Reviews

Single Electron Transfer Reactions in the Synthetic Organometallic Chemistry of First-Row Transition Metals

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The discovery of new applications in small-molecule activation, olefin polymerization, and organic synthesis has stimulated interest in well-defined, paramagnetic, first-row transition-metal organometallic compounds. Single-electron-transfer reactions have proved to be a useful tool in the targeted synthesis of such complexes. In this review, several examples from the recent literature are used to illustrate this strategy. The case studies include β-diketiminato complexes of Cr(II) and Cr(III), three-coordinate Ni(II) species, and β-diketiminato complexes of V(III), V(IV), and V(V).

Introduction

The preparation of well-defined yet catalytically active complexes provides an exciting challenge to synthetic organometallic chemists. Once the fundamental structural requirements for catalytic activity have been identified, the steric and electronic properties of the ancillary ligands can be systematically altered to enhance the reactivity profile of the resulting catalyst. Over the past 25 years, organometallic success stories such as stereoselective olefin polymerization and olefin metathesis have relied on this interplay between inorganic synthesis and catalysis.[1,2] Perhaps the most inspiring example of this relationship has been the ongoing development of d^0 catalysts of molybdenum.[3]

By comparison, the synthetic methodology for paramagnetic organometallic complexes of the first-row transition metals is not nearly as advanced. While this may be due in part to the perception that second-row metals are more important catalytically, there are also significant chemical challenges to be overcome. The stability of several adjacent oxidation states effectively precludes reactions based on two-electron oxidative addition and reductive elimination processes, as are seen in the familiar catalytic cycles based on d^{10} and d^8 complexes of palladium[4] or d^6 and d^4 ruthenium species.[5] Instead, disproportionation and/or radical reactivity is often observed, and single electron transfer (SET) reactivity is common.[6] Even within a single oxidation state, multiple spin states are sometimes accessible.[7] Perhaps most significantly, the presence of unpaired electrons renders NMR spectroscopy less useful in characterizing paramagnetic complexes.[8] As a result of these factors, multistep inorganic syntheses involving paramagnetic first-row metals remain relatively uncommon.[9] Much of the published work concerns the preparation of homoleptic species or the use of redox reactions to generate transient 19e or 17e metalloradical species from diamagnetic 18e organometallic precursors.[10]

The potential for paramagnetic organometallic synthesis has brightened in recent years, in part due to technological advancements. The use of CCD detectors has dramatically decreased the minimum crystal size required for single-crystal X-ray diffraction, to the point where X-ray structural determination has become almost mandatory for confirming the identity of all new paramagnetic products. While it remains difficult to definitively characterize paramagnetic complexes by NMR spectroscopy,[8] more researchers are using NMR as a screening technique. Improvements in computer speed and in commercially available computational packages have led to the increased utility of density functional theory to help explain the structure and reactivity of paramagnetic organometallic complexes.[11]

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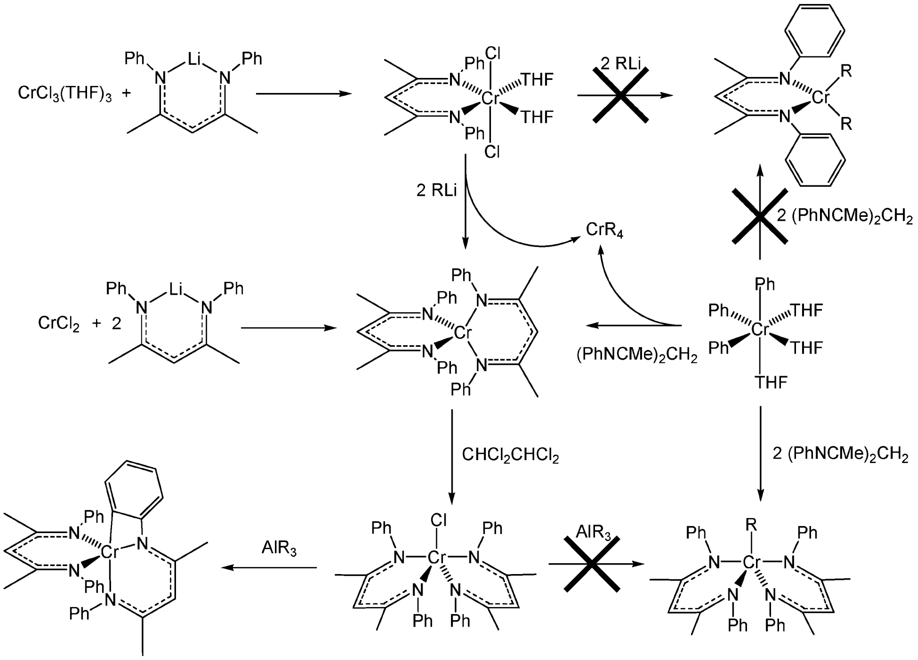
10.1021/om049196s CCC: $30.25

