Hypovalent substrates in transition metal catalysis: C-H bond functionalisation, ring-closing reactions & polymer synthesis

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Chapter 1

Nitrogen-Centred Ligand Radical Complexes;

Classification, Spectroscopic Features, Reactivity and Catalytic Applications.
Abstract

In this chapter the electronic structure, spectroscopic features and (catalytic) reactivity of nitrogen-centred ligand radical complexes are described. Aminyl-radical ([M(•NR$_2$)]), nitrene/imidyl-radical ([M(•NR)]), and nitridyl-radical ([M(•N)]) complexes are shown to be detectable and sometimes even isolable species, and despite their radical nature frequently reveal selective reactivity patterns towards a variety of organic substrates. A classification system of nitrogen-centred ligand radical complexes is introduced on the basis of their electronic structure, leading to a description as one-electron-reduced Fischer-type systems, one-electron oxidised Schrock-type systems or systems with a (nearly) covalent M–N π-bond. Experimental data relevant for the assignment of the radical locus (i.e. metal vs. ligand) are discussed, and the application of nitrogen-centred ligand radical complexes in (catalytic) syntheses of a variety of nitrogen-containing organic molecules, such as aziridines and amines, is demonstrated by recent literature examples. The information in this chapter should contribute to a better understanding of the (catalytic) reactivity of nitrogen-centred ligand radicals and the role they play in tuning the reactivity of coordination compounds.
1.1 Introduction.

Investigations into the ligand-centred reactivity of transition-metal complexes with so-called ‘cooperative’ and ‘redox-active’ ligands is currently among the ‘hot topics’ in coordination chemistry and homogeneous catalysis. In particular, ligands that can assist in catalytic transformations by storing and releasing electrons during catalytic turnover have attracted a lot of interest over the past years. Such ‘redox non-innocent’ behaviour of ligands has received further attention due to the related ligand-centred redox processes observed in several metallo-enzymatic reactions, which has in fact initiated the study of ‘redox noninnocent’ ligands in the first place. Meanwhile, it has resulted in the development of a number of efficient and practically useful ‘bio-inspired’ catalytic transformations.

In the context of the above perspective, the nitrogen-centred redox activity of amido, imido/nitrene, and nitrido ligands is of particular significance and relevance. Complexes bearing open-shell nitrogen-donors are remarkable synthetic targets, and were elusive for a long time due to their high reactivity/instability, making their isolation and sometimes even characterisation challenging. Such species are proposed key-intermediates in catalytic hydrocarbon functionalisation reactions, olefin aziridination and related nitrene-transfer reactions, and are thought to be important in nitrogen-fixation processes (see main text for detailed discussion). Nitrogen-centred ligand radicals are also of interest from a theoretical and spectroscopic point of view. Resolving their electronic structures is rarely trivial, and a combination of spectroscopic measurements and high-level computational studies are usually required to draw any conclusions about the locus of the unpaired electron(s) (ligand vs. metal) in such species. Finally, successful application of nitrogen-centred ligand radicals in new catalytic transformations makes them valuable from a practical point of view. In this review, we will discuss experimentally well defined disubstituted (aminyl-, Figure 1, a), mono- and non-substituted nitrogen ligands.5

![Lewis structures and nomenclature of nitrogen-centred ligand radicals](image-url)

**Figure 1.** Lewis structures and nomenclature of a) di-, b) mono-, and c) non-substituted nitrogen ligands.
substituted (nitrene-, Figure 1, b) and non-substituted (nitridyl, Figure 1c) nitrogen-centred ligand-radicals featured in transition metal complexes. We will also discuss reactivity and experimental characterisation of these species in order to illustrate their practical relevance as well as highlight spectroscopic techniques available for elucidation of their electronic structures.

We start by classifying the specific N-donor ligands by analogy with nomenclature used for carbene species, i.e. as Fischer- and Schrock-type complexes. While unconventional for nitrogen-based systems, this analogy applies well and proves to be useful in the discussion of the electronic structure of the ligand-radical complexes conversed in this review. Nitrogen-centred ligand radicals (aminyl-, imidyl-, and nitridyl-radicals; see Figure 1) can be generated by either one-electron (1e) reduction of nitrenium ions, nitrenes or nitrenates (Figure 1, species on the left) or by 1e-oxidation of azanide, imido or nitrido precursors (Figure 1, species on the right). Similarly, the corresponding metal complexes are formally derived from (hypothetical) nitrenium-, nitrene- or nitrenido complexes (1e-reduction of Fischer-type species with low-lying metal d-orbitals, Figure 2a) or from amido-, imido- or nitrido complexes (1e-oxidation of Schrock-type species with low-lying nitrogen p-orbital, Figure 2b). These systems are stoichiometrically identical, but electronically distinct. In the 1e-reduced Fischer-type complexes, the nitrogen-based SOMO is predominantly an antibonding \( \pi^* \) orbital constructed from a nitrogen p-orbital and a transition metal d-orbital, whereas in the 1e-oxidised Schrock-type case it is a bonding \( \pi \) orbital. Covalent complexes (roughly equal

![Figure 2. MO diagrams of open-shell nitrogen-centred ligand radicals: a) 1e-reduced Fisher-type, b) 1e-oxidised Schrock-type, c) covalent complexes.](image-url)
contribution of metal and nitrogen atomic orbitals to the SOMO) are also possible, which represent the borderlines between ligand radicals and their metallo-radical congeners (Figure 2c).

Several techniques are available to distinguish between metal and ligand-centred radicals, of which EPR spectroscopy is probably the most important one. Ligand-radicals frequently reveal spectroscopic features that resemble those of free organic radicals: rather sharp well-resolved EPR signals, detectable at r.t. and showing well-resolved ligand (super)hyperfine couplings close to the $g$-value of the free electron ($g_e = 2.0023$). An illustrative example of an isotropic (solution phase) EPR spectrum belonging to a ligand-centred radical complex is shown in Figure 3a.$^7$ Such species most often also reveal quite isotropic signals, with small deviations from $g_e$, in frozen solutions. Metal centred radical complexes, on the other hand, generally reveal much broader spectra due to rapid electron-spin relaxation effects. For this reason they are typically recorded at low temperatures (e.g. frozen solutions < 70 K) leading to anisotropic spectra. An example is shown in Figure 3b. Metallo-radical complexes are typically associated with much larger $g$-anisotropies and larger deviations from $g_e$ than ligand radical complexes, but not for all complexes.$^7$ Both metal and ligand (super)hyperfine couplings can be resolved, often of similar magnitude. Similarly, ligand radicals can sometimes reveal rather large hyperfine couplings with the metal to which they bind. Hence, simply inspecting $g$-values and magnitudes of (super)hyperfine interactions is not always enough to discriminate between metal or ligand-centred radicals, and in many cases a more detailed analysis is necessary to draw solid conclusions (for a more detailed discussion, see ref. 7). For this reason correlations between experimental and (DFT) calculated EPR spectra are often very useful.

![Figure 3. Illustrative examples of EPR spectra of (a) ligand- and (b) metal-centred radical complexes.](image-url)
Mössbauer and X-ray absorption spectroscopy (XAS) are also very informative, since they are indicative of the electronic structure and oxidation state of the metal to which the redox-active ligand binds, and thereby these techniques provide important, but indirect information about the electronic structure of the whole complex. Quantum-chemical calculations (in particular population analysis of the spin density) are also extremely useful, especially considering the generally high reactivity of transient ligand-radical species, which often complicates their characterisation. A typical example of the spin density plot of the ligand-radical complex is shown in Figure 4. Here, most of the spin density is located on the ligand (mainly on its nitrogen atom) and involvement of the metal in delocalisation of the unpaired electron is almost negligible.

1.2 Aminyl-radical complexes.

The first example of a experimentally unambiguously detected redox non-innocent aminyl radical complex has been reported by Wieghardt et al. The Co$^{III}$ complex $1^+$ bearing an anilido ligand was electrochemically oxidised, thus producing the dicationic species $1^{2+}$ (Scheme 1). The X-band EPR spectrum (298 K) of $1^{2+}$ reveals an isotropic signal typical for a ligand-centred radical complex, with a $g$-value of 2.0023 with strong hyperfine couplings to cobalt ($A_{iso}^{Co} = 34$ MHz), the NH(Ar) nitrogen atom ($A_{iso}^{N} = 24$ MHz), the hydrogen atom of the NH(Ar) moiety ($A_{iso}^{H} = 29$ MHz) and the benzylic $CH_2$ hydrogen atoms ($A_{iso}^{H} = 26$ MHz). These values are remarkably similar to the ones reported for free ArHN$^•$ radicals, and thus point to an electronic structure that is best described as a ligand-centred aminyl radical complex. The Wieghardt group also reported the related triazacyclononane manganese(IV) complex $2^+$, bearing three anilido substituents. The complex reveals three reversible electrochemical oxidation processes by cyclic voltammetry, Figure 4. Spin density plot of a typical ligand-centred radical complex.

