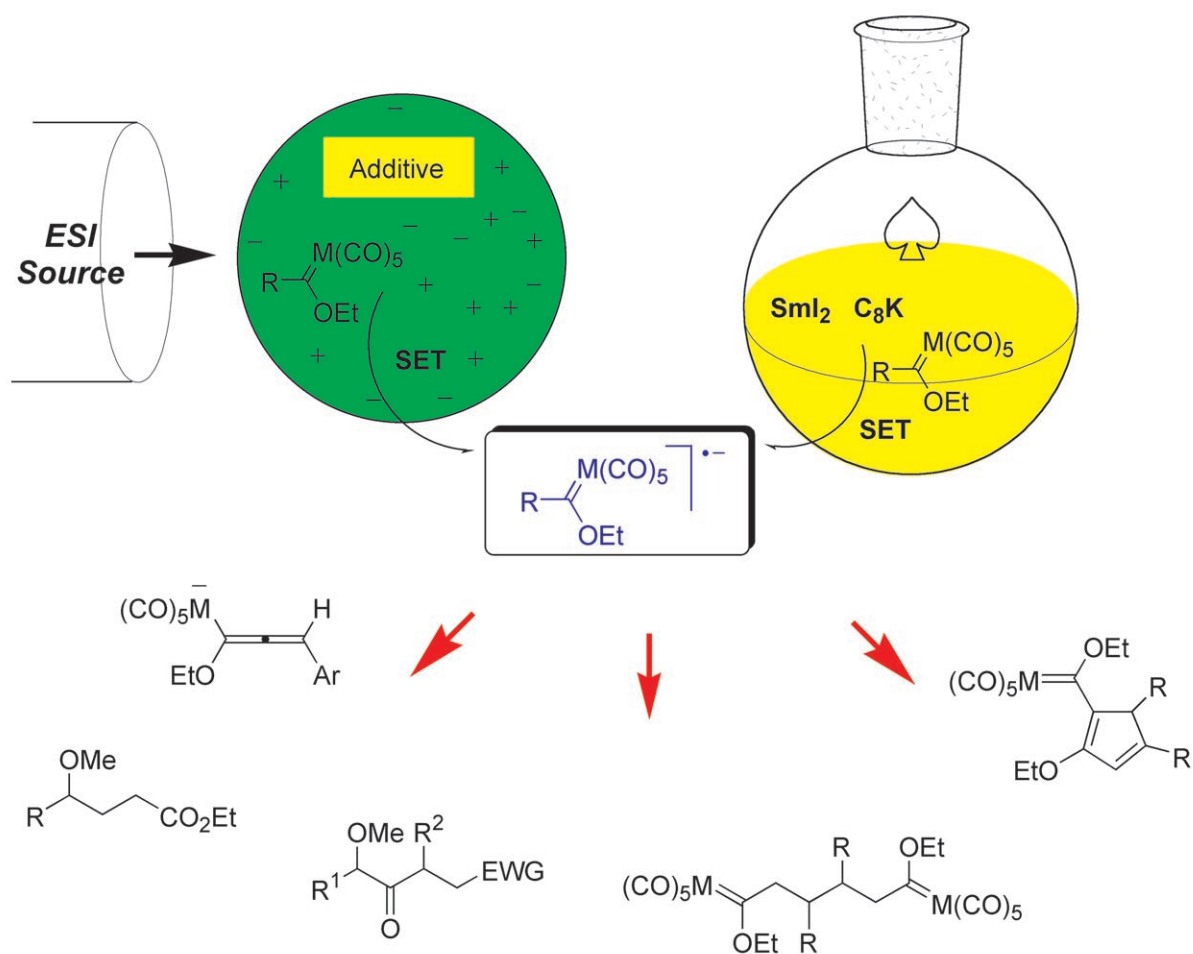


The Origin and Fate of Metal–Carbene Radical Anions



Fischer Carbene Complexes: Beautiful Playgrounds To Study Single Electron Transfer (SET) Reactions

Miguel A. Sierra,* Mar Gómez-Gallego, and Roberto Martínez-Álvarez^[a]

Abstract: The knowledge of the reactivity of Fischer carbene complexes in electron transfer processes is still in the early stage of development, but interesting advances are foreseeable in this young branch of metal-carbene chemistry. Although these compounds have a dual reactivity (which makes them good substrates for oxidation and reduction processes), their behavior towards chemical electron transfer (ET) reagents was unknown until very recently. This article covers the progress accomplished in the reactivity of these compounds towards chemical ET reagents (C_8K or SmI_2), as well as the use of nonconventional sources of electrons, such as electrospray ionization (ESI) to induce ET processes. Special emphasis will be made on the effect of the structure of the starting carbene in the outcome of the reaction and in discussing the different mechanisms proposed.

