

ESI Mass Spectrometry as a Tool for the Study of Electron Transfer in Nonconventional Media: The Case of Bi- and Polymetallic Carbene Complexes[†]

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Intramolecular electron transfer processes in bimetallic Fischer carbene complexes **3–10** have been studied using electrospray ionization mass spectrometry (ESI-MS) as a nonconventional source of electrons. Under ESI-MS conditions, the direct ionization of compounds **3–5** requires both a good donor moiety as the ferrocene group and a conjugated spacer as communication channel with the acceptor M(CO)₅ (M = Cr, W). The electron transfer between the two metallic moieties M(CO)₅ in biscarbenes **6–8** is not observed, and these compounds behave in the ESI source as if the metallic fragments were totally independent from each other. Finally, the ionization of carbene complexes **9** and **10**, having an alkyne-Co₂(CO)₆ moiety, is inhibited even in the presence of additives that have been used previously by us as efficient electron carriers in ESI experiments (hydroquinone or tetrathiafulvalene). These results can be explained considering that the cobalt carbonyl cluster is initially reduced in the ESI source and behaves as an *electron-sink* that hampers the electron transfer process.

Introduction

Electron transfer (ET) processes are essential in chemistry, biology, physics,¹ and the emerging field of molecular electronics² and play a pivotal role in processes that have tremendous relevance to our life such as photosynthesis and respiration.^{3,4} The electron transfer between a donor (D) and an acceptor (A) can be induced by chemical, electrochemical, or photochemical methods.^{1,4} During the past decade, a considerable effort has been invested in determining the factors that control such processes, from both theoretical and experimental

explorations. The understanding of ET processes can be done in light of Marcus theory,⁵ which since postulated, has been applied to a multitude of systems and it is still the subject of revision.⁶

Possibly, the most deeply studied ET processes are those involving the intramolecular electronic interactions between a donor (D) and an acceptor (A). The dependence of the ET dynamics on the nature of the D and A and their relative separation and orientation have been thoroughly discussed. In fact, there is still a debate regarding the extent to which intramolecular ET processes occur by a through-bond^{7,8} or a through-space (solvent mediated)^{9,10} mechanism (eqs 1 and 2 in Figure 1 respectively).

[†] Dedicated to Professor Jose Luis Soto on the occasion of his retirement.

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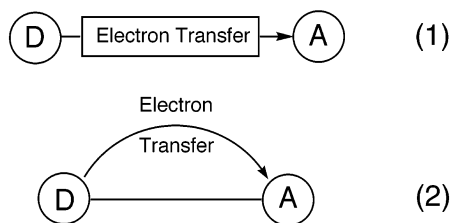
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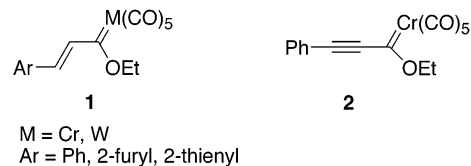
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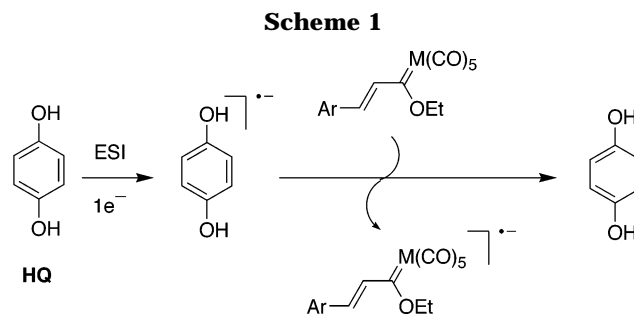
**Figure 1.**

The chemistry of stabilized group 6 Fischer carbene complexes has reached a high level of maturity, and these compounds have become very valuable building blocks in organic synthesis.¹¹ Despite this, studies of electron transfer processes involving this class of compounds are scarce. There are some reports about the behavior of chromium(0) and tungsten(0) Fischer carbene complexes in electron transfer processes chemically induced by Na/K alloy,¹² potassium 1-methylnaphthalenide,¹³ SmI₂,¹⁴ or potassium graphite (C₈K).¹⁵ More recently, our research group has focused its interest on the study of ET reactions involving group 6 Fischer carbene complexes using other less conventional sources of electrons such as electrospray ionization in mass spectrometry (ESI-MS).¹⁶ ESI is a technique that allows the transfer of ions from solution to the gas phase as isolated entities, and these ions can be subjected to mass spectrometric analysis. There are three major steps in the production of ESI ions: first, the production of charged droplets at the ES capillary; second, shrinkage of charged droplets (by the high voltage applied), leading to very small highly charged droplets; and the last step where gas-phase ions are produced from the very small charged droplets. The last step of this general mechanism has proven to be very difficult to establish.^{16,17}

We have recently reported that chromium and tungsten Fischer carbene complexes cannot be ionized under routine ESI conditions. Variations of the ionization potential, flow solution rate, and solvent system (fundamental parameters of this technique) did not produce significant changes in the process. However, we found that the ESI-MS ionization of carbene complexes **1** and **2** (Figure 2) took place by addition of an electron donor such as hydroquinone (HQ) or tetrathiafulvalene (TTF) to the carbene solution.¹⁸