![Figure 4. Spin density plot of a typical ligand-centred radical complex.](image)

**Scheme 1.** Detection of Co$^{III}$-aminyl radical complex $1^{2+}$ formed by electrochemical oxidation of amido complex $1^+$.  

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corresponding to the formation of stable di-
(2\(^{2+}\)), tri-
(2\(^{3+}\)) and tetracationic
(2\(^{4+}\)) complexes,

at least on the timescale of these measurements (Scheme 2). The three redox-processes were
interpreted as ligand centred oxidations, and the oxidised species were all Mn\(^{IV}\) complexes,

bearing one (2\(^{2+}\)), two (2\(^{3+}\)) or three (2\(^{4+}\)) aminyl-radical ligands. The X-band EPR spectrum
(10 K) of the dicationic species 2\(^{2+}\) reveals a signal around \(g \approx 4\). Assignment of the electronic
structure of 2\(^{2+}\) as either a triplet \((S = 1)\) or quintet \((S = 2)\) system solely on the basis of this
EPR spectrum is impossible. However, due to strong antiferromagnetic coupling between the
metal and the ligand radical observed in the analogous [Cr\(^{II}\)(L\(^•\))\(^+\)] complex, a similar
antiferromagnetic coupling between Mn\(^{IV}\) \((S_{Mn} = +3/2)\) and the aminyl radical ligand
\((S = -1/2)\) is expected, which would lead to a triplet \((S = 1)\) electronic structure for 2\(^{2+}\).

The electronic structure of the tricationic species 2\(^{3+}\) was elucidated as an \(S = 1/2\) system.
The EPR spectrum (10 K) of 2\(^{3+}\) \((g_{iso} = 1.965)\) reveals clearly resolved hyperfine coupling
with the metal \((A_{Mn}^{\text{iso}} = 206 \text{ MHz})\). The overall \(S = 1/2\) electronic structure again arises from
antiferromagnetic coupling between the three unpaired electrons on Mn\(^{IV}\) \((S_{Mn} = +3/2)\) and the
two ligand-centred radicals \((S_N = -1/2\) each). In agreement with the aforementioned strong
M–L antiferromagnetic couplings, the tetracation 2\(^{4+}\) is EPR-silent. Unfortunately, the authors
did not report any supporting computational studies, which currently prevent us from
classifying these compounds as Fischer- or Schrock-type systems.

Grützmacher et al. were the first to report a stable and isolable aminyl radical transition
metal complex.\(^9\) Deprotonation of Rh\(^1\) complex 3 followed by oxidation with ferrocenium
hexafluorophosphate (Fe\(^3\)PF\(_6\)) leads to species 4, which has been isolated and thoroughly
characterised by EPR spectroscopy, X-ray diffraction and DFT calculations (Scheme 3). Q-band EPR spectroscopy (15 K) of 4 shows a rather small anisotropy of the \(g\)-tensor \((g_1 =\)
2.0822, \( g_2 = 2.0467, \ g_3 = 2.0247 \), which indicates that spin-orbit interaction in 4 is much weaker than expected for a Rh\(^{10} \) centre.\(^{11} \)

Pulse EPR techniques (Davies-ENDOR and HYSCORE) allowed to detect a relatively large isotropic hyperfine coupling constant of the aminyl-radical ligand nitrogen atom (\( A_{\text{iso}}^N = 45 \) MHz), which is comparable to those observed for short-lived free dialkyl aminyl radicals. Complementary DFT calculations further corroborate the redox non-innocent properties of the trop ligand in 4; \(~54\%\) of the total spin density is localised on the aminyl-radical moiety and \(~30\%\) on the metal atom. The SOMO is predominantly reflecting the Rh–N \( \pi^* \) interaction (see Figure 2, 1e-reduced Fischer-type with a rather strong covalency).

Because most of spin density in the 18e complex 4 is located at the aminyl-radical ligand, it can be expected to undergo ligand-centred radical-type reactivity. This is indeed observed, as 4 reacts quantitatively with hydrogen-atom donors such as Bu\(_3\)SnH and PhSH. Complex 4 is not reactive enough towards PhOH, Ph\(_3\)SiH, or R\(_3\)CH, which can be attributed to the higher E–H bond dissociation energies in these reagents. The Ir analogue of 4, bearing a terpyridine instead of the bipyridine ligand, exhibits a similar electronic structure but with somewhat enhanced reactivity towards hydrogen atom donors and a yet not fully understood intrinsic instability.\(^{12} \)

A few related examples were obtained by deprotonation and oxidation of the 16e ‘trop’ complexes 5 (Scheme 4).\(^{13} \) The thus obtained open-shell species reveal higher reactivity towards solvent compared to 4, which thus far prevented characterisation of the proposed radical species 6 by X-ray structure analysis. The reported EPR data of the rhodium complex were interpreted to correspond with species 6a. Experimental spin population estimated from the hyperfine constants amount to \(~56\%\) of spin density in 6a spread over the

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two nitrogen atoms. The complex is therefore described as a delocalised aminyl-radical complex (calculated spin density per ‘aminyl nitrogen’ 28%) with a considerable degree of covalency (41% spin density on Rh). The EPR spectrum of 6a shows $g$-values close to 2 with a small anisotropy ($g_1 = 2.005$, $g_2 = 1.992$, $g_3 = 1.991$) and rather large hyperfine coupling with the nitrogen atoms ($A_{\text{iso}}^N = 11.1$, $A_{\text{iso}}^\text{Rh} = -0.7$ MHz). The Ir analogue 6b is rather unstable, but EPR (X-band, HYSCORE, ENDOR) spectra could be obtained. The X-band EPR (20 K) spectrum with $g$-values close to 2 ($g_1 = 1.974$, $g_2 = 1.993$, $g_3 = 2.028$), again suggests that the unpaired electron is delocalised over the ligand with minor metal-contribution.

The aminyl-radical species 6 are of interest from a reactivity point of view. Like 4, they react with hydrogen-atom donors such as stannanes, thiols and silanes. Iridium complex 6b is also postulated to be a key-intermediate in the catalytic oxidation of alcohols to aldehydes in the presence of $t$BuOK (Scheme 5). The proposed mechanism resembles the catalytic cycle of enzymatic oxidation of galactose mediated by galactose oxidase. The reaction starts by double deprotonation of the catalyst precursor 5b leading to the monoanionic intermediate 8 (via 7), which is then oxidised by $p$-benzoquinone (BQ) to produce 6b. The latter

Scheme 5. Aminyl ligand-radicals in catalytic alcohol oxidation.\textsuperscript{13c}
coordinates the alcoholate substrate, thus forming intermediate 9, which undergoes intramolecular hydrogen-atom abstraction (HAA) from the coordinated alcoholate to the redox non-innocent aminyl ligand-radical. Subsequent 1e oxidation of complex 10 by semiquinone and elimination of the aldehyde product closes the catalytic cycle. The reaction can be carried out with 1–10 equivalents of the base (KO\textsubscript{t}Bu), 2 equivalents of oxidant (benzoquinone is the most efficient, but oxygen can also be employed) and very low catalyst loadings of 0.01 mol\%, which provides the corresponding aldehyde with a remarkably high TOF (60 000 – 150 000 h\textsuperscript{-1}).

Pincer ligands are commonly used as ancillary ligands in organometallic chemistry,\textsuperscript{15} but can also act as electron-reservoirs by delocalizing excessive (or deficient) electron density.\textsuperscript{2} Incorporation of the amido functionalities into a pincer motif can be employed to stabilise aminyl-ligand radical complexes. As such, Mindiola, Szilagyi, et al. reported the synthesis of [(PNP)NiCl]OTf complex 12a, which was obtained in 87\% yield by oxidation of the neutral precursor 11a with FcOTf (Scheme 6).\textsuperscript{16} X-ray crystallographic analysis of 12a reveals a square planar geometry around Ni, very similar to neutral 11a. Complexes 11a and 12a only differ slightly in their Ni–P–CAr–CAr dihedral angles. The X-band EPR spectrum of 12a in solution (292 K) reveals well-resolved hyperfine couplings stemming from one N ($A_{N}^{\text{iso}} = 27$ MHz), two P and six H atoms ($A_{P}^{\text{iso}} = 22$ MHz, $A_{H}^{\text{iso}} = 14$ MHz, $A_{H}^{\text{iso}} = 9$ MHz). The $g_{\text{iso}}$-value of 2.0238 further points to an electronic structure that is best described as a ligand-centred aminyl radical complex (Ni\textsuperscript{III} species typically reveal $g$-values in the range 2.15–2.20). Cl K-, P K-, and Ni

