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Redox Noninnocence of Carbene Ligands: Carbene Radicals in (Catalytic) C—C Bond Formation

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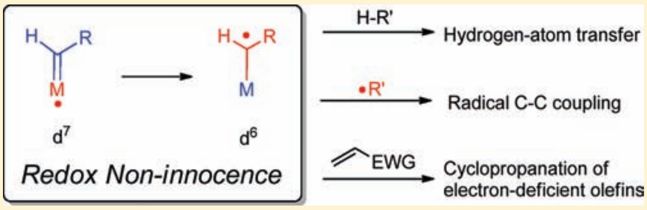
ABSTRACT: In this Forum contribution, we highlight the radical-type reactivities of one-electron-reduced Fischer-type carbenes. Carbene complexes of group 6 transition metals (Cr, Mo, and W) can be relatively easily reduced by an external reducing agent, leading to one-electron reduction of the carbene ligand moiety. This leads to the formation of "carbene-radical" ligands, showing typical radical-type reactivities. Fischer-type carbene ligands are thus clearly redox-active and can behave as so-called "redox noninnocent ligands". The "redox noninnocence" of Fischer-type carbene ligands is most clearly illustrated at group 9 transition metals in the oxidation state II+ (Co^{II}, Rh^{II}, and Ir^{II}). In such carbene complexes, the metal effectively reduces the carbene ligand by one electron in an intramolecular redox process. As a result, the thus formed "carbene radicals" undergo a variety of radical-type C—C and C—H bond formations. The redox noninnocence of Fischer-type carbene ligands is not just a chemical curiosity but, in fact, plays an essential role in catalytic cyclopropanation reactions by cobalt(II) porphyrins. This has led to the successful development of new chiral cobalt(II) porphyrins as highly effective catalysts for asymmetric cyclopropanation with unprecedented reactivity and stereocontrol. The redox noninnocence of the carbene intermediates results in the formation of carbene-radical ligands with nucleophilic character, which explains their effectiveness in the cyclopropanation of electron-deficient olefins and their reduced tendency to mediate carbene dimerization. To the best of our knowledge, this represents the first example in which the redox noninnocence of a reacting ligand plays a key role in a catalytic organometallic reaction. This Forum contribution ends with an outlook on further potential applications of one-electron-activated Fischer-type carbenes in new catalytic reactions.



1. INTRODUCTION

Controlling radical reactivity is a long-standing challenge in synthetic organic and organometallic chemistry. In general, free radicals are not so easy to control and are often considered to be *too reactive to be selective*. In the coordination sphere of a transition metal, however, highly chemo-, regio-, diastereo-, and even enantioselective radical-type reactions become feasible, as demonstrated by the many radical-type bioenzymatic processes mediated by a variety of metalloenzymes.[1] Because selectivity is primarily a matter of relative rates rather than absolute ones, the steric and electronic influences of ligands can be utilized to attain both fast rates and high selectivities in transition-metal-controlled radical reactions. The confined nanospace of enzyme pockets provides a further controlling factor to achieve chemo- and regioselectivity in radical-type reactions.[2]

In the field of synthetic organometallic chemistry, the playground of *catalytic* synthetic organic transformations, controlling the radical-type reactivity of open-shell organometallic compounds offers vast opportunities to develop a wide variety of new, fast, and selective catalytic transformations.[3,4] Organometallic complexes present many ways to form *ligand radicals*, which can play a dominating role in directing the open-shell reactivity of these compounds, thus providing an attractive possibility of achieving selectivity and of uncovering new reactivity in the emerging field of open-shell organometallic chemistry.[5−7] Many new discoveries can be expected from future research in this area, especially in the realm of catalysis.[8−11]

When considering the reactivity of paramagnetic complexes, knowing the location of the unpaired electrons is highly relevant because the sites bearing the largest unpaired spin densities are often the most reactive. This is a nontrivial task and often requires detailed spectroscopic and computational investigations to reveal the information. This holds especially true for complexes bearing redox-active ligands because oxidation state assignments are, per definition, ambiguous in these cases. Because both the ligand and metal can be reduced or oxidized, the apparent (formal) metal oxidation state does not always reflect the actual changes in the metal d-electron count. When rather unexpected reduction or oxidation of the ligand is encountered, the term "redox noninnocence" is used to underline the oxidation state ambiguity of such ligands. Although redox noninnocence of ligands has long been considered a spectroscopic curiosity, the concept proved to be of crucial importance to understanding the reactivity of (synthetic models of) several metalloenzymes[12,13] and a variety of synthetic open-shell organometallic compounds[7−9,14] over the past years. The generation of ligand radicals can lead to interesting

