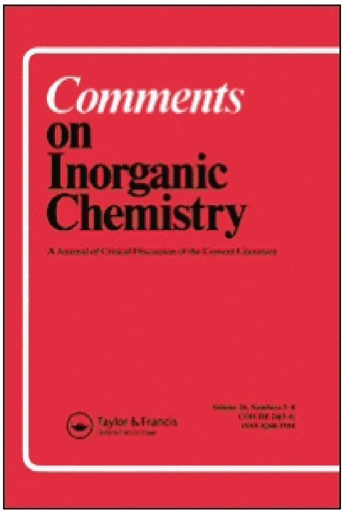

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TERMINAL NITRIDO AND IMIDO COMPLEXES OF THE LATE TRANSITION METALS

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TERMINAL NITRIDO AND IMIDO COMPLEXES OF THE LATE TRANSITION METALS

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Compounds that contain a late transition metal-nitrogen multiple bond represent important reactive intermediate species in many useful organic and inorganic transformations. In order to understand the role that these intermediates play in reactions, it is important to have a full understanding of their electronic structure. This paper reviews the known structural motifs that occur in late transition metal nitrido and imido compounds, and provides a correlation between geometric structure and electronic structure. Also, intermediate species that have been postulated but not yet isolated are discussed, as these compounds represent exciting targets for further efforts in synthetic inorganic chemistry.

INTRODUCTION AND BACKGROUND

Metal-ligand multiple bonding is a common feature of the chemistry of early transition metals in high oxidation states.[1,2] Late transition metal species with metal-ligand multiple bonds are not as common, and tend to be highly reactive, often serving as important intermediate species in reactions involving oxidation of organic substrates. For example, a multiply-bonded Fe=O iron-oxo unit has long been considered as the

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key oxidizing intermediate in cytochromes P450,[3,4] which promote the remarkable hydroxylation of unactivated C–H bonds.

In 1985, a cytochrome P450 from rabbit liver was found to catalyze a new type of reaction that involves insertion of a nitrene (NR) moiety into a C–H bond.[5] Here, the key intermediate that was proposed was a multiply-bonded Fe=NR species.[5] Contemporaneous with this P450 work, several transition metal complexes, including iron and manganese complexes of tetraphenylporphyrin and dirhodium tetraacetate, were found to catalyze intramolecular insertion of nitrenes into C–H bonds.[6] Today, transition metal catalyzed insertion of nitrenes (and carbenes) into C–H bonds has been developed into a viable methodology for synthetic organic chemistry that allows complex structures to be built, often in fewer steps than would be necessary by traditional methods.[7]

A full understanding of the nature and mechanism of these metal-catalyzed nitrene insertion reactions requires detailed knowledge of the preferred geometries and electronic structures of species with metal-nitrogen multiple bonds, because these species are proposed to be important catalytic intermediates. To this end, a major research effort is underway in many laboratories aimed at the synthesis and characterization of late transition metal nitrido ($M\equiv N$) and imido ($M=NR$) complexes. The purpose of this review is to emphasize emerging trends in the geometric and electronic structures of multiply-bonded compounds that are of current interest. For an excellent review of the synthetic aspects and reactivity of nitrido and imido complexes, the reader is referred to a recent paper by Eikey and Abu-Omar,[8] as well as other texts.[1,9–15]

The scope of this review is detailed in Figures 1 and 2. The transition metals discussed in this article will be those in groups 8–11 of the periodic table. Notably, terminal nitrido complexes are only known for Fe, Ru, and Os. Attempts to synthesize nitrido complexes of the later metals have been reported to result in the formation of proposed metal-nitrene ($M=NH$) species.[16–26] Bona fide examples of imido complexes are also rare for metals to the right of group 8; incidentally, a related phenomenon involving metal-oxo compounds has led to the division between groups 8 and 9 being colloquially dubbed “the oxo wall.” Though few well characterized examples are known, metal imido species beyond the oxo wall are often invoked as transient highly reactive intermediates in late metal-catalyzed nitrene transfer chemistry.

The organization of this review will be as follows. Nitrido compounds will be discussed first, and then imido species will be mentioned,

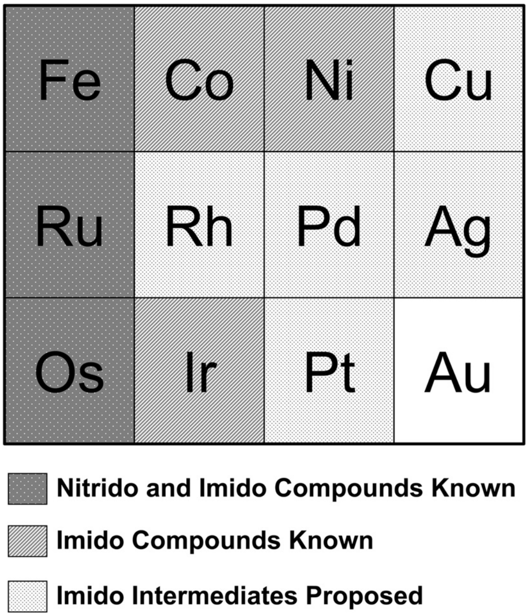


Figure 1. Survey of the known compounds of the late transition metals with terminal nitrido and imido ligands.

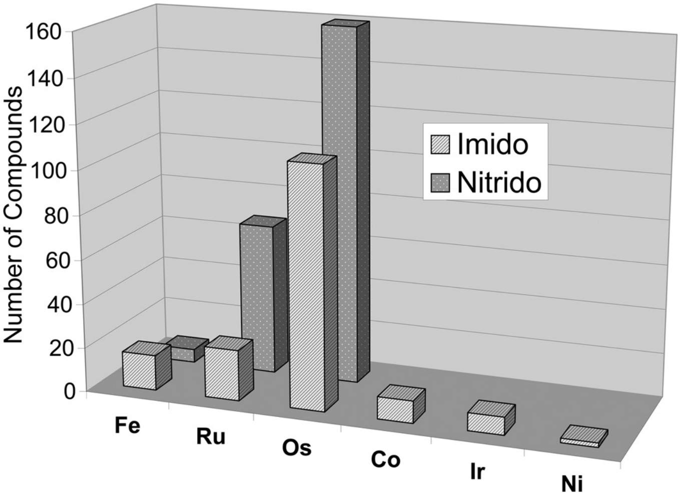
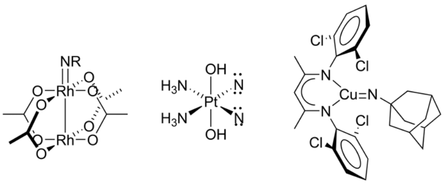


Figure 2. Chart of the number of terminal nitrido and imido compounds known.

followed by di- and tri-imido species. The content will be organized according to molecular geometry, so that compounds with different metals and electron counts but similar structures can be easily compared. Chelating imido species will not be discussed.[27–30] The last section will focus on species that have been postulated in the organic chemistry literature, but do not have any stable analogs that have been characterized. Some of these last species are highly speculative, and open up interesting opportunities as targets for synthetic efforts.

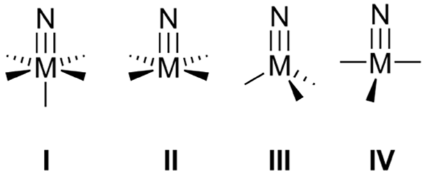
NITRIDO COMPOUNDS

Terminal nitrido compounds are those in which a single nitrogen atom serves as a ligand to a transition metal. As the name implies, significant charge transfer is assumed to take place in these compounds such that the nitrogen atom is thought of as an N^{3-} trianionic ligand, and the metal assumes a high oxidation state. The formalisms of oxidation states, useful though they may be, often do not convey information about the electronic structure of nitrido compounds because there is a significant covalent component to the metal-nitrogen bonds. Nitrido complexes feature metal-nitrogen multiple bonds that can be formed via the orbital overlap shown in Scheme 1. An M–N σ bond may be formed from the interaction between an orbital of σ symmetry on the metal (shown is a d_{z^2} orbital, assuming that the M–N axis is also the z axis) and an N p_z or *sp* hybrid; π bonds can be formed via overlap of the N p_x and p_y with appropriate orbitals of π symmetry on the metal. Overall, an M–N bond order of three is possible. Although equivalent metal and ligand character is shown in the bonding orbital combinations in this scheme, the metal and ligand contributions to a given molecular orbital do not have to be equivalent. Indeed, it is the inequivalence of these contributions that gives each new compound different properties and reactivity.