Scheme 1



There have also been significant discoveries of new applications for first-row complexes, either stoichiometrically in small molecule activation reactions[12] or as catalysts for olefin polymerization or organic synthesis.[13] Important developments in ancillary ligand design have resulted from academic and industrial research in these areas: from olefin polymerization, the use of readily modifiable, multidentate, anionic ligands with sufficient steric bulk to maintain a monomeric catalytically active species,[14] and the wide range of chiral ligands developed for asymmetric catalysis for organic synthesis.[15] While computational studies based on the latest density functional theoretical techniques are undeniably a boon to this area of research, it is reassuring to note that often notions of orbital splitting derived from simple ligand field theory (LFT) concepts can both help explain reactivity and identify appropriate target molecules and geometries. In this regard, ligand design is again critical, as constrained multidentate ligands or interligand steric interactions can be arranged in order to reinforce a specific electronically preferred geometry. Perhaps more interestingly, ligand systems have also been designed to disfavor familiar combinations of electronic state and complex geometry, often leading to exciting new reactivity modes for first-row metal complexes.[16]

This review will examine recent examples of targeted synthetic organometallic chemistry of first-row metals, focusing on strategies involving single electron transfer reactions as key steps. Other advanced inorganic synthetic techniques such as amine or alkyl elimination reactions by protonolysis could have also served as a focus, but SET reactivity is especially appropriate, as it makes use of the adjacent stable oxidation states that are a characteristic trait of first-row metal chemistry. Although this reactivity mode is often viewed as a drawback of these systems, the following case studies illustrate how SET oxidation reactions can be harnessed in directed organometallic synthesis.

β-Diketiminato Complexes of Chromium(II) and Chromium(III)

While the development of non group 4 olefin polymerization catalysts has for the most part been a relatively recent phenomenon,[13] Cr-based systems have a long history of use in the industrial production of polyethylene. Most academic interest has focused on two silica-supported systems: the Union Carbide catalyst, derived from Cp_2Cr, and the Phillips catalyst, based on CrO_3. Pioneering studies by Theopold and co-workers using well-defined, homogeneous organometallic complexes to model the Union Carbide system helped establish that cationic, 13-electron $[Cp^*Cr(R)(L)]^+$ complexes were active single-component catalysts for olefin polymerization.[8]

More recent studies on noncyclopentadienyl compounds to model the Phillips catalyst have employed β-diketiminato ancillary ligands, with the main synthetic target being a cationic Cr(III) alkyl compound which might be an active polymerization catalyst. Scheme 1 outlines the synthetic efforts of Theopold and co-workers toward neutral Cr(III) $Cr[(PhNCMe)_2CH](R)_2$ dialkyl complexes, which would be reasonable precursors to the desired monoalkyl cations.

The synthesis of the neutral Cr(III) monoalkyl species $\{Cr[(PhNCMe)_2CH](R)(\mu\text{-}Cl)\}_2$ from $CrCl_3(THF)_3$ via the Cr(III) dichloro compound $Cr[(PhNCMe)_2CH]Cl_2(THF)_2$ proceeds smoothly. However, attempted alkylation of $Cr[(PhNCMe)_2CH]Cl_2(THF)_2$ with alkyllithium reagents leads to disproportionation to homoleptic, four-coordi-

