π-Bonding and Reactivity in Transition Metal Nitrosyl Complexes, Part 7[+]

Effects of π-Bonding on Stability and Reactivity in [CpCr(NO)] Complexes

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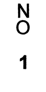
Abstract: Recent synthetic and theoretical investigations of organometallic compounds containing the CpCr(NO) fragment have shown an interdependence of the electronic nature of ancillary ligands and the stability of a given Cr oxidation state. Understanding the correlation between ligand π-bonding properties and the nature of the metal-based frontier orbitals permits the rationalization of observed reactivity patterns, and the identification and preparation of new classes of target molecules.

Keywords: chromium · ligand effects · nitrosyl complexes · pi-interactions · redox chemistry

Introduction

During the 1950s, an enormous synthetic effort by Fischer and Wilkinson laid the foundation for modern organotransition metal chemistry. This torrent of discovery sprang from and was directed by the empirical observation that stable organometallic compounds result from the combination of a low-valent metal, a strongly π-accepting ligand set, and a total valence-electron count of eighteen. Typical of this class are two prototypal molecules containing the CpCr(NO) fragment, **1** and **2**, prepared by the works of Fischer and Wilkinson, respectively.[1] Accordingly, prototypes **1** and **2**, and a range of substituted derivatives, formally contain chromium in a zero-valent state, have at least one strong π-acceptor ligand in addition to the nitrosyl group, and are electronically saturated.



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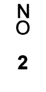

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This “18-electron (18e) rule” was highly useful in identifying reasonable synthetic targets among this emerging class of transition metal compounds—18e compounds tend to be stable.[2] However, this is merely a sufficient condition, not a necessary one—stable compounds need not be 18e. After studying the redox properties and reactivity of species derived from **1** and **2**, we have synthesized a series of nitrosyl complexes of Cr^0, Cr^I, and Cr^{II} with valence-electron counts ranging from 18e to 14e.[3] These species are at the interface between Wilkinson/Fisher-type 18e organometallic compounds and Werner-type, open-shell coordination compounds;[4] their stability depends to a great extent on the π-bonding capabilities of their ancillary ligands. Examination of these complexes by extended Hückel and density functional theoretical techniques has provided a bonding rationale of these trends. As a result of these insights, new types of compounds containing the Cr(NO) moiety have been synthesized.

π-Acceptor and π-Neutral Ligands

Electrochemical oxidation of **1** is irreversible; consistently, chemical oxidation of **1** in MeCN with $[Cp_2Fe]^+$ affords a 17e Cr^I species lacking carbonyl ligands (Scheme 1).[5] The parent carbonyl does not react thermally with MeCN, so these transformations represent a redox-triggered substitution of the strong π-acceptor CO by a σ-donor nitrile. A wide range of similar 17e complexes has now been prepared, including anionic, neutral, and cationic species with amine, phosphine, halide, and alkyl ligands—all groups without strong π-acceptor properties.

Like the 18e complexes discussed above, $[CpCr(NO)(NH_3)_2]^+$ (**3**) is not substitutionally labile in the Cr^I state, but this mode of reactivity can be induced by a redox process. Compound **3** exhibits an irreversible electrochemical reduction, and although **3** is inert under CO atmosphere, treatment with Zn under the same conditions affords dicarbonyl **1**.[5] This

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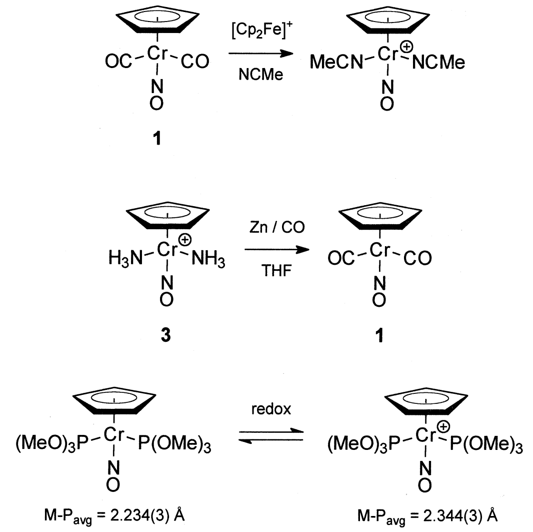


Scheme 1. Redox reactions of Cr^I and Cr^0 complexes.

reaction represents the conceptual reverse of that above, wherein reduction triggers replacement of σ-donor ligands by π-acceptors.