I II III

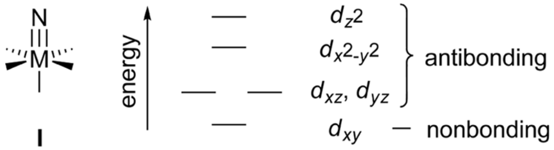
Scheme 1. Metal-nitrogen bonding orbitals.



Scheme 2. Geometry of terminal nitrido compounds.

Four general classes of nitrido compounds will be discussed, and these are listed in Scheme 2 arranged by their coordination number. Species **I** are coordinatively saturated. Because of the larger number of metal-ligand bonds in these compounds, complexes having this geometry are limited in the number of *d* electrons available to the metal. If the metal possesses too many *d* electrons, M–N antibonding orbitals will begin to be populated, causing an inherent instability in the compound. The prevailing method for synthesizing metal-ligand multiply bonded compounds with large *d* electron counts has been to use lower coordination numbers, as in species **II**, **III**, and **IV**. In my lab, we have recently discovered an alternative way of synthesizing compounds that are coordinatively saturated but may also have high *d* electron counts: this is possible by using compounds with metal-metal bonds, and will be described more fully below.

Species of type **I** have idealized C_{4v} symmetry, but the actual symmetry may be lower depending on the nature and identity of the supporting ligands. The energies of the metal *d* orbitals may be approximated from simple ligand field theory as the following: $d_{xy} < d_{xz} \sim d_{yz} < d_{x^2-y^2} < d_{z^2}$ (see Scheme 3). Of these orbitals, the d_{xy} is the only one that is nonbonding with respect to all metal-ligand bonds. The d_{xz} and d_{yz} both have π^* character with respect to the M≡N bond, and the $d_{x^2-y^2}$ and d_{z^2} orbitals both have σ^* character. Therefore we may expect that the maximum number of *d* electrons that can be comfortably accommodated

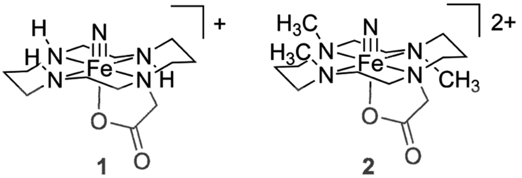


Scheme 3. Valence orbital splitting diagram for **1**.

in this bonding manifold is two. For Fe, Ru, and Os, this means that stable compounds with the geometry of type **I** should have the metal in the oxidation state of +6 or higher. Since higher oxidation states are more common for the second- or third-row metals, there are many more nitrido compounds of Ru and Os of type **I** that are known. In fact, the first and only Fe(VI)-nitrido compound has just very recently been discovered.[31]

The first iron nitrido complexes of type **I** that were found to be synthetically accessible were complexes of Fe(V). After earlier resonance Raman studies suggested the existence of Fe(V)-nitrido porphyrin complexes,[32–35] further spectroscopic evidence for the formation of nitrido-iron(V) species stabilized by cyclam-type ligands (**1**) was presented by Wieghardt and coworkers (see Scheme 4).[36,37] Further spectroscopic work on **1** was undertaken using X-ray absorption spectroscopy, magnetic susceptibility, and nuclear resonant vibrational spectroscopy in combination with DFT calculations.[38,39] This work has resulted in a good understanding of the electronic structure of **1**, which, as a low-spin d^3 system, has one unpaired electron and a $(d_{xy})^2(d_{xz}, d_{yz})^1$ ground state electron configuration. This configuration leads to a ^2E ground state, and many of the magnetic properties of this compound are perturbed by Jahn-Teller splitting. Notably, this electron configuration implies a formal Fe≡N bond order of 2.5 in **1**, leaving significant radical character on the nitrogen atom. The reactivity of a nitrido-iron(V) species toward C−H and N−H bond activations and alkyne metathesis has recently been explored using gas-phase mass spectrometric techniques.[40,41]

Addition of steric bulk to **1** has made it possible to synthesize the Fe(VI) complex **2**, which is metastable, decomposing slowly at temperatures of –40°C.[31] Notably, **2** is only the second Fe(VI) species to be discovered, the first being the ferrate ion, FeO_4^{2-}. As expected from the orbital diagram in Scheme 3, **2** is diamagnetic, and its Fe≡N bond



1 **2**

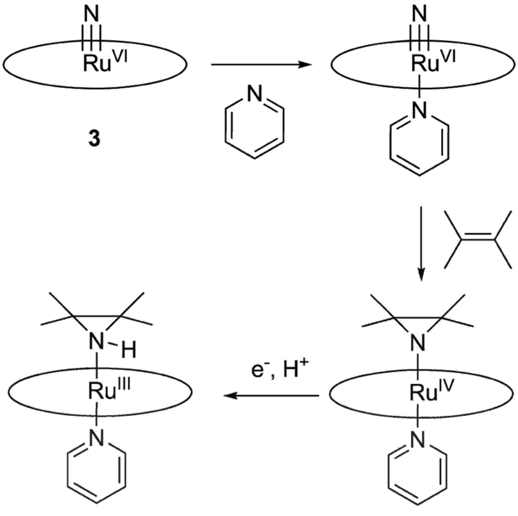
Scheme 4. Structures of **1** and **2**.

length, 1.57 Å (determined from EXAFS), is significantly shorter than the 1.61 Å distance found in **1**.[31,38] Trends in a series of hypothetical *trans*-$[Fe{\equiv}N(NH_3)_4(OH)]^{n+}$ compounds have been examined by computational methods.[42] These compounds span the oxidation states Fe(IV), Fe(V), and Fe(VI) corresponding to d^4, d^3, and d^2 systems. While the computed Fe(V) and Fe(VI) species reproduce the trends found in **1** and **2**, the Fe(IV) species was anomalous in that its electronic structure did not have the "expected" $(d_{xy})^2(d_{xz}, d_{yz})^2$ configuration but instead had a $(d_{xy})^2(d_{x^2-y^2})^1(d_{xz}, d_{yz})^1$ configuration.[42] This unusual orbital ordering results from a large splitting between the d_{xy} and (d_{xz}, d_{yz}) orbitals as well as elongation of the equatorial metal-ligand bonds, stabilizing the $d_{x^2-y^2}$ orbital. Since the anticipated electron configuration would lead to an Fe=N bond order of only 2, it was suggested that the molecular distortion in this compound was a result of attempts by the nitrogen atom to increase its valency to three.[42] Needless to say, these results strongly suggest that a complex with geometry type **I** and four *d* electrons or more would be either highly unstable, or highly distorted.

For ruthenium, compounds of type **I** are not as numerous as those of type **II**, but there are nevertheless many type **I** compounds that are known, all of Ru(VI).[43–48] Importantly, the addition of a new ligand *trans* to the nitride (i.e. changing from type **II** to type **I** geometry) substantially increases the reactivity of the complex. For example, Lau has recently shown that a (salen)Ru≡N species, **3**, which ordinarily does not react with alkenes, will do so upon addition of an axial pyridine donor ligand to produce an N-bound aziridine, **4** (Scheme 5).[49]

As illustrated by the above example, the coordination of a ligand *trans* to a nitrido group weakens the Ru≡N bond. We have recently used this concept to design a new type of reactive Ru-nitrido complex, **5**, which has an axial Ru−Ru bond *trans* to the nitride, resulting in an extraordinarily weak Ru≡N bond.[50] The resulting structure of this Ru−Ru≡N complex has a Ru≡N bond length that lies between what is observed for mononuclear Ru(VI) nitrido complexes and for N atoms bound to a bulk Ru metal surface (Figure 3, Scheme 6).