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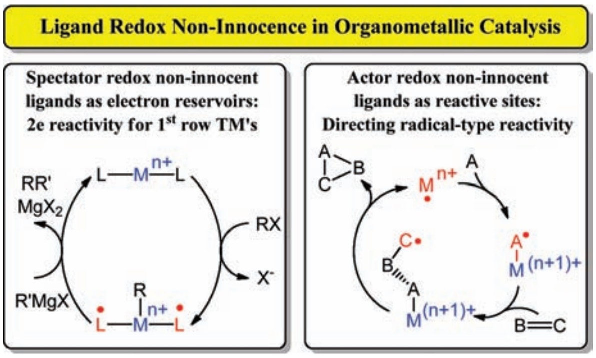

Figure 1. Complementary approaches in using redox-active ligands to steer and control catalytic reactions.

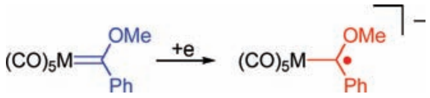

Figure 2. Formation of carbon-centered radicals by the one-electron reduction of group 6 transition-metal carbene complexes (M = Cr, Mo, and W).

ligand-centered reactivity, especially in the field of organometallic chemistry, where redox-active ligands offer ample opportunities for new and fast (catalytic) transformations.

While the concept of redox noninnocence in synthetic organometallic chemistry is still dominated by stoichiometric examples, it is swiftly penetrating into the realm of catalytic processes. Ligand redox noninnocence is clearly becoming a useful synthetic concept to enhance reactivity and steer selectivity.[8,10,11] The field is currently evolving along two important and emerging research lines.[11] On the one hand, *nonreactive* redox noninnocent (spectator) ligands can be used as electron reservoirs (the "electron-borrowing" principle) to facilitate two-electron reactivity for (cheap, first-row) transition metals that have an intrinsic tendency to react via one-electron pathways (Figure 1, left).[15−17] On the other hand, redox-active ligands can also be used to generate *reactive* (actor) ligand radicals to impose controlled ligand-centered radical-type reactivity in catalysis (Figure 1, right).

In this Forum contribution, we draw our attention to the topic of directing radical-type reactivity to ligands in order to steer and control radical-type reactions. In particular, we will focus on the redox noninnocent behavior of (Fischer-type) carbene ligands.[18]

Reactive (Fischer-type) carbene complexes are key intermediates in several catalytic reactions, such as alkene metathesis,[19] cyclopropanation,[20] C−H bond insertion,[21] carbene polymerization[22] and many more, and their closed-shell organometallic reactivity has been intensively studied. Their open-shell reactivity and potential redox noninnocence have received comparably much less attention. Herein we show that carbene-radical ligands can play a crucial role in open-shell organometallic catalysis.

2. REDOX ACTIVITY AND STOICHIOMETRIC REACTIVITY OF CARBENE LIGANDS IN GROUP 6 TRANSITION-METAL COMPLEXES

The redox activity of carbene ligands was first addressed in the late 1970s for Fischer-type carbene complexes with group 6 metals.[23] The lowest unoccupied molecular orbital (LUMO) of Fischer-type carbene complexes is carbene-carbon-centered, which gives rise to the typical electrophilic character of the ligands. This property also

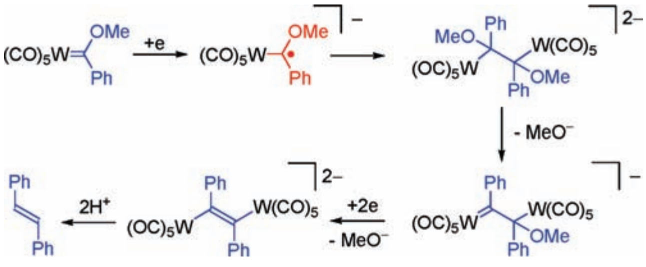

Figure 3. Formation of *trans*-stilbene via dimerization of one-electron-reduced Fischer-type tungsten carbenes.

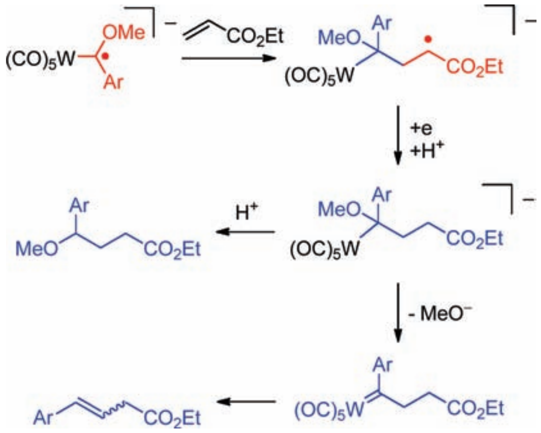

Figure 4. Reaction of one-electron-reduced Fischer-type carbenes with ethyl acrylate.

