Computational and experimental tools in solving some mechanistic problems in the chemistry of Fischer carbene complexes

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Well-established bonding situations of organometallic complexes and extensive applications in synthesis have been achieved during the past 25 years. In contrast, very little attention has been devoted to the intimate understanding of their reaction mechanisms. In this *feature article*, we show how the combined use of experimental and computational tools can be used to explore some reaction mechanisms of Fischer-type carbene complexes. The results obtained clearly demonstrate the usefulness of these combined tools to unravel the intimacies of different thermal and photochemical transformations, not only to explain already known processes but to predict new reactivity involving these fascinating complexes.

1. Introduction

The understanding of organic reaction mechanisms has fully matured during the past 50 years, and this ‘‘corps of doctrine’’ is based in very solid experimental and theoretical grounds.[1] This asseveration is far from the truth in the case of organometallic chemistry. The so-called ‘‘Hegedus’ syndrome[2] enunciated in 1988 stated (sentence in bold in the paragraph) ‘‘*Several factors contributed to the initial reluctance of synthetic organic chemists to use organometallic reagents. Lacking education and experience in the ways of elements having d electrons, synthetic chemists viewed organometallic processes as something mysterious and unpredictable, and not to be discussed in polite society. Organometallic chemists did not help matters by advertising their latest advances as useful synthetic methodology, but* ***restricting their studies to very simple organic systems lacking any serious functionality (e.g., the methyl, ethyl, butyl, futile syndrome)****. Happily, things have changed. Organometallic chemists have turned their attention to more complex systems, and more recently trained organic chemists have benefited from exposure to the application of transition metals. This combination has set the stage for major advances in the use of transition metals in the synthesis of complex organic compounds*’’. In fact, major advances in the use of transition metals in the synthesis of complex organic molecules have been achieved during the past 20 years.[3] However, the understanding of organometallic reaction mechanisms has not paralleled the explosive advance in their use in organic synthesis. The task is beyond doubt formidable since the standard kinetic methods are of little use in most reactions, due to the fact that the limiting step is at the initial stages of the reaction (usually a ligand dissociation). Therefore, little information has been extracted from these studies that has been pivotal in the elucidation of organic reaction mechanisms.[1]

The advent of computational tools, particularly DFT methodologies has provided the needed push ahead to achieve


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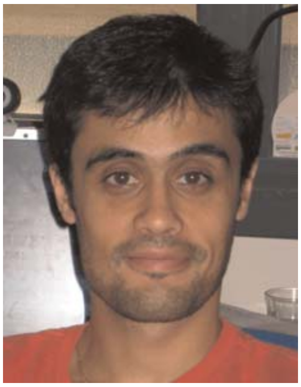
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significant advances in elucidating organometallic reaction mechanisms. Modern and well defined quantum chemical charge and energy partitioning methods such as natural bond orbital analysis (NBO),[4] charge decomposition analysis (CDA),[5] atoms in molecules (AIM),[6] and energy decomposition analysis (EDA),[7] provide a quantitative answer to questions about the bonding situation in terms of simple bonding models. Recent improvements in methodology and computer hardware[8] allow scientists to begin the computational description of complex organometallic reaction mechanisms.

Group 6 metal–carbene complexes[9] (Fischer[10] carbene complexes, Fig. 1) offer an exceptional opportunity to test the synergy of computational and experimental methods to study quite different reaction mechanisms. The enormous number of different processes experienced by these complexes has earned them the appellative of "chemical multitalents".[9l]

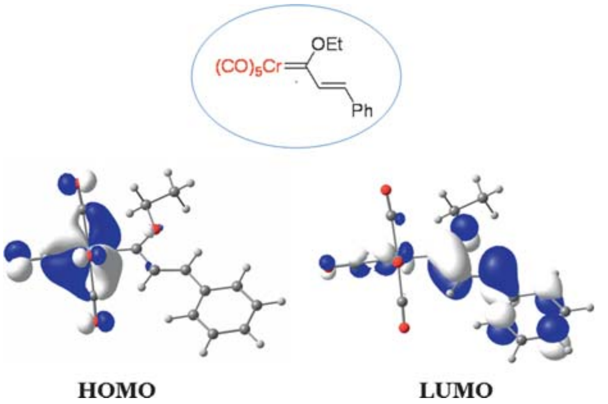
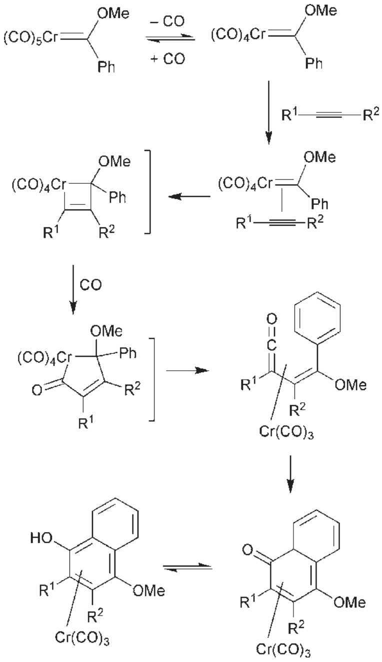


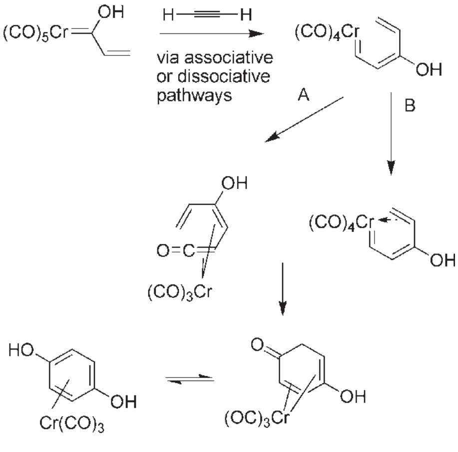
Fig. 1 A representative chromium(0) carbene complex and its HOMO and LUMO orbitals.