The Ru_2^{7+} core present in **5** can be described to a first-order approximation as consisting of a Ru^{3+} and a Ru^{4+} ion. Since six-coordinate nitrido complexes of Ru in these oxidation states should be unstable due to occupation of Ru≡N antibonding orbitals, it is clear that the metal-metal bond in **5** contributes to the stability of this species. The electronic structure of **5** was examined by DFT methods and was found



3

4

Scheme 5. The equatorial disc represents a salen-type ligand.

to differ significantly from that anticipated in Scheme 3. Specifically, the d_{z^2} orbitals of both Ru atoms, along with the N p_z orbital were shown to form three-center orbital combinations; three-center π orbitals were likewise formed from the Ru d_{xz}, d_{yz} and N p_x, p_y orbitals (Scheme 7). For the σ and two orthogonal π sets, the bonding and non-bonding

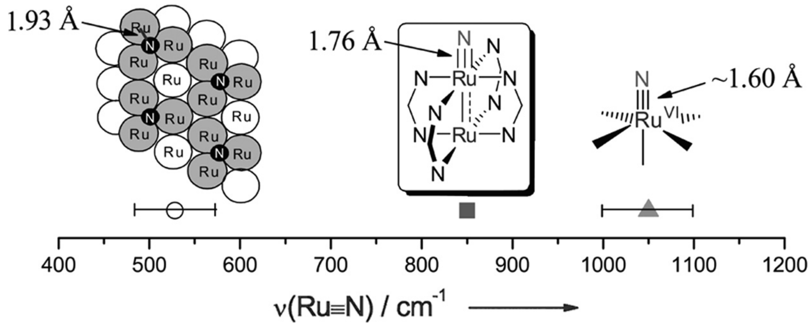
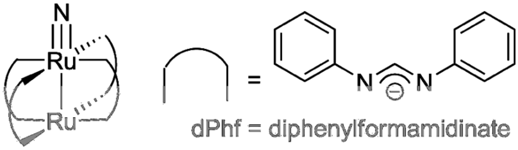


Figure 3. Comparison of the Ru≡N bond lengths and observed Ru≡N stretching frequencies for mononuclear Ru(VI)-nitrido complexes (right), N atoms bound to Ru metal surfaces (left), and **5** (center). Reproduced with permission from reference 49. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

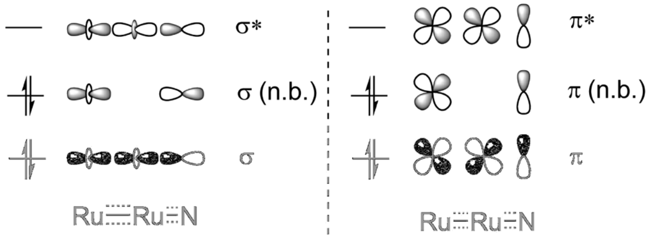


5

Scheme 6. Structure of **5**.

orbital combinations each house a pair of electrons. Thus, the Ru−Ru≡N bonding may be described as consisting of a three-center four-electron σ bond and two orthogonal three-center four-electron π bonds.

The calculated molecular orbitals are shown in Figure 4, which displays the full energetic ordering of these orbitals and the Ru_2 δ orbitals, which do not have the appropriate symmetry to interact with any of the N orbitals. The disposition of the δ orbitals is important, however, as one of them contains the molecule's unpaired electron. The electronic structure in Figure 4 does help us to understand some of the unique features of **5**. The unusually high electron count of the Ru_2^{7+} unit is accommodated in both Ru_2N bonding and Ru_2N *non-bonding* orbitals. Since σ and π nonbonding orbitals are not available for mononuclear Ru-nitrido species, these mononuclear species cannot accommodate as many valence electrons as the metal-metal bonded system. The Ru−Ru and Ru≡N bonds are both longer than they would be in isolated systems. This effect comes from the fact that we are no longer dealing with isolated Ru−Ru multiple bonds or Ru≡N multiple bonds, but a *delocalized* Ru−Ru≡N system built upon three-center four-electron bonds. It is this delocalization that causes the Ru−Ru and Ru≡N bonds to be longer and weaker than what is normally observed.



Scheme 7. Three-center σ and π orbitals.

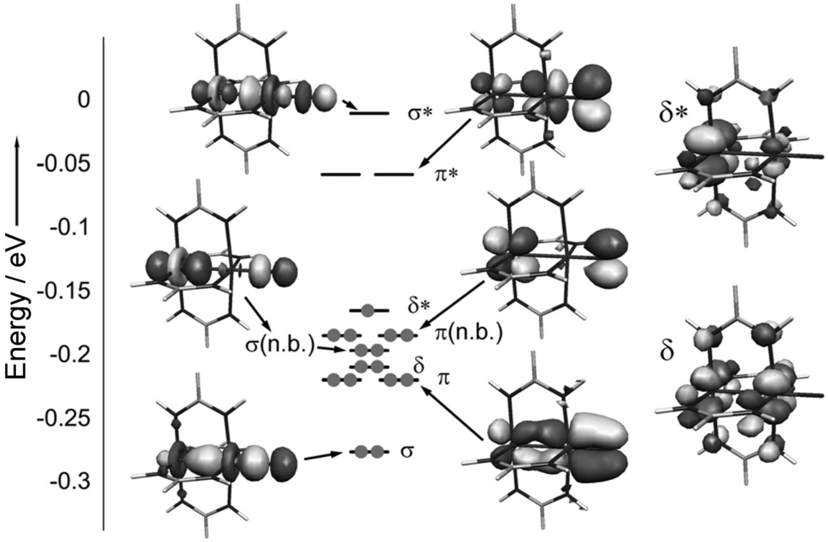


Figure 4. Molecular orbital diagram for $Ru_2(HNCHNH)_4N$, a model for **5**, calculated from DFT. Reproduced with permission from reference 49. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

There are two important implications for the weaker-than-normal Ru−Ru and Ru≡N bonds in **5**. The first is that δ bonding in the Ru_2 unit is not very strong, as evidenced by the meager splitting between the δ and δ^* levels in Figure 4. Secondly, in contrast to most mononuclear Ru-nitrido species that are very stable and can be characterized by X-ray crystallography, compound **5** is *unstable* and decomposes readily. Consequently, structural information on **5** was only obtainable by EXAFS methods.[50] Although decomposition products from **5** have not yet been identified, it is likely that they result from reactivity associated with the weakly-bound nitrido ligand.

It is important to mention that the reactivity of **5** is relevant to proposed intermediate species in dirhodium-catalyzed organic reactions. Specifically, Rh−Rh bonded compounds such as $Rh_2(OAc)_4$ are good catalysts for the insertion of a nitrene (NR) moiety into unreactive C−H bonds.[7,51] The key intermediate species implicated in these reactions are Rh−Rh=NR species, which have never been isolated (vide infra). It is suggested that the Rh=NR bonding in these intermediates is weakened via electron delocalization, similar to what occurs in **5**.[50]

Osmium nitrido complexes are much more numerous than their ruthenium analogs, and those having a structure of type **I** are the most numerous of all of the structurally characterized Os species. A broad range of ligands have been used to support Os(VI) nitrido species. These may be generally classified as halogen and pseudohalogen ligands,[51–60] amines,[62,63] alkoxides,[64,65] polypyridyl ligands,[66–72] and polyoxometallates.[73–76] Organometallic Os(VI) nitrido species are also known.[77–79]

Because of the stability and kinetic inertness of these osmium complexes, these complexes have been extensively used to explore the reactivity of the nitrido group. In general, Os(VI) nitrido complexes are electrophilic (though organometallic nitrides are nucleophillic)[79] and react with various nucleophiles to form products with new bonds to the nitride nitrogen atom (Scheme 8).[80–98] The nitrido group in these Os compounds does not display significant nucleophilicity. In fact, Os-nitrido species react with electrophilic acylating reagents via ligand substitution pathways that keep the Os≡N bond intact.[99] Another stunning example of the inability for the Os-nitrido unit to act as a nucleophile is its reaction toward BPh_3 (Scheme 9). Instead of forming a simple Lewis acid-base complex, i.e., $Os{\equiv}N{\rightarrow}BPh_3$, the nitride N atom in $TpOsNCl_2$, **6**, is inserted into one of the B–C bonds.[100]