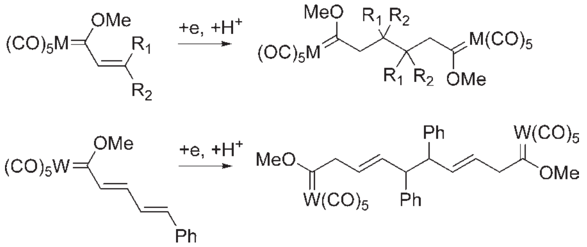

Figure 5. Remote reductive ligand−ligand coupling of unsaturated carbene complexes (M = Cr, W; R_1 = Me, Ph; R_2 = Me, H).

makes it possible to form carbon-centered "carbene radicals" upon one-electron reduction of these complexes.[24] The redox activity of Fischer-type carbene ligands was first demonstrated experimentally by Casey et al.[25] They showed that one-electron reduction of the pentacarbonyl(alkoxyaryl)carbene complexes of group 6 transition metals with a sodium/potassium alloy leads to the formation of carbon-centered radical anions (Figure 2), which are persistent in solution at low temperatures (−50 °C and below), as evidenced by electron paramagnetic resonance (EPR) spectroscopy.[25]

Only recently, the radical-type reactivity of these carbene ligands has been reinvestigated in a broader scope of stoichiometric transformations. These carbon-centered radicals could be employed in C−C bond-forming reactions. Fuchibe and Iwasawa reported that tungsten aryl- or silylcarbene complexes dimerize (Figure 3) or undergo radical addition to electron-poor olefins (Figure 4) after one-electron reduction with SmI_2.[26] The nature of the para substituent on the aryl group of the alkoxycarbene was shown to influence the outcome of the reaction with ethyl acrylate. Electron-withdrawing groups lead to subsequent protonolysis, whereas electron-donating groups affect the loss of MeO^- to form a tungsten carbene species. Similar results were obtained with a tungsten (diphenylmethylsilyl)methoxycarbene complex.

For conjugated carbene complexes (Figure 5), one-electron reduction leads to radical-type ligand—ligand coupling reactions at more remote distances from the metal, presumably for steric reasons. One-electron reduction of chromium or tungsten α,β-unsaturated carbene complexes results in the formation of dinuclear bis(carbene) species by radical coupling between the γ-carbon atoms, followed by protonation (in protic media) or quenching with another electrophile.[26,27] Reduction of tungsten dienylcarbene complexes causes radical-type C—C coupling at the terminal olefinic carbon atoms most distant from the metal. Stabilization of the intermediate ligand radical density by the phenyl substituent at this carbon likely also plays a role in directing the reaction toward this remote ligand-based coupling (Figure 5).[26]

Somewhat related ligand radicals could be obtained by deprotonation of Fischer-type carbene complexes bearing β-hydrogen-containing substituents, followed by one-electron oxidation of the resulting anionic intermediates. For example, deprotonation of the chromium(0) pentacarbonyl(methoxymethyl)carbene complex generates an anionic carbene complex that undergoes radical-type C—C coupling after one-electron oxidation (Figure 6).[28,29] The related manganese carbene complexes exhibited a similar reactivity.[30] However, this type of reactivity is perhaps not unique for Fischer-type carbenes because similar deprotonation/oxidation-induced radical-type reactivity is also known for the methyl group of acetylferrocene.[29]

3. "REDOX NONINNOCENCE" OF FISCHER-TYPE CARBENES IN THE (CATALYTIC) OPEN-SHELL ORGANOMETALLIC REACTIVITY OF COBALT(II), RHODIUM(II), AND IRIDIUM(II)

Stoichiometric Reactions Involving "Carbene-Radical Ligands". Quite remarkably, Fischer-type carbene ligands formed at paramagnetic metal(II) complexes of group 9 transition metals seem to reveal an intrinsic "redox noninnocent" behavior. Carbene ligands generated from diazo compounds at low-spin iridium(II), rhodium(II), and cobalt(II) complexes seem to have a clear carbon-radical (carbene-radical) character, even without one-electron reduction by an external reducing agent. These "carbene-radical" intermediates are capable of hydrogen-atom abstraction from the reaction medium to form diamagnetic metal(II) alkyl complexes, for example. This reactivity has been observed for $Co^{II}(TPP)$ (TPP = tetraphenylporphinato), which forms the diamagnetic alkyl species $Co^{III}(TPP)(CH_2COOEt)$ upon prolonged exposure to ethyl diazoacetate.[31] A similar hydrogen-atom-abstraction reactivity was disclosed for Rh^{II}(TMP) (TMP = tetramesitylporphinato; Figure 7).[32]