The seemingly general trend represented by [CpCr(NO)] species, namely that compounds with π-acceptor groups are only stable as 18e Cr^0 species while compounds with π-neutral ligands are stable only in the 17e Cr^I state, can be rationalized with a qualitative molecular-orbital diagram based on extended Hückel calculations (Figure 1). The frontier orbitals of all these compounds follow a "two-below-one" pattern, where the two orbitals representing the M–NO π-bonding interaction are lower in energy than another metal-centered orbital, labeled **A**. The latter is orthogonal to the M–NO vector, and is also of π-symmetry. In 18e complexes such as **1**, orbital **A** is a doubly occupied HOMO, whereas in 17e species such as **3**, **A** is singly occupied. Essentially, a stable complex with two electrons in the HOMO requires bonding with strong π-acceptor ligands, both to reduce electron density at the metal and lower the energy of orbital **A**. One-electron oxidation of such a Cr^0 compound therefore involves partial depopulation of a strongly bonding orbital, destabilizing the complex generally and weakening the π-acceptor bond in particular—the oxidation is therefore irreversible because the π-acceptor ligands will be lost. On the other hand, for a complex without such π-interactions, orbital **A** is nonbonding. A half-filled nonbonding orbital does not represent a destabilization and the Cr^I form is stable in that case. However, a nonbonding HOMO is also localized entirely on the metal, such that one-electron reduction of a Cr^I species forces additional electron density on a metal center without ligands of sufficient electron-withdrawing character—thus the reduction is also irreversible, resulting in loss of the strong σ-donor, π-neutral groups.[5]

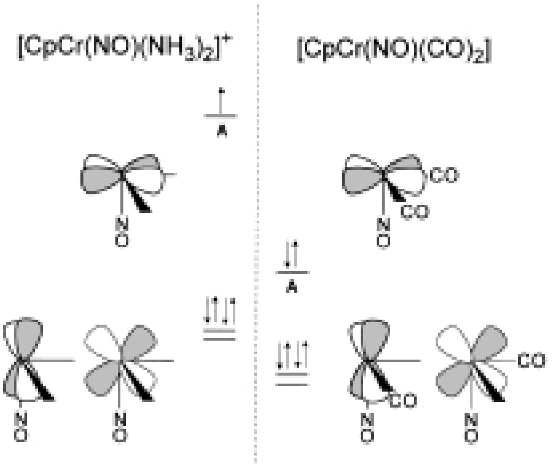
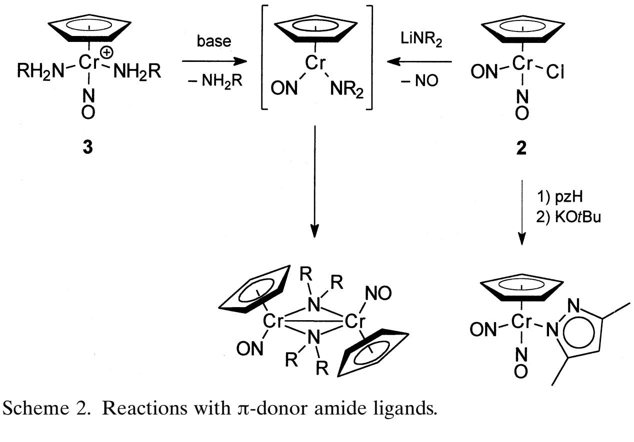


Figure 1. Frontier orbitals, energies, and occupancies of **1** and **3**.