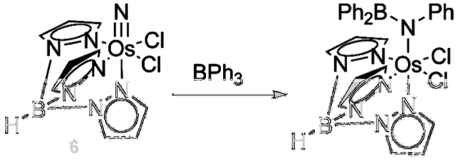
As a further display of the electrophilic nature of Os≡N species, **6** has been shown to react with a nucleophilic early-metal nitrido species, $(Et_2NCS_2)_3MoN$, to produce molecular N_2.[101] N–N coupling has also been observed in the chemical reduction of **6** with cobaltocene,[102] although in acid solution reduction to the Os(II)–NH_3 complex is observed.[103] Electrochemical studies of these Os(VI)-nitrido species therefore typically exhibit irreversible reductions; oxidations to the presumed Os(VII) species are reversible, albeit at extraordinarily high potentials, >1.3 V vs Fc/Fc^+.[104]

In the structures of type **I** species, the metal-ligand bond *trans* to the M≡N bond is typically longer than normal, due to the strong *trans* influence of the nitride ligand. Due to the intrinsic weakness of these *trans*

$$L_5Os{\equiv}N \;+\; \mathbf{Nuc} \longrightarrow L_5Os{-}N{=}\mathbf{Nuc}$$

Nuc = OH^-, $S_2O_3^{2-}$, olefin, carbene, diene, Grignard, NO, S_8, Se_8, CN^-, amines, N_3^-, thiol, PR_3, SPR_3

Scheme 8. Electrophilic reactivity of Os nitrido compounds.

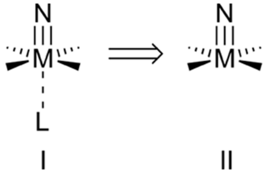


Scheme 9. Reaction of 6 with BPh_3.

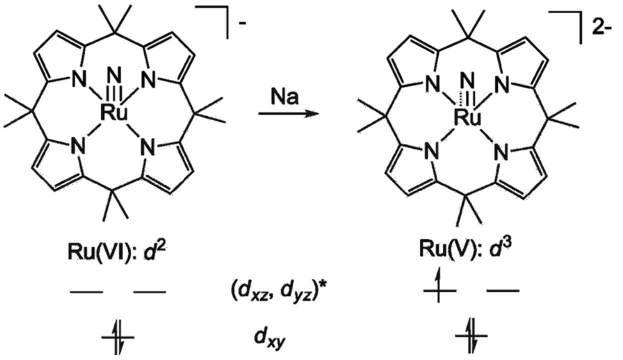
metal-ligand bonds, it is not surprising that many five-coordinate complexes (type II) are known in which the *trans* axial ligand is absent (Scheme 10). These complexes are most numerous for Ru and Os; to date no Fe analogs have been synthesized.

For ruthenium and osmium, type II species are known with many different types of equatorial ligands: halogens,[105–112] alkyl,[113–122] N- or O-donors,[55,123–129] and thiolates[130–135] are known. Reactivity of these species is similar to those of type I, though it should be mentioned that the $[OsNCl_4]^-$ anion has been recently used as a cocatalyst (along with $FeCl_3$) for the oxidation of alkanes.[136] One particularly noteworthy result of relevance to electronic structure is a Ru(VI)-porphyrinogen nitrido complex that has also been isolated in its one-electron reduced Ru(V) form (Scheme 11).[137] As one would expect from the addition of an electron to one of the d_{xz}, d_{yz} π^* orbitals, the Ru≡N bond length in the Ru(V) species, ~1.76 Å, is significantly longer than in the Ru(VI) case, 1.57 Å.[137] The Ru(V) species is also paramagnetic, having a room temperature μ_{eff} value of 1.84 μ_B, consistent with the presence of a single unpaired electron.[137]

Tetrahedral, or distorted tetrahedral nitrido complexes (III) are best known for the Os(VIII) species OsO_3N^-, which has been characterized in many salts.[138–142] The OsO_3N^- ion has also been found to coordinate to metal ions through the N atom,[143–145] and, like the $OsNCl_4^-$ ion described above, has been recently used in catalytic alkane oxidations.[146]



Scheme 10. Conversion of I to II.

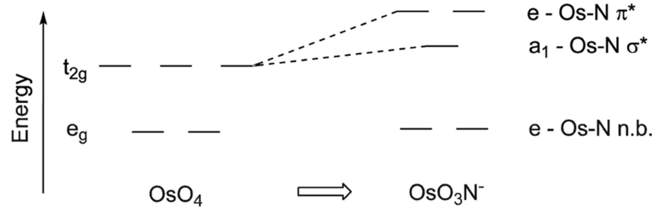


Scheme 11. Ruthenium porphyrinogen nitrido compounds.

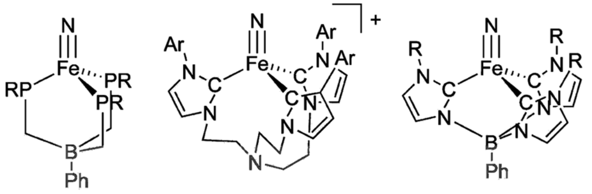
The electronic properties of the OsO_3N^- ion, like those of OsO_4, are dominated by LMCT features, though the spectral features are consistent with the lowering of symmetry from O_h (OsO_4) to C_{3v} (OsO_3N^-), as shown in Scheme 12.[147]

One of the most exciting recent developments in late transition metal nitrido chemistry has been the preparation of distorted tetrahedral Fe(IV)-nitrido species. Specifically, the new complexes **7**,[148–150] **8**,[151] and **9**[152] shown in Scheme 13 have all been prepared, in which the Fe≡N unit is chelated by a polydentate ligand bearing soft donor groups: phosphines in **7**, and *N*-heterocyclic carbene moieties in **8** and **9**. Because of the pseudo-tetrahedral symmetry of these complexes, the four valence *d* electrons of the Fe(IV) ion are housed in the non-bonding *e* orbitals (Scheme 13), which are the d_{xy} and $d_{x^2-y^2}$.

As expected, these Fe-nitrido species react readily with nucleophiles to form products similar to those depicted in Scheme 8.[148,152] Notably, binuclear N–N coupling to produce N_2 is observed for species that do not contain protective sterically bulky substituents.[148] Consequently,



Scheme 12. Qualitative molecular orbital diagram for OsO_4 and OsO_3N^-.



7 8 9

Scheme 13. Pseudotetrahedral iron nitrido compounds.

it has thus far not been possible to obtain structural information on **7** via X-ray crystallography, though EXAFS analysis has established a very short Fe$\equiv$N bond distance of 1.51 Å.[150] This short Fe$\equiv$N bond has been confirmed by crystallographic data on the bulkier and more stable complexes **8** and **9**, which have bond distances of 1.53 Å and 1.51 Å, respectively.[151,152] These Fe$\equiv$N bond distances are shorter than the Fe$\equiv$N distance observed for the octahedral Fe(VI)-nitrido species by up to 0.06 Å, an effect that is attributed to the lower coordination number of the cases of **7**–**9**.

The somewhat unusual ordering of the Fe$-$N σ^* and π^* orbitals has been addressed by Kirk and Smith.[152] Because of the very short Fe$\equiv$N distances in these compounds, one might expect that the Fe$-$N σ bond would be strong enough to raise the a_1 σ^* orbital higher in energy above the e π^* orbitals. However, the observed energetic ordering is reversed as shown in Scheme 12. This ordering is attributed to two main effects: (1) the N$\equiv$Fe$-$L angle in these compounds is balanced such that the electron pairs of the L ligands point toward the radial node of the Fe d_{z^2} orbital, reducing its Fe$-$L antibonding character. Also, (2) hybridization of the d_{z^2} orbital by mixing with the 4s and 4p_z orbitals mitigates the Fe$\equiv$N antibonding nature of this orbital.[152]

Another exciting recent development in the chemistry of four-coordinate nitrido complexes is the complex $(\mathrm{N(SiMe_2CH_2P^tBu_2)_2)RuN}$, **10** (Figure 5), which has been reported by Caulton to form via thermolysis of the corresponding azido complex at ∼–30°C.[153] This complex utilizes a meridional-tridentate supporting ligand that binds through two phosphine arm groups and a central amide N atom (PNP), and has been used to form planar four-coordinate Ru(II) complexes that adopt an intermediate spin state ($S = 1$).[154] The d^4 Ru(IV) nitrido complex, however, shows significant deviations from planarity: the Ru$\equiv$N bond is roughly 25° out of the plane of the PNP ligand (**IV**).