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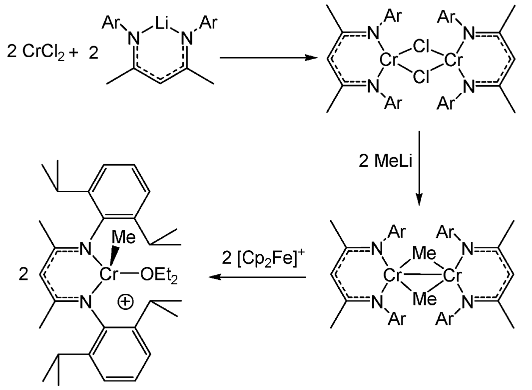
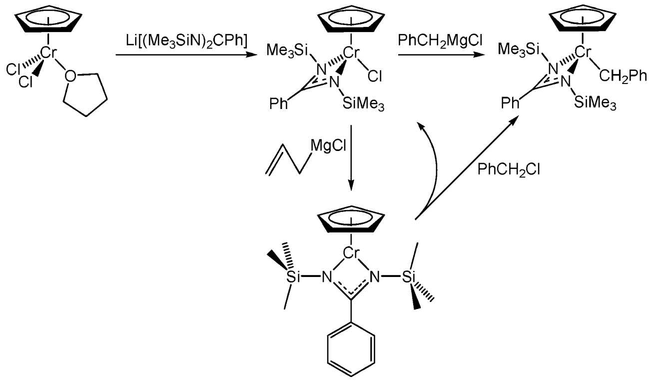
Scheme 2



Scheme 3



nate Cr(II) Cr[$(PhNCMe)_2CH]_2$ and Cr(IV) CrR_4 complexes. The problem can be partially remedied by using $CrPh_3(THF)_3$ as a precursor for an arene elimination reaction. However, while treatment of $CrPh_3(THF)_3$ with 2 equiv of the neutral $(PhNCMe)_2CH_2$ ligand leads to the expected Cr[$(PhNCMe)_2CH]_2$(Ph) species, reaction with only 1 equiv of $(PhNCMe)_2CH_2$ again results in disproportionation rather than the Cr(III) Cr[(PhNCMe)$_2$CH](Ph)$_2$ diphenyl compound.[17]

The Cr(II) Cr[$(PhNCMe)_2CH]_2$ compound can be independently synthesized from $CrCl_2$ and the lithium salt of the anionic β-diketiminato ligand. Instead of the electronically preferred square-planar geometry expected for a high-spin d^4 four-coordinate complex, steric interactions between the two bulky ancillary ligands lead to a geometry that is nearly tetrahedral. The Cr(II) bis(ligand) complex can be cleanly oxidized to the five-coordinate Cr(III) Cr[$(PhNCMe)_2CH]_2$Cl complex using 1,1,2,2-tetrachloroethane. This provides an excellent example of how a SET oxidation reaction can be used to access a mixed-ligand complex without the complications that may accompany a more traditional salt metathesis route (e.g. formation of the mono(ligand) or tris(ligand) complex, solvent coordination, "ate" complex formation, etc.). However, attempts to alkylate Cr[$(PhNCMe)_2CH]_2$Cl with RLi or RMgX reagents lead to reduction back to the Cr(II) complex Cr[$(PhNCMe)_2CH]_2$, while addition of less reducing AlR_3 reagents results in ortho metalation of one of the NPh groups of the β-diketiminato ligand. Despite the sophisticated synthetic methodology brought to bear, and the excellent characterization of the products obtained, a synthetic route to Cr(III) dialkyl compounds has yet to be reported for this particular variant of the β-diketiminato ligand.[17]

Interestingly, Cr(III) Cr[$(ArNCMe)_2CH](CH_2SiMe_3)_2$ dialkyl complexes can be prepared if Ar = 2,6-$Me_2C_6H_3$ is used instead of phenyl.[18] Related Cr[$(ArNCMe)_2CH](R)_2$ dialkyl compounds are not obtained for Ar = 2,6-$^iPr_2C_6H_3$; treatment of the Cr(III) dichloro precursor with alkylating agents instead leads to reduction to Cr(II) monochloro species. Scheme 2 illustrates how a cationic Cr(III) alkyl complex was ultimately prepared by Theopold and co-workers.[19] Salt metathesis with $CrCl_2$ affords the Cr(II) monochloro species as a dimer, {Cr[$(ArNCMe)_2CH](\mu$-Cl)}$_2$, for Ar = 2,6-$^iPr_2C_6H_3$. The steric bulk of the 2,6-^{i}Pr-substituted NAr groups is presumably critical in the synthesis of the mono(ligand) Cr(II) complex, instead of the Cr[$(PhNCMe)_2CH]_2$ complex obtained with the smaller phenyl substituents (Scheme 1). The Cr(III) cationic species is then obtained in two steps as a diethyl ether adduct by first alkylating and then performing a SET oxidation reaction on the resulting Cr(II) mono(alkyl) dimer using ferrocenium. This synthetic strategy has been used previously (e.g. in the oxidation of the neutral Ti(III) species $Cp^*{}_2TiMe$ with $AgBPh_4$ in THF to give $[Cp^*{}_2Ti(Me)(THF)][BPh_4]$)[20] and promises to be a particularly powerful route to well-defined, highly unsaturated cationic Cr(III) alkyl complexes in cases where the corresponding neutral Cr(III) bis(alkyl) complexes are not directly accessible. Gratifyingly, $\{Cr[(ArNCMe)_2CH](CH_3)(OEt_2)\}^+$ does in fact act as a single-component olefin polymerization catalyst.[19]