**Figure 2.**

The proposed mechanism for the ESI ionization process involves the capture of an electron by the addition of HQ or TTF at the surface of the capillary. The species HQ^{•-} or TTF^{•-} promotes the formation of a carbene radical anion, which loses a hydrogen radical to form the detected [M – H]⁻ ions (Scheme 1). It is important to note that this reaction takes place only on the surface of the capillary during the ESI experiment and that no reaction is observed in solution when mixing carbenes **1** and **2** with the additives. As only conjugated carbene complexes **1** and **2** were ionized in the presence of HQ or TTF, we proposed that the stabilization of the intermediate radical anions produced by the conjugation of the carbene moiety with the aromatic rings is essential for the formation of such entities and hence for their subsequent detection by MS. Thus, pentacarbonyl-[(ethoxy)(phenyl)carbene]chromium(0) did not ionize even in the presence of external additives. Although other compounds known as electron acceptors have been tested as additives (TCNQ, Toluidine Blue O), they were ineffective in promoting the ionization process. It seems that under ESI conditions HQ and TTF (both electron donors) can be forced to accept an electron, leading to a highly reductive species that is responsible for the ET to the carbene complex.¹⁹



In this context, we were interested in studying the ESI-induced electron transfer reactions in group 6 Fischer carbene complexes that incorporate in their structures an extra metallic center. This study will allow us to determine the participation of the two metals in intramolecular ET reactions under ESI-MS conditions, as well as the influence of the spacer between the two metallic moieties in the process. For the study, we have selected a series of bimetallic complexes, **3–10**, with different spacers linking the two metals (M and M') (Figure 3). To establish the role of the metal in the intramolecular ET process, compounds **3–10** incorporate different metallic moieties. Thus, complexes **3–5** include in their structures a ferrocene, a well-known donor in electron transfer reactions.²⁰ The possible

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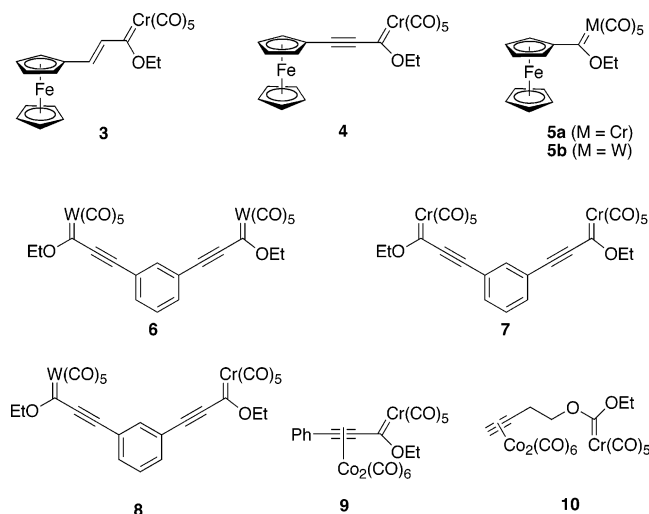


Figure 3.

interaction between the two $M(\text{CO})_5$ moieties ($M = \text{Cr}, \text{W}$) will be established in biscarbenes **6–8**, and finally, compounds **9** and **10** incorporate the good electron acceptor $\text{Co}_2(\text{CO})_6$ moiety.

Results and Discussion

First we checked the behavior of ferrocenyl carbene complexes **3–5**. Solutions of carbene complexes **3** and **4** were directly sprayed under routine ESI conditions, and the corresponding quasimolecular ions $[\text{M} - \text{H}]^-$ or $[(\text{M} - \text{H}) - \text{CO}]^-$ were detected respectively in the mass spectra. The formation of quasimolecular ions of different compositions is a well-known process that is influenced by many factors such as the facility to form adducts with the solvent or the ability to lose ligands. Moreover, ligand fragmentation and ligand oxidation are also observed processes in the ESI of organometallic compounds, and it is not rare that structurally related compounds could lead to different quasimolecular ions. The ESI mass spectrum of **4** is displayed in Figure 4. The quasimolecular ions were also detected when the ESI-MS of **3** and **4** were done in the presence of HQ or TTF. These results contrast with those previously observed for the structurally related compounds **1** and **2** (Figure 2), which could be ionized, and hence their mass spectra recorded, only in the presence of HQ or TTF as additive.¹⁸

A reasonable explanation to understand why compounds **3** and **4** do not need an additive to be ionized in the ESI source could be based on the ability of such complexes toward reduction. The reduction potentials of compounds **1–5** are summarized in Table 1, and their cyclic voltammograms are provided as Supporting Information. The comparison between the E_{pc} values of the different phenyl and ferrocenyl α,β -unsaturated carbene complexes displayed in Table 1 does not justify why carbenes **3** and **4** ionize directly under ESI conditions whereas their phenyl counterparts **1** and **2** require

an additive for the ionization. Compounds **3** and **4** are push–pull complexes²¹ in which the ferrocene is the donor and the $\text{Cr}(\text{CO})_5$ 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 **3** and **4** is not just being a substituent conjugated with the metal carbene fragment. Ferrocene is a good electron donor that could be playing the same role as HQ or TTF in the ESI process (see above). In fact it could be considered as an *internal electron carrier* that makes possible the direct formation of the carbene radical anion in the ESI source (Scheme 2).

To evaluate the influence of the conjugation between the two metal centers in the ET process, nonconjugated carbene complex **5a** ($M = \text{Cr}$) was studied next. In this case, the direct electrospray ionization did not take place, but the quasimolecular ion $[(\text{M} - \text{H}) - \text{CO}]^-$ could be detected when HQ or TTF was added (Figure 5). Identical results were obtained when the experiments were carried out with **5b** ($M = \text{W}$). Again, the presence of a ferrocene moiety provokes a dramatic change in the behavior of the carbene complexes **5** in ESI-MS, as their phenyl counterpart (pentacarbonyl[(ethoxy)(phenyl)carbene]chromium(0), $E_{\text{pc}} = -1.78 \text{ V}$)¹⁸ cannot be ionized even in the presence of additives.