Keywords: carbenes · electron transfer · electrospray ionization · nonconventional media · set reagents

Introduction

Development of modern chemistry intimately parallels our understanding of single electron transfer (SET) processes.^[1] In fact, one of the key landmarks in Chemistry is the Marcus theory^[2] rationalizing SET processes in different fields of knowledge. SET reactions in organic synthesis are generally mediated by metals or metal complexes^[3,4] (for example, SmI_2 and Na-naphthalenide), charge transfer interac-

tions^[3] or induced by light.^[5] The synthetic utility of these processes has been profusely demonstrated during the last century. By contrast, the knowledge of the mechanisms of reaction of transition metals towards chemical SET reagents is still in the early stages of understanding. Within this context the study of SET processes between organometallic complexes and organic or organometallic additives in a non-conventional media such as electrospray ionization sources (ESI) is also an emerging research area.

Transition metal Fischer carbene complexes^[6] are paramount to study both, the chemical and ESI induced SET processes considering that the electron-withdrawing effect of the $[M(CO)_5]$ moiety in these compounds makes the carbene carbon very electrophilic, and hence a extremely good electron acceptor. The LUMO orbital (Figure 1) is centered

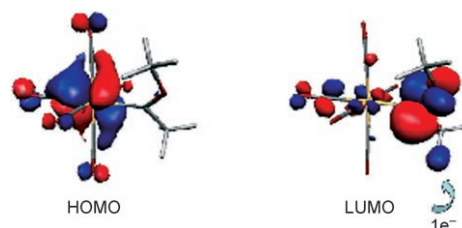


Figure 1. HOMO and LUMO orbitals of $(CO)_5Cr(OMe)Me$ complex showing the highly centered nature (HOMO metal and LUMO carbene carbon) of both orbitals.

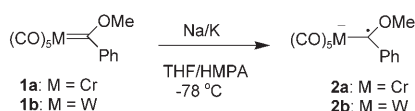
in the carbene carbon and the capture of one electron will thence succeed in a much more localized site of the molecule, while the negative charge will be centered in the metal. Highly stabilized species may thereof arise from the capture of one electron.

In this concept we present the behavior of Fischer carbene complexes in the scarcely explored conventional (chemically induced) and nonconventional (ESI) SET reactions, as well as an outlook on the perspectives of this area of research in the near future.

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Chemically Induced Electron Transfer Reactions: Metal Carbene Complexes as the Acceptors

The orbital distribution represented in Figure 1^[7] predicts the reactivity of Fischer carbene complexes towards a chemical electron transfer reagent first reported by Casey in the reduction of alkoxyaryl carbene complexes **1** by Na/K alloy (Scheme 1).^[8] The ESR of radical anion **2** (-50°C under

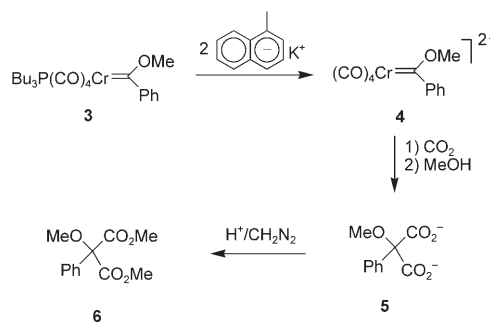


Scheme 1. Reaction of chromium- and tungsten(0)-carbene complexes to form stable radical anions.

high dilution conditions) indicated that it was a carbon centered radical, with the odd electron localized on the carbene ligand, and that the effect of the metal on the electron density distribution was small.

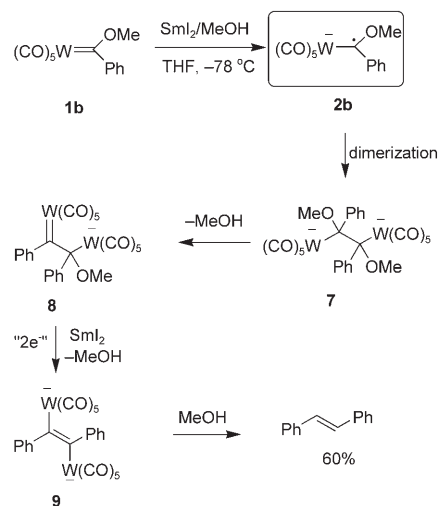
The one-electron reduction of **1** causes the umpolung of the electrophilic carbene carbon in **2** (now it becomes nucleophile), which means a total change in the reactivity pattern of the starting complex. In spite of this fact, the first attempt of exploring the reactivity of the radical anion obtained from a Fischer carbene complex was made by Cooper in 1990.^[9] Treatment of $[\text{Bu}_3\text{P}(\text{CO})_4\text{CrC}(\text{OMe})\text{Ph}]$ **3**, with excess potassium 1-methylnaphthalenide yields the highly reduced carbene complex **4**. This species reacts with CO_2 as an electrophile to yield malonate **5**, isolated as its methyl ester **6** (Scheme 2). Since this initial report, it was necessary to wait for more than a decade to find new studies about the reactivity of Fischer carbene complexes under electron transfer conditions, and of their synthetic applications, particularly in the formation of C–C bonds.