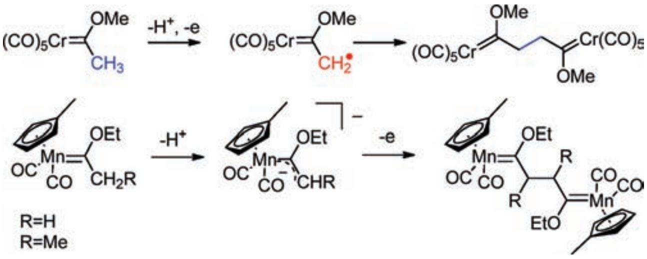

Figure 6. Deprotonation/oxidation-induced radical-type reactivity of β-hydrogen-containing carbene complexes.

The carbene's *redox noninnocent behavior* was examined in more detail for paramagnetic $(Me_3tpa)Ir^{II}$ complexes [Me_3tpa = *N,N,N*-tri(6-methyl-2-pyridylmethyl)amine]. In MeCN, the metalloradical complex $[(Me_3tpa)Ir^{II\bullet}(ethene)]^{2+}$ is converted to the "ethene-ligand-radical" complex $[(Me_3tpa)Ir^{III}(CH_2CH_2^\bullet)(NCMe)]^{2+}$ in small amounts, which readily loses ethene through Ir—C bond homolysis. In the presence of diazo compounds ($N_2{=}CHR$), the more open and more reactive metalloradical $[(Me_3tpa)Ir^{II\bullet}(NCMe)]^{2+}$ forms the "carbene-ligand-radical" intermediate $[(Me_3tpa)Ir^{III}(CHR^\bullet)]^{2+}$. With sterically nondemanding diazo compounds, such as ethyl diazoacetate, the thus formed "carbene radical" readily and selectively couples with the "ethene-ligand-radical" species $[(Me_3tpa)Ir^{III}(-CH_2CH_2^\bullet)(NCMe)]^{2+}$ to form a binuclear diamagnetic $Ir^{III}—CHR—CH_2—CH_2—Ir^{III}$-bridged complex. The use of more bulky diazo compounds such as Me_3SiCHN_2 leads to hydrogen-atom abstraction from the reaction medium (Figure 8).[33]

Catalytic Olefin Cyclopropanation via "Carbene Radical Ligands". The above stoichiometric reactions indicate that carbene ligands behave as redox *noninnocent ligands* upon coordination to (low-spin) iridium(II), rhodium(II), and cobalt(II) complexes and thus spontaneously form "carbene radicals" through intramolecular reduction of the carbene carbon atom by the transition metal. This behavior can be understood in terms of the generalized and simplified orbital interaction scheme shown in Figure 9.

The interaction with the (singlet) carbene moiety (:CHR) pushes the energy of the metal d_{z^2} orbital above the energy of the antibonding molecular orbital constructed from the carbon p_y orbital and the metal d_π orbital, thus resulting in intramolecular electron transfer from the metal to the carbene moiety (Figure 9). Partial occupation of the M—C π^*-antibonding orbital thus substantially reduces the M—C bond order. Consequently, the "carbene" species loses its typical Fischer-type character, gains unusual radical reactivity, and becomes more nucleophilic. However, its open-shell radical character, putting a discrete

Figure 7. Formation of "carbene radicals" upon the reaction of diazo compounds with Co^{II}(por) and Rh^{II}(por) complexes with subsequent hydrogen-atom transfer to the carbon-centered radical.