The results obtained for compounds **5a,b** show that the ferrocene moiety is essential for the ESI-MS ionization process, but only when the ferrocenyl and the $\text{Cr}(\text{CO})_5$ moieties are linked by a π -system is the efficient direct ET from the ESI source observed.

Once the ESI-MS spectra of ferrocenyl carbene complexes **3–5** were recorded, the corresponding quasimolecular ions were isolated and their fragmentations studied by the collision-induced dissociation (CID) technique. All of them undergo in the first fragmentation stage (MS^2) a double simultaneous decarbonylation process. This simultaneous removal of two CO ligands has been observed in organometallic complexes only in exceptional cases in electron-impact mass spectrometry (EI)²² and was previously detected by us in ESI-MS for carbene complexes **1** and **2**.¹⁸ The MS^3 fragmentation stage leads to a new monodecarbonylation process, and compound **3** also exhibits at this stage the loss of a cyclopentadiene molecule.

The behavior of compounds having two $M(\text{CO})_5$ moieties ($M = \text{Cr}, \text{W}$) in ESI-MS conditions was studied next. Thus, biscarbenes **6**, **7**, and **8** were obtained and their ESI mass spectra recorded. In all cases the direct ionization failed and the expected quasimolecular ions $[\text{M} - \text{H}]^-$ or $[(\text{M} - \text{H}) - \text{CO}]^-$ could only be detected in the presence of additives (HQ or TTF) (Figure 6). Therefore, biscarbenes **6–8** behave in ESI-MS like the parent monocarbene **2** (Scheme 3).

Spectroscopic studies on polymetallic π -bridged carbene complexes of the type $\text{M}-\pi-\text{M}'-\pi-\text{M}''$ suggested only a weak interaction between the carbene fragments and the central metal nucleus.²³ Similar conclusions

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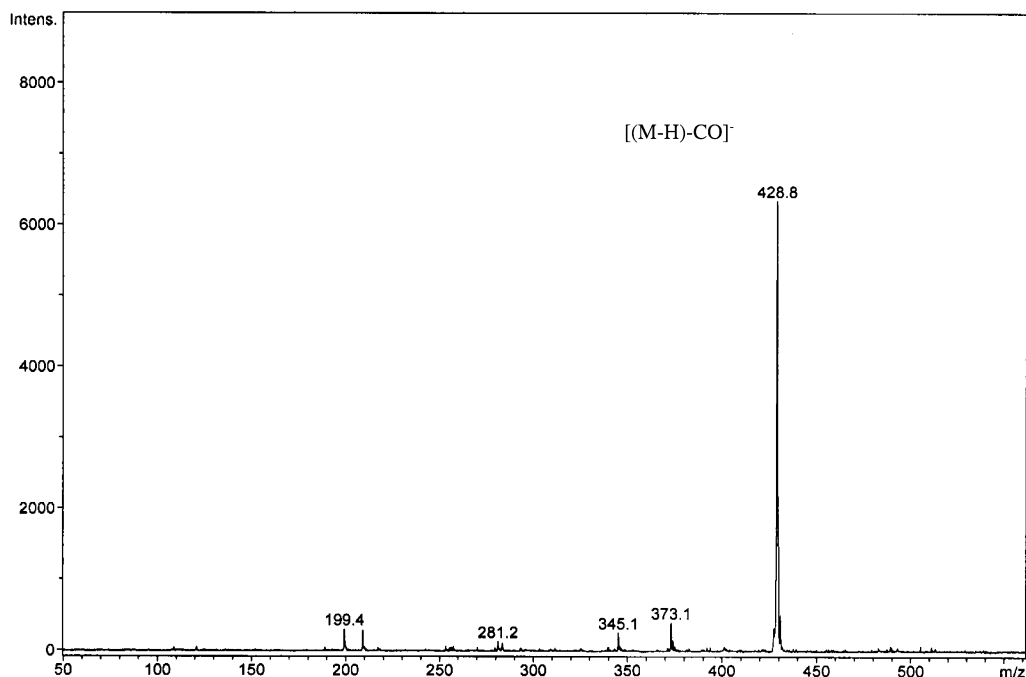


Figure 4. ESI mass spectrum of complex **4** showing the quasimolecular ion $[(M - H) - CO]^-$ (m/z 429).

Scheme 2

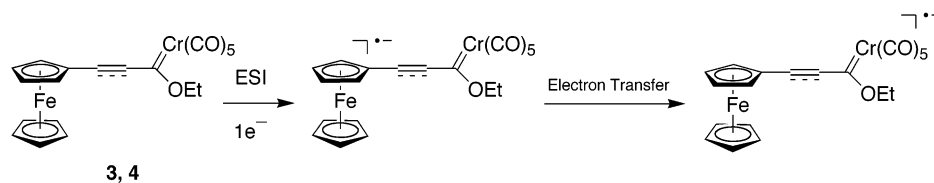


Table 1^a

compound	1st E_{pc}	2nd E_{pc}
1^b	-1.25	
2^b	-1.15	
3^c	-1.22	
4	-1.29	
5a	-1.71	
5b	-1.61	
6	-0.92	-1.19
7	-0.99	-1.26
8	-1.00	-1.29

^a Cyclic voltammograms in 0.1 M $Bu_4NClO_4-CH_2Cl_2$ at a scan rate of 0.1 V/s at 25 °C. ^b See ref 18. ^c See ref 21.

were obtained for π -conjugated bisaminocarbene complexes, whereas π -bridged alkoxy amino biscarbene complexes showed a significant interaction between the two metallic fragments through the bridge.²⁴ The electrochemical properties of biscarbenes **6–8** are summarized in Table 1, and their cyclic voltammograms are included as Supporting Information.