The reactivity of radical anions **2** not only is related to their nucleophilicity (and hence to the electrophile present in the reaction medium) but also depends on the nature of



Scheme 2. Highly reduced complex **4** reacts as nucleophile with CO_2 .

the metal. Thus, tungsten-based anion radical **2b** generated by reaction of **1b** with SmI_2 dimerizes to form dianion **7** in the absence of electrophiles. Intermediate **7** extrudes MeOH to form a new anionic carbene **8**, which captures two more electrons to form dianion **9**. Finally, protonation of **9** lead to stilbene as reaction product (Scheme 3).^[10]

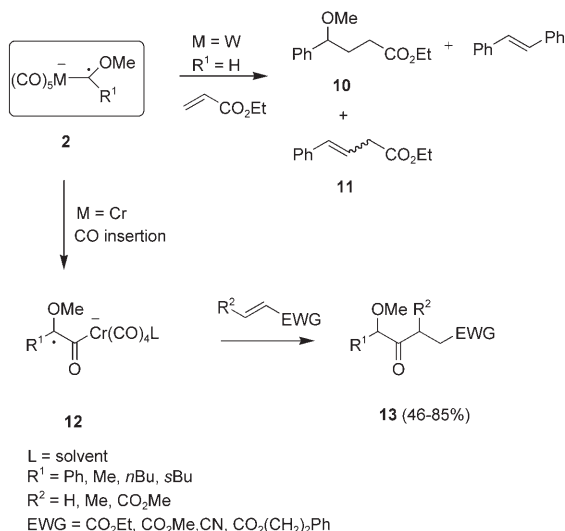


Scheme 3. Reaction of radical anion **2b** in the absence of radical acceptors.

Abstract in Spanish: *A pesar de que los complejos metal-carbena de Fischer tienen una reactividad dual (que les convierte en excelentes sustratos para procesos de oxidación y de reducción), el estudio de su reactividad en procesos de transferencia electrónica está todavía en sus inicios, aunque es de esperar que se produzcan interesantes progresos en esta rama de la química de compuestos organometálicos. Este artículo recoge los avances en el conocimiento de la reactividad de estos complejos en procesos de transferencia electrónica, tanto inducidos por vía química (C_8K o SmI_2), como en medios no-convencionales, como es el caso de una fuente de ionización por electrospray (ESI). El artículo hace también especial hincapié en la influencia de la estructura del complejo de partida sobre el curso de la reacción y discute los diferentes mecanismos propuestos.*

The presence of electrophiles modifies the reactivity of intermediates **2**. Thus, **2b** can be trapped with ethyl acrylate in a competitive process to the dimerization to form mixtures of **10** and **11** (in variable amounts depending on the complex/acrylate ratio) and stilbene. Radical-anion **2a** derived from chromium(0)-carbene complex **1a** shows a different reactivity towards electron-poor alkenes. The rate of reduction is now slower than that observed for the tungsten complexes, and a carbonylation pathway competes with the direct addition of the anion radical to the alkene. This carbonylation reaction leads to the formation of α -methoxyketones **13** through intermediates **12**, together with the products analogous to **10** and **11** (Scheme 4).

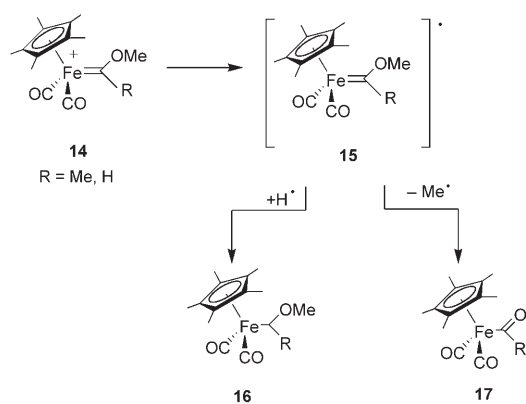
The different behavior of chromium- and tungsten-carbene complexes towards the insertion of a CO ligand has

Scheme 4. Reaction of radical anions **2** in the presence of electrophiles.

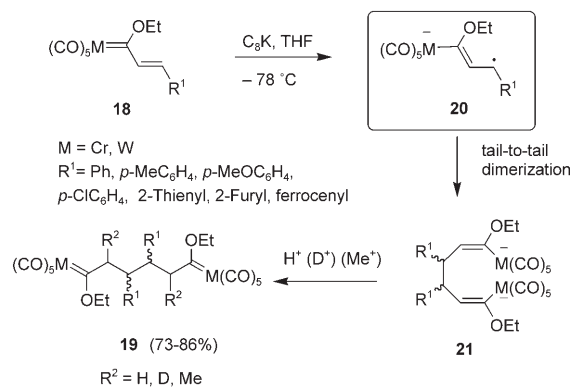
been explained considering the differences in metal–CO bond strength, through backbonding, that makes chromium complexes more prone to carbonyl insertion than their tungsten counterparts.^[11] The CO insertion pathway can be favored by adding the ethyl acrylate after reduction of the carbene complex (SmI₂, –78 °C, THF/MeOH, stirring overnight). Under these conditions α -methoxyketones **13** were isolated exclusively in good yields.