The application of computational methods to the study of group 6 carbene complexes has mainly focused on the structure and bonding situation of these compounds. The nature of the chemical bonding of Fischer and Schrock type carbene complexes has been recently reviewed.[11] We have theoretically studied the structure and conformations of alkoxy- and mercaptoxy-Fischer carbene complexes.[12] However, very little is known about the reaction mechanisms of these complexes. The paradigmatic and illustrative example is the Dötz reaction.[13] This process builds an aromatic ring by heating an alkoxychromium(0) carbene complex in the presence of an alkyne in a one-pot reaction. This powerful reaction has been repeatedly used for the synthesis of very different compounds[9c,f] ranging from cyclophanes[14] to natural products.[15] Apart from the formation of aromatic rings, more than 15 different classes of compounds may be formed in this reaction, depending mainly on the nature of the substituents tethered to the carbene carbon.[16] It is not surprising that every elementary step of the Dötz reaction remains the subject of extensive experimental and theoretical studies aimed at explaining the different reaction pathways leading to the most important by-products.[17] Scheme 1 shows the original reaction pathway proposed by Dötz and Fischer *et al.* in 1982.[17a,18]



Scheme 1 Mechanism for the Dötz reaction proposed in 1982.

After 25 years of extensive experimental and computational mechanistic studies, the resulting most probable mechanism for the Dötz reaction is depicted in Scheme 2. The mechanism has been maintained almost unaltered, except for the exclusion of the formation of the highly unstable chromacyclobutene, and the proposal of a new metallatriene as a potential intermediate in the electrocyclization step.[17]

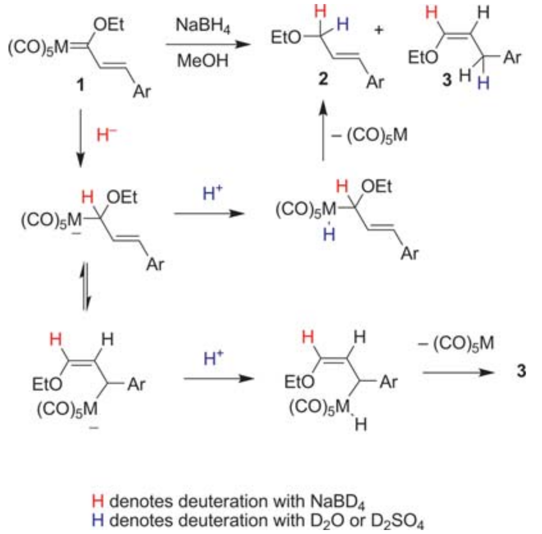


Scheme 2 Current proposed mechanism for the Dötz reaction.

Schemes 1 and 2 show how formidable a task is the understanding of organometallic reaction mechanisms. In this *feature article* we will summarize the efforts undertaken by our laboratories to understand essentially the role of the metal of group 6 metal–carbene complexes in simple nucleophilic addition reactions, cycloadditions, as well as the combined computational–experimental approach to understand the photochemistry of these complexes and to discover new reactions.

2. The isolobal analogy[19] in group 6 metal carbene chemistry

Group 6 Fischer carbene complexes have been traditionally considered the isolobal analogues of organic esters. Whether or not this analogy is maintained even in simple reactions has to be carefully considered. In fact, apparently simple processes such as the addition of nucleophiles to α,β-unsaturated Fischer carbene complexes occur by pathways more complex than the simple addition to a carbon moiety, showing that the metal fragment is not a mere spectator in the progress of the transformation.[20] Within this context the most evident divergence from the classical vision of the metal as an spectator is the addition of hydrides to α,β-unsaturated chromium(0) and tungsten(0) carbenes.[20a,b] In fact, the addition of $NaBH_4$ to carbene complex **1** forms two different reaction products **2** and **3**. While formation of the minor product **2** is easily explained by the conventional conjugated addition, product **3** should be formed through an unpredictable (based on the isolobal analogy with esters) 1,3-chromatropy. The extensive deuteration studies demonstrated to be exceedingly useful to elucidate this reaction mechanism (Scheme 3).



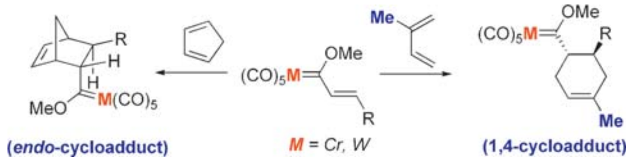
Scheme 3 1,3-Metallatropy observed in hydride addition to α,β-unsaturated group 6 Fischer carbenes.

The scenario is different when cycloaddition to double or triple bonds conjugated to the carbene carbon is considered. In these cases the situation is that predicted by the isolobal analogy, and group 6 metal (Fischer) carbene complexes behave as activated esters. This fact was early experimentally demonstrated but only recently has the systematic computational study of these processes been undertaken.

2.1 [4 + 2] Reactions involving α,β-unsaturated Fischer carbene complexes and dienophiles

The [4 + 2] Diels–Alder cycloaddition between alkenyl- or alkynyl group 6 carbene complexes and 1,3-dienes occurs smoothly and efficiently and it has been used repeatedly in the synthesis of new organic and organometallic compounds.[21] The origin of this success is the compatibility of Fischer carbene complexes with sensitive functionalities, which are not tolerated for metal-free or Lewis-acid catalyzed Diels–Alder reactions. The reaction rates, the *endo*/*exo* selectivities, and the regioselectivities of the Diels–Alder reaction involving Fischer complexes were experimentally found to be comparable to the Lewis-acid catalyzed reactions of their corresponding organic esters.[21d]

DFT calculations (B3LYP/6-31+G(d)&LanL2DZ) carried out[22] on the Diels–Alder reaction between Fischer carbene complexes and neutral 1,3-dienes (isoprene and cyclopentadiene) nicely agree with the experimental findings. These processes are regioselective, leading to cycloadducts where the pentacarbonylmetal fragment and the methyl group of the isoprene are in a 1,4-relative disposition or to *endo*-cycloadducts in the case of cyclopentadiene as a diene (Scheme 4). The computed activation barriers were higher for the pathways leading to the corresponding 1,3- or *exo*-cycloadducts than those for the 1,4- or *endo*-adducts, showing that the origin of the selectivity in these reactions has to be kinetic.



Scheme 4 The selectivity of the Diels–Alder reaction between carbene complexes and neutral dienes.