\begin{align*}
\text{Scheme 6. Oxidation of electron-rich transition metal amido complexes leading to aminyl radical complexes classified as ‘1e-reduced Fischer-type’ species.}\textsuperscript{16,17}
\end{align*}
L_{III}-edge XAS spectra were also recorded. The latter proved highly informative for the electronic structure of 12a. Only a slight change in the ‘2p_{Ni} → LUMO (3d_{Ni})’ excitation energy is observed upon oxidation of 11a to 12a, which indicates presence of a Ni^{II} centre in 12a, and therefore the redox process must be mainly ligand-centred. In accordance with these experiments, DFT calculations reveal 69% spin density on the aminyl pincer moiety (32% on the nitrogen atom, 37% in the aromatic rings) and only 26% on the nickel atom. The HOMO of the amido precursor 11a is dominated by a high-lying filled nitrogen p-orbital in \pi-conflict with a filled metal d-orbital. Removal of one electron from the HOMO of 11a partially reduces this \pi-conflict and leads to a net \pi-bond-order of \sim \frac{1}{2} between the metal and the aminyl radical nitrogen. The unpaired electron resides predominantly in an anti-bonding \pi^* Ni–N molecular orbital (SOMO), which is dominated by the nitrogen p-orbital contribution (albeit with significant delocalisation over the adjacent aryl-rings). Species 12a can therefore be classified as a ‘1e-reduced Fischer-type’ species (Figure 2a; Scheme 6).

The groups of Nocera and Ozerov collaboratively employed the same type of pincer ligand to generate Mn and Re aminyl complexes.\textsuperscript{17} AgOTf was used as an oxidant in this case, which gave 12b and 12c in 98% and 86% yield, respectively (Scheme 6). Comparable to the nickel couple 11a/12a, the manganese and rhenium complexes undergo only a slight change in geometry on going from the neutral species 11b, c to the cationic aminyl radicals 12b, c (based on X-ray crystallography). Also the carbonyl C≡O stretch vibrations in the IR spectra reveal only a relatively small change upon oxidation of 11b, c to 12b, c (Δν \sim 30–40 cm\textsuperscript{-1}), thus pointing to electronic structures of 12b, c that are best described as ligand- (not metal-) centred radicals. Frozen solution (4 K) X-band EPR spectroscopic characterisation of 12b, c reveals g-values close to 2.00 (g_{iso} = 2.004 (12b) and 2.013 (12c)). The hyperfine couplings with the metal and N atom for 12b are resolved at room temperature (A_{Mn}^{iso} = 52 MHz; A_{N}^{iso} = 25 MHz, r.t.), whereas 12c revealed only metal-hyperfine coupling (A_{Re}^{iso} = 169 MHz, r.t.). DFT calculations confirmed the ligand-centred radical descriptions: For 12b, only 14% spin density is localised on the Mn centre and about 50% on the aminyl nitrogen; 12c has about 7% spin density on

![Scheme 7. Ligand-centred radical-type reactivity of 12 b, c.\textsuperscript{17}](image-url)
Re and 50\% on N. The electronic structure of 12b, c is very similar to that of 12a (1e-reduced Fischer-type, see Figure 2a, Scheme 6).

These species exhibit quite interesting radical-type reactivity. They proved unreactive toward PhSH and Et3SiH but reactions with hydrogen-atom donors such as Bu3SnH lead to formation of the neutral species 11b, c, likely by deprotonation of the intermediate hydrogen-atom abstraction (HAA) products. Employing Bu3Sn(CH2CH=CH2) instead of Bu3SnH leads to the allyl-radical abstraction products 13b, c (Scheme 7), which are stable under reaction conditions and can be isolated. The observed attack at the aryl ring of the pincer ligand underlines the delocalised nature of the aminyl-radical.

Application of a related PNP pincer ligand in Cu-chemistry is reported by Peters and Szilagyi (Scheme 8).\textsuperscript{18} In this case, however, a dinuclear dimeric structure 14 is formed with two bridging amido nitrogen atoms. Oxidation of 14 with 1 equiv. of a ferrocenium salt leads to monocationic Cu\textsuperscript{I} complex 14\textsuperscript{+} (78\% yield), in which one of the amido moieties of the pincer ligand is oxidised to an aminyl-radical. Using 2 equiv. of a nitrosonium salt as the oxidant leads to oxidation of both ligands (14\textsuperscript{2+}, 47\% yield). Due to the radical character of the pincer (aminy1) ligand(s) in 14\textsuperscript{+} and 14\textsuperscript{2+}, the presence of tert-butyl groups is essential to prevent dimerisation at the aryl-rings (para-position with respect to the aminy1 nitrogen atoms).

Oxidation of 14 to 14\textsuperscript{+} leads to shortening of the Cu–Cu distance by ca. 0.2 Å (from 2.72 to 2.53 Å, X-ray), whereas the second oxidation (to 14\textsuperscript{2+}) does not alter Cu–Cu distance significantly (d\textsubscript{Cu–Cu}(14\textsuperscript{2+}) = 2.53 Å). The EPR spectrum of complex 14\textsuperscript{+} features a broad signal without resolved hyperfine couplings and a rather small g-anisotropy (g\textsubscript{1} = 1.987, g\textsubscript{2} = 2.025, g\textsubscript{3} = 2.098). The EPR spectrum of 14\textsuperscript{2+} is typical for an S = 1 system, with effective g-values at g\textsubscript{1} = 1.998 and g\textsubscript{2} = 4.02 (featureless).

\textbf{Scheme 8.} Bridged aminyl-radical ligands in Cu\textsuperscript{I}-chemistry.\textsuperscript{18}
Further evidence for the ligand redox non-innocent behaviour in $^{14+}$ and $^{142+}$ was obtained from XAS spectroscopy. A negligible shift ($< 0.5$ eV) of the Cu K-edge inflection point on going from $^{14}$ to $^{14+}$ indicates that the Cu centres have the same oxidation state in both species (Cu$^1$). However, oxidation to $^{142+}$ leads to a somewhat larger shift of 1.7 eV in the Cu K-edge spectrum, which is attributed (based on comparison with related species) to an asymmetric distortion of the Cu$_2$(μ-NR$_2$)$_2$ core. The authors concluded from these data that $^{142+}$ is indeed a Cu$^1$-(bis-aminyl) complex.

The electronic structure of triplet species $^{142+}$ was further investigated computationally with DFT calculations, which is in agreement with the experimental data. The two copper atoms carried only 35% of the total spin density, and most of the spin density (165%, two unpaired electrons correspond to 200%) of $^{142+}$ is computed to be delocalised over the pincer ligands with each of the two nitrogen atoms bearing 77% spin density, which signifies rather delocalised ligand-centred radicals with a pronounced aminyl character. The strong covalency of Cu–N bond in the cluster complicates an unambiguous assignment of the formal oxidation state in the mono-cationic compound $^{14+}$.

The above-described aminyl-radical complexes all contain chelating aminyl moieties. The first complex with a non-chelating aminyl ligand radical has been reported by Peters and Szilagyi in 2009. Anionic copper species $^{15a}$ was oxidised with a ferrocenium salt, yielding neutral paramagnetic complex $^{16a}$ (25% yield) (Scheme 9). The molecular structures obtained from X-ray crystallography reveal a trigonal planar coordination geometry around the metal centre for both species, with overall minor differences in the Cu–P bond lengths and P–Cu–P bond angles on going from $^{15a}$ to $^{16a}$. However, shortening (~0.1 Å) of the Cu–N bond is evident upon oxidation of $^{15a}$ to $^{16a}$. This points to (partial) removal of the π-conflict between filled metal d-orbitals and the filled nitrogen p-orbitals (2e-reduced Fischer-type system) upon formation of the aminyl-radical ligands (1e-reduced Fischer-type). The reported DFT calculations seem to be in agreement with this interpretation, although the picture is slightly blurred due to the somewhat strained bridging interactions and substantial delocalisation over the ligand π-system.

Cu K-edge XAS experiments show similar pre-edge and rising-edge energies for $^{15a}$ and $^{16a}$, which indicates a similar ‘spectroscopic’ oxidation state (d-electron configuration) of both species (i.e. Cu$^1$). Additionally, integration of the area under the pre-edge feature in the Cu L-edge XAS spectrum of $^{16a}$ and comparison with the corresponding XAS area of CuCl$_2$,
shows that the redox-active molecular orbital in 16a has only ~14% 3d-orbital character. These data correlate well with a ligand-centred oxidation on going from 15a to 16a.

Further, the EPR spectrum of 16a in frozen solution shows g-values close to 2 and substantial, well-resolved hyperfine couplings with nitrogen (g x, g y, g z = 2.008, 2.008, 2.030; A N x, A N y, A N z = 24, 100, 24 MHz). The DFT calculated spin density on nitrogen is 49%, and only 13% on copper (the residual spin density is delocalised over the tolyl moiety and PriBu-groups), which further supports the aminyl ligand radical description of 16a.