In contrast to this reactivity, 19-electron iron–carbene complexes **15**, generated by reaction of cationic heterocarbene iron complexes **14** and Cp₂Co as electron transfer reagent, either captures a hydrogen atom from the medium or loses the methyl group of the methoxy fragment, leading to complexes **16** and **17**, respectively. The generation of the intermediates **15** can be also induced electrochemically (Scheme 5).^[12] Therefore, the outcome of the reactions of nonconjugated carbene complexes and ET reagents appears to be very metal-dependent.

The evolution of the radical anions derived from the capture of an electron by α,β -unsaturated Fischer carbene com-

Scheme 5. Alternate reaction pathways in the evolution of 19-electron Fe-carbene **15**.

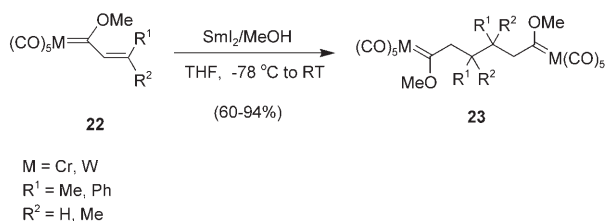
plexes is different. The work by our group^[13] has shown that treatment of α,β -unsaturated Fischer carbene complexes **18** with C₈K^[14] (THF, –78 °C) followed by quenching with 10% H₂SO₄, gives biscarbene complexes **19** in good yields as inseparable (60:40) diastereomeric mixtures (Scheme 6). The

Scheme 6. Reaction of α,β -unsaturated Group 6 carbene complexes with heterogeneous ET-reagent C₈K.

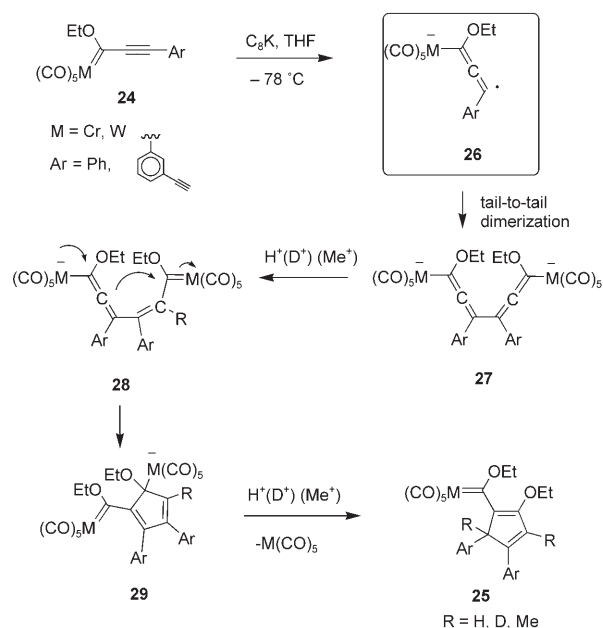
reaction occurs by one-electron transfer from the C₈K to the α,β -unsaturated complexes **18** to form key intermediate radical anion **20**, which are vinylogous to Casey's intermediates **2**. Radical anion **20** gives biscarbene dianion **21** by tail to tail dimerization. Now, while the intermediates derived from nonconjugated carbene complexes evolve by extrusion of MeOH (see Scheme 3), quenching of **21** with an electrophile yields biscarbene complexes **19** (Scheme 6). Quenching with [D₂]H₂SO₄ or CF₃SO₃Me yielded the expected α,α' -dideuterated or α,α' -dimethylated biscarbene complexes in good yields thus confirming the proposed mechanism. The differential reactivity of intermediates **7** and **21** may be attributable to the lesser delocalization of the negative charge in **7** compared to that in **21**. This results in much more stable intermediate species **21**, which can be protonated before the extrusion of alcohol.

Iwasawa^[10] further demonstrated the generality of the electron capture by α,β -unsaturated complexes to form anion radical intermediates such as **20**, by reacting Fischer carbene complexes with samarium(II) iodide. Now, the reaction of α,β -unsaturated chromium- and tungsten–carbene complexes **22** with SmI₂/MeOH, affords the corresponding biscarbene complexes **23** in yields comparable to those obtained in the dimerizations with C₈K (Scheme 7).

Alkynyl chromium(0)carbene complexes **24** did not afford dimerization products in the presence of C₈K. Instead, in these cases cyclic carbene complexes **25** were obtained in good yields (Scheme 8).^[13] The reaction is restricted to aryl substituted alkynyl carbene complexes. Alkyl and TMS derivatives analogous to **24** only yielded complex reaction mixtures, from which the expected cyclic carbene complexes could not be obtained. The mechanism of formation of cyclic compounds **25** involves the generation of an allenyl radical anion **26** analogous to **20** by ET from the C₈K, fol-



Scheme 7. Reaction of α,β -unsaturated Group 6 carbene complexes with homogeneous ET-reagent SmI_2 .