The ESI-MS spectra of bimetallic complexes **6** and **7** reveal similar $[(M - H) - CO]^-$ quasimolecular ions, whereas **8** leads to $[(M + CH_3OH - H) - 2CO]^-$ ion under the same conditions. However, the differences in the composition of quasimolecular ions are not induced by metallic interactions and can be assumed considering the stability of the different adducts formed in the gas-phase reactions.^{17,25} The observation of ions attributable

to noncovalently bonded species only suggests the existence of associations between analyte and solvent. The species that appear in the mass spectra are not necessarily present in solution, and it is also known that in some cases the effect of gas-phase proton transfer reaction can explain the formation of the different adducts.²⁵ The MS² spectra of biscarbenes **6**, **7**, and **8** reveal the formation of alkynyl monocarbene ions $[C_{18}H_9O_6M]^-$, which seem to be originated by the loss of an alkoxy carbene moiety. This fragmentation is independent of the nature of the metal (Cr or W) in symmetrical biscarbenes **6** and **7**, but two different fragments of similar abundance, corresponding to the elimination of the two possible metallic moieties, were detected for mixed biscarbene **8**. The double simultaneous decarbonylation process takes place in a further stage from the $[C_{18}H_9O_6M]^-$ ions, which behave in ESI-MS like the simple alkynyl monocarbene **2**.

The effect of the incorporation of a dicobalt hexacarbonyl moiety ($Co_2(CO)_6$) in the ESI ionization of group 6 Fischer carbene complexes was studied in complex **9**, obtained by coordination of the carbon-carbon triple bond of **2** with dicobalt octacarbonyl.

It is well known that metal carbonyls are easy to reduce due to the ability of carbonyl ligands to stabilize low oxidation states.²⁶ Octacarbonyl dicobalt ($Co_2(CO)_8$) forms $Co(CO)_4^-$ in the presence of reducing agents such as SmI_2 (THF) or borohydrides,^{26b,27} and being electron rich, most reactions of $Co(CO)_4^-$ result in the cobalt

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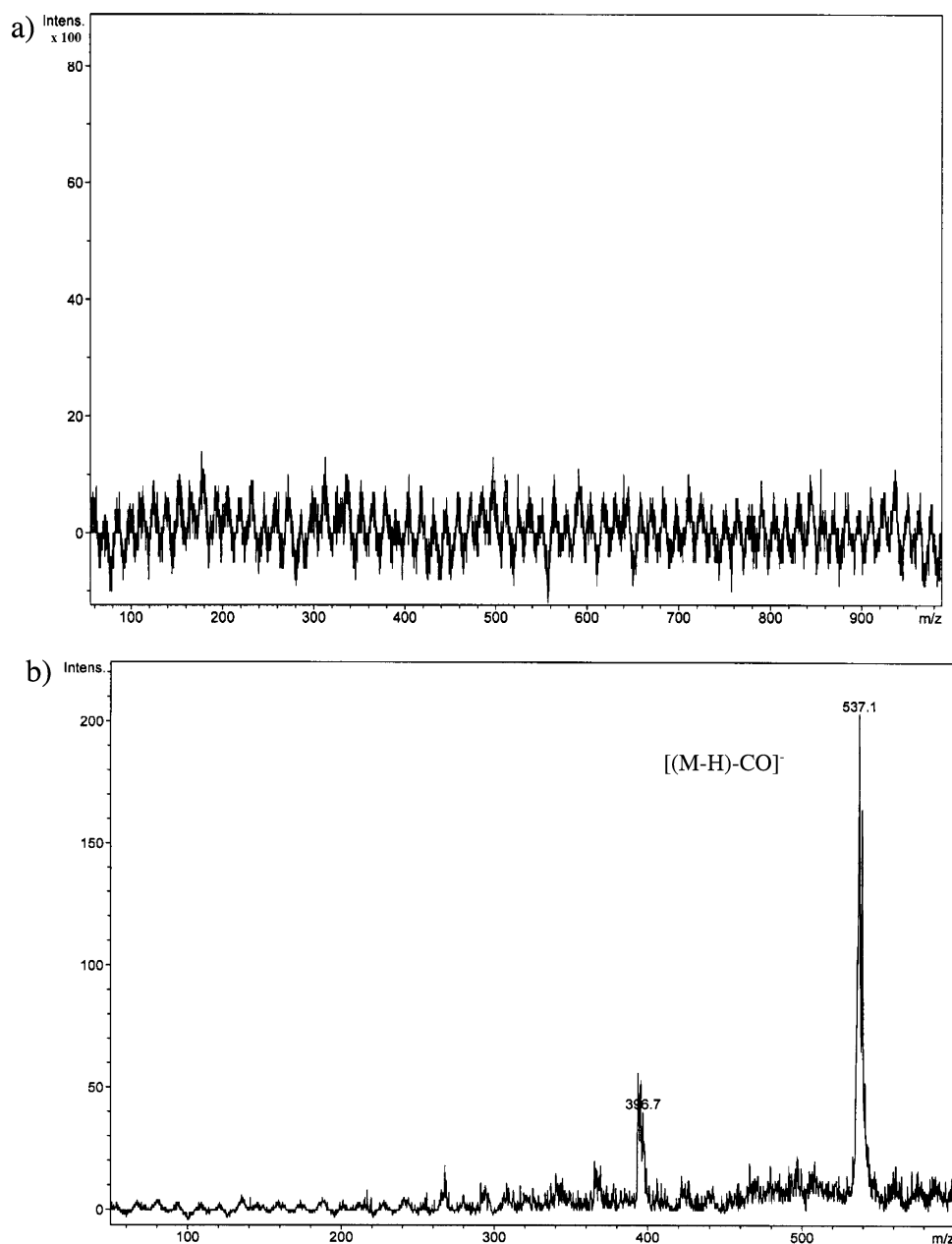