The transition states of the cycloadditions of Fischer carbenes and neutral dienes have geometrical features resembling the transition states of the analogous Lewis-acid catalyzed [4 + 2] reactions. Thus, it is not surprising that both kinds of compounds present quite similar barrier energies, reaction rates, and regioselectivities and therefore, it can be concluded that, in terms of the isolobal analogy model,[19] carbene complexes act in this reaction as organometallic analogues of Lewis-acid complexed organic acrylates. In fact, the long ago coined term "super ester" for these complexes is then fully applicable to these cycloadditions. This resemblance is extended to the similar computed low synchronicities[23] (S_y = 0.74–0.77, which is actually close to the limit between concerted and stepwise mechanisms) and to the similar computed aromaticities of the corresponding transition states[24] (computed nuclear independent chemical shifts,[25] NICS = −13.1 to −18.2 ppm). Fig. 2 depicts the distribution of the frontier

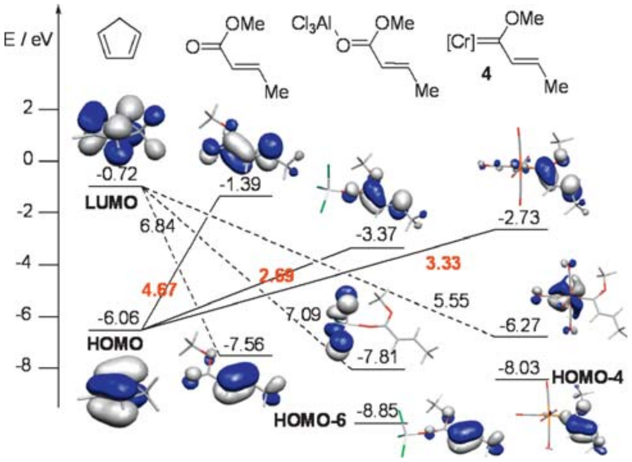


Fig. 2 Frontier orbitals of complex **4** and its organic analogues (values in eV).

orbitals for the reaction of complex **4**, methyl crotonate, and the complex $AlCl_3$–methyl crotonate. It is clear there are strong analogies between the reactions on **4** and complexed crotonate, which are electronically closer to each other than to the free crotonate ester.

Furthermore, the strongly increased *endo*-selectivity in the case of the reaction of complex **4** and cyclopentadiene compared to that of methyl crotonate is due in part to the presence of secondary orbital interactions (SOI),[26] which are stronger in the complex than in the corresponding metal-free processes (Fig. 3).

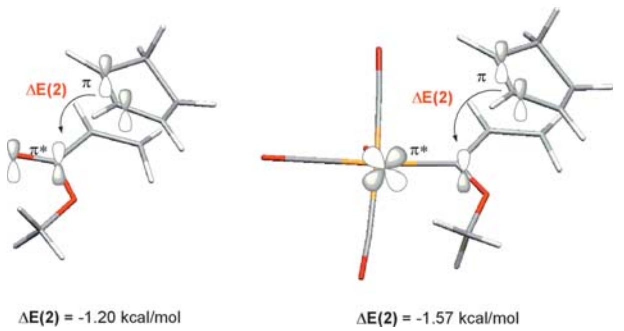


Fig. 3 Stabilizing secondary orbital interactions (SOI) in the reactions of methyl crotonate (left) and carbene complex **4** (right) with butadiene.

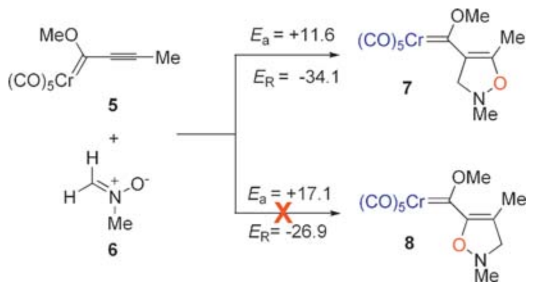
2.2 [3 + 2] Reactions involving α,β-unsaturated Fischer carbene complexes as dipolarophiles[27]

Group 6 Fischer carbene complexes are also exceptional dipolarophiles. The more thoroughly studied 1,3-dipolar cycloaddition of group 6 α,β-unsaturated Fischer carbene complexes is the reaction of alkynyl Fischer carbene complexes and nitrones leading to 2,3-dihydroisoxazole carbene complexes in excellent yields with rate enhancements of 10^4 fold over the analogous alkynyl organic esters. Thorough mechanistic experiments have shown that this is a bimolecular process occurring through a one-step, polar, and concerted pathway.[27e]

Computational tools (B3LYP/6-31+G(d)&LanL2DZ) show[28] that the reaction between carbene complex **5** and nitrone **6** produces the cycloadduct **7** where the Fischer carbene moiety and the oxygen of the nitrone are in a 1,4-relative position. This regioselectivity takes place under both kinetic and thermodynamic control, in view of the considerably higher computed activation barrier required for the formation of cycloadduct **8**, as well as the lower reaction energy calculated for this latter cycloadduct compared to **7** (Scheme 5).

The [3 + 2] cycloaddition reactions,[28] are more asynchronous (S_y = 0.61–0.69) and occur *via* transition states that are less aromatic (NICS = −10.1 to −13.4 ppm) than the corresponding all-carbon analogues. Furthermore, the synchronicity of the transformation, the aromaticity, and geometry of the transition states involving Fischer carbene complexes are similar to those for the reaction of nitrones and propiolates in the presence of Lewis acids. Fig. 4 shows the orbital distribution for the reaction of carbene complex **5**, methyl propiolate, and the complex $AlCl_3$–methyl propiolate with nitrone **6**. The most favorable HOMO (nitrone)–LUMO (dipolarophile) interaction occurs for the Lewis acid catalyzed reaction of methyl but-2-ynoate. The energy difference of the frontier orbitals for carbene **5** and nitrone **6** is only 10.6 kcal mol^{-1} (0.46 eV) higher than the energy gap of the methyl but-2-ynoate–$AlCl_3$ complex and the same nitrone. It can reasonably be concluded that the metal fragment acts as a Lewis acid for the organic moiety in the [3 + 2] cycloadditions of Fischer carbenes and nitrones. This behavior explains the observed rate enhancement of the process compared to organic esters, and the geometrical similarities which were found between the transition states of metal carbene complexes and the Lewis acid catalyzed cycloadditions.

The results obtained for [4 + 2] and [3 + 2] thermal cycloadditions of α,β-unsaturated Fischer carbene complexes are consistent with the role of the Fischer carbene moiety as an electron withdrawing group. The pentacarbonyl metal moiety enhances the reactivity of the alkene or alkyne group, and controls the selectivity of the reactions, in a similar fashion to the complexation of a Lewis acid to the carbonyl group of an α,β-unsaturated ester. Additionally, the strong effect in the distribution of the frontier orbitals of the carbene complex exerted by the $(CO)_5M$, which determinates the regiochemistry of the cycloaddition, is also analogous to that of the Lewis acid complexed α,β-unsaturated esters. Therefore, the isolobal analogy is fully applicable to these cycloaddition reactions.



Scheme 5 Regioselectivity of the [3 + 2] cycloaddition between complex **5** and nitrone **6** (values in kcal mol^{-1}).