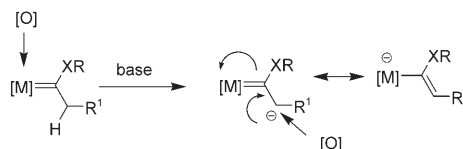
Scheme 8. Reaction of alkynyl-substituted Group 6 carbene complexes with heterogeneous ET-reagent C_8K .

lowed by dimerization to give a bisallenyl intermediate **27**. To this point the process is identical to that of α,β -unsaturated complexes **18**. However, upon protonation intermediate **27** forms **28**, which cyclizes to **29**. Protonation and cyclization with loss of a $\text{M}(\text{CO})_5$ fragment finally leads to products **25** (Scheme 8). The proposed mechanism is also supported by quenching experiments carried out with $[\text{D}_2]\text{H}_2\text{SO}_4$ and Me_3OBF_4 to unambiguously establish the deuterated positions of the ring in **25**. This time, Me_3OBF_4 turned to be more efficient quenching agent than $\text{CF}_3\text{SO}_3\text{Me}$, although the yields of the methylated products **25** (R = Me) only reached 53%.

Chemically Induced Electron Transfer Reactions: Metal Carbene Complexes as the Donors

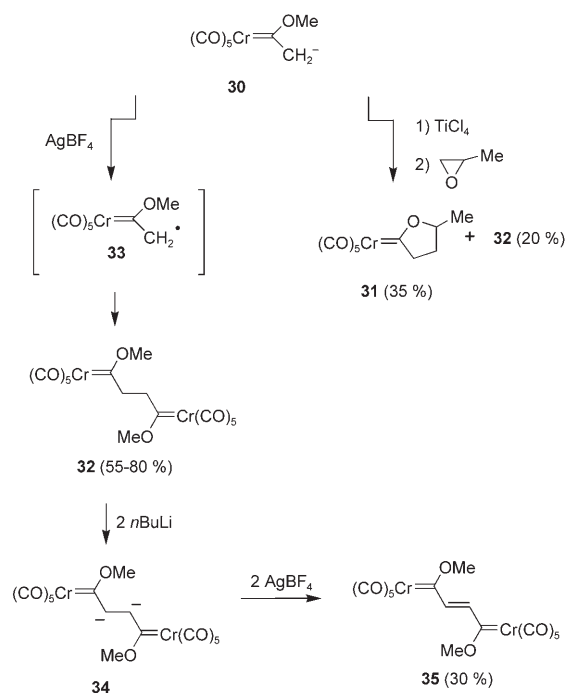
The orbital distribution of metal–carbene complexes (Figure 1) and the electrochemical data for metal(0) Fischer carbene complexes^[15] show that these compounds are very prone to oxidation. However, the oxidation occurs at the

metal and usually leads to metal removal producing organic materials. Oxidation at the metal may be avoided by using the strong acidity of the hydrogen atoms attached to the α -carbon.^[16] The carbanions derived from alkyl metal carbene complexes are oxidized at the carbon centre thwarting the oxidation at the metal. Thence, the final products keep the metal moiety, albeit the chemistry arising from these species has been scarcely studied (Scheme 9).



Scheme 9. Site-selectivity control of the oxidation of metal–carbene complexes by formation of a metal(0)–carbene carbanion.

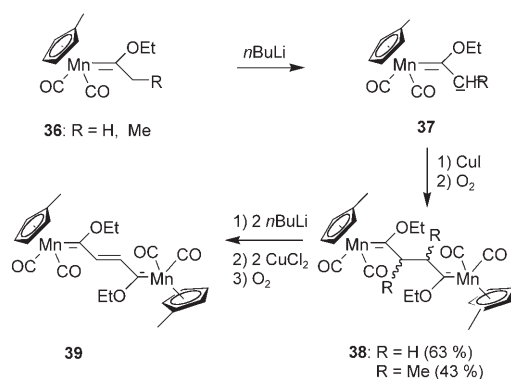
Thus, anions derived from Fischer carbene complexes are exceptionally reactive towards SET reactions leading to oxidative coupling processes. The first example of these couplings was serendipitously discovered while using TiCl_4 to activate the ring opening of ethylene oxide towards the nucleophilic attack of chromium carbene anion **30** (Scheme 10). This reaction formed the expected complex **31** together with biscarbene complex **32**. Compound **32** was unexpected and it was formed by the oxidation of anion **30** by Ti^{IV} to yield the radical species **33** that undergoes dimerization to the carbene **32**. No improvement in the yield of complex **32** was observed when the reaction was carried out in the absence of the oxirane (Scheme 10).^[17] A controlled oxi-



Scheme 10. Serendipitous and controlled oxidation of the anion derived from chromium(0)–carbene complex

dation of carbanion **30** was achieved by using AgBF_4 .^[18] These conditions lead to complex **32** in 50–80% yields. Evidently, biscarbene complex **32** could be deprotonated to form dianion **34** which is then oxidized by AgBF_4 to yield α,β -unsaturated biscarbene complex **35**. These reactions demonstrate the ability of carbene complexes derived carbon centered anions to transfer one electron.

