes to in situ spectroscopic ones.[13] Thus it appeared that genuine, isolable metal aminyl radical complexes were elusive species, lost somewhere between the pitfalls of instability and conversion to the metal amide configuration (Figure 1 b).

Figure 1. Limiting electronic structures of M−NR$_2$ fragments: a) metal aminyl radical and b) metal amide.

The first isolable aminyl radical complex was reported by Grützmacher and co-workers in 2005.[14] Deprotonation of the NH group of the cationic rhodium(I) amine compound **1** affords the neutral rhodium(I) amide complex **2** (Scheme 1). The latter can be easily oxidized ($E^0 = -0.55$ V vs. ferrocene/ferrocenium in DMSO) and thus, treatment of **2** with ferrocenium cation generates cation **3** (as its $CF_3SO_3^-$ salt) as a stable entity in the solid state and in solution. EPR spectroscopy studies indicate that the majority of spin density resides on the nitrogen atom, supporting the formulation of **3** as a rhodium(I) complex of a neutral aminyl radical rather than a rhodium(II) amido compound. The EPR data are corroborated by DFT calculations, which predict a spin density of 57 % on nitrogen and 30 % on rhodium (Figure 2 a). The singly occupied molecular orbital (SOMO) of **3** (Fig-



1 **2** **3**

Scheme 1. Synthesis of rhodium(I) aminyl complex **3**. bipy = 2,2′-bipyridine, Fc$^+$ = ferrocenium.

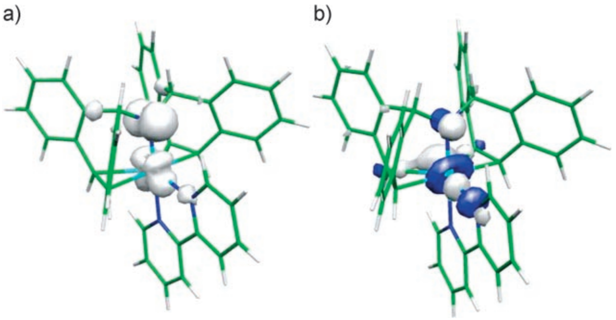


Figure 2. a) Spin density plot and b) SOMO for **3**. Rh teal, N blue, C green, H white. From reference [14]. Reprinted with permission from AAAS.

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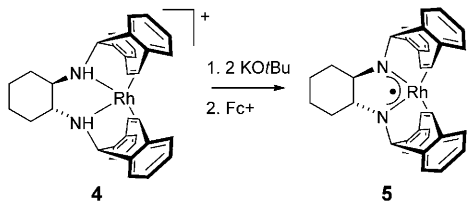
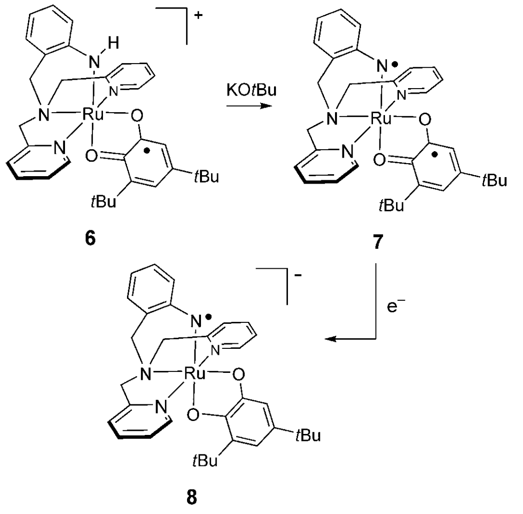
ure 2b) is largely based on the nitrogen 2p orbital but does possess some antibonding Rh–N character, a finding which is experimentally supported by the shorter Rh–N bond in **3** (1.936(3) Å) than **2** (2.045(3) Å), in which the SOMO becomes doubly occupied.

The stability of **3** arises in part from the specific substituents of the aminyl group $R_2N^{\bullet}$. The nitrogen atom bears two 5-*H*-dibenzo[*a,d*]cyclohepten-5-yl or "trop" groups, which likely provide some steric protection. Furthermore, the pendant olefin groups provide additional coordination sites for the metal, thereby allowing the (now tridentate) ligand to bind more strongly and to "lock" the conformation of the amin(yl) donor so as to maximize its interaction with the metal ion. The trop substituent figures prominently in the related aminyl complex **5** also reported by Grützmacher and co-workers.[15] In this example, double deprotonation of cationic rhodium(I) diamine complex **4** yields the corresponding anionic diamide complex (not shown). One-electron oxidation of the diamide affords **5** (Scheme 2), which can be formally described as a rhodium(I) species with one amide and one neutral aminyl donor. EPR and DFT data suggest that the spin density is shared between the two nitrogen atoms (56 % total) and the metal (41 %). As such, **5** can be described as a delocalized radical anion ligand, though one in which the delocalization pathway is "through metal". Curiously, the added delocalization in **5** (relative to **3**) does not appear to correlate with the stabilities of the two aminyl complexes: Complex **5** abstracts hydrogen atoms from solvent, thereby precluding its structural characterization by X-ray analysis, and **5** is also somewhat more reactive as a hydrogen-atom abstractor (see below).