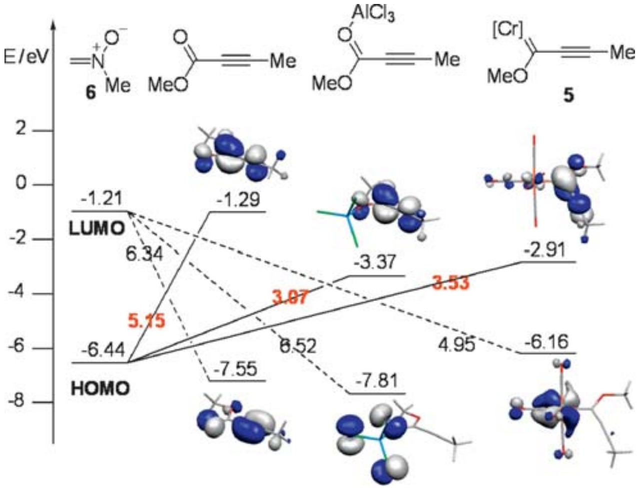
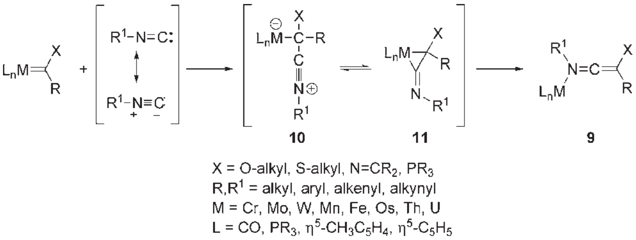


Fig. 4 Frontier orbitals of complex **5** and its organic analogues (values in eV).

3. The reaction of Fischer carbene complexes with isonitriles: a bridge between thermal and photochemical reactivity

Fischer carbene complexes react thermally with isonitriles to produce metal complexed ketenimines **9**.[29] The mechanism for the formation of complexes **9** was proposed to occur by a 1,2-insertion of the $\text{N}{\equiv}\text{C}$ bond into the $\text{M}{=}\text{C}$ bond, *via* ylide complexes **10** and/or (with charge neutralization) *via* metallacyclopropanes **11**. Intermediates **10** and **11** are formed by nucleophilic attack of the isocyanide carbon atom on the electrophilic carbene carbon (Scheme 6). This proposal was based on the experimental observation that alkoxychromium(0) carbene complexes having carbene and isocyanide ligands in a *cis* arrangement are stable under the reaction conditions.[29,30] This fact ruled out an hypothetical reaction pathway in which the isocyanide first coordinates to the metal atom and further evolves to intermediates **10** and **11**. Furthermore, the stability and thence the possibility of isolation of species **9–11** is metal dependent. Thus, the species **9** has been characterized crystallographically for chromium[31] while metallacyclopropanimine **11** has been isolated for iron.[32] Moreover, the coexistence of a mixture of species **9–11** in solution has been reported for manganese based on NMR data.[33] Therefore, with these experimental data in hand the apparently simple scenario sketched in Scheme 6 becomes much more complicated.



Scheme 6 Reaction of Fischer carbene complexes and isonitriles.

The potential energy surface (PES)[34] for the reaction of methylisonitrile with chromium, tungsten, and iron Fischer carbene complexes **12** (Fig. 5) clearly indicates that the insertion of the isocyanide into the $\text{M}{=}\text{C}$ bond of the chromium(0) Fischer carbene complexes to produce ketenimine complexes **9** occurs *via* the metallacyclopropanimine **11**, rather than the ylide complex **10** (Scheme 6), followed by a 1,2-metallotropic rearrangement. Moreover, the energy barrier for the 1,2-[Fe] migration from intermediate **11** to **9** is 15.6 kcal mol^{-1}, which renders this process unfavorable compared to the corresponding chromium or tungsten metallotropic processes (E_a = 3.4 kcal mol^{-1} for chromium and E_a = 8.1 kcal mol^{-1} for tungsten complexes, see Fig. 5). Moreover, the global minimum on the PES is the species **9** for M = Cr, W while for M = Fe it is **11**. According to these results, the isolable compounds in the case of iron should be metallacyclopropanimines **11** and not metal-coordinated ketenimines **9**. This is in full agreement with the isolation and crystallographic characterization of Fe–cyclopropanimines[32] and Cr–ketenimines.[31]

4. Photochemical reactivity

The irradiation of group 6 (Fischer) metal carbene complexes with visible light in the presence of nucleophiles leads to the formation of β-lactams,[35] cyclobutanones,[36] amino acids and peptides,[37] polynuclear hydrocarbons,[38] and β-lactones[39] (Scheme 7). This rich and synthetically powerful photoreactivity[9i] has no paragon in the photochemistry of any other class of organometallic compounds. Nevertheless, the synthetically useful photochemistry of chromium(0) and molybdenum(0) carbene complexes (but not tungsten(0) carbene complexes) relies exclusively on the reversible