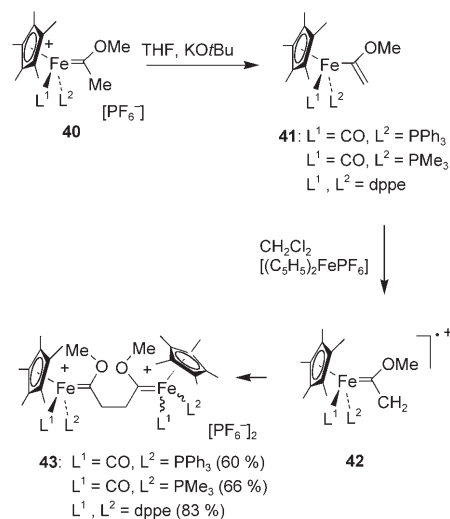
The sequence oxidative dimerization–deprotonation–oxidative generation of a C=C bond is generally applicable. Thus, the oxidation of the anions **37** derived from Mn–carbene complexes **36** with CuI and O_2 yields biscarbene complexes **38**, which are subsequently deprotonated and oxidized with CuCl_2 and O_2 , to form conjugated complexes **39** (Scheme 11). Alternatively, transformation of **38** to **39** can be achieved by electrochemical oxidation. This sequence has been applied to the preparation of diverse manganese–biscarbene complexes.^[19]



Scheme 11. Sequence deprotonation–oxidation–deprotonation–oxidation leading to biscarbene complexes.

Iron–carbene complexes also participate of this chemistry. 17-Electron iron carbenes **42** have been generated from cationic carbene complexes **40** through neutral vinyl complexes **41** obtained by deprotonation of these complexes with $\text{KO}t\text{Bu}$ at -80°C . Now, reaction of complexes **42** with a stoichiometric amount of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2\text{PF}_6]$ gave **43** as a mixture of two diastereomers (Scheme 12).^[20] Dimerization of **42** occurs upon warming in the solid state. When **42** remained in solution, the hydrogen abstraction from the solvent favorably competes with the dimerization to produce starting materials **41**. Dimerization of two 17-electron species having a CO ligand is rather interesting, since this ligand is exceptionally labile in these compounds, and often evolves with decoordination of CO and finally to decomposition (Scheme 12).

The examples discussed in this section show the ability of anions derived from different Fischer carbene complexes, including 17-electron intermediates, to behave as electron donors leading to dimerization of the corresponding radical intermediates. However, apart from the self-dimerization no other chemistry has been reported for these radicals.



Scheme 12. Biscarbene complexes are also obtained by dimerization of 17-electron intermediates **42**.

Metal Carbene Complexes as the Electron Transfer Acceptors in Nonconventional Media

Fischer carbene complexes also act as good electron acceptors in noncondensed media. Electrospray ionization mass spectrometry (ESI-MS) is a technique that allows the transfer of ions from solution to the gas phase as isolated entities, before these ions are subjected to mass spectrometric analysis (generally detected as $[M-H]^-$ or $[M+H]^+$ ions).^[21] Since supercharged droplets are produced in a ESI source, the study of the behavior of Group 6 metal carbenes under these conditions results very attractive. The initial drawback for these studies is the fact that metal–carbene complexes are frequently thermolabile compounds, possessing a great ability to lose carbon monoxide, and hence prone to decompose within the MS source. These facts either make impossible to obtain their MS spectra or reduce considerably the intensity of their molecular ions. The situation is exacerbated for neutral carbene complexes lacking acidic positions (able to deprotonate) or basic centers (able to protonate) that facilitate their ESI-MS analysis. This is the case for compound **44** whose ESI-MS spectrum is shown in Figure 2a. However, in the presence of an additive such as tetrathiafulvalene (TTF) or hydroquinone (HQ) the situation changes dramatically and in both cases the expected pseudomolecular $[M-H]^-$ ions can be clearly detected (negative mode) (Figure 2b,c).^[15b] Clearly, the additives have allowed the ionization of the complex **44** in the ESI source.

As shown in Scheme 13 for α,β -unsaturated Fischer carbene complex **45**, the role of the additive is undoubtedly to facilitate the ionization process. TTF and HQ act as electron carriers that efficiently transfer one electron to the carbene, leading to the formation of a radical anion species **46** that evolves in the ESI conditions to the detected $[M-H]^-$ species.