Such an argument suggests a ligand with both good σ-donor and π-acceptor properties should support the CpCr(NO) fragment in both oxidation states, although no such complex had been previously prepared. The synthesis and structural characterization of both d^5 17e and d^6 18e $[CpCr(NO)\{P(OMe)_3\}_2]^{+/0}$ species (Scheme 1)[5] reveals that the only significant difference between the structures involves the phosphite ligands. The reduced Cr^0 form has Cr–P bonds shorter by about 0.11 Å, and P–O bonds longer by about 0.03 Å. As well, the O-P-O angles of the phosphite ligands contract upon reduction, by an average of 5.0°. All these structural distortions are consistent with increased π-bonding to the phosphite ligands in the lower oxidation state.[6]

π-Donors with Cr^0 and Cr^I

The conclusion drawn from the previous section is that Cr^0 complexes of [CpCr(NO)] require π-acceptor ligands to be stable, while Cr^I complexes require π-neutral groups. Consistently, reactions that generate *π-donor* ligands in either of these oxidation states result in unstable compounds. For example, deprotonation of Cr^I $[CpCr(NO)(NH_2R)_2]^+$ species affords dimeric $[CpCr(NO)(\mu\text{-}NHR)]_2$ complexes, and not monomeric amido compounds.[7] Similar bridging amide complexes had been previously isolated from the treatment of dinitrosyl **2** with lithium amide reagents.[8] A possible common intermediate to both reactions may be an unsaturated d^5 $[CpCr(NO)(NR_2)]$ complex, resulting from the loss of amine from Cr^I or NO from Cr^0, the latter dissociation effecting the one-electron oxidation of Cr (Scheme 2).



Scheme 2. Reactions with π-donor amide ligands.

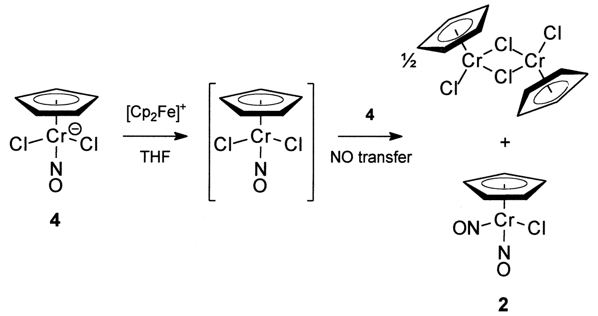
In each case, introduction of a π-donor lone pair on the ligand nitrogen atom induces the dissociation of another ligand. A rationale for this result follows readily from the above orbital analysis. For both of the proposed [CpCr(NO)(NH$_2$R)(NHR)] and [CpCr(NO)$_2$(NR$_2$)] intermediates, occupied orbital **A** cannot accept amide π-donation. The resulting filled–filled (or -half filled) repulsion leads to two effects that promote ligand dissociation: destabilization of the ground-state due to the population of an orbital antibonding to the π-donor, and stabilization of the ligand-loss transition-state because reduction of the coordination number creates a vacant orbital, allowing formation of a favorable π-bond with the amide.[9]

Whereas Cr^0 requires its two-electron HOMO to be low-energy and bonding, and Cr^I its one-electron HOMO nonbonding, a π-donor group will render either orbital high in energy and antibonding, resulting in an unstable complex. This can be avoided if the electron density on the π-donor ligand can be reduced, as illustrated by the stability of [CpCr(NO)$_2$(N$_2$C$_3$Me$_2$)] where the filled orbital on the coordinated N is attenuated via delocalization onto the aromatic ring of the pyrazolyl ligand (Scheme 2).[10]

Oxidation of Cr^I

Another possible solution to the above problem is to remove *both* electrons from orbital **A**—adopt a d^4 Cr^{II} configuration with a vacant metal orbital available for π-donation. Indeed, two compounds fitting this description had been previously reported, namely [CpCr(NO)(NPh$_2$)I][11] and [Cp*Cr(NO)(O*i*Pr)$_2$].[12] Both complexes were prepared unexpectedly from Cr^0 dinitrosyl compounds, but the reactions were neither general nor easily rationalized. An alternative synthetic route to Cr^{II} amides would be the oxidation of a suitable Cr^I halide precursor, followed by metathesis of the halide for amide.

To this end, we prepared the Cr^I dihalide [CpCr(NO)Cl$_2$]$^-$ (**4**) and studied its electrochemical and chemical oxidation chemistry.[13] Just as with reduction of our Cr^I cations, the oxidation of this Cr^I anion proves to be irreversible. Complete consumption of dichloride **4** requires only one-half equivalent of [Cp$_2$Fe]$^+$, and affords Cr^{III} [{CpCrCl$_2$}$_2$] and Cr^0 dinitrosyl **2**—a formal disproportionation resulting from transfer of a NO ligand. A possible mechanism for this reaction is shown in Scheme 3.