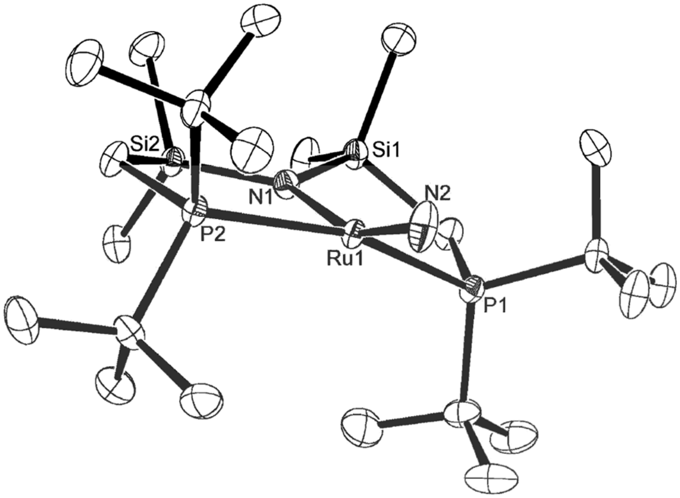
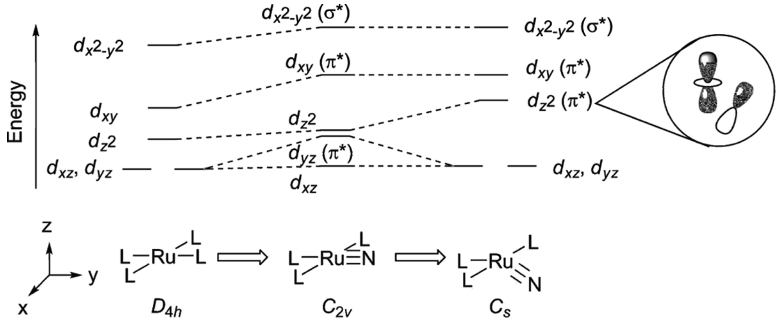


Figure 5. X-ray crystal structure of compound **10** reprinted with permission from reference 152. Copyright 2005 American Chemical Society.

The molecular distortion in this compound and its ability to house four *d* electrons may be rationalized through molecular orbital analysis. Shown in the left-hand side of Scheme 14 is the typical MO splitting for the valence *d* orbitals of a square planar complex as derived from simple ligand field theory. In changing one of the four ligands in a square planar complex to a nitride (N^{3-}), resulting in a change to C_{2v} symmetry, a strong σ interaction destabilizes the $d_{x^2-y^2}$ orbital, and the d_{xy} and d_{yz} orbitals are destabilized by π interactions. The C_{2v} orbital diagram (center of Scheme 14) is not compatible with a d^4 electron count for two reasons: (1)



Scheme 14. Molecular orbital analysis of **10**.

this would necessitate adding electrons to the d_{yz} π^* orbital, weakening the Ru≡N bond; and (2) the singlet state would be orbitally degenerate, or very nearly so, leading to a Jahn-Teller state that would be prone to distortion. Relaxing the molecular geometry to C_s symmetry by bending the Ru≡N bond obviates these problems: instead of having a destabilizing π interaction with the d_{yz} orbital, now the N p_y orbital may overlap with the Ru d_{z^2} yielding the π interaction shown in the far right of Scheme 14. This leaves two non-bonding orbitals, the d_{xz} and d_{yz} low in energy to house the four valence d electrons.

Because of the open coordination sites in **10**, the complex is able to react with small molecules such as NO and N_2O. Interestingly, both reactions yield the same (PNP)RuNO nitrosyl complex.[155] Attempts to form the analogous (PNP)FeN complex have led to the isolation of a complex in which the N atom has inserted into one of the Fe–P bonds, yielding a new P=N–Fe connectivity.[156] The strategy of using lower coordination numbers to synthesize metal-ligand multiply bonded compounds with high *d* electron counts has proven to be a very fruitful area of study, and has recently resulted in the synthesis of a (PCP)Pt(IV)-oxo complex that is structurally analogous to **10**, but has six valence electrons.[157]

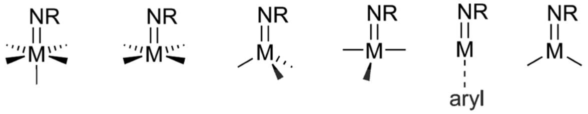
IMIDO COMPOUNDS

In principle, an M=N–R complex can have the same bonding characteristics of the corresponding nitrido species, with the formation of one σ and two π bonds. However, this analysis assumes an M–N–R angle of 180°, which is not always true. Bent M=N–R species are especially more common with electron-rich late transition metals, and will only be able to have one σ and one π bond. However, it should be mentioned here that the energy required to change the M=N–R angle to and from linearity is often very small. It should also be noted that in some cases the M=NR bond order can approach a value of three, prompting an M=NR description. For simplicity, the structures of all imido compounds as having an M=NR structure have been illustrated, even though this may not been appropriate bonding description in every case.

The polarities of both the σ and π bonds are important factors that govern reactivity,[14] though in general the late metal imido species are electrophilic. Indeed, in some cases the bent M=NR species are so electrophilic that they are considered to consist of a nitrene coordinated to a metal. The difference between an imido species and a metal nitrene complex is that of the formal oxidation state of the metal atom. An imido species suggests the combination of (M^{2+}) with (NR^{2-}) whereas a metal nitrene complex represents neutral NR coordinated to M. Only recently has the intermediate case where an $(NR)^{\bullet -}$ radical is coordinated to M^+ been postulated by Wieghardt.[158] Given these possibilities, there are many possible interpretations for the electronic structures of M=NR complexes, which will need to be examined on a case-by-case basis. Presented here is a general overview of the electronic structures that have been found to be useful in describing the reactivity of classes of compounds. Specifically, the classes of imido compounds we will discuss are those whose structures are given in Scheme 15.

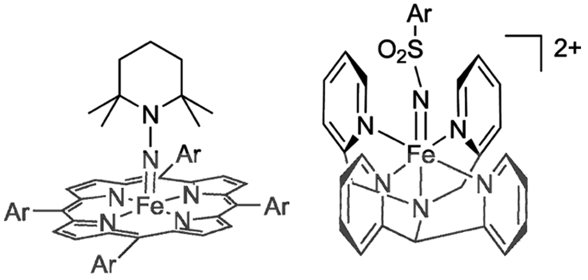
Iron-porphyrin species with structure **V** or **VI** are proposed intermediates in nitrene insertions into C–H bonds catalyzed by Cytochromes P450.[6,159,160] Significant early efforts were therefore made to isolate such a species,[161–164] leading to the isolation of one species that was characterized by crystallography:[164] compound **11** (Scheme 16). The Fe=N–N group in **11** is linear with an Fe=N distance of 1.81 Å, and Mössbauer parameters for the complex suggest a high-spin Fe(II) ground state ($S = 2$).[163] The properties and electronic structure of this compound are inconsistent with true imido compounds as described below; it is likely that significant N—Nπ bonding in the hydrazido ligand stabilizes this ligand and minmizes the effects of F_e=N multiple bonding.