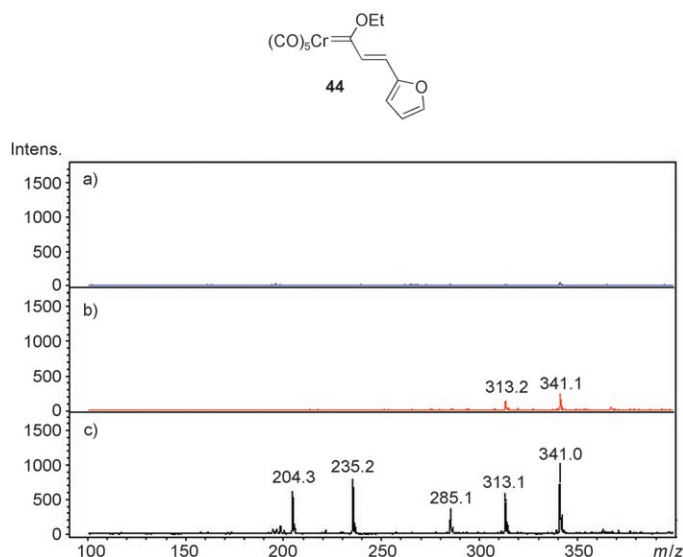
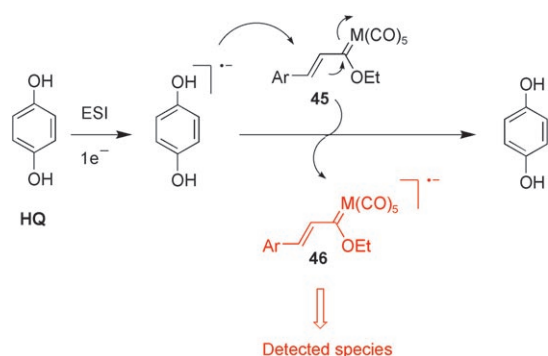


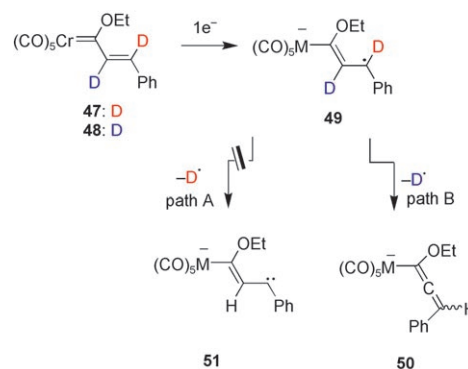
Figure 2. Spectra of carbene complex **44** in a) absence of additives, b) in the presence of HQ and c) in the presence of TTF.



Scheme 13. Mechanism of ionization of a neutral carbene complex **45** in the presence of an electron carrier (HQ).

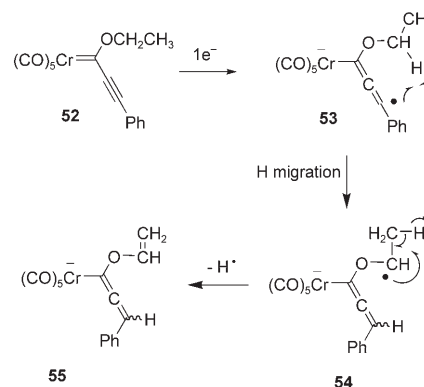
The evolution of radical anion **46** to the detected $[M-H]^-$ ion has been the subject of a mechanistic study by means of classical deuterium labeling experiments carried on substrate, solvent and additive ($[D_6]HQ$).^[22] Complexes **47** and **48** were used in these studies and confirmed that radical anions **49** formed after initial HQ or TTF mediated ET to the carbene complex, evolves by extrusion of a hydrogen radical (path B) to form an allenylchromium anion **50** that is detected as $[M-H]^-$ ion in the ESI-mass spectrum (Scheme 14). The alternative formation of carbene anion **51** by loss of the β -hydrogen atom (path A) was discarded by the experiments. Additionally, the higher stability of allenyl anion **50** compared to carbene anion **51** was demonstrated by DFT calculations.^[22]

Alkynyl carbene complex **52** behaves in a similar way. These complexes do not ionize without additive but they ionize efficiently in the presence of either HQ or TTF. Now, the initial ET mediated by the additive to the complex **52**



Scheme 14. ESI-SET reaction pathway of α,β -unsaturated Group 6 metal carbene complexes.

forms the anion radical **53**, which evolves by intramolecular H transfer from the alkoxy group to form **54**. Extrusion of a hydrogen radical leads to allenyl anion **55** that is the species detected in the ESI-MS spectrum as $[M-H-CO]^-$ (Scheme 15).^[15b]



Scheme 15. Ionization of complex **52** in the presence of additives.

Noteworthy radical anions **46** and **53** are identical to those obtained by reaction of Fischer carbenes **18** and **24** with chemical SET reagents (C_8K , SmI_2 , see above). However, their evolution within a droplet in the gas phase, under the nonconventional SET conditions of the ESI source, leads to observe a totally different reactivity of such species without further dimerization processes.