Scheme 3. Oxidation of **4**.

The most interesting feature of this reaction is that oxidation of the Cr^I species results in loss of NO from the presumed Cr^{II} [CpCr(NO)Cl$_2$] intermediate, yielding the observed Cr^{III} dimeric complex. Transfer of the NO to unconverted **4** then gives formal reduction of the d^5 dihalide compound, affording d^6 **2** after chloride loss. The loss of NO in this reaction is surprising. The redox-induced ligand substitution reactions discussed above always preserve the [CpCr(NO)] fragment, and the oxidation of Cr^I involves removal of the single electron from the orbital not engaged in NO bonding—so why is the NO bond affected? A possible rationale is a spin-state change—oxidation to Cr^{II} makes orbital **A** a low-lying LUMO, such that the complex may then adopt a triplet ground state (Figure 2). Such a configuration promotes an electron out of the NO bonding framework, weakening the Cr–NO bond. To evaluate this possibility, we undertook a study of this reaction using density functional theory (DFT).

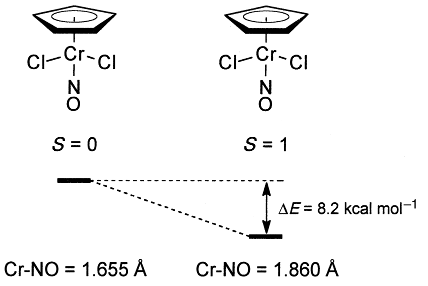


Figure 2. Relative energies of singlet and triplet [CpCr(NO)Cl$_2$].

DFT energies of the singlet and triplet spin states for [CpCr(NO)Cl$_2$] are depicted in Figure 2.[14] As expected, the triplet form of this molecule is calculated to be 8.20 kcal mol^{-1} below the excited singlet state. The only major structural difference between the two optimized geometries is a dramatic elongation of the Cr–NO bond in the triplet structure (1.860 Å vs. 1.655 Å), signaling a critical weakening of the Cr–NO bond in the triplet state. Thus, the ground-state triplet configuration of the transient Cr^{II} [CpCr(NO)Cl$_2$] leads to a labilization of the nitrosyl, consistent with the observed oxidation products. Presumably, a complex with a singlet ground state would avoid this decomposition pathway.

This hypothesis is consistent with the known Cr^{II} [CpCr(NO)] complexes, which have π-donor ligands. The effect of amide π-donation is illustrated in Figure 3, which compares the orbital energies of [CpCr(NO)Cl$_2$] and the hypothetical [CpCr(NO)(NH$_2$)Cl]. The LUMO becomes the antibonding combination of the amide π-bond—an unfavorable interaction for Cr^I or Cr^0, but one that serves to increase the HOMO–LUMO gap in Cr^{II}. The result is a stabilization of the relative energy of the singlet configuration: although singlet [CpCr(NO)(NH$_2$)Cl] is still calculated to be the excited state, it is within 0.95 kcal mol^{-1} of the triplet state. Further stabilization is conferred by alkyl groups: [CpCr(NO)Me$_2$] and [CpCr(NO)(NH$_2$)(Me)] are both calculated to have singlet ground states.[14]

Thus, a π-donor ligand and the Cr^{II} state appear to be mutually dependent. In a lower oxidation state a π-donor