In contrast, Que has recently synthesized a non-heme Fe=NR complex stabilized by a tetrapyridyl amine ligand, **12**, that has Mössbauer parameters indicative of an Fe(IV) species.[165] Though **12** was not isolated in crystalline form, the Fe=N distance was resolved by EXAFS analysis and found to be 1.73 Å, considerably shorter than in **11**. The structure of **12** was calculated using DFT methods, and the computed geometry and spectroscopic properties were found to be in good agreement with those observed experimentally. The computed Fe=N–S angle of 160° is not quite linear; nevertheless, the electronic structure is described as having a $(d_{xy})^2(d_{xz}, d_{yz})^2$ ground state ($S = 1$).[165]



V **VI** **VII** **VIII** **IX** **X**

Scheme 15. Structures of imido compounds.



11 **12**

Scheme 16. Structures of **11** and **12**.

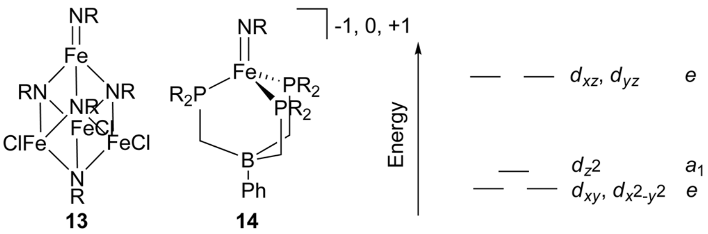
Other Fe-imido/nitrene complexes of types **V** or **VI** have been identified in gas-phase reactions,[166,167] and in iron-catalyzed organic reactions.[168–171] No concrete structural data on these species have yet been presented, nor for a proposed Fe-imido species with trigonal bipyramidal geometry.[172] Ruthenium imido/nitrene complexes with structure types **V** or **VI** have also been proposed in several instances but not isolated.[173–178]

Osmium imido species with structure **V** have been prepared from the corresponding Os(VI)-nitrido species; an example with Os in each of the three oxidation states Os(IV), Os(V), and Os(VI) is known. The Os(IV) complex, [(tpy)(bpy)Os=N−NEt$_2$]$^{2+}$, has been characterized by X-ray crystallography.[179] An Os=N distance of 1.89 Å and an Os=N−N angle of 137° were observed.[179] Thaking these observations together with the observed diamagnetism of the compound suggests an electronic structure with only one Os−N π bond. One-electron reduction of (Tp)Os(Cl)$_2$N, **6**, in acidic conditions produces the Os(V)-imido species (Tp)Os(Cl)$_2$ NH.[180] This compound, which is presumably paramagnetic, has an Os=N distance of 1.75 Å, shorter than in the Os(IV) case due to additional Os=N π interactions that can take place. Compound **6** also undergoes a reaction with phenyl-magnesium bromide producing the postulated Os(VI) species [(Tp)Os(Cl)$_2$NPh]$^-$, though, due to its rapid reaction with water, the complex was not isolated and characterized.[181] Other Os compounds that have been prepared include OsF$_5$(NCl),[182] in addition to several organometallic compounds.[183–186]

Pseudotetrahedral imido complexes (**VII**), have been known since 1959, when Milas and Iliopulos discovered that the Os=O groups in OsO$_4$ could be exchanged for Os=NR groups.[187] The use of OsO$_3$(NR) compounds in amino-hydroxylation of alkenes was pioneered by Sharpless.[188–190] As is the case in the OsO_3N^- anion, the Os=E bonds in OsO_3NR compounds are not equivalent: the Os=N bond shows more triple-bond character than do the Os=O bonds, as evidenced by shorter Os=N bond lengths.[191] This trend is also visible in Os(VI)-oxo-imido compounds.[186,192]

Recently, several new examples of pseudotetrahedral iron imido compounds have been reported. Two types of compouds, one with an $Fe_4(NR)_4$ cubane core (**13**, Scheme 17),[193] and another in which the Fe center is supported by a chelating phosphine ligand (**14**),[194,195] are known. Whereas the former complex is known in the valence-trapped $[Fe(III)]_3/Fe(IV)$ state (with the Fe=NR species presumably being the Fe(IV) site),[193] **14** has been isolated by Peters in three different oxidation states, Fe(II), Fe(III), and Fe(IV).[194,196–198] Reactivity of these compounds with hydrogen[199] and analysis of their vibrational spectra[200] have been investigated. Smith has isolated the chelating carbene analog of **14** in both the Fe(III) and Fe(IV) states and determined the rate constant for electron transfer between the two, which is large ($\sim$ 107 M-1 s-1), consistent with the lack of structural reorganization between the Fe(III) and Fe(IV) states.[195] The electron transfer energy barrier, along with an estimated pK_a of the corresponding Fe(III) amido compound, were used to determine the thermodynamic driving force to hydrogen atom abstraction of the Fe(IV) imido complex.[195]

The electronic structure of the $[\mathbf{14}]^-/\mathbf{14}/[\mathbf{14}]^+$ electron transfer series may be understood in terms of the orbital splitting diagram shown to the right in Scheme 17.[194,196–198]> The d^6 Fe(II) species $[\mathbf{14}]^-$ is diamagnetic, its six electrons filling the δ-type d_{xy} and $d_{x^2-y^2}$ orbitals and the σ-type d_{z^2} orbital.[197] Interestingly, calculations have shown that the d_{z^2} orbital in these complexes is very low in energy, and as in the case of the nitrido complexes described above, is essentially *non-bonding* with, respect to the NR group. The Fe(III) species is again low-spin, having one unpaired electron in the



Scheme 17. Pseudotetrahedral iron imido compounds, with a qualitative molecular orbital diagram.

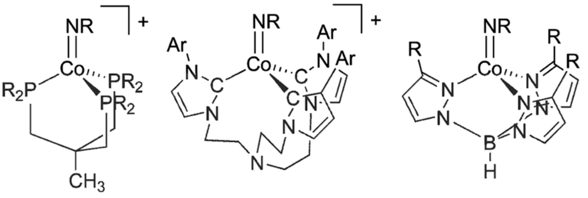
a_1 orbital,[194] and the Fe(IV) complex has an $S = 1$ ground state. The ground state is a ^{3}E state derived from a $(e)^3(a_1)^1$ electronic configuration. This Jahn-Teller active state has been stabilized experimentally by making one phosphine arm of the supporting ligand different from the other two.[198] The Fe=N bond distances in the Fe(II), Fe(III), and Fe(IV) compounds are all roughly 1.64 Å, in agreement with the non-bonding character of the orbitals involved in the redox processes.

The electronic structure of the Fe(III)/Fe(IV) imido species have been recently investigated computationally by Ghosh.[201] Geometry optimization of simple models for species such as **14** has shown that there is an electronic preference for a bent Fe=N−R geometry. This bending results from a pseudo-Jahn-Teller distortion derived from the near degeneracy of the e and a_1 orbitals. It is suggested that this distortion is not observed experimentally due to steric encumbrance of the imido substituent and the supporting ligand.[201] The unusually stable d_{z^2} orbital was also examined, and it was found that significant Fe $3d_{z^2}/4p_z$ orbital mixing mitigates the σ^* character of this orbital by enlarging the bottom lobe of the d_{z^2} orbital as well as the "donut", which actually becomes large enough to have a bonding interaction with the σ lone pair of the imido N atom.[201]

Pseudotetrahedral Co=NR compounds are also known, which represent the first well-characterized metal-ligand multiply bonded compounds to the right of the oxo wall that we shall discuss. Notably, a cobalt complex with structure **V** or **VI** is expected to be unstable because of the population of Co−N antibonding orbitals, though such species have been suggested as intermediates in photochemical reactions[202] or cobalt-catalyzed organic reactions.[203,204] By changing the geometry of the complex from **V** or **VI** to **VII**, more orbitals become available to hold electrons in these compounds, and electrons that would have occupied antibonding orbitals in the case of **V** or **VI** may occupy non-bonding orbitals in **VII**.