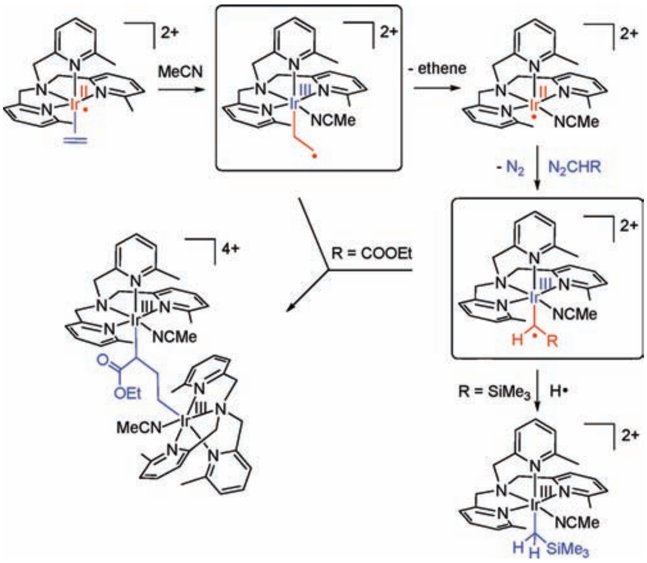

Figure 8. Coupling of "carbene radicals" with "ethene radicals" in the open-shell reactivity of $\mathrm{Ir^{II}}$(ethene) species with ethyl diazoacetate. The use of more bulky diazo compounds results in hydrogen-atom abstraction.

unpaired spin density on the "carbene" carbon atom, is fundamentally different from closed-shell Fischer- or Schrock-type carbene descriptions. This typical behavior of group 9 transition-metal carbene complexes in the II+ oxidation state was recently disclosed to be of crucial importance in $\mathrm{Co^{II}}$(por)-catalyzed olefin cyclopropanation reactions.[34]

Paramagnetic $\mathrm{Co^{II}}$(salen)[35] and, in particular, $\mathrm{Co^{II}}$(por) complexes[31,36] are effective catalysts for olefin cyclopropanation. Since the discovery that they are capable of diastereo- and enantioselective olefin cyclopropanation reactions, various cobalt(II)-based catalytic systems have been developed. So far, the most effective cobalt-based catalysts are the cobalt(II) complexes of D_2-symmetric chiral porphyrins developed by Zhang and co-workers.[36] Among them, [Co(3,5-Di^{t}Bu-ChenPhyrin)] (Figure 10) is unprecedented in its reactivity, stereocontrol, and ability to affect cyclopropanation with (near) stoichiometric amounts of alkenes, avoiding carbene dimer formation. Another intriguing feature of the cobalt(II) porphyrin systems is their effectiveness in cyclopropanation of electron-deficient olefins such as α,β-unsaturated carbonyl compounds and nitriles.[36d,f−h] This remarkable reactivity differs significantly from the typical electrophilic Fischer-type carbene intermediate associated with $\mathrm{Cu^{I}}$- and $\mathrm{Rh_2}$-based systems, thus pointing to a fundamentally different character of the carbene-transfer intermediate for $\mathrm{Co^{II}}$(por)-based systems.

Recent EPR spectroscopic and DFT computational investigations confirmed[34] the previously reported hypothesis[36a,37] that the catalytically active cobalt carbene complex has a strong carbon-radical character. The active intermediate is indeed a "carbene radical" similar to the iridium carbene radicals described above and reveals the same orbital configuration as that shown in Figure 9. Its nucleophilic radical character facilitates the cyclopropanation of electron-deficient olefins and, at the same time, suppresses the carbene dimerization activity. To the best of our knowledge, this represents the first documented example in which ligand redox noninnocence plays a key role in an organometallic catalytic transformation. Cyclopropanation clearly proceeds via a radical-type mechanism (Figure 11), which involves the formation of reactive carbon-centered radicals within the coordination sphere of cobalt. Addition of the "carbene radical" to the olefin is followed by a low-barrier transition state for cyclopropane ring closure.[38] The latter step is best described as a radical-type C−C bond coupling with simultaneous homolytic splitting of the Co−C bond (intramolecular homolytic radical substitution). Besides the "redox noninnocence" of the carbene, it is apparent that the intrinsic relative weakness of the Co−C bond plays a crucial role in this reaction.[39]

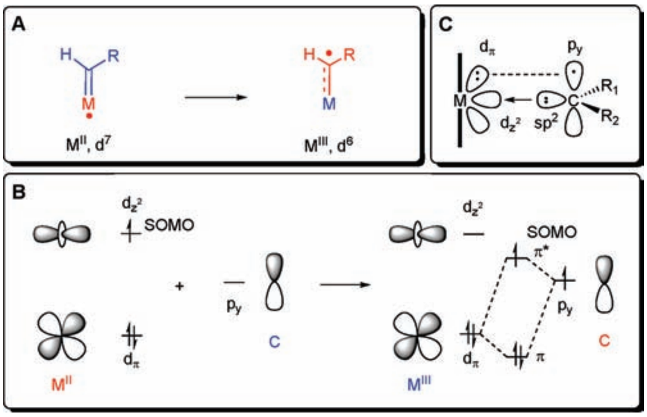

Figure 9. Simplified orbital interaction scheme explaining the redox noninnocent behavior of carbene ligands with the formation of "carbene radicals" upon coordination to cobalt(II), rhodium(II), and iridium(II).