Figure 5. (a) ESI mass spectrum of complex **5b**. Neither molecular peak nor fragments were observed. (b) ESI mass spectrum of complex **5b** after addition of HQ showing the quasimolecular ion $[(M - H) - CO]^-$ (m/z 537) and a fragment at m/z 397.

being oxidized. It has been reported that the one-electron electrochemical oxidation of $Co(CO)_4^-$ is irreversible, with formation of $Co_2(CO)_8$. On the other hand, electron transfer reactions have been presumed to lead to two molecules of $Co(CO)_4$ as disproportionation products of $Co_2(CO)_8$.²⁸

Considering all these precedents, the introduction of the $Co_2(CO)_6$ moiety in a group 6 Fischer carbene

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complex should inhibit the electrospray ionization of this compound. In fact, treatment of alkynyl cobalt complex **9** under standard ESI-MS conditions did not produce the expected $[M - H]^-$ ion, in either the presence or absence of HQ as additive. Then, it seems clear that the cobalt moiety is behaving as an *electron-sink* that inhibits any possible electron transfer to the $Cr(CO)_5$ fragment. Very likely, the $Co_2(CO)_6$ moiety is initially reduced either in the ESI source or by means of the $HQ^{\bullet-}$ and subsequently oxidized without interacting with the Cr–C bond. This fact is confirmed by the detection of a peak (m/z 171) corresponding to $Co(CO)_4^+$ in the mass spectrum.

The redox properties of carbene complex **9** were also examined. Figure 7 shows the cyclic voltammograms of alkynyl complex **2**, alkynyl cobalt complex **9**, and Co_2-

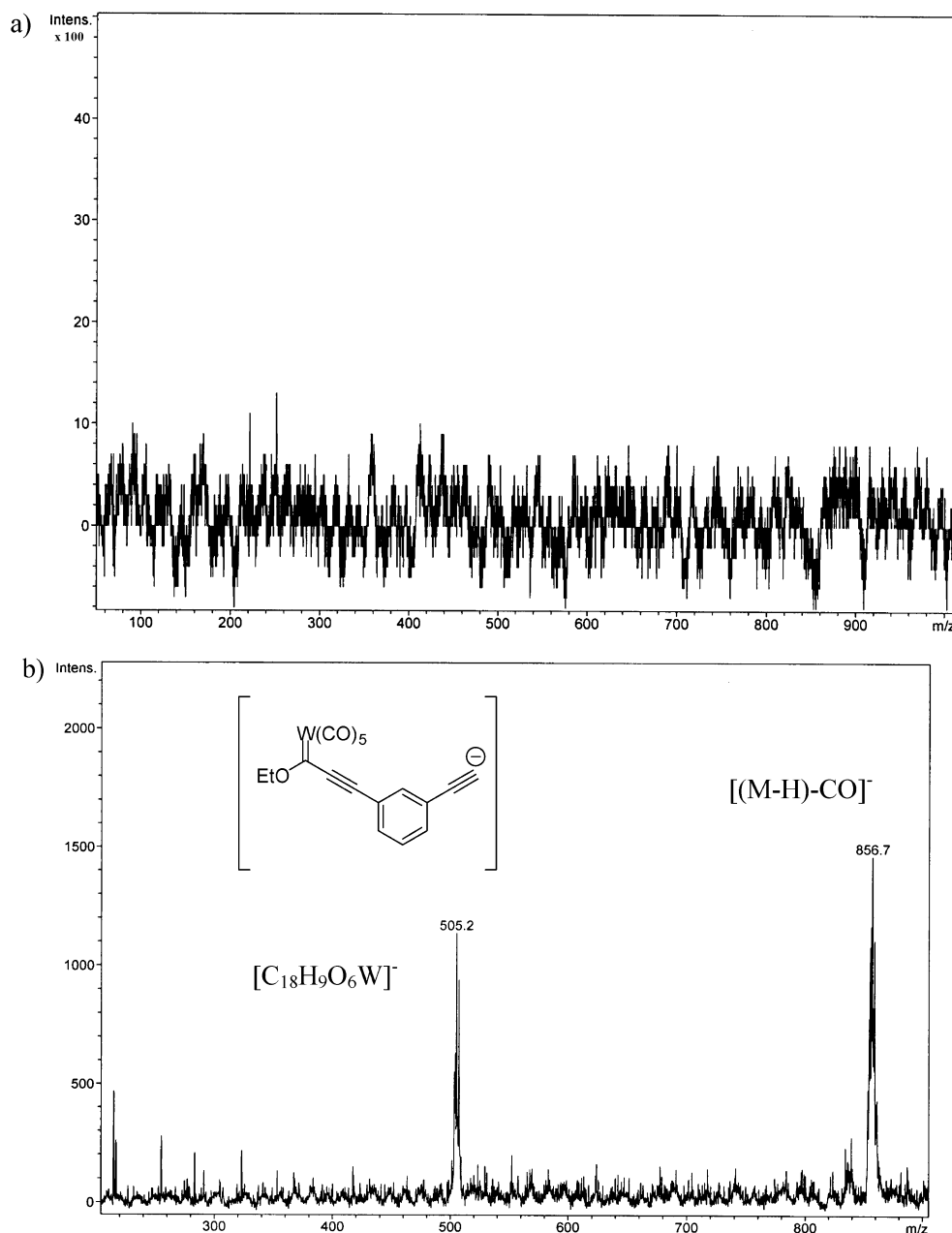
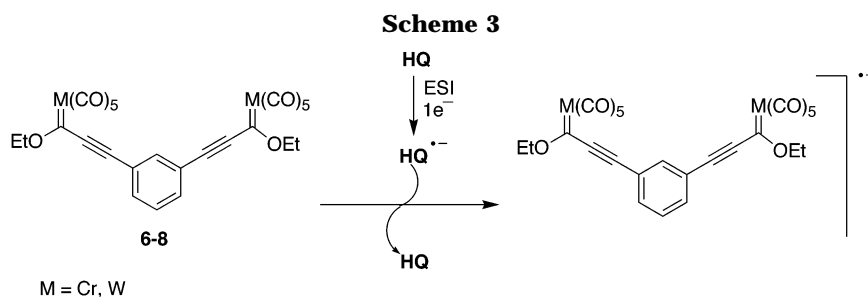