Consistent with its ligand-radical character, complex 16a demonstrates HAA reactivity towards hydrogen-donors such as thiophenol and tributyl tin, which yields product 17a. Notably, if the tolyl group on the aminyl nitrogen moiety is substituted by a phenyl group (15b), oxidation by ferrocenium-salts leads to a dimerisation product 18. Both reactions demonstrate the radical-type reactivity of aminyl radical species 16 (Scheme 9).

Another example of a non-chelating aminyl radical copper complex (although with a more covalent N–Cu bond) is reported by Warren et al. in 2010.20 The target compound 20 can be prepared by reaction of lithium diphenylazanide (LiNPh2) with CuII-precursor 19, which gives ‘aminyl-radical’ complex 20 in 81% yield (Scheme 10). Alternatively, 20 can be isolated (albeit in a lower yield of 31%) as byproduct of the reaction of diphenylnitrosamine (Ph2NNO) with the Cu-dimer \([\{(Me2NN)Cu\}_2\] \). X-ray crystallographic analysis reveals a shorter Cu–N distance (1.841 Å) in 20 than in 16 (1.906 Å), and the anisotropy of the EPR
Nitrogen-Centred Ligand Radical Complexes

spectrum (at 30 K) of 20 ($g_1 = 2.146$, $g_2 = 2.043$ and $g_3 = 2.018$; $A_{Cu}^1 = 298$ MHz) is much larger than observed for 16. The room temperature EPR spectrum shows a relatively small hyperfine coupling with the aminyl nitrogen ($A_{Niso}^N = 14$ MHz) and a large one with Cu ($A_{Cuiso}^Cu = 103$ MHz). DFT analysis also shows a stronger involvement of a copper d-orbital in the SOMO, leading to similar spin densities on Cu (30%) and N (27%). The unpaired electron is further substantially delocalised over the two aryl rings. These data suggest that the Cu–N bond in 20 is rather covalent (Figure 2c). Nonetheless, complex 20 reacts as a ligand radical with other radicals such as NO, leading to the formation of Ph$_2$NNO. The locus of initial NO-attack (Cu or N) is presently unclear.

Many of the above examples describe ‘aminyl radical’ complexes in which the aminyl moiety bears conjugated substituents capable of delocalizing the unpaired spin density of the aminyl radical. This typically results in substantial delocalisation of the spin density over a larger ligand area, as described for most of the above examples. The Rh$^I$-aminyl radical complex 4 described by Grützmacher is a notable exception (Scheme 3). The rather strong covalency of the Rh–N bond in 4 nonetheless leads to substantial ‘delocalisation of spin density’.10 Warren and Cundari recently reported another remarkable example wherein the aminyl moiety contains non-conjugated substituents.21 Here, reaction of dinuclear copper complex 21 with the lithium salt of 1-adamantyl amine leads to aminyl radical complex 22 in 50–70% yield (Scheme 11). The X-band EPR (51 K) spectrum of 22 reveals a rather anisotropic $g$-tensor ($g_1 = 2.133$, $g_2 = 2.036$, $g_3 = 2.031$). Also the hyperfine tensors are rather anisotropic, showing a large Cu hyperfine ($A_{Cu}^1 = 365$ MHz) and a substantial N$_{aminyl}$ hyperfine splitting ($A_{N}^N = 65$ MHz). These data all point to a rather strong covalency of the Cu–N bond (Figure 2c), which was confirmed by supporting DFT calculations. Spin density calculations reveal 49% spin density on the aminyl nitrogen atom and 30% on copper. The unpaired electron is located in a $\pi$* Cu–N MO (1e-reduced Fischer-type with strong covalency; see Figure 2 and Scheme 6). Interestingly, the aminyl moiety in 22 participates in ‘nitrene’ insertion reactions into the C–H bonds of ethylbenzene or indane producing PhCH–(NHAd)Me or (1-indanyl)NHAd in 87% and 81% yield, respectively. These
Conversions were proposed to proceed via a binuclear mechanism, which reflects the importance of the $[\text{R}^1\text{R}^2\text{N}^-\text{Cu}^1]$ resonance structure in the $[\text{R}^1\text{R}^2\text{N}^-\text{Cu}^1] \leftrightarrow [\text{R}^1\text{R}^2\text{N}^-\text{Cu}^1]$ resonance description of the nearly covalent Cu–N π-interaction. HAA from the substrate (C–H bond) by the ‘aminyl radical’ $[\text{R}^1\text{R}^2\text{N}^-\text{Cu}^1]$ leads to formation of a CuI-amine species $[\text{R}^1\text{R}^2\text{NH}^-\text{Cu}^1]$ and an organic radical $R^2^*$. The latter reacts with another equivalent of the ‘aminyl radical’ $[\text{R}^1\text{R}^2\text{N}^-\text{Cu}^1]$ to form a CuI-amine product $[\text{R}^1\text{R}^2\text{NR}^2^-\text{Cu}^1]$ (see Scheme 11).

The amine products easily dissociate from the CuI centre.

Complex 22 could also be prepared directly from the free amine using tBuO-complex 23 (Scheme 11). The latter was obtained by reacting benzene-bridged binuclear copper(I) complex 24 with tert-butyl peroxide. Subsequent reaction of 23 with adamantyl amine yielded 22. This method allows remarkable direct catalytic amination of C–H bonds with amines, proceeding via the net ‘nitrene insertion’ activity of 22. In a typical procedure the amine (1 equiv.), tert-butyl peroxide (1.2 equiv.), the C–H substrate (10 equiv.) and catalytic amounts of 24 (0.5 mol%) are heated at 90 ºC, giving the corresponding amines in high yields (Scheme 11). Not only substrates with activated C–H bonds such as indane and ethylbenzene can be employed, but also unactivated cyclohexane gives high yields of the corresponding amine product. Aliphatic amines such as Ad–NH$_2$, c-Hex–NH$_2$, PhCH$_2$CH$_2$–NH$_2$ and morpholine were evaluated as amines, leading in all cases to C–H amination products in good

![Scheme 11. ‘Nitrene transfer’ activity of ‘aminyl radical’ copper species 22 in direct catalytic amination of C–H bonds with amines.](image_url)
yields. The scope of the reaction also includes aromatic amines, but formation of diazene decreases the yield, particularly for electron-rich anilines. Thus, optimum yields are obtained using anilines with electron withdrawing groups (EWG) on the aromatic rings and low catalyst loadings in order to avoid dimerisation. Remarkably, secondary amines can also be used since the reaction proceeds via the aminyl complex $[R^1R^2\text{N}•\text{CuI}]^{22}$, without formation of the nitrene precursor.

### 1.3 Nitrene radical complexes.

Imido-complexes are commonly proposed as intermediates in transition metal-catalysed nitrene transfer reactions. However, it has been recognised (and proven) rather recently that in some cases such intermediates can have a considerable radical character on imido (nitrene) nitrogen, which at least in part explains their reactivity.

Warren and co-workers were one of the first to recognise the potential redox non-innocent character of nitrene/imido ligands in a nickel complex. The reported nickel imido complex 26 (Scheme 12) was prepared in 52% yield by reacting 2,4-lutidine nickel complex 25 with 1-adamantyl azide (AdN$_3$). X-ray crystallographic analysis of 26 reveals a slightly bended structure with a Ni–N–C(Ad) angle of 164.5°. The frozen solution EPR (77 K) spectrum of 26 features a rhombic pattern ($g_1 = 2.161$, $g_2 = 2.038$, $g_3 = 1.937$), where the central ($g_2$) signal is split into a triplet (1:1:1, $A = 63$ MHz) due to nitrogen hyperfine coupling, supporting substantial participation of the nitrene/imido nitrogen atom ($I(^{15}\text{N}) = 1$) in delocalisation of the unpaired electron. However, the quite large $g$-anisotropy at low temperatures suggests considerable metal-contribution to the SOMO. In accordance with the recorded EPR spectrum, DFT population analysis indicates that approximately 57% of the spin density is localised on the ‘nitrene’ nitrogen. According to these same calculations, the unpaired electron in 26 is located in an anti-bonding $\pi^*$ orbital, thus allowing the classification of 26 being a 1e-reduced Fischer-type nitrene complex (Figure 2a) albeit with a large covalent character of the M–N $\pi$ bond. The ‘nitrene’ moiety of complex 26 can be transferred to CO, PMe$_3$ and CNtBu to form the corresponding AdN=X (27) ($X = \text{Lewis base molecule}$) organic products. Reaction of 26 with the single-electron reducing agent cobaltocene unexpectedly produced $[\text{Me}_2\text{NN}]\text{Ni–N(Ad)}–\text{Cp–CoCp}$ 28 as the product, further illustrating radical character of 26. The radical character of 26 is also reflected in its HAA reactivity towards 1,4-cyclohexadiene leading to the amido complex $[\text{Me}_2\text{NN}]\text{Ni–NHAd}$ 29 and benzene. The HAA reactivity was investigated with other benzylic C–H substrates in stoichiometric...
reactions. Radical-capture of the generated alkyl radical R²• via a rebound mechanism was demonstrated to lead to amino complex 31. However, 26 has a similar affinity for the radical R²• to produce amido complex 30 (Scheme 12).²⁴ Noteworthy is the non-selective C–H functionalisation reactivity of 26 compared to 22 and its putative \{[Cl₂NN]Cu\}_2(μ–NAd) precursor. The somewhat enhanced selectivity of R²• towards 26 compared to \{[Cl₂NN]Cu\}_2(μ–NAd) likely correlates to the amidyl character of 26.