The synthesis of {Cr[$(ArNCMe)_2CH](\mu$-Cl)}$_2$ (Ar = 2,6-$^iPr_2C_6H_3$) from $CrCl_2$ and Li[$(ArNCMe)_2CH$] has utility for applications other than olefin polymerization. Well-defined complexes derived from this precursor have been used to study the activation of organic halides by 2 equiv of Cr(II) to form Cr(III) halides and Cr(III) organometallics. This SET oxidation process is the key step in the Nozaki–Hiyama–Kishi reaction, a chromium-mediated coupling of organic halides and aldehydes.[21] Useful in natural product total syntheses due to its selectivity and functional group tolerance, the reaction has been widely studied in the past decade as first catalytic[22] and then catalytic asymmetric versions have been developed.[23] An example from Smith and co-workers using the benzamidinato ancillary ligand is outlined in Scheme 3 and involves the reaction of benzyl chloride with a paramagnetic high-spin Cr(II) complex, CpCr[$(Me_3SiN)_2CPh$], resulting in a mixture of the Cr(III) chloro and Cr(III) benzyl complexes.[24] The reaction of $CpCrCl_2(THF)$ and (tmeda)Li[$(Me_3SiN)_2CPh$] yields the Cr(III) chloro complex, which in turn reacts

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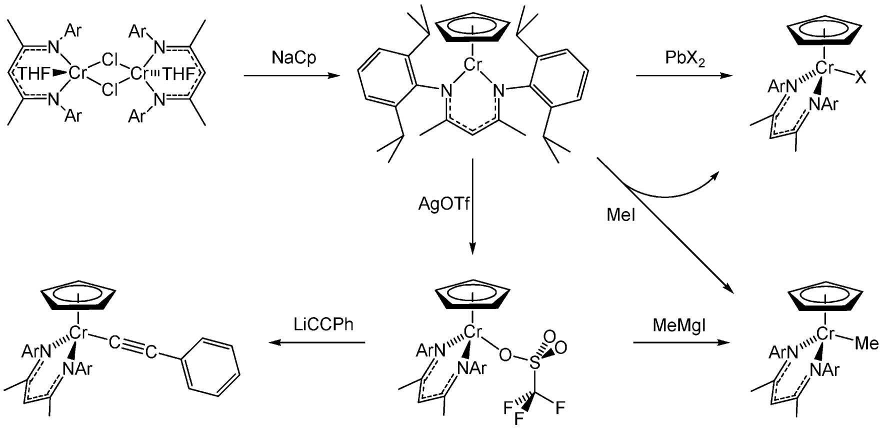
Scheme 4



cleanly with $PhCH_2MgCl$ to provide an independent synthesis of the Cr(III) benzyl complex. The Cr(II) complex $CpCr[(Me_3SiN)_2CPh]$ was prepared by the reduction of $CpCr[(Me_3SiN)_2CPh]Cl$ with $H_2C{=}CHCH_2MgCl$.