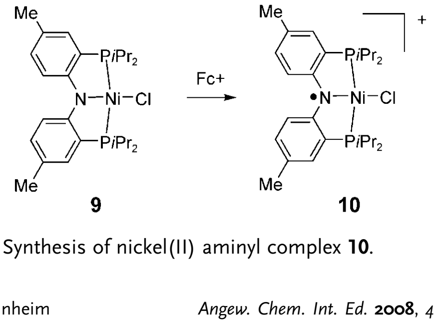
Scheme 2. Synthesis of rhodium(I) aminyl complex **5**.

A substantially different type of aminyl complex has been reported by Tanaka and co-workers.[16] The radical precursor complex is cation **6**, a ruthenium(III) species with a semiquinone radical anion and a coordinated anilide anion $ArNH^-$ as one arm of a tetradentate ligand (Scheme 3). The NH proton of **6** can be removed (KO*t*Bu) to afford neutral species **7** which could be described as a ruthenium(III) semiquinone complex of an imide ArN^{2-} ligand. However, the low-temperature EPR spectrum is consistent with a triplet species which cannot arise from a ruthenium(III) semiquinone complex, as such species are EPR silent owing to the strong ruthenium–semiquinone antiferromagnetic coupling. Resonance Raman spectroscopy and computational studies also indicate that **7** is best formulated as a ruthenium(II) semiquinone complex with an aminyl radical anion $ArN^{\bullet-}$, which must arise from intramolecular electron transfer from the putative imide ArN^{2-} to the ruthenium(III) center. Partial aminyl radical anion character has been noted in other metal imido complexes,[17,18] but in **7** it is $ArN^{\bullet-}$ which represents the dominant contribution to the electronic structure. Electrochemical reduction of **7** gives anionic complex **8**, in which the semiquinone moiety has been reduced to a dianionic catecholate, leaving one unpaired electron on the aminyl anion $ArN^{\bullet-}$, as evidenced by the EPR spectrum with $g \approx 2$ and a substantial hyperfine coupling constant to a lone nitrogen atom. DFT calculations place nearly two thirds of the spin density on the nitrogen atom and, importantly, essentially no spin on the catecholate.



Scheme 3. Synthesis of ruthenium(II) aminyl complexes **7** and **8**.

A distinctive feature of the coordinated aminyl radical anion $ArN^{\bullet-}$ in **7** and **8** is the substantial spin density found on the aromatic substituent on the nitrogen atom. This feature is shared by the most recently reported aminyl complex, a nickel(II) system reported by Mindiola and co-workers.[19] The square-planar complex **9**, containing a tridentate PNP-based amido ligand, can be oxidized to give cation **10** (Scheme 4) as its $CF_3SO_3^-$ salt. Once again, this species was probed using a variety of techniques, notable among which was X-ray absorption spectroscopy (XAS), a very effective probe of local (atomic) electronic structure. The similarities of the nickel L-edge XAS profiles of **9** and **10** is particularly compelling evidence that oxidation of **9** does not occur at the metal center. Collectively, the characterization of **10** suggests it is best described as a nickel(II) aminyl radical complex, that is, reaction of **9** with ferrocenium removes an electron from



Scheme 4. Synthesis of nickel(II) aminyl complex **10**.

the amide nitrogen atom. Most of the spin density (69 %) in **10** resides on the ligand, but this is divided nearly equally between the nitrogen atom and the two aromatic substituents (Figure 3). A smaller but still significant proportion of spin density (26 %) resides on the nickel ion.

The collection of aminyl radical complexes described above share an important feature. Although all of the complexes can be best described as metal-coordinated aminyl radicals, there is inevitably substantial spin density on the metal ion (and also elsewhere on the ligand where appropriate), and the metal orbitals make non-negligible contributions to the SOMO. In other words, the canonical forms in Figure 1 should be thought of as limiting resonance structures, with the real structure being some weighted average of the two, rendering aminyl radicals as new examples of non-innocent ligands. This aspect of metal aminyl complexes also highlights the challenges of elucidating their electronic structure, challenges which are met through the use of as many relevant techniques as possible to probe them. The use of computational studies to complement experimental work is clearly indispensable as well.

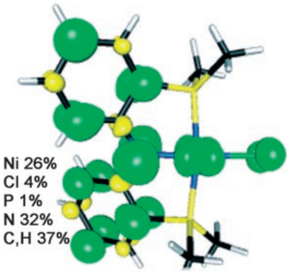


Figure 3. Spin density plot for a model complex of **10.** Ni blue, Cl green, P yellow, N blue, C black, H white. From reference [19]. Reprinted with permission from the American Chemical Society.

The metal aminyl complexes described herein share another common trait, namely that they are all prepared by oxidation of corresponding metal amido (or imido) precursor complexes. Given the widespread occurrence and use of chelating amido ligands in transition-metal chemistry, it seems likely that many more aminyl radical complexes will be discovered. The possibility of employing these complexes—with their spin-bearing, non-innocent ligands[20]—for chemical transformations also looms. Indeed, the investigations by Tanaka and co-workers into the ruthenium anilidyl complexes **7** and **8** were motivated by the catalytic activity demonstrated by closely related species.[21,22]. Aminyl complexes **3** and **5** have been shown to react stoichiometrically with EH substrates to give EE dimers ($E = SnR_3$, SR; $E = SiR_3$ for **5** only) and the corresponding amine complexes **1** and **4**, respectively.[14,15] Iridium analogues of **5** have also been recently reported to act as cocatalysts for the oxidation of alcohols to aldehydes,[23,24] thus highlighting a potential role for metal aminyl complexes in catalysis as well.

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