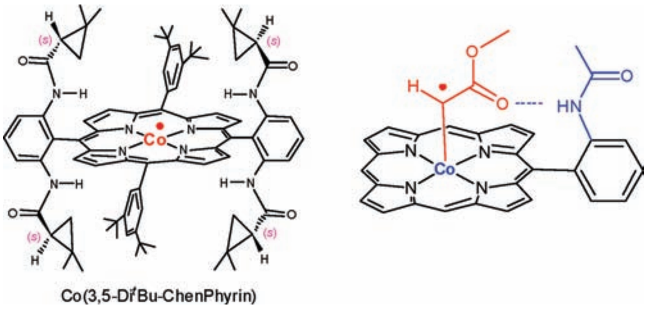

Figure 10. Left: Arylbis(cyclopropane carboxamide) functionalities of [$\mathrm{Co^{II}}$(3,5-Di^{t}Bu-ChenPhyrin)] providing a confined, protective, and chiral nanospace around the cobalt active site. Right: Hydrogen-bond donation to the diazo ester substrate that lowers the activation barrier for "carbene-radical" formation.

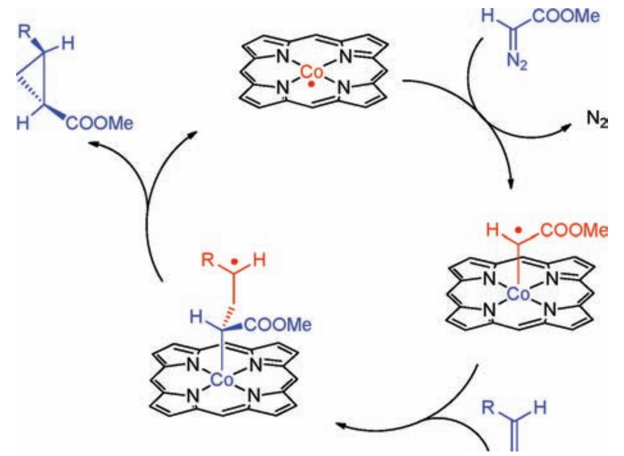

Figure 11. Radical-type mechanism of $\mathrm{Co^{II}}$(por)-catalyzed cyclopropanation of olefins.

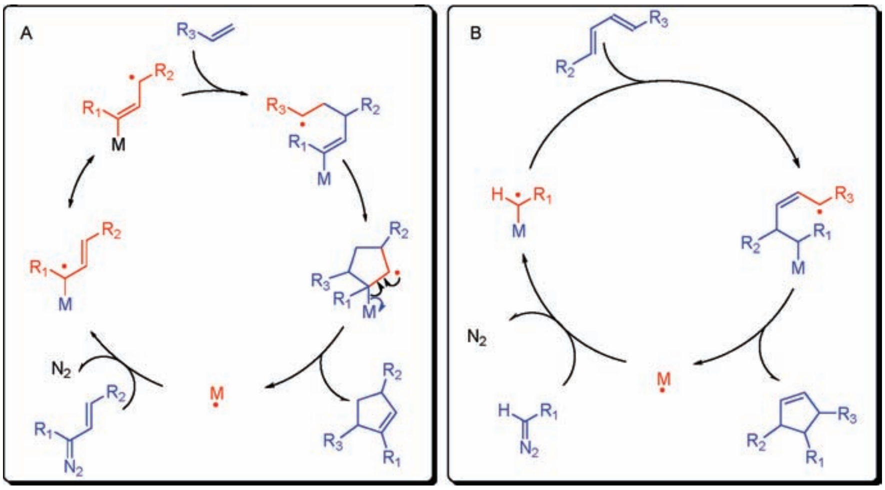

Figure 12. Proposed new radical reactions involving redox noninnocence of carbenes, leading to highly functionalized cyclopentenes.