It was expected that the reaction of NaCp and $\{Cr[(ArNCMe)_2CH](THF)(\mu\text{-}Cl)\}_2$[25] would provide a more direct synthetic route to Cr(II) monocyclopentadienyl species and that the enhanced steric protection afforded by the large β-diketiminato ligand would also enhance the stability of the $CpCr^{II}$ product. While this proved to be the case, problems arose in the attempted synthesis of $CpCr^{III}$ alkyl complexes with the 2,6-$^iPr_2C_6H_3$-substituted ligand. The reaction of the ligand lithium salt and $CpCrCl_2(THF)$ was sluggish, and the reactions of the resulting Cr(III) chloro complex with Grignard reagents were also quite slow and low yielding. Scheme 4 illustrates the synthetic route developed by Smith and co-workers to circumvent these difficulties.[26] SET oxidation of the Cr(II) complex $CpCr[(ArNCMe)_2CH]$ with PbX_2 reagents (X = Cl, Br, I) gives the corresponding Cr(III) halides, following the use of $PbCl_2$ and $PbBr_2$ by Teuben and co-workers to oxidize $Cp^*{}_2Ti^{III}$ complexes to diamagnetic Ti(IV) d^0 halide derivatives for improved ^1H NMR analysis.[27] Oxidation of $CpCr[(ArNCMe)_2CH]$ with AgOTf gives the Cr(III) triflate complex, which proved to be a better precursor than the halides for subsequent salt metathesis reactions. When $CpCr[(ArNCMe)_2CH](OTf)$ was treated with MeMgI or LiCCPh, the corresponding Cr(III) carbyl species could be prepared. The reaction of $CpCr[(ArNCMe)_2CH]$ with iodomethane in pentane was followed using UV−visible absorption spectroscopy, and the second-order rate constant for the alkyl halide activation process was determined.[26]

Further studies are currently in progress to quantify how varying the steric and electronic properties of the bidentate, monoanionic (LX) ligands in these CpCr(LX) complexes changes their reactivity toward alkyl halide activation and pinacol coupling reactions.[28] This requires the use of ancillary ligands that are amenable to systematic variation. A less obvious limitation is presented by the effects of ligand modification on the crystallinity of the resulting organometallic complexes. While incorporation of a p-CF_3 substituent on the benzamidinato complexes shown in Scheme 3 proved useful for screening the benzyl chloride activation process by ^{19}F NMR,[24] the resulting complexes are markedly more difficult to crystallize. A more general route to active high-spin CpCr(LX) Cr(II) compounds would also be useful for this system, in contrast to the ligand-specific syntheses illustrated in Schemes 3 and 4.

Three-Coordinate Nickel(II) Complexes

Monomeric late-transition-metal complexes with terminal imido ligands, while rare compared to their early-metal counterparts, are potentially useful for “NR” group transfer reactions. The relative instability of such species can be attributed to a mismatch between soft Lewis acid and hard Lewis base and to the lack of empty metal d orbitals to accept π-donation from the imido group. On the basis of the thermal reactivity of $Ni(PR_3)_2(SH)(Ph)$ complexes,[29] Hillhouse and co-workers targeted (dtbpe)Ni(NHR)X complexes (dtbpe = bis(di-*tert*-butylphosphino)ethane, $(Me_3C)_2PCH_2CH_2P(CMe_3)_2$) as precursors to Ni(II) imido compounds via net loss of HX. However, $(dtbpe)NiCl_2$ reacted with LiNHAr (Ar = 2,6-$^iPr_2C_6H_3$) to give a mixture of products, including paramagnetic species. As shown in Scheme 5, reduction of the Ni(II) dichloro complex with KC_8 gave $[(dtbpe)Ni(\mu\text{-}Cl)]_2$, which then reacts cleanly with LiNHAr to give a monomeric, paramagnetic three-coordinate Ni(I) amido complex. Oxidation of Ni(I) gives the cationic amido complex, which can then be deprotonated to give the three-coordinate Ni(II) imido complex.[30]

Scheme 5 contains several important features that warrant further discussion. A key factor in the ultimate success of the synthesis was the recognition that ligand-to-metal π-donation is in fact possible for d^8 systems if they are three-coordinate. This conclusion can be arrived at using relatively straightforward ligand field theory considerations. The structural evidence for the ligand-to-metal π interactions are particularly pronounced in