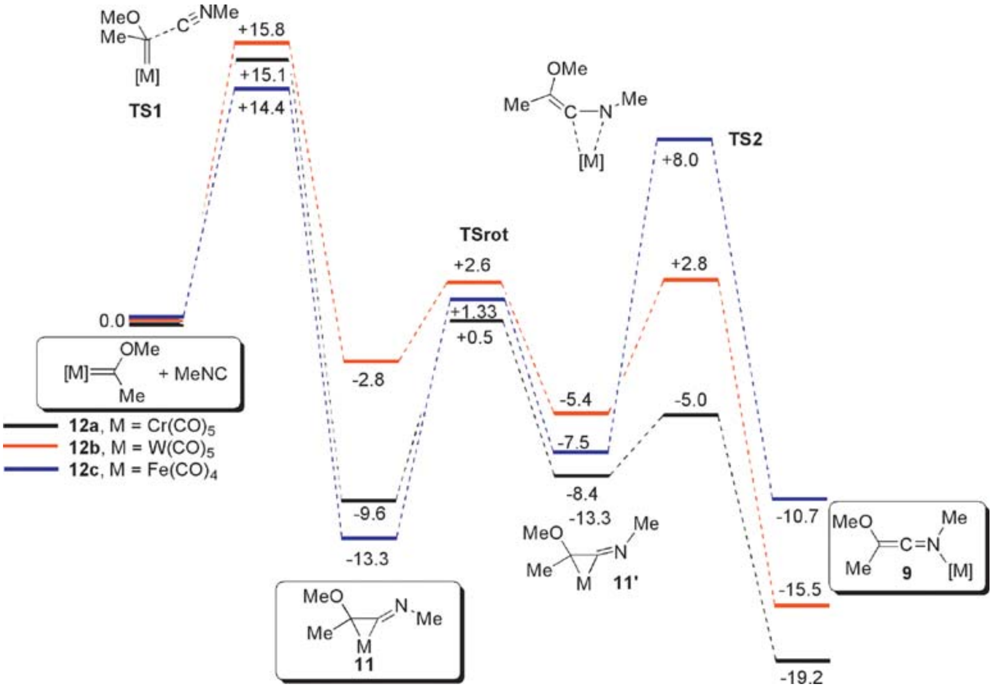
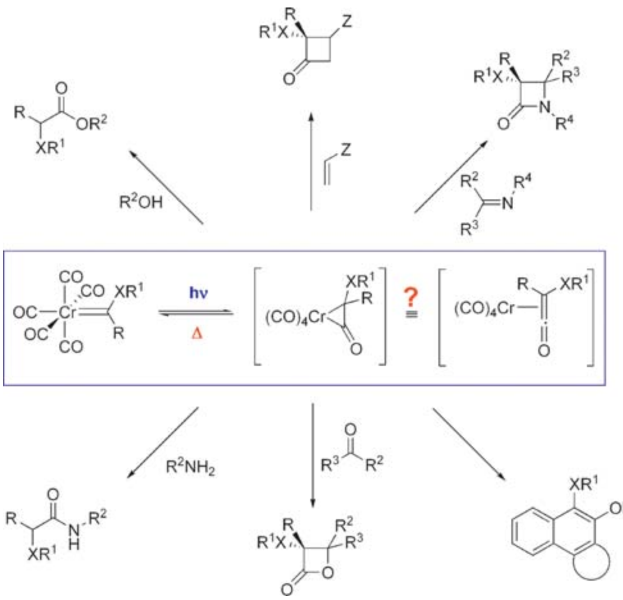


Fig. 5 Computed reaction pathways for the reaction of complexes **12** and methylisonitrile (values in kcal mol^{-1}).



Scheme 7 Some products obtained in the photochemical reaction of group 6 Fischer carbene complexes and different nucleophiles.

insertion of a CO ligand into the M$=$C bond to yield ketene-like species.[40] This mechanistic insight was reported by Hegedus *et al.* in 1988[41] who systematized the photochemistry of group 6 carbene complexes in the presence of nucleophiles (Scheme 7). Despite the close parallelism of the ketenes derived from the irradiation of group 6 metal carbene complexes and free ketenes, the different efforts directed towards the detection of these elusive intermediates were fruitless,[42] and during almost 20 years the mechanism of these processes remained unexplored. Furthermore, no other photoprocesses were ever reported for group 6 Fischer carbene complexes.

Difficulties in the experimental study of these transformations led to the use of a combination of computational–experimental methods to shed some light on the photochemistry of these complexes. The problem was sequentially (albeit not chronologically) studied throughout the following steps:

- Study of the electronic spectroscopy of group 6 Fischer carbene complexes.
- Photocarbonylation step.
- Reaction of the metallaketenes with nucleophiles.
- Search for other photoreactions.

4.1 Electronic spectroscopy of group 6 Fischer carbene complexes

Chromium(0) carbene complexes are strongly colored compounds, their color ranging from pale yellow to dark red. The UV-visible spectra of Fischer metal–carbene complexes show three well defined absorptions: a spin-forbidden metal–ligand charge transfer (MLCT) absorption around 500 nm, the spin-allowed and moderately intense ligand-field (LF) absorption in the range of 350–450 nm, and one additional LF transition in the range of 300–350 nm (Fig. 6).[9a] There is a lower energy LF transition usually masked by the intense MLCT absorption, although it has been observed in the non-heteroatom stabilized carbene complex $(CO)_5W{=}CPh(p\text{-}MeOPh)$.[43] Based on earlier molecular orbital calculations,[44] the MLCT band has been assigned to the promotion of an electron from the non-bonding metal-centered HOMO to the carbene-carbon p-atomic orbital centered LUMO, while the LF band was attributed to the more energetic population of the metal centered LUMO + 1.

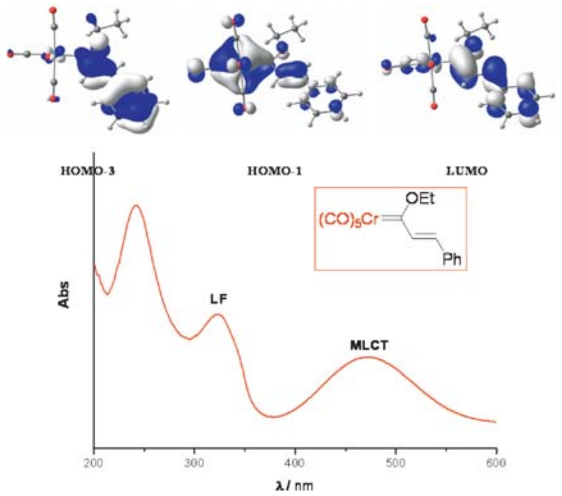


Fig. 6 UV-Vis spectrum and molecular orbitals of pentacarbonylethoxystyrylchromium(0) carbene complex.

TD-DFT (time-dependent density functional theory) calculations show appealing differences with respect to the earlier work.[45] The MLCT band was ascribed to the promotion of one electron from the metal-centered HOMO$-$1 to the LUMO which is a π-extended orbital involving the p-atomic orbital of the carbene carbon atom (Fig. 6). The presence of a π-link between the phenyl group and the metal moiety provokes a strong red-shift of this absorption. The LF transition is assigned to the promotion of one electron from the HOMO$-$3 (centered in the π-system of the carbene ligand, Fig. 6) to the LUMO.

Furthermore, both the LF and the MLCT band have a remarkable π–π* character, which was demonstrated by the strong dependence of the absorptions on the donor/acceptor nature of the substituent in *p*-substituted styrylchromium(0) carbene complexes. The effect of the substituent was also related to the equilibrium geometry of the complexes. The reassignment of the electronic spectroscopy of group 6 Fischer carbene complexes should have interesting consequences in the interpretation of the photochemistry of these and related compounds and constitutes the first step to fully understand the photochemistry of these compounds.