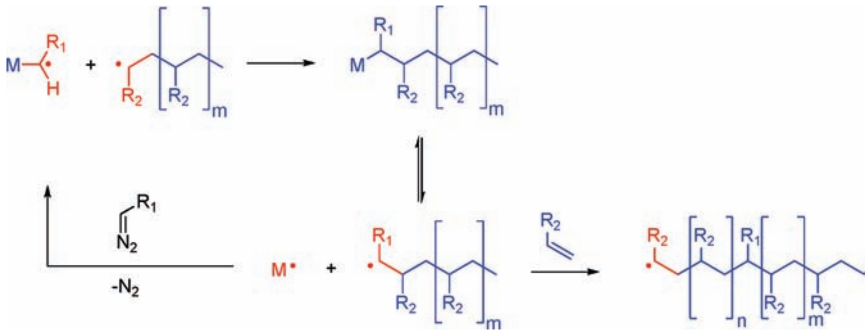

Figure 13. Possible incorporation of carbene-radical ligands into the growing polyolefin chain.

The metal obviously also plays an important role as the template to bring together the substrates and serves as a reservoir for the essential unpaired electron. An additional interesting feature of this catalyst is that the arylbis(cyclopropane carboxamide) functionalities of the 3,5-Di^{t}Bu-ChenPhyrin ligand (Figure 10) provide a confined, protective, and chiral nanospace around the active site. This type of chiral environment is important to controlling the enantioselectivity but likely also prevents unwanted side reactions, leading to catalyst deactivation. Furthermore, the amido functionalities serve as potent hydrogen-bond donors to lower the activation barrier for formation of the carbene radicals from the diazo reagents, leading to faster reactions and higher selectivities. Hence, the catalytic system makes combined use of several enzyme-like "tricks", approaching those applied by natural enzymes. With this radical-type mechanism being firmly established, Co^{II}(por)-catalyzed olefin cyclopropanation provides an illustrative example of a synthetically useful catalytic reaction that operates via a radical process but still allows for highly chemo-, regio-, diastereo-, and even enantioselective turnover.[40]

4. DIAGNOSTIC FEATURES OF REDOX-ACTIVE CARBENE LIGANDS

All of the complexes of "radical carbenes" known to date are transient, and therefore their structural analyses have so far been limited to in situ EPR and IR spectroscopy. Only a few spectroscopic studies on open-shell metal carbene complexes have been performed and, in many cases, the radical character of the carbon atom has been established by analysis of the products formed from these reactive species. EPR spectroscopy is a valuable tool for studying the electronic structure of paramagnetic molecules in general and therefore can be used to investigate the redox noninnocence of carbene ligands. Carbene-radical ligands generally reveal small g anisotropy, with g values close to the free-electron value ($g \sim 2.00$) and at the same time clear hyperfine couplings with the metal to which they bind (and relevant substituents having a nuclear spin).[25,34] These features are characteristic for the formation of carbon-centered radicals and hence establish the redox activity of the carbene ligand. In some cases, however, the carbene-radical complex appears to be EPR-silent[34] or is simply too reactive to be directly detected.[33]

In several cases, the carbonyl substituent of ester-based carbenes could be used as a probe for transfer of the electron density from the metal to the carbene. One-electron reduction of the carbene results in a clear shift of the IR C=O stretch frequency to lower wavenumbers compared to analogous closed-shell carbene complexes.[37,41] Apart from the above experimental diagnostic features, (quantum mechanical) computational methods are highly useful to shed light on the electronic structure of compounds containing carbene-radical ligands (singly occupied molecular orbital and spin-density distributions),[25,33,34,42] especially in combination with spectral property calculations when compared to spectral data from experimental studies.[34,37,41,43]

5. OUTLOOK

Other Metals. The chemistry of one-electron-activated Fischer-type carbenes is currently limited to group 6 and 9 transition metals. These open-shell species are carbon-centered radicals and have a d^6 electron configuration on the metal. Despite the fact that many stable Fischer-type carbene complexes with other metals exist [most notably the catalytically active ruthenium(II) or copper(I) complexes], quite surprisingly, their electrochemical behavior has not yet been investigated. It is likely that one-electron activation of carbenes bound to metals of other groups will lead to fascinating (catalytic) reactivity and should be a topic of increasing interest in the coming years.

New Reactions. The redox noninnocence of Fischer-type carbenes is well established now. It is also clear that the Co(por)-mediated cyclopropanation of (electron-deficient) olefins follows a *controlled, fast, and selective radical-type pathway*.[34,36d,36f] Together, it is interesting and tempting to think about other radical-type reactions involving radical carbenes. For example, related radical-type ring-closure reactions, as depicted in Figure 12, should be possible with properly designed catalysts. The use of suitable carbene precursors (i.e., leading to radicals being highly stabilized at the carbon containing the R_2 group) should allow for radical addition of the γ-carbon radical to olefin substrates (Figure 12A). This would produce an ε-carbon radical, and its subsequent ring closure should yield a cyclopentene derivative. Another possible route toward the formation of highly substituted cyclopentenes is carbene-radical addition to functionalized conjugated dienes (Figure 12B). This would yield intermediates similar to the ones in pathway A. The combination of the proper catalyst design with the right choice of the diene substrate will be key to allowing for such reactivity by preventing the competing binuclear radical−radical deactivation pathways.