Another interesting nickel species that is shown to participate in nitrene transfer reactions is the (dtbpe)Ni=NR (dtbpe = 1,2-bis(di-tert-butylphosphino)ethane) family of complexes reported by Hillhouse and co-workers.²⁵ These Ni^{II} imides (32) with a closed-shell configuration can undergo 1e chemical oxidation to afford their cationic analogues (33a) in 1,2-difluorobenzene (DFB) (Scheme 13).²⁶ The HAA ability of 33a is remarkable, and even in the presence of ethereal solvents, the Ni^{II}-amide complex 34a is obtained. SQUID data for compound 33a suggested a mixed spin state, and it was demonstrated that the doublet and quartet spin states of 33a are involved in a temperature dependent spin-crossover equilibrium (ratio LS : HS is 1:4 at room temperature). Complex 33b with a bulkier substituent on imido moiety shows greater stability and does not reveal any spin-crossover over a broad temperature range. The geometrical differences between complexes 33a and 33b (angle Ni–N–R is 164.2° for 33a and 178.4° for 33b) suggests that the aromatic ring in 33b contributes in the delocalisation of the electron density at the imido moiety, hence enlarging the Ni–N–R angle, which leads to enhanced orbital overlap. The reported EPR data of 33a (broad isotropic
line around $g \approx 2$) and

33b

(overlapping patterns with features at $g = \sim 4$ and $\sim 2$) did not allow the authors to distinguish between a metal- or ligand-centred radical, due to unresolved hyperfine couplings and since metal-centred Ni$^{III}$ radicals have $g$-values in the range of 2.15–2.20. However, DFT calculations on simplified models reveal that the spin density is delocalised over the nitrogen and nickel atoms, with more than 50% spin density located at the nitrogen atom in both alkyl- and aryl-substituted species (69% for alkyl-nitrene radical and 53% for aryl-nitrene radical). Hence, the authors attribute the difference in reactivity of 33a and 33b to the radical character of the nitrogen atom. The theoretical model further suggests that the barrier for rotation around the Ni=NR bond is $\sim 3$ kcal mol$^{-1}$ larger for the aryl-imido complex compared to the alkyl-imido species, which supports spin delocalisation over the aryl ring in complex 33b. In these DFT models the SOMO is located at the $\pi^* (d_{xz}-p_x)$ with major nitrogen character in the alkyl substituted complex pointing to a 1e-reduced imido complex (Fisher-type nitrene radical). The aryl-substituted compound, however, has a more covalent Fe=NR $\pi$-bond. Further characterisation is needed to fully comprehend the electronic structure of these species.

Tanaka et al. prepared Ru-semiquinone-anilido complex 35 (Scheme 14), which after deprotonation with tBuOK gave the nitrene biradical species 36. EPR spectra of biradicals are generally not very illustrative for the locus of the unpaired electrons (and hence the redox non-innocent behavior of the ligands). However, the fact that 36 is EPR non-silent (two main
transitions with \( g \)-values \(-2\) and \(-4\) can be taken as indirect evidence for predominance of the \([\text{R} \cdot \text{N} - \text{Ru}^{\text{II}}]\) resonance structure over \([\text{RN} = \text{Ru}^{\text{III}}]\), because Ru\(^{\text{III}}\)-semiquinone (SQ) species are expected to have strong antiferromagnetic Ru\(^{\text{III}}\)-SQ couplings and are typically EPR silent. In accordance, DFT calculations show about 43\% spin density on the nitrene nitrogen atom. Interestingly, compound 36 can be further reduced electrochemically leading to the anionic species 37. The latter also appears to be a ligand-centred radical with 64\% spin density on the ‘nitrene’ nitrogen atom and 31\% on ruthenium (DFT). Complex 37 shows a rhombic \( g \)-tensor \((g_1 = 2.175, g_2 = 2.105, g_3 = 1.950)\) in the EPR spectrum, with \( g_3 \) split into a triplet due to substantial hyperfine coupling with nitrogen \((A_N = 224 \text{ MHz})\). Again, a rather large \( g \)-anisotropy illustrates considerable metal-radical character of the SOMO.

An open-shell system with several ligand-centred unpaired electrons was recently reported by Wieghardt, Lu et al. (Scheme 15).\(^{28}\) Reaction of chromium bis-(\(\alpha\)-imino-pyridine) biradical complex 38 (containing two 1e-reduced \(\alpha\)-imine-pyridine ligands) with 1-adamantyl azide leads to formation of the neutral diamagnetic nitrene complex 39, which in turn can be oxidised by two equivalents of ferrocenium salts to generate compound \(39^{2+}\) \((S = 1)\). The latter contains two non-reduced \(\alpha\)-imine-pyridine ligands and one 1e-oxidised ‘imido’ ligand antiferromagnetically coupled to the three unpaired electrons on Cr\(^{\text{III}}\). X-ray crystallographic analysis of \(39^{2+}\) reveals a distorted trigonal-bipyramidal geometry around Cr, and a more linear Cr–N–C(Ad) fragment than in 39 (angle Cr–N–C(Ad) = 163.6º (39), 176.6º (\(39^{2+}\))). In this case, EPR spectroscopy did not allow the authors to distinguish between metal- and ligand-centred radicals. The authors therefore relied on Cr K-edge XAS, which indicates chromium in oxidation state +3 (Scheme 15). DFT calculations further corroborated the redox non-innocent behavior of the nitrene ligand, revealing 89\% spin density on the ‘imido’ nitrogen atom. Surprisingly, despite a considerable calculated spin density on the ‘imido’ nitrogen atom in neutral 39 (78\%, \(S = 0\)) and the mono-cationic \(39^+\) (72\%, \(S = 1/2\)), Cr K-edge

![Scheme 15](image)

**Scheme 15.** Switching ‘non-innocence’ from \(\alpha\)-imino-pyridine to imido upon oxidation.\(^{28}\)
XAS indicates chromium in these complexes to be in oxidation state +IV (based on pre-edge and rising edge energies), which points to a ‘classic’ imido AdN$_2^-$ fragment in 39 and 39$^+$. From the qualitative MO diagrams presented by the authors, it appears that the $\pi^*(M$–$N$Ad) MO is empty, which indeed indicates a 1e-oxidised imido (1e-oxidised Schrock-type) radical ligand (Figure 2b). However, a more detailed quantitative analysis of the MOs may be necessary to reach a final conclusion.

Multiple bonds between a metal and an imido ligand can be achieved in a pseudo-tetrahedral environment of tris(phosphine-$_2$ or NHC-based$_3$) boranes 40 (Scheme 16). Substitution of the boron atom in 40 by silicon alters the geometry to trigonal bipyramidal or square pyramidal, leading in some cases to a nitrene-radical complexes. In this way, Peters and co-workers prepared a series of nitrene ligand-radical complexes of the group 8 elements. Thus, treatment of Ru or Os complexes 41a, b with para-trifluoromethyl phenylazide 42-CF$_3$ (Scheme 16, R = CF$_3$) gives rise to formation of the nitrene complexes 43a-CF$_3$ (46% yield) and 43b-CF$_3$ (41% yield). The room temperature EPR spectra (low temperature spectra were also recorded) revealed sharp patterns with $g_{\text{iso}}$-values close to 2.0 and large hyperfine constants with nitrogen ($g_{\text{iso}} = 2.020$, $A_{\text{iso}}^N = 98$, $A_{\text{iso}}^P = 64$, $A_{\text{iso}}^{\text{Ru}} = 48$ MHz for 43a-CF$_3$; $g_{\text{iso}} = 2.013$, $A_{\text{iso}}^N = 93$, $A_{\text{iso}}^P = 58$, $A_{\text{iso}}^{\text{Os}} = 155$ MHz for 43b-CF$_3$). Species 43a-CF$_3$ and 43b-CF$_3$ were further characterised by X-ray structure analysis, which showed highly distorted trigonal bipyramidal geometries around the metal atoms (i.e. $\tau(43a$-$\text{CF}_3) = 0.54$) and almost linear M–N–C bonds (~170°). According to population analysis (DFT), about 25% of the spin density is located at the nitrogen atoms in 43a-, b-CF$_3$ while the total ligand spin density amounts to 54%. Hence, the radical is substantially delocalised over the metal and the NAr moiety. Noteworthy, species 43a, b also have some negative spin density on the nitrene substituent, which actually reduces the total ligand spin density.