On a historical note, it should be mentioned that the use of lower coordination numbers to stabilize structurally characterized metal-ligand multiply bonded compounds to the right of the oxo wall was first demonstrated with the synthesis of trimesityl-oxo-iridium[205] and Cp$*$Ir=NR complexes (structure type **IX**).[206–208] Subsequently, other examples of d^6 imido compounds of type **IX** were discovered: (arene)M=NR species with M=Ru or Os.[209–213]

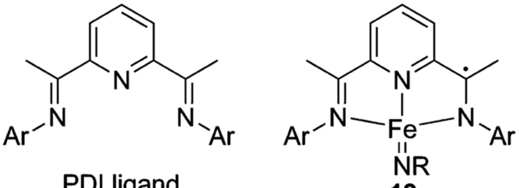
Three main ligand classes have been used to stabilize Co compounds of type **VII**: chelating phosphine ligands,[196,214,215] chelating *N*-heterocyclic carbene ligands,[216,217] and tris-pyrazolyl borate ligands



Scheme 18. Pseudotetrahedral cobalt imido compounds.

(Scheme 18).[218,219] In the case of the phosphine and carbene complexes, the diamagnetic d^6 Co(III) species are stable, which have an $(e)^4(a_1)^2$ ground state. In contrast, **17** has an $S=1$ ground state,[218,219] in agreement with the expected lesser ligand field strength of the supporting *N*-donor ligand.[220]

Another four-coordinate Fe=NR complex, **18**, is known that has geometry **VIII**. This geometry is enforced by a pyridine-di-imine (PDI) ligand as shown in Scheme 19.[221] The distortion of this complex away from square planar geometry likely occurs for the same reasons discussed above for **10**. Magnetic susceptibility and Mössbauer spectroscopy data suggest that **18** contains an Fe(III) ion instead of Fe(II), which requires that the PDI ligand be reduced to its radical anionic form.[221] This results in a $(d_{xz}, d_{yz})^3(d_{z^2})^1(d_{xy})^1$ electronic configuration for the Fe atom and thus an Fe=N bond order of two. The lower Fe=N bond order is reflected in the longer Fe=N bond distance, ~1.71 Å, observed for **18**, as compared to the pseudotetrahedral **14**. It should be mentioned that attempts to synthesize a Co(III)-imido species with geometry **VIII** have been made using a (PNP)Co cobalt(I) source. An imido intermediate was not isolated, but was postulated due to the observation of insertion of an NR group into one of the Co–P bonds.[222]



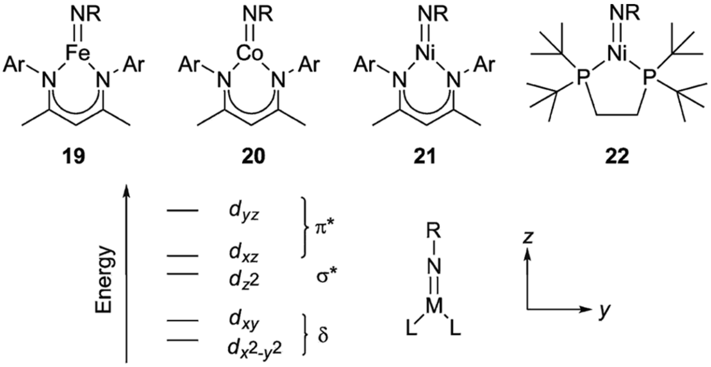
Scheme 19. Structure of 18.

The recent development of a number of bulky bidentate ligands has allowed successful syntheses of a number of new M=NR compounds having geometry X that span nearly the entire set of late first-row transition metals. As seen in Scheme 20, the majority of these new compounds have been made using bulky β-diketiminate ligands. The splitting of the d orbitals in C_{2v} symmetry is also shown in Scheme 20; this diagram reflects the inclusion of the NR group as a strong π donor as explained nicely by Holland in a recent review.[223] As in the case of the pseudotetrahedral compounds described above, the σ^* character of the d_{z^2} orbital is somewhat muted and this orbital is fairly low in energy.[224]

Although it has not been structurally characterized, spectroscopic evidence corroborated by DFT calculations supporting the preparation of **19** has been reported by Holland.[225] This compound shows a rhombic EPR spectrum consistent with an $S = 3/2$ ground state for the molecule, which is rationalized by the proposed $(d_{x^2-y^2}, d_{xy})^3(d_{z^2}, d_{xz})^2$ electron configuration, and an overall formal Fe=N bond order of two.[225]

Compound **20** has been characterized by X-ray crystallography by Warren and features a fairly short Co=N bond distance of 1.62 Å, shorter than the ~1.65 Å distances observed in pseudotetrahedral Co=NR species described above.[226] The shortness of this Co=N bond may be attributed to the lower coordination number in **20** as well as similar bonding characteristics. Like most of the pseudotetrahedral compounds, **20** is diamagnetic with the three non-bonding d orbitals filled.

Three-coordinate Ni-imido compounds have also been prepared. Ni(II) and Ni(III) species are known, with the metal oxidation state



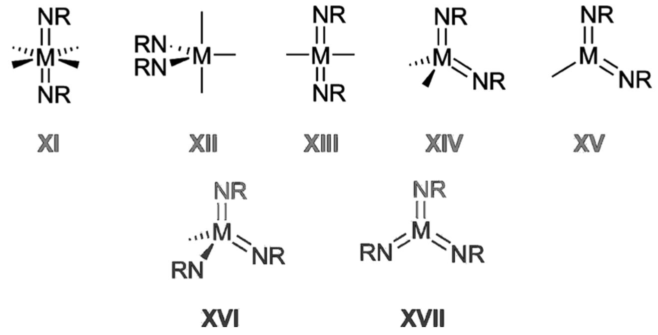
Scheme 20. Geometry and molecular orbital diagram for **19–22**.

depending highly on the nature of the bidentate ligand used. The Ni(III) β-diketiminato complex **21** has been prepared and characterized by X-ray crystallography and EPR spectroscopy.[227] The latter technique shows the complex to display rhombic symmetry, as expected, with an $S = 1/2$ ground state and significant hyperfine coupling of the unpaired electron to the ^{14}N nucleus of the imido group.[227] This result is rationalized by the placement of the unpaired electron into the π^* d_{xz} orbital, which also explains the longer Ni=N bond distance (1.66 Å) as compared to the analogous distance in **20**.[227]

Compound **22** is an analog of Pd and Pt imido complexes that were proposed by Stone in 1970.[228] Though Stone's complexes have never been structurally characterized, Hillhouse has reported the crystal structure of the Ni analog,[229] and has also reported a study of its formation[230] and reactivity.[231–233] The relationship between **22**, which is diamagnetic, and **21** can be rationalized in terms of the extra electron in **22** being added to the π^* d_{xz} orbital, thus reducing the Ni=N bond order in the compound. This view is consistent with the structural result that the Ni=N bond distance in **22**, 1.70 Å, is ~0.04 Å longer than that in **21**.

DI- AND TRI-IMIDO COMPOUNDS

Di- and tri-imido complexes are not as numerous as mono-imido species, and have been studied to a lesser degree. This is most likely due to a dearth of examples where such species play an important role in catalytic reactivity. Nevertheless, these compounds have interesting structural features, as seen in Scheme 21. In general, these compounds are known only for metals of the second or third transition series, though the first



Scheme 21. Structures of di- and tri-imido compounds.

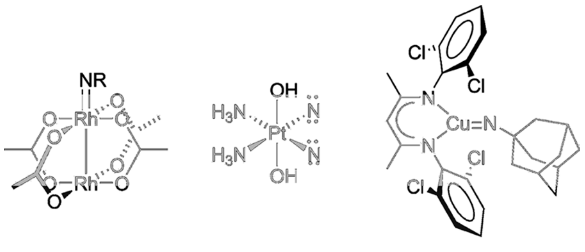
example of a di-imido iron complex (**XV**) has been recently reported by Power.[234]

In contrast to the isoelectronic oxo ligand, the maximum number of terminal imido groups that has to date been found around a single metal center is three. Thus, the tetraimido analog of OsO_4 is unknown, though all of the other $OsO_x(NR)_{4-x}$ and related compounds are known, with structures **VII**, **XIV**, and **XVI**.[186,192,235,236] Some of these compounds have seen recent use in functionalization of organic molecules.[237,238] The only homoleptic tris-imido osmium compound is also known (**XVII**), which is an Os(VI) complex that is diamagnetic with its two d electrons paired in the d_{z^2} orbital.[239] The diamagnetic *trans*-square planar complexes of Ru(IV) and Os(IV) are also known (**XIII**),[239,240] but a full investigation of their electronic structure was never made.