4.2 Photocarbonylation step

Irradiation of alkoxychromium(0) carbene complexes **13**, either in the LF band followed by relaxation to the MLCT band, or directly in the MLCT band, results in the excitation of these complexes to the S$_1$ state, which readily decays to T$_1$ by intersystem crossing (ISC) due to spin–orbit coupling.[46] These triplet species have a chromacyclopropanone structure **14** whose unpaired electrons are mainly localized in the metal fragment and in the former carbene carbon atom. The triplet coordinative unsaturated complexes change their multiplicity prior to evolving to the ketene-derived products. This is accomplished by filling the corresponding free coordination site with a molecule of a coordinating solvent in the apical position. The geometrical features and the NBO analysis carried out on these species clearly show that they possess a structure which corresponds to a ketene species **15** coordinated to chromium with a highly polarized Cr–C (former carbene carbon atom) bond. From these acylchromate complexes, ketene-derived products can now be formed in the presence of ketenophiles on the S_0 hypersurface, while in their absence, these species revert to the starting carbene complex in a very exothermic process (Fig. 7).

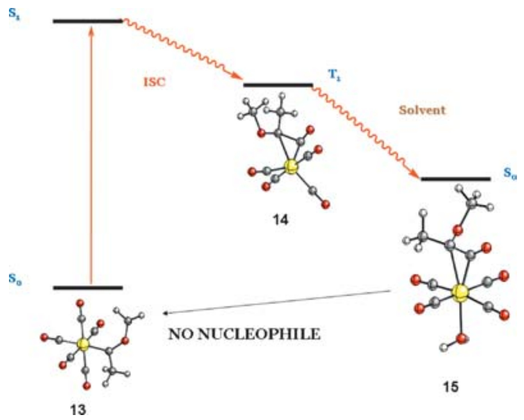


Fig. 7 The photocarbonylation of chromium(0) carbene complexes.

The solvent-induced T_1–S_0 crossing of chromoketene **16** was further appealing. Relaxed scans (UB3LYP/LANL2DZ& 6-31G(d)) of this complex at different Cr–OH_2 distances, where the OH_2 ligand models an ethereal coordinating solvent (Fig. 8), showed that the T_1 state of **16** exhibits a very swallow Morse-like curve, whose minimum is located at $r = 3.746$ Å, r being the Cr–OH_2 distance (Fig. 8). The harmonic analysis of this structure shows two low-frequency vibrations associated with stretching of the Cr–O interaction and symmetrical bending of two carbonyls to achieve the octahedral coordination. This result, together with the negligible energy difference between both states at large Cr–OH_2 distances, indicates that the available thermal energy is enough for the molecule to pass from the T_1 to the S_0 potential energy surface. This radiationless intersystem crossing does not take place through a narrow conical intersection (a photochemical funnel)[47] but occurs at r values larger than 4.0 Å along a large energy plateau shared by both spin states. This situation has no known precedents in the photochemistry of metal complexes.

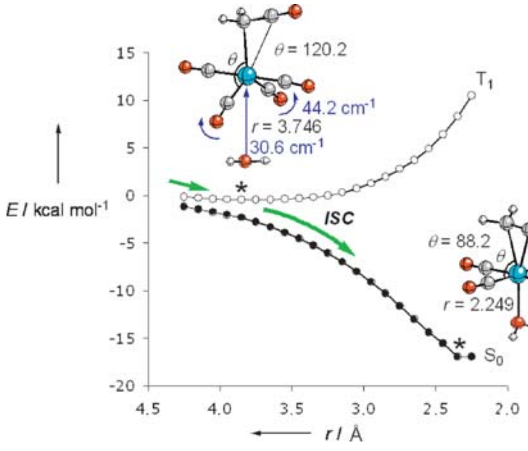


Fig. 8 Fully relaxed scans for the chromoketene **16** coordinated with a water molecule as a model for a coordinating ethereal solvent. The energies and geometries were computed at different Cr–OH_2 distances, denoted as r. Open and black circles indicate calculations at T_1 and S_0 states, respectively. Blue arrows indicate the stretching and bending vibrations associated with the T_1–S_0 radiationless intersystem crossing, represented by the green arrows. Blue numbers correspond to the wavenumbers associated with these vibrations.

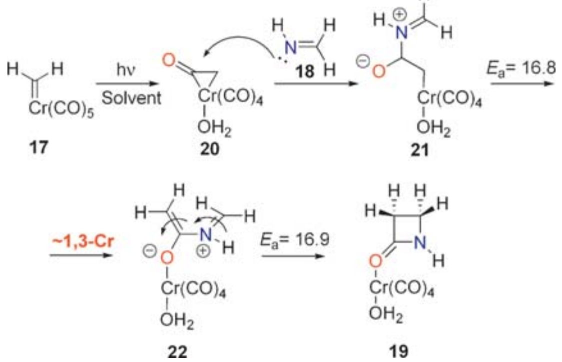
The computational model predicts that group 6 carbene complexes having soft or strong σ-donor ligands (such as phosphines) may carbonylate but not alkoxypentacarbonyltungsten(0) carbene complexes.

4.3 Reaction of metallaketenes with nucleophiles

The photolysis of Fischer carbene complexes with imines led to 2-azetidinones in good yields and free of by-products.[35] The reaction is highly diastereoselective since under these conditions Fischer carbene complexes form β-lactams where the larger substituent of the ketene is placed *cis* to the *anti*-substituent of the imine. This contrasteric bias has been claimed to be due to the presence of the metal moiety during the cycloaddition.[9j]

The PES of the reaction of the model complex **17** with methanimine $CH_2{=}NH$ **18** to yield the cycloadduct **19** was calculated to achieve some data about the mechanism of the reaction of metallaketenes and imines (Scheme 8).[48] Similarly to the classical Staudinger reaction between ketenes and imines,[49] a stepwise mechanism was obtained. The reaction starts with the nucleophilic attack of the nitrogen atom of the imine on the carbon atom of the photogenerated acylchromate species **20**. The likeness to the classical Staudinger reaction stops at this point. Now a 1,3-metallatropic process connects **21** to **22**. Intermediate **22** is a chromium enolate–iminium zwitterionic complex. The final step converts **22** to the cycloadduct **19** through a saddle point associated with a conrotatory ring closure and therefore is subjected to torquoelectronic effects.[50]

However, this mechanism may be flawed since it predicts that chromium(0) carbene complexes having σ-donor ligands should carbonylate and thence be reactive towards imines.

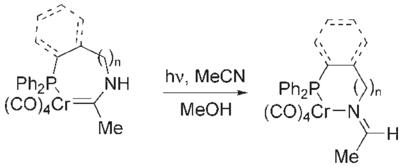


Scheme 8 Computed reaction pathway for the reaction of complex **17** and imine **18** (values in kcal mol^{-1}).