Scheme 16. ‘Delocalised nitrene radical ligands’ reported by Peters and co-workers.$^{31-33}$
Further studies showed that the nature of the organic group on the azide 42-R has a big impact on the course of the reaction with 41a. Addition of para-methoxyphenylazide 42-OMe (instead of 42-CF3) to 41a yields para-(methoxy) azobenzene 45 and only a small amount of complex 43a-OMe (Scheme 17). Remarkably, formation of azoarene 45 does not proceed via complex 43a-OMe, but via a free triplet aryl nitrone 44, which either dimerises or reacts with another molecule of aryl azide 42-OMe to yield the azoarene. Nitrene species 43a-OMe can however be prepared in 52% yield via reduction of cationic complex 46 with cobaltocene (Scheme 17). Like 43a-CF3, complex 43a-OMe can be described as a nitrone-ligand radical species. The EPR spectrum of 43a-OMe at r.t. reveals a three-line pattern with large nitrogen hyperfines ($g_{iso} = 2.002$, $A_{Niso} = 119$ MHz, $A_{Ruiso} = 38$ MHz, $A_{Piso} = 48$ MHz).

The analogous Fe complex 43c-Me is found to be rather unstable, and can be generated only by photolysis of the corresponding azide complex in frozen 2-(methyl)tetrahydrofuran glass at 77 K. The EPR spectrum (77 K) of 43c-Me has a somewhat anisotropic $g$-value ($g_o$, $g_p$, $g_z = 1.990$, 2.032, 2.098), but close to the value of 2.0, pointing to strong ligand involvement for the SOMO. DFT calculations on a simplified model (low spin, ground state) showed about 16% spin density on nitrogen and again a strong delocalisation into the adjacent aryl moiety. Similarly to complexes 43a, b-CF3, some negative spin density is found on the ligand, likely caused by spin polarisation, which in turn results from antiferromagnetic coupling of the five unpaired electrons (total $S = \frac{1}{2}$, 3α and 2β electrons). This reduces the total spin density on the ‘nitrone’ moiety. DFT also predicted a closely lying intermediate quartet spin state ($S = \frac{3}{2}$) only approx. 2.8 kcal mol$^{-1}$ higher in energy than the doublet ($S = \frac{1}{2}$). The total nitrogen spin density in the quartet ($S = \frac{3}{2}$) species is 82%. The unpaired
electron of the lower-energy doublet \((S = \frac{1}{2})\) species is located in the antibonding \(\pi^*\) orbital, and hence we classify this species as a 1e-reduced Fischer-type nitrene ligand (Figure 2, a).

The iron species \(43c\text{-Me}\) is too unstable to further study its reactivity directly. However, it is the most likely key-intermediate in a number of reactions observed for mixtures of species \(41c\) and azides \(42\). The proposed intermediate \(43c\text{-Me}\) is capable of HAA from 9,10-dihydroantracene to yield antracene and Fe(NHTol)(SiP\(_{iPr}\_3\)). Nitrene transfer to tert-butyl isocyanide (\(t\text{BuNC}\)) to give the corresponding carbodiimide (\(t\text{BuN}=C=\text{NTol}\)), azoarene (\(\text{TolN}=\text{NTol}\)) and the isonitrile complex Fe(SiP\(_{iPr}\_3\))(CN\(_{tBu}\)), is proposed to proceed via the same nitrene-radical intermediate. In the absence of other reagents, reaction of \(41c\) with tolylazide \(42\text{-Me}\) lead to the formation of para-methyazobenzene (\(\text{TolN}=\text{NTol}\)), which was proposed to proceed also via the intermediate \(43c\text{-Me}\).

Another interesting Fe-nitrene complex, \(48\) (Scheme 18) was recently reported by Betley et al. This species exhibits higher stability than \(43c\), and hence could be characterised using X-ray crystallography.\(^{34}\) Complex \(48a\) features a slightly elongated Fe–N bond (1.768 Å) compared to previously reported iron-imido complexes (1.66–1.73 Å), suggesting a decreased Fe–N bond order in \(48a\). Mössbauer spectroscopy indicates an Fe\(^{III}\) d\(^5\)-configuration in \(48a\), which likely correlates to transfer of a single electron from the metal to the ligand. DFT calculations reveal considerable positive, as well as negative, spin density on the ‘imido’ nitrogen atom. Based on these data, species \(48a\) was identified to have six unpaired electrons. One electron, localised on the ‘imido’ moiety \((S_N = \frac{1}{2})\), is antiferromagnetically coupled with one of the other five unpaired electrons localised on the iron atom \((S_{Fe} = \frac{5}{2})\), thus giving a total quintet \((S_{total} = 2)\) spin multiplicity. This ‘imido’ unpaired electron is located in a predominantly \(\pi\)-bonding orbital between the metal and the ‘imido’ nitrogen, allowing the classification of this system as a Schrock-type 1e-oxidised imido ligand. However, the picture is somewhat blurred due to substantial delocalisation of spin.

\[
\text{Scheme 18. ‘Half-porphyrin’ stabilised iron- and cobalt-nitrene radical complexes reported by Betley.}^{34,35}
\]
The reactivity of \(48a, b\) further supports its nitrene radical nature. The nitrene moiety of \(48a, b\) can be transferred to organic substrates, and be used either for nitrene-insertion into benzylic C–H bonds of toluene (producing \(\text{PhCH}_2\text{–NH}(p\text{-C}_6\text{H}_4\text{tBu})\)) or in aziridination of styrene (producing \(\text{Ph}[\text{CHCH}_2]\text{N}(p\text{-C}_6\text{H}_4\text{tBu})\)). The catalytic activity of \(47\) has also been briefly studied in the amination of toluene using adamantyl azide as a nitrene source. The best results were obtained with 1-adamantyl derived complex \(47b\), which gives 95% yield of (benzyl)(adamantyl)amine \((\text{PhCH}_2\text{–NHAd})\) at room temperature \((\text{TON} = 6.7)\). Catalytic aziridination with \(47b\) is also possible, as styrene is converted into the corresponding aziridine in 85% yield \((\text{neat styrene, r.t., 20 equiv. of AdN}_3, \text{TON} = 17)\).

In line with the ability of the weak-field dipyrrin ligand to stabilise low coordination in \(47a, b\), Betley and co-workers investigated the Co analogues \(47d,c\) and the parent imido species \(48c, d\).\(^{35}\) Despite that most Co complexes display low-spin ground states, species \(48c\) has a partial population of the high-spin state \((S = 2)\) (35% at r.t.) and undergo a spin crossover behavior from singlet to quintet state. This, however, is not the case for the aromatic analogue \(48d\), which has an intermediate spin \((S = 1)\). This is attributed to the conjugation of the of the nitrogen p-orbital with the coplanar aromatic ring in \(48d\), which changes the orbital energy diagram of the species. Complex \(48c\) shows imido/nitrene group transfer to phosphines, but no C–H bond activation of 1,4-cyclohexadiene or dihydroanthracene. Complex \(48d\), however, is able to activate intramolecularly the C–H bond of the ortho-methyl group of the mesityl substituent at the imido ligand. Based on so far available data the authors interpreted species \(48c, d\) as metal-centred radical complexes. Thus, decrease in HAA reactivity of \(48\), when iron is substituted with cobalt, may point to the importance of ligand-centred radical complexes in this type of reactions.

Chirik and co-workers reported a series of Fe(nitrene) species \(50\) (Scheme 19), bearing the redox non-innocent pyridine-2,6-diimine ligand \((\text{PDI})\). These complexes were prepared by reacting \textit{bis}-dinitrogen complex \(49\) with the corresponding azide. The substituent

\[
\text{Scheme 19. Iron ‘imido’ complexes stabilised by the redox non-innocent PDI ligand.}\quad ^{36,37}
\]
on the nitrene nitrogen atom was found to have a big influence on the properties of the resulting species. Thus, in case of $R = \text{Ar}$ (Scheme 19), complexes 50-Ar exhibit a relatively long Fe–N$\text{nitrene}$ bond (~1.705–1.717 Å) and a non-linear N$\text{Py}$–Fe–N$\text{nitrene}$ structure ($\theta$ ~139–155º, Scheme 19).\textsuperscript{36} Those species are found (based on X-ray, Mössbauer- and SQUID magnetic studies) to have a triplet ($S = 1$) spin multiplicity, and thus best described as Fe$^{\text{III}}$ intermediate spin-state ($S_{\text{Fe}} = +3/2$) systems antiferromagnetically coupled to a PDI-monoanion radical ligand ($S_{\text{PDI}} = -1/2$). As a consequence, the NAr moiety in these complexes behaves as a ‘classical’ [NAr]$^{2-}$ imido fragment (I, Figure 5), with a rather covalent Fe–N$\text{nitrene}$ bond and the presence of a 2-centre-3e bond.