By far the most well-known and useful di-imido complexes are the octahedral *trans*-di-imido Ru(VI) species, mainly supported by porphyrin-type ligands, which have been extensively studied by Che.[241–243] Although Os analogs are known,[241,244–247] the Ru di-imido complexes have been found to catalyze a number of organic reactions, including olefin aziridination and NR insertion into C−H bonds.[248–251] In analogy to the well-known *trans*-dioxo-Ru(VI) complexes, a $(d_{xy})^2$ ground state is expected for these di-imido compounds.

THE FRONTIER: SPECIES THAT HAVE BEEN PROPOSED, BUT NOT ISOLATED

Scheme 22 shows a few specific examples of species that have been postulated but not yet isolated and characterized. As mentioned earlier, Breslow and Gellman recognized early on that $Rh_2(OAc)_4$ serves as an



XVIII **XIX** **XX**

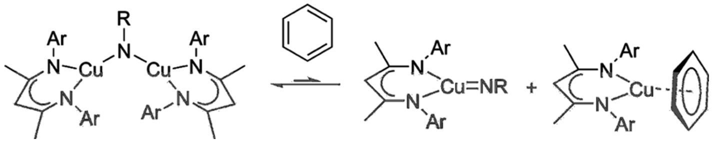
Scheme 22. Proposed structures of **XVIII**, **XIX**, and **XX**.

excellent catalyst for nitrene insertion into C–H bonds.[6] This chemistry has since been greatly expanded to include many different dirhodium carboxylates as catalysts.[51,252–255] Regardless of the specific catalyst used, however, a nitrenoid species such as **XVIII** is invariably invoked as being the key reactive intermediate in the catalytic cycle.[51,252] Although such a species has never been isolated, recently we have reported a metal-metal bonded nitrido complex with a related linear Ru–Ru≡N structure;[50] this compound is the closest structural analog to **XVIII** that has yet been prepared.

Coordinated nitrenoid intermediates of unspecified geometry have also been proposed in amidation reactions catalyzed by palladium(II) acetate,[256] and in the reduction of organo-nitrogen compounds by palladium clusters.[257] The unusual species **XIX**, which features coordination of two nitrene-like nitrogen mono-anions (N^-) to platinum, has been proposed based on nitrene trapping studies with dimethyl sulfide.[258] Binding of nitrenes to platinum electrode surfaces has been proposed in electrochemical olefin aziridination reactions.[259,260] A (diphosphine)Ni$(N_3)_2$ complex is proposed to form a nitrene-type intermediate upon photolysis that has been shown to react with CO and hydrocarbons.[261]

The coinage metals, Cu, Ag, and Au, have also been shown to promote reactions involving nitrenes.[262] Copper has been the most extensively studied of these metals.[263–268] In 1967, copper(I) sources were shown to catalyze the decomposition of benzenesulfonyl azide through a suggested copper-nitrene complex,[269] and copper complexes were shown in 1995 to catalyze olefin aziridination via a putative (di-imine)Cu=NR intermediate.[270] Such nitrene complexes have remained elusive, though recent work from the Warren lab has provided strong evidence for a terminal nitrene species such as **XX**, described below.[271,272]

Warren has reported the synthesis of an interesting class of di-imine ligated dicopper nitrene/imido complexes through the reaction of (di-imine)Cu(arene) complexes with organic azides.[271] The resulting dicopper complexes contain a single nitrene or imido group that bridges the two Cu ions, as shown in Scheme 23. The oxidation state of the copper atoms, and hence the nitrene/imido moiety, is not yet clear. Thus, the complexes may be described as containing two Cu(I) ions with a bridging nitrene, or two Cu(II) ions with a bridging imido group. Either formulation would be consistent with the observed diamagnetic ground state, though the Cu(II) formulation would necessitate very strong antiferromagnetic coupling between the Cu(II) ions.



Scheme 23. Equilibrium formation of a putative copper imido complex.

A dissociation equilibrium, which would form a terminal nitrene/imido species, has been proposed for these compounds (Scheme 23).[271] This equilibrium is proposed to be heavily reactant-favored, which has precluded isolation and characterization of the terminal nitrenoid species. This equilibrium is, however, supported by two important experimental observations: (1) formation of unsymmetrical dicopper species is observed when a Cu-arene complex ligated by a different di-imine is added to a solution of the original dimer;[271] (2) increasing the steric bulk of the nitrenoid NR group causes reaction mixtures to become more unstable.[272]

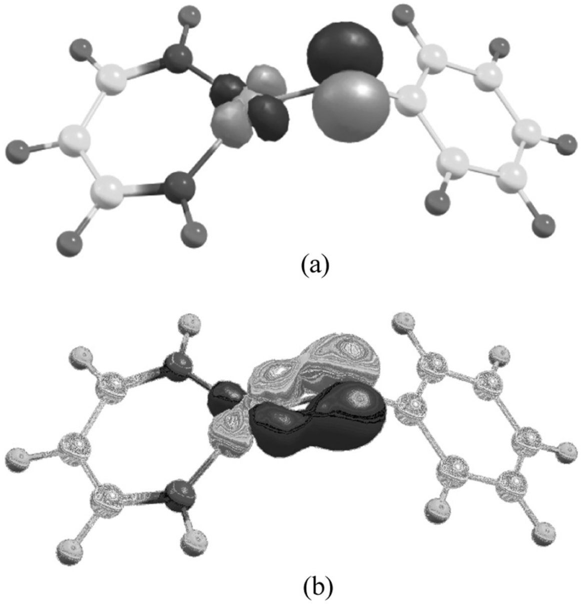


Figure 6. Plot of the CASSCF calculated, partially occupied Cu–N π (b) and π^* (a) orbitals for the model (di-imine)Cu=NPh species. Reproduced with permission from reference 272. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

The electronic structure of the suggested (di-imine)Cu-nitrenoid intermediate has been investigated by several groups.[224,273,274] Whereas DFT calculations suggest a triplet ground state for the nitrenoid species,[224,273] more sophisticated CASSCF methods suggest a singlet ground state with a bent Cu–N–C angle of 132° and substantial *N*-radical character.[274] The radical character stems from the observation of two partially occupied orbitals: the Cu(d_{xy})–N(p_x) π and π^* combinations, which are shown in Figure 6. The computed natural orbital occupation numbers of the π and π^* combinations were 1.5 and 0.5, respectively,[274] which suggest an electronic structure for the complex that falls between the two extreme descriptions as either a Cu(I)–nitrene species or a Cu(II)–NR$^\bullet$ species.

A terminal nitrenoid intermediate has been implicated in silver-catalyzed nitrene transfer reactions.[275,276] By analogy to the copper species described above, the Ag=NR unit is proposed to behave as a diradical; this mechanistic proposal is supported by the fact that the silver-catalyzed alkane functionalization process is selective for tertiary C–H bonds over secondary or primary ones.[276] Gold compounds have been shown to catalyze nitrene insertion reactions into weak C–H bonds as well, though no terminal gold-nitrenoid intermediates have been proposed.[277]

CONCLUSION

The preparation, isolation, and characterization of new types of reactive and unstable compounds will always define one of the frontiers of synthetic inorganic chemistry. In the case of late transition metal nitrido and imido compounds, this frontier has a strong intersection and synergy with ongoing efforts in synthetic organic chemistry, as new methods for adding nitrogen functionality to unfunctionalized organic substrates continue to be developed. Understanding the electronic structure of these metal-ligand multiply bonded compounds is therefore of interest to both the synthetic inorganic as well as the synthetic organic community, as it serves as a guide in making new types of transition metal compounds, and understanding how they react with substrates. This review is meant to give a clear picture of both the state of the art, as well as a look toward potential future synthetic endeavors.

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