Experimental evidence[48] demonstrated that alkoxychromium(0) carbene complexes having a CO ligand substituted by a PPh_3 are less reactive than their pentacarbonylchromium(0) analogues, while those complexes having a CO substituted either by Bu_3P or the bidentate phosphine $Ph_2PCH_2CH_2PPh_2$ are not reactive. Efforts to fully develop a general experimental–theoretical model which explains the influence of the chromium ligands and substituents at the carbene carbon atom on the reactivity and the *cis*/*trans* ratio of the final 2-azetidiones are currently underway.[51]

4.4 Search for other photoreactions

The search for photoreactivity different from the photocarbonylation has been a long-standing quest in group 6 Fischer carbene chemistry. With the, at that time, somewhat naïve idea in mind of hampering the photocarbonylation process, the chromium(0) carbene complexes **23** were synthesized. The idea was that the tether may geometrically hamper the insertion of CO into the M=C double bond (the resemblance between a metallacyclopropanone and a linear ketene was assumed as the starting point of the work). Therefore, evolution of the excited species through pathways different from carbonylation was expected. In fact, complexes **23** reacted by photolysis in the presence of MeOH to yield new organometallic complexes **24** lacking the carbene moiety (Scheme 9).[52] Therefore, instead of a photocarbonylation process a new carbene to imine photorearrangement took place.



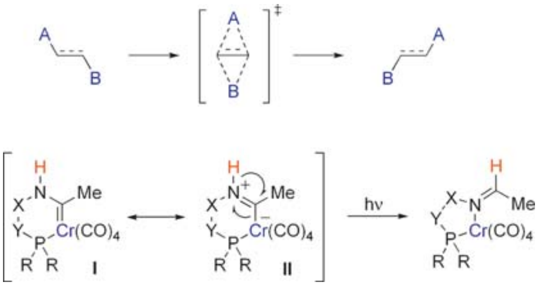
23
n= 0,1

24

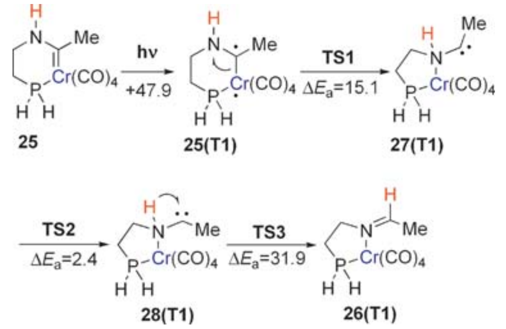
Scheme 9 The carbene complex to imine rearrangement.

This transformation is formally a 1,2-dyotropic rearrangement of type I according to the definition by M. T. Reetz.[53] Both C–Cr and N–H bonds migrate intramolecularly, and the Cr and H atoms interchange their positions, the C=N moiety (structure II contributes significantly to the description of the complex) being the static scaffold (Scheme 10).

All our attempts to locate and characterize a concerted transition state that connects the model complex **25** with the *syn*-N-metallated imine **26** in either the S_0 or T_1 potential energy hypersurfaces met with no success. Instead, a stepwise mechanism that starts with a short-lived triplet state **25(T₁)**, formed after initial photo-excitation of the singlet ground state S_0 to the excited singlet state S_1 and subsequent intersystem crossing, was found (Scheme 11). **25(T₁)** evolves to uncoordinated triplet carbene species **27(T₁)** in the triplet hypersurface *via* a transition state which is associated with the 1,2-migration of the metal moiety from the carbene carbon atom to the nitrogen atom. Carbene **27(T₁)** isomerizes to **28(T₁)** *via* rotation about the N–C(Me) bond. The species **28(T₁)** yields the final product **26(T₁)** through a transition state associated with the migration of the hydrogen atom from the nitrogen atom to the carbene moiety.

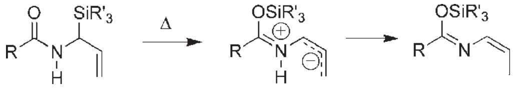


Scheme 10 Simplified mechanistic pathway for the type I chromadyotropic rearrangement.



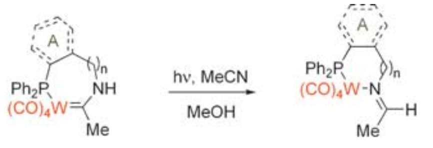
Scheme 11 Computed reaction pathway for the photoreaction of complex **25** (values in kcal mol^{-1}).

To the best of our knowledge, this process, together with the *N*-(α-silyl)allyl amide → *cis*-enamide transformation (Scheme 12) reported by Houk, Danishefsky, and co-workers,[54] constitute the unique examples of stepwise dyotropic rearrangements reported so far.



Scheme 12 *N*-(α-Silyl)allyl amide → *cis*-enamide transformation.

The dyotropic reaction is not restricted to chromium(0) carbene complexes. In fact, the aminotungsten(0) carbene complexes **29** analogous to **23** also form *syn*-N-metallated imines **30** (Scheme 13).[55] This process represents ***the very first photoreaction reported for Fischer type tungsten(0) carbene complexes****, which have been traditionally considered as photo-inert compounds*. We computed the corresponding PES of this type I dyotropic rearrangement and we found that, with the exception of the relative energies of the starting biradical species with respect to the ground state complexes (4.8 kcal mol^{-1} higher in



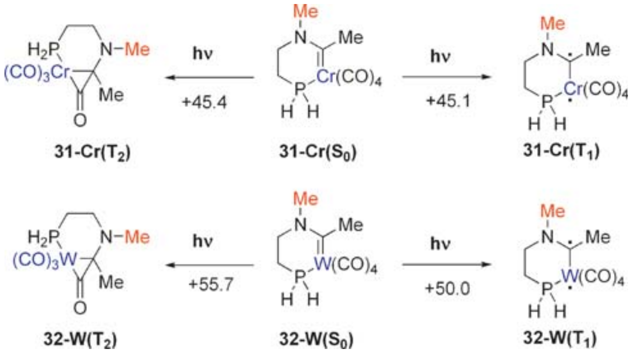
29a n = 0, A = none
29b n = 1, A = none
29c n = 1, A = *o*-Ph

30a n = 0, A = none (71%)
30b n = 1, A = none (55%)
30c n = 1, A = *o*-Ph (38%)

Scheme 13 First tungsten(0) carbene complex photoreactions.