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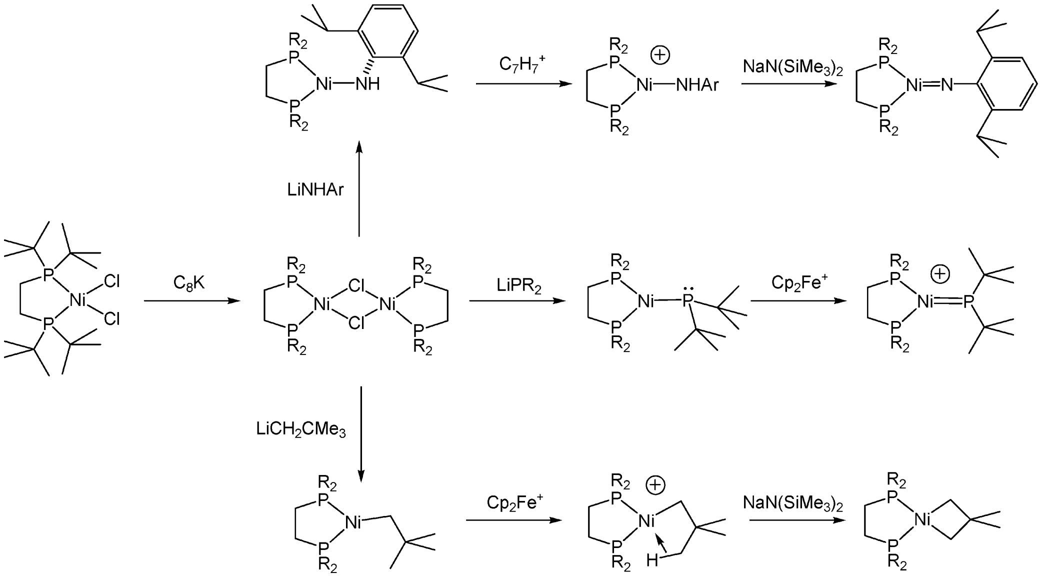
Scheme 5



the Ni(I) and Ni(II) phosphido complexes.[31] The examples in the previous section used SET reactions to convert paramagnetic, high-spin Cr(II) d^4 compounds to paramagnetic, high-spin Cr(III) d^3 species. For the Ni complexes, however, both the initial starting material and final product are diamagnetic Ni(II) d^8 complexes. It seems likely that synthetic strategies involving SET to and from paramagnetic intermediates might profitably be considered in other diamagnetic first-row organometallic systems. The use of cyclic voltammetry to identify the redox potential required for a chemical oxidant to convert the Ni(I) amido to its cationic Ni(II) form is also a significant step in optimizing the synthesis. It is especially crucial in this case, where much decomposition is observed if too powerful an oxidant is employed and where the actual oxidant eventually identified, the tropylium cation, is a fairly exotic one for synthetic inorganic chemists.

The importance of ligand steric bulk to prevent bimolecular decomposition pathways has been implicitly considered in the design of the synthesis of the Ni(II) imido complex. While this critical feature has been firmly established by recent work in olefin polymerization and metathesis catalysts, it is not exclusively a new insight: Hillhouse points out that the three-coordinate Ni(I) amido complex Ni(PPh$_3$)$_2$[N(SiMe$_3$)$_2$] was reported in 1972.[32] As well as furnishing the requisite steric bulk, the multiple equivalent CH$_3$ groups with relatively unhindered rotation in the P^{t}Bu and NAr substituents are useful for aiding in the interpretation of the paramagnetic ^{1}H NMR spectra. In addition, the chosen ligands evidently lead to crystalline products: this is obviously important in obtaining single crystals suitable for X-ray diffraction, since definitive identification of paramagnetic complexes without structural characterization is often quite difficult. Highly crystalline products are also critical in multistep inorganic syntheses in order to isolate each intermediate in a pure state and an acceptable yield before proceeding with the next reaction. The overall yield of ~35% for (dtbpe)Ni(NAr) based on (dtbpe)NiCl$_2$ over four steps is remarkably high and is based on pure, recrystallized product obtained after each reaction. Subsequent studies by Hillhouse and co-workers have demonstrated group transfer reactions of the multiply bonded ligands in the complexes in Scheme 5 from Ni(II) to organic substrates.[33]

Scheme 5 also shows how the same SET synthetic strategy has been applied to prepare cationic Ni(II) alkyl complexes. Alkylation of [(dtbpe)Ni(μ-Cl)]$_2$ gives monomeric Ni(I) complexes that are distorted from an ideal trigonal-planar geometry but do not show any agostic interactions. Oxidation with ferrocenium salts gives cationic Ni(II) complexes that have agostic interactions with the alkyl ligands. Reaction of the Ni(II) alkyls with NaN(SiMe$_3$)$_2$ does not remove a proton from the α-carbon atom, as expected by analogy with the previously described cationic amido and phosphido compounds. Instead, deprotonation at the γ-carbon results in neutral Ni(II) metallacyclobutane products.[34]