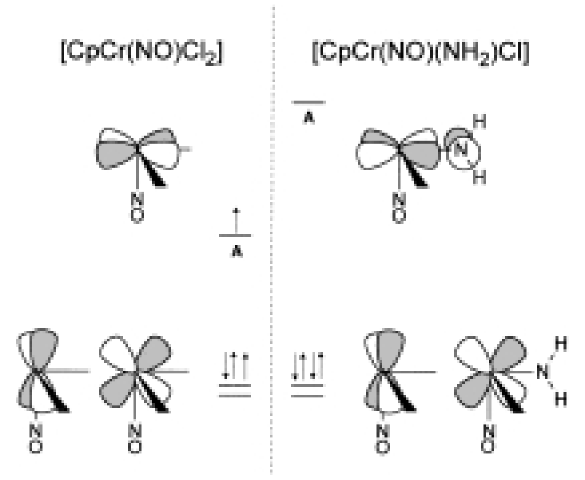
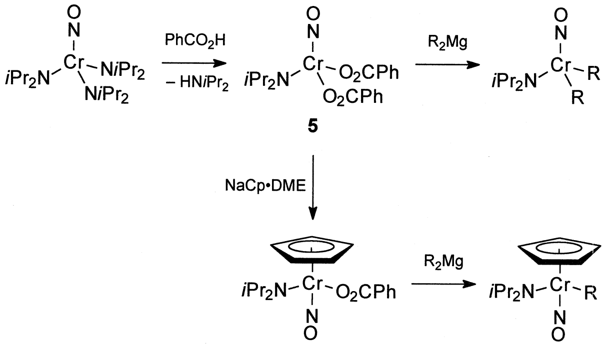


Figure 3. Frontier orbitals, energies, and occupancies of [CpCr(NO)(X)Cl], X = Cl, NH_2.

ligand must overlap with a filled or half-filled orbital, destabilizing the complex and resulting in decomposition by ligand dissociation. In contrast, the orbital is available to form a π-bond for Cr^{II}, increasing the HOMO–LUMO gap. Without this stabilizing interaction, the complex is prone to adopt a triplet configuration, resulting in depopulation of Cr–NO orbitals and consequent labilization of NO.[15]

π-Donors with Cr^{II}

The above argument suggests that Cr^{II} amide complexes of [CpCr(NO)] should be stable molecules. Because attempts to prepare them from lower valent mononitrosyl compounds were unsuccessful, we chose to employ a precursor already containing the Cr^{II} [Cr(NO)(NR_2)] fragment. A simple reaction with [Cr(NO)(N*i*Pr_2)$_3$][16] yields [Cr(NO)(N*i*Pr)(O_2CPh)$_2$] (**5**) (Scheme 4), a precursor for complexes



Scheme 4. Synthesis of organometallic Cr^{II} nitrosyl amides.

such as [CpCr(NO)(N*i*Pr_2)CH_2SiMe_3].[17] As expected, these amide alkyl complexes have a singlet configuration, and a geometry consistent with strong amide π-donation: a short Cr–N distance and a planar Cr–NR_2 unit aligned coplanar with the Cr–NO vector. This Cr–amide interaction renders the complex effectively saturated, as evidenced by a lack of reactivity with Lewis bases such as CN*t*Bu. Thus, [CpCr(NO)(N*i*Pr_2)CH_2SiMe_3] is best considered to be an 18e complex, albeit of a different type than the d^6 Cr^0 species such as **1** and **2**: the saturation is achieved by the combination of a Cr^{II} oxidation state and the π-donor amide group.

However, **5** is also a precursor to 14e alkyl complexes such as [Cr(NO)(N*i*Pr_2)(CH_2SiMe_3)$_2$], a diamagnetic complex despite its low coordination number and high degree of unsaturation.[17] Although the utility of Cr compounds as reagents for organic synthesis[18] and olefin polymerization[19] has been recognized, their investigation has been hindered by the paramagnetism of mid-valent organochromium compounds.[19] Understanding how unsaturated Cr compounds may be rendered diamagnetic, and therefore more amenable to study by NMR techniques, could have significant repercussions in the development of these applications.

Conclusion

Complexes containing the [CpCr(NO)] fragment can exist in Cr oxidation states ranging from Cr^0 to Cr^{II}, the relative stability of which is determined by a simple property of the ancillary ligands: π-acceptor ligands give stable Cr^0 species, π-neutral ligands afford paramagnetic Cr^I complexes, and π-donor groups yield higher valent Cr^{II} compounds. The stability of the latter compounds with respect to nitrosyl dissociation is determined by the relative energies of singlet and triplet spin states.

The use of advanced computational techniques is required to evaluate the spin-state effects, but a grasp of the frontier orbital structure—and a resultant understanding of the above oxidation-state stability trends—is available with a very simple and qualitative overlap description. These bonding principles not only allow the rational synthesis of stable non-18e complexes, such as highly unsaturated, and diamagnetic, Cr^{II} alkyl complexes, but also unify a continuum of organometallic molecules, ranging from species adhering rigorously to the 18e rule, to higher valent open-shell complexes[4] of reduced electron count.