The ESI-ET behavior of metal-carbene complexes can be influenced by the presence of additional metal centers. Thus, the presence of two nonconjugated metal-carbene moieties in homo and heterobimetallic biscarbene complexes **56** (Figure 3) does not alter the general reactivity and these compounds behave in a similar fashion as **52** in the presence of additives. It is noteworthy that in the electrochemical studies carried out on complexes **56** they also behave as two independent monocarbene entities.^[15d] However, the presence of a conjugated ferrocene moiety in the structure of the Fischer carbene complex, has a noticeable effect in the course of the ESI ionization. Ferrocenyl car-

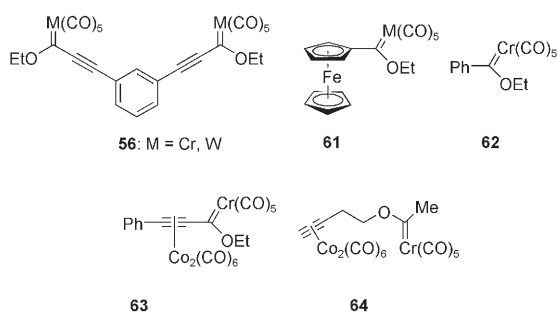
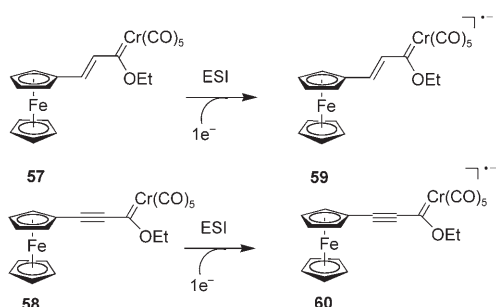


Figure 3. Effect of additional metal centers in ESI processes in metal–carbene complexes.

bene complexes **57** and **58** ionize under ESI conditions in the absence of HQ or TTF leading to radical anions **59** and **60**, respectively (Scheme 16). The experimental results could be understood considering the push–pull nature of these complexes.^[15d] The ferrocene moiety is an electron donor and the Cr(CO)₅ group behaves like a large electron depleted group, since the five CO ligands are strong π -acceptors. It seems clear that during the ESI process, the role of the ferrocene moiety in **57** and **58** is not just being a substituent conjugated with the metal fragment. The ferrocene could be considered as an *internal* electron carrier that makes possible the direct formation of the carbene radical anion in the ESI source (Scheme 15).



Scheme 16. Ferrocene behaves as an internal electron carrier in conjugated bimetallic carbene complexes **57** and **58**.

To behave as an internal electron carrier the ferrocene nucleus needs to be linked by a π -tether between the two metals. This feature is missing in carbene complexes **61** and the direct electrospray ionization did not take place. The quasimolecular ion $[(M-H)-CO]^-$ was detected when HQ or TTF were added. Nevertheless, the presence of a ferrocene moiety provokes a dramatic change on the behavior of the carbene complexes in ESI-MS, as their phenyl counterpart, (pentacarbonyl[(ethoxy)(phenyl)carbene]chromium(0), **62** cannot be ionized even in the presence of additives (Figure 3).

The presence of a cobalt cluster exercises a radical effect in the ESI ionization of Group 6 Fischer carbenes.^[15d] When the Co₂(CO)₆ moiety is included in the structure of the com-

plex (as in **63** and **64**, Figure 3) the electron transfer process from the additive is hampered. The ability of [Co₂(CO)₈] towards reduction is well known^[23] and therefore the bimetallic cluster is behaving as an electron sink inhibiting the ionization process. The electron sink also works when incorporated as an external additive to a running experiment. The quasimolecular ions observed in the ESI-MS spectrum of a solution containing alkenyl carbene **18** and HQ disappear by addition of [Co₂(CO)₈].

Conclusions and Outlook

The electrophilic character of Fischer carbene complexes makes them ideal substrates for the study of electron transfer processes. Although there are still scarce data about the possibilities offered by this promising area of chemistry, the results we have in hand indicate that depending on the stability of the radical anion formed, the electrophile present in the reaction medium and the nature of the metal, different reaction products can be observed, from CO₂ trapping, to addition to electron-poor olefins, CO insertions and dimerizations. Other ET processes can result from the hampering of the oxidation of the metal–carbene fragment. Thus, by deprotonation of the acidic α -position, dimerization products resulting from oxidative coupling can be obtained.

Finally, the use of nonconventional sources of electrons (electrospray ionization) leads to species analogues to that obtained with chemical SET reagents. The SET to Fischer carbene complexes in the ESI source is mediated by an electron carrier that makes possible the ionization of the complex, while the presence of other metal moieties such as Co₂(CO)₆ inhibit the process. Terms like electron carrier induced ET and electron sink, respectively, have been coined to describe these two processes.

Overall, the reactivity of Fischer carbene complexes in electron transfer processes shows promising perspectives in the near future, both as probes to study novel mechanisms and as scaffolds to prepare new molecules. In this regard, the possibility of studying the interaction between metal centers in polymetallic carbene complexes, the interaction of organic molecules and metal centers in the supercharged droplets formed in the ESI source, and the parallel processes in condensed media, are appealing perspectives foreseeable in this area of chemistry to be developed.

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