Figure 6. (a) ESI mass spectrum of bis carbene **6**. Neither molecular peak nor fragments were observed. (b) ESI mass spectrum of bis carbene **6** with HQ as additive, showing the quasimolecular ion $[(M-H)-CO]^-$ (m/z 857) and a fragment at m/z 505.



$(CO)_8$, all in $Bu_4NClO_4-CH_2Cl_2$. Whereas complex **2** shows a clear irreversible reduction wave of the $Cr(CO)_5$ moiety at $E_{pc} = -1.15$ V, in the voltammogram of alkyne cobalt complex **9** appear two irreversible oxidation waves at $E_{pa}^1 = 0.11$ V and $E_{pa}^2 = 1.16$ V, together with an irreversible reduction wave at $E_{pc} = -0.79$ V, all of them attributable to the cobalt moiety. These

results reveal that the redox properties of complex **9** are due to the complexation of the $Co_2(CO)_8$ fragment with the C–C triple bond. This point is further supported by the electrochemical study of alkyne complex **2** in the presence of $Co_2(CO)_8$. The voltammogram (displayed in Figure 8) shows the two-step irreversible oxidation at $E_{pa}^1 = 0.12$ V and $E_{pa}^2 = 1.24$ V and irreversible reduc-

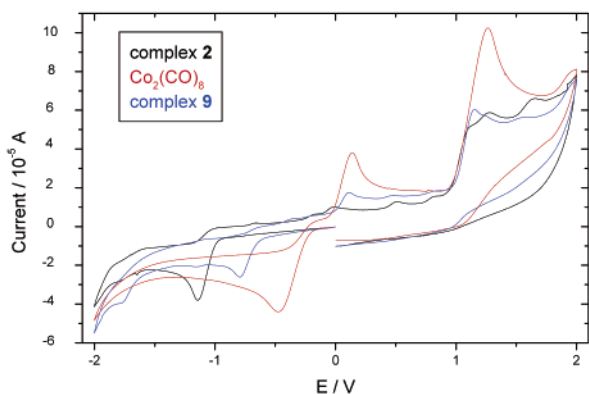


Figure 7. Cyclic voltammograms in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ at a scan rate of 0.1 V/s at 25 °C.

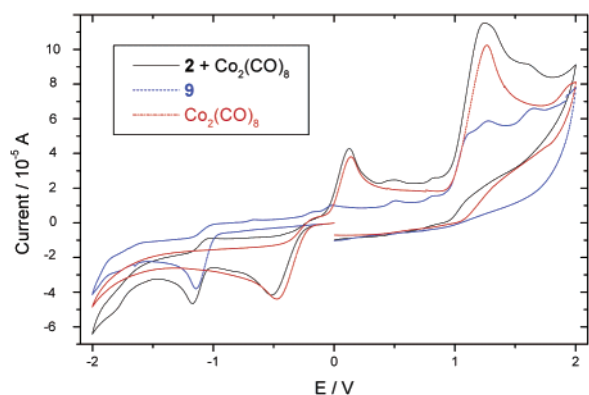


Figure 8. Cyclic voltammograms in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ at a scan rate of 0.1 V/s at 25 °C.

Table 2

compound	1st E_{pc}	2nd E_{pc}	1st E_{pa}	2nd E_{pa}
2	-1.15			
$\text{Co}_2(\text{CO})_8$	-0.47		0.14	1.26
9	-0.79		0.11	1.16
2 + $\text{Co}_2(\text{CO})_8$	-0.51	-1.17	0.12	1.24

tion at $E_{pc} = -0.51$ V of the $\text{Co}_2(\text{CO})_8$ together with the irreversible reduction of complex **2** at $E_{pc} = -1.17$ V. The electrochemical data are summarized in Table 2.