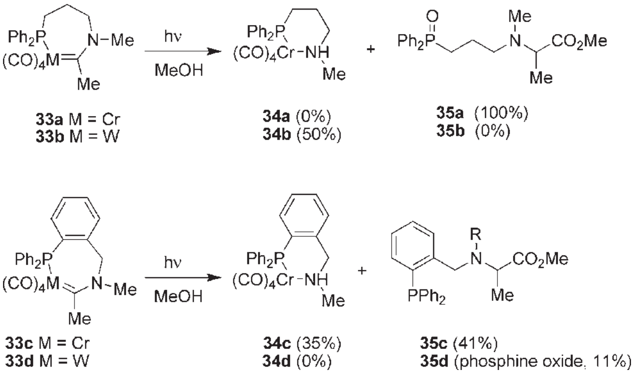
tungsten complexes than in their chromium analogues), no systematic differences were observed between the isostructural chromium and tungsten complexes, which is a very remarkable and unusual result.[56]

The results above show the fundamental influence of the ligands in the photochemistry of Fischer carbene complexes. The ability of our computational methodology to predict the behaviour of other types of complexes was demonstrated by using the model complexes **31** and **32**. Now, two coexistent triplet species, namely the biradicals **31Cr(T$_1$)** and **32W(T$_1$)**, and the metallacyclopropanone complexes **31Cr(T$_2$)** and **32W(T$_2$)**, were found (Scheme 14). Both activated species are nearly isoenergetic ($\Delta E_{\mathrm{T1-T2}}$ = 0.3 kcal mol^{-1}) for chromium(0) carbene complexes. Therefore, chromium(0) carbene complexes should lead to mixtures of ketene-derived (aminoesters) derived from **31Cr(T$_2$)** and products derived from **31Cr(T$_2$)**. In contrast, the computed energy difference between the respective activated species for the model tungsten complex **32** was + 5.7 kcal mol^{-1} being the biradical **32W(T$_1$)**, the most stable excited species (Scheme 14). This higher difference in energy should result in a clear bias for the formation of products derived from biradical **32W(T$_1$)**, but the possibility of photocarbonylation is not excluded in these cases.



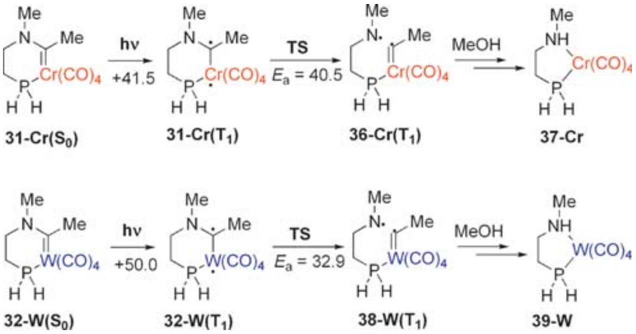
Scheme 14 Coexisting metallacyclopropanone and biradical triplets in the photochemistry of group 6 carbene complexes.

In fact and as predicted, N-alkyl substituted chromium(0) and tungsten(0) aminocarbene complexes **33** upon irradiation lead to mixtures of tetracarbonylmetal(0)-*N*-aminophosphine complexes **34** and *N*-alkylaminoesters **35** (Scheme 15). Compounds **35** derive from a photocarbonylation process, which is especially important for the case of tungsten complexes **33**. *In fact, this is the first reported example of a photocarbonylation process of the hitherto fore "photoinert" tungsten(0) carbene complex*. Tetracarbonylmetal(0)-*N*-aminophosphine complexes **34** are formed from the cleavage of the N–C bond of the starting carbene complex. This process is the organometallic analog of the α-fragmentation of amides.[57]



Scheme 15 The non-carbonylative photochemistry of chromium(0) and tungsten(0) carbene complexes.

The evolution of the short-lived species **31(T$_1$)** occurs *via* a transition state associated to the cleavage of the N–C bond, like in the α-fragmentation of amides.[58] Amazingly, the energy barrier of the N–C bond cleavage is 7.9 kcal mol^{-1} lower for tungsten complexes than for isostructural chromium species, making this step easier for tungsten than for chromium. The stronger N–C bond in **31(T$_1$)** (M = Cr) compared to that in the tungsten species accounts for this observation (Scheme 16).

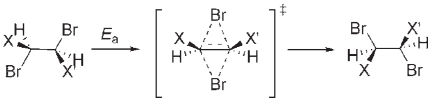


Scheme 16 Comparative reaction pathways for chromium(0) and tungsten(0) carbene complexes.

5. Corollary

As discussed through this *feature article*, the isolobal analogy between group 6 Fischer carbene complexes and organic esters or amides should be excluded when the metal is directly involved in the reaction. This is true even in the simplest addition reaction of hydride to an α,β-unsaturated carbene. Otherwise the reactions occurring outside the participation of the metal finely respond to the isolobal analogy.

With the aim of checking this asseveration also for the well-established type I dyotropic rearrangement, which is fundamentally concerted in organic systems but stepwise in group 6 carbene complexes, the effects of different substituents on type I dyotropic rearrangements were studied by means of DFT calculations in the search for a non-concerted reaction pathway (Scheme 17).[58] Although clear correlations between the donor ability of the heteroatom bonded to the reactive system (measured by the Hammett σ_p substituent constants) and the activation barriers needed for the rearrangement were obtained (higher values of σ_p resulting in lower E_a and longer C–C and C–Br bond distances in the corresponding transition



Scheme 17 Type 1,2-dyotropic rearrangement in vicinal 1,2-dibromides.

states), no discrete intermediates were found. Strikingly, the computed values of the synchronicity (S_y) were high in all the studied systems rendering 1,2-dyotropic reactions synchronous and mostly independent of the substituents.

It can be concluded that the presence of the metal is decisive for the stepwise nature of the type I metalladyotropic rearrangement, even if the nature of the final products is as expected for a concerted process.

6. Summary and conclusions

The knowledge of many organometallic reaction mechanisms is still in its early stages of development, which is in sharp contrast with the worldwide use of organometallic reagents in organic synthesis. The situation is even more dramatic in photochemical processes using organometallic reactions, which results in the almost lack of synthetically useful organometallic reagents for preparative photochemistry. The situation contrasts with the well-established bonding situation of many organometallic complexes. This knowledge gap undoubtedly has its origin in the experimental difficulties found in studying the different organometallic transformations and because most of the reported experimental and/or theoretical studies have been traditionally focused on the bonding situation and application in synthesis of these compounds. In the present *feature article*, we have shown the combined use of experimental and computational tools to explore some reaction mechanisms of Fischer-type carbene complexes. The results obtained clearly demonstrate the usefulness of these combined tools to unravel the intimacies of different thermal and photochemical transformations, not only to explain already known processes but to predict new reactivity involving these amazing complexes.

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