Carbene-radical ligands could also be utilized for (radical) copolymerization of olefins with C1 monomers (Figure 13),[22,44] as exemplified in organometallic radical polymerization (OMRP) reactions. In these reactions, carbene radicals can be anticipated to react occasionally with the growing polymer radical chain, thus allowing the partial incorporation of functionalized C1 units into a polymer chain built primarily from the vinylic C2 units. Subsequent homolytic cleavage of the M−C bond should regenerate the active polymer radical chain, in the same way as the more conventional OMRP reactions. Such C1/C2 copolymerization reactions should lead to novel polymers with interesting properties.

6. CONCLUSIONS

The redox activity of ("redox noninnocent") ligands is emerging as a useful synthetic concept to enhance reactivity and steer selectivity in catalysis. *Nonreactive* redox noninnocent (spectator) ligands can be used as electron reservoirs ("electron borrowing" principle) to facilitate two-electron reactivity for (cheap, first-row) transition metals that have an intrinsic tendency to react via one-electron pathways. Redox-active ligands can also be used to generate *reactive* (actor) ligand radicals to impose controlled ligand-centered radical-type reactivity in catalytic reactions. Fischer-type carbene ligands provide an excellent example of "redox noninnocent" ligands that allow for controlled radical-type reactions in the coordination sphere of transition metals.

The carbene-carbon-centered LUMO of Fischer-type carbene complexes gives them typical electrophilic character but also makes it possible to form carbon-centered "carbene radical ligands" upon one-electron reduction. Carbene complexes of group 6 transition metals (Cr, Mo, and W) are relatively easily reduced by an external reducing agent, leading to one-electron reduction of the carbene ligand moiety. This leads to the formation of "carbene radical" ligands showing typical radical-type reactivity. Fischer-type carbene ligands are thus clearly redox-active and can behave as so-called "redox noninnocent ligands". The "redox noninnocence" of Fischer-type carbene ligands has been clearly demonstrated by group 9 transition metals in the oxidation state II+ [cobalt(II), rhodium(II), and iridium(II)]. In these carbene complexes, the metal effectively reduces the carbene ligand by one electron in an intramolecular redox process. As a result, the thus formed "carbene radicals" undergo a variety of radical-type C−C and C−H bond formations.

The redox noninnocence of Fischer-type carbene ligands is not just a chemical curiosity but, in fact, plays an essential role in catalytic cyclopropanation reactions by cobalt(II) porphyrins. This has led to the development of chiral cobalt porphyrins as highly successful cyclopropanation catalysts, showing unprecedented reactivity and stereoselectivity. The "redox noninnocence" of the carbene intermediates leads to the formation of carbene radicals with nucleophilic character, which explains their effectiveness in the cyclopropanation of electron-deficient olefins and their reduced tendency to mediate carbene dimerization. To the best of our knowledge, this constitutes the first catalytic organometallic reaction in which the "redox noninnocence" of the terminal carbene ligand plays a crucial role. The cooperative action of the "carbene radical" and the transition metal is an essential feature of the catalytic process for substrate activation and subsequent conversion. This process is, in fact, very similar to the mechanisms by which several metalloenzymes gain control over radical-type reactions. An additional interesting feature of these catalysts is that the employed bulky porphyrin ligands create a confined, protective, and chiral nanospace around the active site, allowing enantioselectivity while preventing unwanted side reactions. Furthermore, hydrogen-bond-donating functionalities at the porphyrin periphery lower the activation barrier for formation of the carbene radicals (transition state stabilization), thereby leading to faster reactions and higher selectivities. These new insights clearly show that several "enzyme-like tricks" can be employed in synthetic organometallic catalysis to achieve selectivity in radical-type transformations. If this is possible for radical-type olefin cyclopropanation reactions, why should it not be possible for other radical-type transformations? Hence, we believe that open-shell organometallic chemistry, in general, has a bright (catalytic) future. Much can be expected from future computational studies and conscientious spectroscopic investigations of open-shell organometallic compounds, which should provide valuable and detailed new information about their intriguing and unusual electronic structures. This will be of crucial importance for further synthetic developments, especially to pave the road for controlled catalytic radical-type reactions.

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