The ability of $\text{Co}_2(\text{CO})_8$ as an inhibitor of the ionization process was tested in an ESI-MS experiment with alkenyl carbene **1**, $\text{Co}_2(\text{CO})_8$, and HQ as electron carrier.²⁸ The quasimolecular ions observed in the ESI-MS spectrum of a solution containing alkenyl carbene **1** and HQ disappear by addition of $\text{Co}_2(\text{CO})_8$. This result confirms that the cobalt carbonyl moiety is easily reduced by the $\text{HQ}^{\bullet-}$ and behaves as an *electron-sink*, unable to take part in any electron transfer process to the M-C bond and hence responsible for the total inhibition of the ionization of the carbene complex in ESI-MS. The incorporation of a heteroatom in the spacer linking the $\text{Co}_2(\text{CO})_6$ and the Cr-C moieties in Fischer carbene complex **10** did not produce any modifications in the previous results. This complex was also unable to show any molecular ions or fragments in the mass spectrum under standard ESI-MS conditions either in the presence or in the absence of additives.

In conclusion, electrospray ionization mass spectrometry (ESI-MS) has been revealed as a valuable tool in the study of ET reactions in bi- and polymetallic carbene complexes. Using the ESI as a nonconventional source of electrons we have shown that the direct ionization of

these compounds requires both a good donor as the ferrocene group and a conjugated π -spacer as communication channel with the acceptor. The incorporation of the $\text{Co}_2(\text{CO})_6$ cluster in the structure of a Fischer carbene complex inhibits ionization even in the presence of external additives. In these cases the $\text{Co}_2(\text{CO})_6$ moiety can be regarded as an *electron-sink*. An analogous effect is observed when $\text{Co}_2(\text{CO})_8$ is sprayed together with the conjugated complex in the ESI source. Further work directed to investigate the usefulness of ESI-MS as a nonconventional source of electrons in the study of the reactivity of bi- and polymetallic complexes is currently under way in our laboratories.

Experimental Section

General Procedures. ^1H NMR and ^{13}C NMR spectra were recorded at 22 °C in CDCl_3 , on Varian XL-300S (300.1 and 75.4 MHz), Bruker Avance 300 (300.1 and 75.4 MHz), and Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H , 0.0 ppm) or CDCl_3 (^{13}C , 77.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. All solvents used in this work were purified by distillation and were freshly distilled immediately before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone and CH_2Cl_2 from CaH_2 . Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Merck silica gel (230–400 mesh) was used as the stationary phase for purification of crude reaction mixtures by flash column chromatography. The identification of products was made by TLC (kieselgel 60F-254). UV light ($\lambda = 254$ nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. All commercially available compounds were used without further purification. Compounds **3**,²¹ **4**,³⁰ **5**,³¹ **6**,^{24b} **7**,³² and **9**³³ were obtained following the procedures reported in the literature.

Preparation of Compound 8. To a solution of 1,3-diethynylbenzene (500 mg, 3.96 mmol) in dry Et_2O (38 mL) at -78 °C was added dropwise *n*-butyllithium (1.6 M in hexanes, 5.5 mL, 8.7 mmol). The mixture was stirred at -78 °C for 45 min, and then chromium hexacarbonyl (0.87 g, 3.96 mmol) and tungsten hexacarbonyl (1.40 g, 3.96 mmol) were added in one portion at 0 °C. The mixture was allowed to reach room temperature and stirred for 15 min. Afterward, anhydrous THF (20 mL) was added, and the mixture was allowed to stir at room temperature overnight. The reaction mixture was quenched by addition of Et_3OBF_4 (3.01 g, 15.9 mmol) in one portion at -78 °C. The solution was stirred at this temperature for 15 min and then allowed to reach room temperature for an additional hour. Solvents were removed under reduced pressure, and the residue was dissolved in Et_2O and filtered through silica gel. The solvent was evaporated, and the residue was submitted to flash column chromatography under argon pressure (SiO_2 , hexane) to give **8** (251 mg, 8%) as a dark green solid. ^1H NMR (300 MHz, CDCl_3): δ 7.98 (s, 1H), 7.70–7.50 (m, 3H), 4.91 (q, $J = 7.1$ Hz, 2H), 4.70 (q, $J = 7.1$ Hz, 2H), 1.59 (t, $J = 7.1$ Hz, 3H), 1.53 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75.5 MHz, CDCl_3): δ 313.7, 286.4, 225.6, 216.0, 202.9, 197.1, 136.9, 134.8, 129.7, 122.2, 91.5, 81.7, 79.4, 76.2, 73.0, 15.4, 15.0.

(29) Before the experiment, the compatibility of the reagents was checked by keeping a dichloromethane solution of equimolar amounts of HQ and $\text{Co}_2(\text{CO})_8$ for 48 h at room temperature. After this time both reagents remained unaltered.

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IR (CCl₄): ν 2150, 2062, 2006, 1925 cm⁻¹. Anal. Calcd (%) for C₂₆H₁₄CrO₁₂W: C 41.40, H 1.87. Found: C 41.51, H 1.75.

Preparation of Compound 10. Pentacarbonyl[(1-butynoxy)(methyl)carbene]chromium(0) (11). This compound was synthesized following the method previously described by Hegedus.³⁴ A solution of pentacarbonyl[(tetramethylammonium)carbene]chromium salt (1.5 g, 4.8 mmol) in dry CH₂Cl₂ (37.5 mL) under an argon atmosphere was cooled to -40 °C with an acetone/dry ice bath. To the faint yellow solution was added acetyl bromide (4.8 mmol) by syringe. The reaction mixture was stirred at -35 °C for 1 h, and after this time a solution of 3-butyn-1-ol (0.34 g, 4.8 mmol) in 10 mL of CH₂Cl₂ was added by syringe. The solution was stirred at -35 °C for 3 h and allowed to slowly reach room temperature without removing the cold bath. To the resulting bright orange solution was added ca. 2 g of silica gel, the solvent was removed under reduced pressure, and the crude was submitted to flash column chromatography under argon pressure (hexane) to give complex **11** (0.98 g, 71%) as an orange solid. ¹H NMR (300 MHz, CDCl₃): δ 4.93 (br s, 2H), 2.92 (s, 3H), 2.83 (br s, 2H), 2.03 (s, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ 359.6 (Cr=C), 223.2 (CO trans), 216.2 (CO cis), 92.8, 78.5, 71.0, 49.4, 19.8. IR (CCl₄): ν 2064, 1982, 1944 cm⁻¹. Anal. Calcd (%) for C₁₁H₈-CrO₆: C 45.85, H 2.80. Found: C 46.03, H 2.97.