β-Diketiminato Complexes of Vanadium(III), Vanadium(IV), and Vanadium(V)

The preparation of high-oxidation-state alkylidene and alkylidyne complexes by Mindiola and co-workers (Scheme 6) provides excellent examples of SET oxidation reactions in multistep, target-oriented inorganic synthesis. The initial starting material is a β-diketiminato dichloro complex, V[(ArNCMe)$_2$CH]Cl$_2$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$), initially prepared by Budzelaar and co-workers as a precatalyst for olefin polymerization.[35] Alkylation with neopentyllithium gives the bis(alkyl) complex V[(ArNCMe)$_2$CH](CH$_2$CMe$_3$)$_2$. The V(III) complex has a reversible oxidation wave in its cyclic voltammogram,

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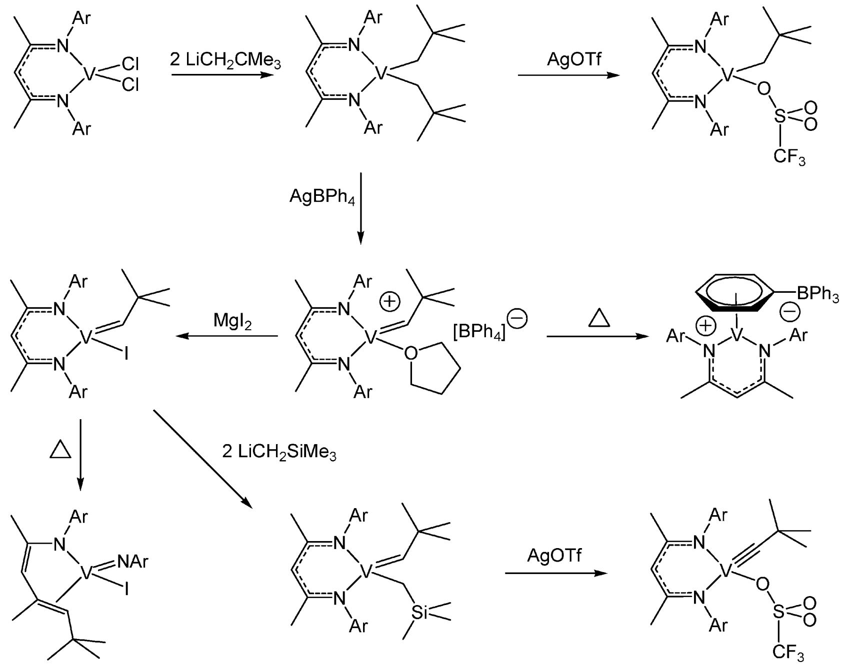
Scheme 6



and chemical oxidation with $AgBPh_4$ in THF gives the cationic V(IV) alkylidene $\{V[(ArNCMe)_2CH](CHCMe_3)(THF)\}^+$ as the tetraphenylborate salt.[36] Analogous SET oxidation reactions with Ti(III) bis(alkyl) and Ti(III) bis(amido) complexes to induce similar α-H abstraction reactions had previously been reported by Mindiola and co-workers.[37] For vanadium, the choice of oxidant proved to be critical, as reaction of $V[(ArNCMe)_2CH](CH_2CMe_3)_2$ with AgOTf gave the V(III) monoalkyl species $V[(ArNCMe)_2CH](CH_2CMe_3)(OTf)$ rather than the alkylidene. A V(IV) complex suitable for subsequent salt metathesis reactions is obtained when the cationic THF adduct is treated with MgI_2 to form neutral $V[(ArNCMe)_2CH](CHCMe_3)I$. Both cationic and neutral V(IV) alkylidene complexes show interesting thermolysis chemistry in THF at 60 °C, resulting in zwiterionic V(II) and V(IV) imido complexes, respectively, as shown in Scheme 6.[36]

Treatment of $V[(ArNCMe)_2CH](CHCMe_3)I$ with $LiCH_2SiMe_3$ gives the V(IV) alkyl/alkylidene complex. Once again, SET oxidation leads to α-H abstraction, as $V[(ArNCMe)_2CH](CHCMe_3)(CH_2SiMe_3)$ reacts with AgOTf to give $V[(ArNCMe)_2CH](CCMe_3)(OTf)$ and with $AgBPh_4$ to give $\{V[(ArNCMe)_2CH](CCMe_3)(THF\}[BPh_4]$. Like the related V(IV) and Ti(IV) alkylidene species, the V(V) alkylidyne complexes undergo intramolecular rearrangement upon thermolysis to generate V(V) imido complexes.[38]