Quite a different picture is observed when the ‘nitrene’ nitrogen carries an alkyl substituent.\textsuperscript{37} Thus, species 50-Alk with $R = 1$-adamantyl, cyclooctyl or 2-adamantyl display relatively short Fe–N$\text{nitrene}$ bonds of ~1.65–1.66 Å and more linear N$\text{Py}$–Fe–N$\text{nitrene}$ angles ($\theta$ ~168–175º), compared to $R = \text{Ar}$. These systems exhibit spin-crossover behaviour. Complex 50-Ad\textsuperscript{1}, in contrast to 50-Ar, is found to be (almost) diamagnetic ($S = 0$) at room temperature (based on SQUID-magnetic measurements), but spin-crossover to a triplet ($S = 1$) system occurs at elevated temperatures (~8% the $S = 1$ spin state between 50 and 200 K, with increased $S = 1 / S = 0$ ratios at higher temperatures). In all cases incomplete transitions toward the triplet spin state were observed at the temperatures studied. The 2-adamantyl derivative 50-Ad\textsuperscript{2} shows similar behaviour, with an $S = 1$ ground state at room temperature and spin-crossover to $S = 0$ at lower temperatures.

Revealing and understanding the electronic structures of 50-Alk species is not a trivial exercise. Both iron and the redox-active PDI ligand may adopt multiple redox states, and DFT calculations do not always reliably reproduce the relative energies of open-shell spin-
crossover systems (with the commonly applied B3LYP functional frequently giving an artificial preference for the higher-spin states). Based on the collected experimental data thus far, the 50-Ad\(^1\) (\(S = 0\)) can be interpreted either as a low-spin Fe\(^{II}\) or Fe\(^{IV}\) complex (II or III, Figure 5) or as Fe\(^{III}\) species IV (Figure 5) with a low-spin Fe\(^{III}\) (\(S_{Fe} = +\frac{1}{2}\)) system antiferromagnetically coupled to a nitrene radical ligand (\(S_{N} = -\frac{1}{2}\)) (Figure 5). An Fe\(^{III}\) species with an intermediate spin state (\(S_{Fe} = +\frac{3}{2}\)) could be excluded on the basis of Mössbauer spectroscopic data.

The electronic structure of 50-Ad\(^2\) is even less clear. Although it has the same total spin (\(S = 1\)) as 50-Ar, the spectroscopic and geometrical differences between these two species did not allow the authors to classify the electronic structure of 50-Ad\(^2\) as for 50-Ar (I, Figure 5). The three possible candidates for the electronic structure of 50-Ad\(^2\) include: 1) intermediate spin (\(S_{Fe} = +1\)) Fe\(^{II}\) (or Fe\(^{IV}\)) species with closed-shell PDI (\(S_{PDI} = 0\)) and nitrene ligands (\(S_{N} = 0\)); 2) 50-Ad\(^2\) could contain a diamagnetic PDI fragment (\(S_{PDI} = 0\)) and a ferric (Fe\(^{III}\)) centre (\(S_{Fe} = +\frac{3}{2}\)) antiferromagnetically coupled to a nitrene radical moiety (\(S_{N} = -\frac{1}{2}\)); and 3) a low-spin Fe\(^{III}\) centre (\(S_{Fe} = +\frac{1}{2}\)) ferromagnetically coupled with a nitrene radical moiety (\(S_{N} = +\frac{1}{2}\)) as in electronic structure IV that also correlate with experimental data.

The Fe–N\(_{nitrene}\) bonds must display a considerable degree of covalency (more close to Figure 2c). The differences between aryl and alkyl-substituted nitrene species 50 most probably relate to steric factors, as the \(N-Ar\) substituent protrudes out of the Fe-PDI plane, due to its steric bulk, which decreases the Fe–N\(_{nitrene}\) electronic overlap and consequently leads to a higher spin state on Fe. On the other hand, the \(N-Alk\) substituent is more in the Fe-PDI plane, leading to a stronger orbital overlap between Fe and N\(_{nitrene}\), which further increases the Fe–N bond covalency and the nitrene field strength, leading to a low-spin iron configuration.

Holland and co-workers reported an iron imido-complex stabilised by a beta-diketiminate (nacnac) ligand,\(^{39}\) that is rather redox-inert compared to the PDI ligand. Nitrene complex 52 is formed by reacting dinitrogen complex 51 (Scheme 20) with 1-adamantyl azide. Species 52 was thoroughly characterised by X-ray, EPR, K-edge XAS, EXAFS and Mössbauer spectroscopy and supporting DFT-calculations. According to the DFT data, about 23% of the spin density of 52 (\(S = \frac{3}{2}\)) is localised on the ‘nitrene’ nitrogen atom. Addition of several equivalents of \(p-(tert\text{-}butyl)\)pyridine changes the spin multiplicity of the species from quartet to sextet, increasing the spin density on the ‘nitrene’ nitrogen to 82% in 53. Noteworthy,
coordination of a pyridine ligand to 52 is essential to induce further reactivity, whereby 53 is capable of intra- or intermolecular (from 1,4-cyclohexadiene derivatives) HAA producing 54 or 55, respectively (Scheme 20). Based on the reported experimental and computational studies, the role of the coordinated pyridine in promoting HAA activity of the complex 53 is explained by (1) weakening of Fe=NAd bond in 53, and (2) stabilisation of the HAA products 55 and 54 through coordination of the pyridine ligand (thermodynamically driven reaction). The quartet ($S = \frac{3}{2}$) and sextet ($S = \frac{5}{2}$) electronic structures of 52 and 53 are interpreted as stemming from ferromagnetic coupling between the metal and ligand unpaired electrons.

A strategy to circumvent the unwanted intramolecular reactivity was to avoid the presence of weak C–H bonds nearby the imido moiety in 52. Complex 57, which features β-diketiminato ligand with phenyl instead of isopropyl substituents, can be prepared from FeI precursor 56 (Scheme 21). Species 57 presents similar to 52 rhombic X-band EPR (8 K) spectrum (57a: $g_{\text{eff}} = 7.11, 1.55, 1.26$; 57b: 7.42, 1.05, 0.9), hence suggesting similar electronic structure in 52 and 57. The phenyl
moiety at the diketiminato ligand in 57 has remarkable repercussions on the reactivity. Thus, while the stability of 52 is relatively low, complex 57 is stable for several days in benzene solution. More importantly, 57 shows much higher HAA reactivity (factor 145) than 52, and addition of pyridine was no longer necessary. Two factors contribute to such differences in reactivity: 1) Steric factor, rotation of the aromatic 2,4,6-triphenylphenyl substituent decreases steric bulk at one side of the (N,N)Fe–NR plane of the compound, thus enabling an easier approach of the substrate. The metal centre in 57, however, is more crowded than in 52, which lowers the affinity of 57 for pyridine; 2) 57 has a more bended compared to 52 Fe–N–R angle of 151° (for R = Ad: angle Fe–N–R is 151° in 57, and 170° in 52) and a longer Fe–N nitrene bond (for R = Ad: d_{Fe,N(nitrene)} = 1.70 Å in 57 and 1.67 Å in 52). This makes complex 57 closer in geometry to the TS for HAA, which is predicted (QM/MM calculations) to have Fe–N nitrene distance of ~1.90 Å and Fe=N–R angle of 140°.