Complex 10. To a solution of complex **11** (150 mg, 0.52 mmol) in dry CH₂Cl₂ (10 mL) was added Co₂(CO)₈ (178 mg, 0.52 mmol) in one portion. The mixture was stirred at room temperature for 30 min, and the solvent was removed under reduced pressure to yield complex **10** (298 mg, quantitative yield) as a brown solid. ¹H NMR (300 MHz, CDCl₃): δ 6.06 (s, 1H), 5.10 (br s, 2H), 3.47 (br s, 2H), 2.92 (s, 3H). ¹³C NMR (75.5 MHz, CDCl₃): δ 359.8 (Cr=C), 223.1 (CO trans), 216.2 (CO cis), 199.3, 89.6, 80.4, 73.7, 49.6, 33.3. IR (CCl₄): ν 2095, 2056, 2031, 1985, 1944 cm⁻¹. Anal. Calcd (%) for C₁₇H₈Co₂-CrO₁₂: C 35.57, H 1.40. Found: C 35.98, H 1.56.

Electrochemical Measurements. Cyclic voltammetric experiments were performed in CH₂Cl₂ at room temperature with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte and glassy carbon as a working electrode. A platinum wire was used as a counter electrode and Ag/Ag⁺ as a reference electrode. All measurements were performed with potentiostat/galvanostat Autolab PGSTAT30, and ferrocene was used as an internal standard.

ESI-MS Experiments. All the ESI-MS experiments were carried out using an ESQUIRE-LC (Bruker Daltonic, Bremen, Germany) ion trap spectrometer in negative mode of detection. A syringe pump (model 74900, Cole-Palmer, Vernon Hills, IL) was used to deliver chloroform solutions (1.5 × 10⁻⁵ mol L⁻¹)

of the corresponding Fischer carbene complex through a short length of 254 mm i.d. PEEK tubing (Upchurch Scientific, Oak Harbor, WA) with a flow rate of 3 mL min⁻¹. The stainless steel capillary was held at a potential of 5.0 kV. Nitrogen was used as nebulizer gas in a flow rate of 3.98 l min⁻¹ (nebulizer pressure 11 psi) at 150 °C. Solutions (chloroform-methanol, 1:1 v/v) containing 25 mM hydroquinone (HQ), tetrathiafulvalene (TTF), ferrocene (Fc), or Co₂(CO)₈ were used. The spectra reported are the averages of 15 scans using 450 ms as the accumulation time. MSⁿ spectra were carried out using collision-induced dissociation (CID) with helium after isolation of the appropriate precursor ions. An isolation width of 0.4 *m/z* was used, and the fragmentation amplitude was maintained at 0.60 V with a fragmentation time of 40 ms.

No differences were observed in the ESI mass spectra when HQ or TTF was used as additive. The HQ was detected as *m/z* 109 [HQ - H]⁻, whereas TTF was observed as *m/z* 204 [TTF]⁻.

Carbene 3: (ESI-MS) *m/z* MS¹ = 459 [M - H]⁻; MS² = 403 [459 - 2 CO]⁻; MS³ = 375 [403 - CO]⁻; 337 [403 - C₅H₆]⁻; MS⁴ = 319 [375 - 2 CO]⁻.

Carbene 4: (ESI-MS) *m/z* MS¹ = 429 [(M - H) - CO]⁻; MS² = 373 [429 - 2 CO]⁻.

Carbene 5a: (registered with additive) (ESI-MS) *m/z* MS¹ = 405 [(M - H) - CO]⁻; MS² = 377 [405 - CO]⁻; MS³ = 349 [377 - CO]⁻; MS⁴ = 321 [349 - CO]⁻.

Carbene 5b: (registered with additive) (ESI-MS) *m/z* MS¹ = 537 [(M - H) - CO]⁻; 397 [537 - (5CO + C₂H₄)]⁻; MS² = 509 [537 - CO]⁻; MS³ = 481 [509 - CO]⁻.

Carbene 6: (registered with additive) (ESI-MS) *m/z* MS¹ = 857 [(M - H) - CO]⁻; MS² = 505 [C₁₈H₉O₆W]⁻; MS³ = 449 [505 - 2CO]⁻.

Carbene 7: (registered with additive) (ESI-MS) *m/z* MS¹ = 593 [(M - H) - CO]⁻; MS² = 373 [C₁₈H₉O₆Cr]⁻.

Carbene 8: (registered with additive) (ESI-MS) *m/z* MS¹ = 729 [(M + MeOH - H) - 2 CO]⁻; MS² = 505 [C₁₈H₉O₆W]⁻; 373 [C₁₈H₉O₆Cr]⁻; MS³ = 449 [505 - 2 CO], 317 [373 - 2 CO]⁻.

Carbenes 9 and 10. No peaks were detected either directly or with addition of HQ.

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Supporting Information Available: Cyclic voltammograms of compounds **4–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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