The thermolysis reactions exhibited by the *β*-diketiminato alkylidene complexes of Ti and V are certainly spectacular, and Mindiola and co-workers have made excellent use of DFT studies to explore the intramolecular rearrangement of the V alkylidyne complex in Scheme 6. However, it is the construction of this alkylidyne compound by sequential alkylation and SET oxidation induced α-H abstraction reactions that makes this chemistry such an inspiring example of targeted organometallic synthesis. The final observation by Mindiola and co-workers that, when treated with 1 equiv of $LiCH_2CMe_3$, the $V[(ArNCMe)_2CH](CCMe_3)(OTf)$ species acts as a polymerization catalyst for phenylacetylene ensures that more exciting work on this system will be forthcoming.[38]

Conclusions

The case studies described above illustrate several of the benefits of applying SET oxidation reactions to the synthesis of paramagnetic organometallic complexes. Using first-row metal starting materials in a lower oxidation state is often advantageous in order to prevent unwanted reduction during salt metathesis reactions. It can also help avoid other potential pitfalls such as “ate” complex formation or undesired metal−ligand stoichiometry. Once formed, SET oxidation of a ML_n complex is useful in the synthesis of ML_nX species (X = halide, OTf, etc.). Such halide complexes might be synthetic targets in their own right or may serve as useful precursors for subsequent salt metathesis reactions. This stepwise strategy facilitates the construction of target molecules with distinct ancillary and reactive ligands, an important requirement in the preparation of well-defined catalysts generally, as well as in the independent synthesis of intermediates believed to participate in a proposed catalytic cycle. Alternatively, SET oxidation reactions performed using weakly coordinating anions permit the generation of $[ML_n]^+$ cations from neutral ML_n complexes. These cationic species may be amenable to the formation of metal−ligand multiple bonds via intermolecular (Scheme 5) or intramolecular (Scheme 6) α-H abstraction reactions. The preparation of active, well-defined, single-component catalysts by a

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SET oxidation process, as shown in Scheme 2, is particularly useful for studying paramagnetic polymerization systems, where the nature of the catalytically active species generated in situ with excess alkylaluminum cocatalysts is often debatable.

SET processes are also important for metals other than those mentioned above. It was initially thought that bis(imino)pyridyl complexes of $CoCl_2$ remained as Co(II) when activated with MAO in polymerization reactions.[39,40] Recent studies from the research groups of Gibson,[41] Budzelaar,[42] and Erker,[43] however, have indicated that reduction to Co(I) occurs under alkylation conditions and that well-defined Co(I) complexes are active single-component polymerization catalysts. Some of the most exciting new paramagnetic organometallic chemistry is being conducted on iron complexes, with relevance for a range of applications,[44] including ethylene,[39] styrene,[45] and acrylonitrile[46] polymerization, hydrogenation and hydrosilation,[47] cross-coupling reactions,[48] reversible β-H elimination,[49] and N_2 activation.[50,51] The preparation of well-defined, paramagnetic Fe complexes should help illuminate connections between these various applications, as well as delineate the role of different possible electronic configurations in these reactions.

In two recent reviews, Lee and Holm emphasized the advances in synthetic methodology that have come from the efforts of inorganic chemists to model the active site of nitrogenase.[52] Similar progress in the preparation of well-defined paramagnetic organometallic complexes will continue to accelerate as the applications of these species are further developed. Some of this research will arise from the exploration of current catalytic processes that are now only poorly understood, such as Cr-based olefin trimerization.[53] However, it seems likely that DFT studies will prove useful in suggesting new synthetic targets with potential catalytic activity, such as Cr(IV) bis(amido) olefin polymerization catalysts.[54]

The chemistry addressed in this article serves to underscore the contention that open-shell organometallic complexes lie at the interface between diamagnetic organometallic compounds and nonorganometallic, Werner-type d-metal complexes.[7,9] From this perspective, it is perhaps unsurprising that both the synthetic methodology (e.g. SET reactions) and conceptual framework (e.g. LFT) that were initially developed for coordination complexes are equally valid for paramagnetic organometallic compounds.

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