The growing number of such open-shell species fits neatly into neither of the two traditional classifications of transition metal complexes, namely Werner-style coordination compounds and traditional Fischer/Wilkinson organometallic compounds. As a result, an understanding of the factors that lead to stable compounds of this type requires the use of ideas from both areas: the d^n electron count and spin state considerations of Werner chemistry, and an appreciation of π-bonding and covalent molecular orbitals in organometallic chemistry.

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[1] a) E. O. Fischer, O. Beckert, W. Hafner, O. Stahl, *Z. Naturforsch. B* **1955**, *10*, 598–599; b) T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1956**, *2*, 38–45.

[2] G. Wilkinson, F. A. Cotton, *Prog. Inorg. Chem.* **1959**, *1*, 1–124.

[3] Linear mononitrosyl compounds of Cr^0, Cr^I, and Cr^{II} are more accurately described as having electronic configurations $\{Cr(NO)\}^6$, $\{Cr(NO)\}^5$ and $\{Cr(NO)\}^4$, respectively, using Enemark-Feltham notation.[4a] The NO^+ oxidation state formalism (as opposed to considering the ligand as NO^- or NO radical) is employed without implications for the exact distribution of electron density in the Cr–NO bond.[4b] a) J. H. Enemark, R. D. Feltham, *Coord. Chem. Rev.* **1974**, *13*, 339–406. b) M. Ogasawara, D. Huang, W. E. Streib, J. C. Huffman, N. Gallego-Planas, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 8642–8651.

[4] R. Poli, *Chem. Rev.* **1996**, *96*, 2135–2204.

[5] P. Legzdins, W. S. McNeil, R. J. Batchelor, F. W. B. Einstein, *J. Am. Chem. Soc.* **1995**, *117*, 10521–10530.

[6] A. G. Orpen, N. G. Connelly, *Organometallics* **1990**, *9*, 1206–1210.

[7] W. S. McNeil, Ph. D. Dissertation, University of British Columbia, Vancouver, British Columbia, **1995**.

[8] M. A. Bush, G. A. Sim, *J. Chem. Soc. A* **1970**, 611–616.

[9] K. G. Caulton, *New J. Chem.* **1994**, *18*, 25–41.

[10] P. Legzdins, S. J. Rettig, K. M. Smith, V. Tong, V. G. Young, Jr., *J. Chem. Soc. Dalton Trans.* **1997**, 3269–3276.

[11] G. A. Sim, D. I. Woodhouse, G. R. Knox, *J. Chem. Soc. Dalton Trans.* **1979**, 83–86.

[12] J. L. Hubbard, W. K. McVicar, *Inorg. Chem.* **1992**, *31*, 910–913.

[13] P. Legzdins, W. S. McNeil, S. J. Rettig, K. M. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 3513–3522.

[14] P. Legzdins, W. S. McNeil, K. M. Smith, R. Poli, *Organometallics* **1998**, *17*, 615–622.

[15] Note that from a simple orbital overlap point of view, this result may seem counter-intuitive: a π-donor (and therefore "weak field") ligand is leading to a larger HOMO–LUMO gap and enforcing a low-spin configuration. This result is due to the nature of the orbital splitting in question: not the usually encountered $t_{2g}-e_g$ gap in an octahedral coordination complex, but rather a splitting *within* the "t_{2g}" set of π-symmetry orbitals. Two are lowered in energy by the π-acceptor NO, and one is raised by the π-donor group.

[16] D. C. Bradley, C. W. Newing, *J. Chem. Soc. Chem. Commun.* **1970**, 219–220.

[17] E. W. Jandciu, J. Kuzelka, P. Legzdins, S. J. Rettig, K. M. Smith, *Organometallics* **1999**, *18*, 1994–2004.

[18] a) L. A. Wessjohann, G. Scheid, *Synthesis* **1999**, 1–36; b) A. Fürstner, *Chem. Rev.* **1999**, *99*, 991–1045.

[19] K. H. Theopold, *Eur. J. Inorg. Chem.* **1998**, 15–24.