A related stabilizing effect by different Lewis acids was recently reported by Ray et al. in case of a Cu-nitrene-radical species. Here, reaction of CuI complex 58 (Scheme 22) with a soluble iodosobenzene derivative PhI=NTs immediately leads to formation of CuII complex 60, presumably via abstraction of a hydrogen-atom from the solvent (or traces of moisture) by ‘nitrene radical’ intermediate 59. To stabilise species 59 for further characterisation and

![Scheme 22. Stabilizing effect of ScIII ions slowing down the HAA activity of CuII-nitrene radical species 59.](image-url)
reactivity studies, different Lewis acids were added, with scandium(III) triflate proving most efficient. The thus stabilised ‘nitrene radical’ species $59$-$\text{Sc}$ is capable of oxidising 2 equiv. of ferrocene to ferrocenium (yield of $\text{Fc}^+$ is 180%), showing that $59$-$\text{Sc}$ is two oxidation levels above the starting compound $58$. XAS measurements reveal that $59$-$\text{Sc}$ posses an almost identical pre-edge energy (ca. 8978 eV) compared to $60$. This allowed the authors to assign $59$-$\text{Sc}$ as a Cu$^{II}$-nitrene radical species. Complex $59$-$\text{Sc}$ also participates in HAA (with dihydroantracene and 1,4-cyclohexadiene) to give $60$ and the corresponding aromatic organic compounds. $59$-$\text{Sc}$ is also active in nitrene C–H-bond insertion reactions with toluene and cyclohexane, yielding amine derivatives with some amount of imines (Scheme 22). The stabilizing effect of Sc$^{III}$ ions is most probably the result of the reduced electron density on the nitrene nitrogen atom of $59$, which also decreases its HAA reactivity.

Besides the discussed experimentally characterised nitrene-centred radical complexes, there is a number of additional mechanistic studies on transition-metal-catalysed aziridination and amination reactions, where nitrene-centred ligand-radicals are proposed (or computationally found) to be key intermediates. These calculations mainly focused on Cu$^{I}$,$^{42}$ Cu$^{II}$- or Ag$^{I}$-catalysed aziridination and nitrene insertion reactions.$^{43}$ Also nitrene species derived from $40$ as well as Fe and Co$^{44}$ porphyrin species bearing nitrenes have been studied computationally. Redox non-innocent NAr fragments might also be present in some Ni–NAr species related to $26$ and $33$.${}^{45}$

1.3 Nitridyl ligand-radical complexes.

From the above sections it is clear that nitrogen-centred aminyl and nitrene-based ligand radicals, although being less stable than their metallo-radical imido and amido counterparts, can reveal selective reactivity and ‘controlled’ by the metal d-orbitals. This concept is highly interesting from a synthetic point of view, and is (at least conceptually) worth to consider in view of dinitrogen activation with open-shell transition metal complexes. As such, formation of nitridyl radical complexes ([M(•N)]) from $\text{N}_2$ can be expected (Figure 1c), possibly allowing subsequent reactivity with other (organic) substrates. This possibility has thus far been scarcely investigated, but some recent examples reveal the potential.

In this context, detection of an iridium-nitridyl radical and its inherent radical-type reactivity, as recently reported by Schneider and de Bruin, is of particular interest. The synthesis of Ir$^{II}$ azide complex $61$ is disclosed, which upon irradiation produces neutral iridium ‘nitridyl radical’ complex $62$ (Scheme 23).${}^{46}$ Alternatively, species $62$ can be
generated upon reduction of cationic nitrido complex 63, which in turn is obtained by oxidation of 61 with a ferrocenium salt. The EPR (20 K) spectrum of 62 reveals a rhombic signal with large $g$-anisotropy ($g_1 = 1.885$, $g_2 = 1.632$, $g_3 = 1.320$). Remarkably, all $g$-values of 62 are below 2.0, indicating that spin-orbit coupling interactions with empty d-orbitals are strong, but negligible with filled d-orbitals.

DFT calculations showed an almost covalent Ir–N bond with about 50% of the total spin density on the non-PNP nitrogen atom and 40% on iridium, thus indicating a substantial contribution of the Ir–N$^*$ nitridyl radical resonance structure. The unpaired electron is located in a $\pi^*$ Ir–N molecular orbital, and hence this system might be best described as a 1e-reduced Fischer-type species. The substantial covalent character of this system so far precludes a definitive assignment or classification.

Compound 62 is stable at room temperature for several minutes, but with longer reaction times dimerisation to the dinuclear N$_2$-bridged binuclear Ir$^3$-complex 64.$^{46}$ Compound 62 is not reactive towards C–H bonds of 1,4-cyclohexane, and gives only 64 and 65, which is probably due to the kinetic preference of dimerisation over HAA.

Wieghardt and co-workers reported the synthesis of a related ‘nitridyl radical’ species 67 (together with some related species), prepared by photolysis of the corresponding azide 66.$^{47}$ Here, complex 67 is interpreted as predominantly nitrido Fe$^V$ species by the authors, but their DFT calculations show
that the SOMO of 67 has about 75% ‘nitridyl radical’ character. Hence, species 67 might as well have been described as nitridyl radical Fe\textsuperscript{IV}-species.

The previously discussed nitrido (nitridyl) complexes were prepared from azido precursors. A recent example reported by Holland and co-workers\textsuperscript{48} is especially noteworthy, since it was obtained by stoichiometric activation of N\textsubscript{2} by an iron \(\beta\)-diketiminate complex (68). This led to the formation of bridging \textit{bis}(nitrido)iron-cluster 69 (Scheme 26). The tetranuclear cluster is only formed in THF, and includes two potassium cations stemming from the reductant (KC\textsubscript{8}). X-ray crystallographic studies of 69 reveal an N–N distance of 2.799(2) \(\text{Å}\), consistent with the absence of any N–N bond. Based on Mössbauer spectroscopy and magnetic susceptibility measurements, Fe(1) and Fe(2) are both assigned as high-spin Fe\textsuperscript{III} centres, whereas Fe(3) and Fe(4) are high-spin Fe\textsuperscript{II} centres (Scheme 26). The calculations, performed on a simplified model, show quite high contribution of nitrogen-based atomic orbitals in the HOMO (exact numbers are not reported), which suggests that unpaired electron is probably delocalised over the nitrido moieties and the Fe-centres. A more detailed analysis of the electronic structure of 71 would be required to confirm this. Complex 71 is able to activate H\textsubscript{2} at room temperature, yielding ammonia in 42% yield.

1.4 Conclusions.

The detection and targeted synthesis of nitrogen-centred ligand radical complexes has attracted a lot of attention over the past decade. The relevance of these intriguing species lies in their reactivity, and several aminyl- ([M(•NR\textsubscript{2})]) and nitrene/imido-radical complexes ([M(•NR)]) have been found to be active intermediates in different catalytic and stoichiometric nitrogen-group transfer processes. These species often reveal selective radical-type reactivity, including addition to unsaturated bonds, radical-radical coupling as well as...
hydrogen atom abstraction reactions. The full benefit of such radical-type reactivity becomes obvious when considering transformations of non-activated substrates such as alkanes, which lack donor atoms and are not prone to form anionic or cationic intermediates, but nonetheless can be successfully transformed into amines using aminyl- or nitrene/imido-radical complexes via radical C–H functionalisation pathways. In fact, a recent study by Pérez and co-workers suggests that spin state transitions occur easily during nitrene transfer reactions and might actually be more general.\textsuperscript{42g} Hence, radicaloid pathways involving exited triplet states could even be expected for a closed-shell ground state imido/nitrene species reacting via triplet- or singlet-biradical exited states. Qualitatively, the reactivity of the doublet ligand-radical complexes highlighted in this review seems to correlate roughly with the amount of nitrogen-centred spin density.

Resolving the electronic structures of nitrogen-centred radical complexes is generally based on a number of spectroscopic techniques such as EPR, X-ray absorption and Mössbauer spectroscopy as well as X-ray crystallography, often combined with DFT calculations. This allows a classification of these ligand radical species as 1e-reduced Fischer-type, 1e-oxidised Schrock-type or covalent systems. Most of the reported complexes represent either a 1e-reduced Fischer-type systems or have rather covalent M–N bonds, while 1e-oxidised Schrock-species are scarce. Although it is tempting to think that the 1e-oxidised Schrock-type systems may reveal quite different reactivity patterns from those reported for the 1e-reduced Fischer-type systems, at this point no comparative reactivity studies and too few examples describing (the reactivity of) 1e-oxidised Schrock-type systems are available to make any fair comparisons. Future investigations should shine more light on this matter, and hence we encourage scientists in this field to consider these aspects and to not only report the spin density of the calculated nitrogen-centred ligand radical complexes but also the nature of metal-nitrogen π-bond.

Among the family of aminyl, nitrene/imidyl radical and nitridyl metal complexes, the latter are remarkably scarce. This is not unexpected in view of the low steric protection of the ‘naked’ nitrogen atom in nitridyl species. However, despite obvious difficulties in the synthesis and isolation of such nitridyl radical complexes, the role they might play in e.g. dinitrogen fixation makes them valuable synthetic targets for future reactivity studies. Their potential reactivity towards other small molecules and organic substrates is also of particular interest.
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1.6 Notes and References.


6 Ligand radicals based on highly delocalised (one-electron oxidised or reduced) π-systems, such as o-phenylenediamines, α-dimines, α-imino-pyridines, pyridine-2,6-dimines, bipyridine or terpyridine (and alike) are excluded from this review (despite the fact that some of these systems bear significant spin density at their nitrogen atoms).


