JOC Article

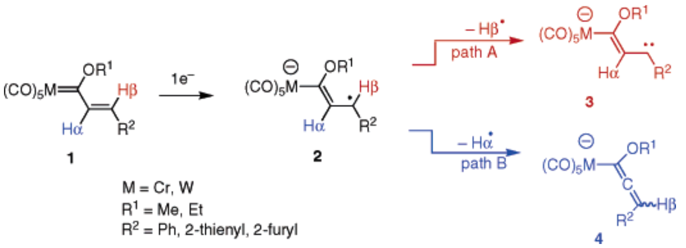
Study of the ESI-Mass Spectrometry Ionization Mechanism of Fischer Carbene Complexes

William D. Wulff,*,† Keith A. Korthals,† Roberto Martínez-Álvarez,‡ Mar Gómez-Gallego,‡
Israel Fernández,‡ and Miguel A. Sierra*,‡

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, and Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040 Madrid, Spain

wulff@chemistry.msu.edu; sierraor@quim.ucm.es

Received March 18, 2005



By means of deuterium-labeling experiments, we have carried out a systematic ESI-MS study to determine the mechanism of ESI ionization of alkenyl and alkynyl group 6 Fischer carbene complexes. These compounds can be ionized under ESI conditions only in the presence of additives such as hydroquinone (HQ) or tetrathiafulvalene (TTF). Our results demonstrate that in the ESI source an anion-radical is formed after the initial HQ- or TTF-mediated electron transfer to the metallic carbene complex. For alkenyl carbene complexes, this species evolves by extrusion of a hydrogen radical to form an allenylchromium anion that is detected as the $[M - H]^-$ ion in the mass spectrum. The preference for this mechanistic pathway could be rationalized by DFT calculations. In the case of alkynyl carbene complexes, experiments combining deuterated substrate, additive, and solvent demonstrate that the previously proposed allene−anion carbene complex is not formed. Instead, the H transfer from the ethoxy group in the anion radical, followed by extrusion of a hydrogen radical, leads to an allenyl anion that is detected in the ESI-MS as $[M - H - CO]^-$.

Introduction

Electron spray ionization mass spectrometry (ESI-MS) is a standard tool for the analysis of the composition of solutions of organic, inorganic, and bioorganic materials.[1] Different areas of chemistry ranging from host−guest chemistry[2] to structural biology[3] benefit from the advantages of this powerful analytical technique that is the method of choice in the case of highly polar or labile compounds. The ESI-MS is also a useful tool in the detection of reactive intermediates of chemical reactions.[4] 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. The production of ESI ions involves three key steps. The first event is the production of charged droplets at the ES capillary, which is followed by the shrinkage of the charged droplet due to the high voltage applied. These two sequential steps lead to very small, highly charged droplets in which the gas-phase ions are formed. This last step has proven to be very difficult to establish.[5] We have recently become aware of the potential of the electrospray ionization source to study electron-transfer processes in nonconventional media.[6] In fact, the behavior of mono- and polymetallic group 6 (Fischer) carbene complexes under ESI conditions clearly differs from that observed with conventional electron-transfer (ET) re-

---

† Michigan State University.

‡ Universidad Complutense.

[1] Gaskell, S. J. *Mass Spectrom.* **1997**, *32*, 677.

[2] Vincenti, M. *Mass Spectrom.* **1995**, *30*, 925.

[3] Schiller, J.; Arnold, K. *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; Wiley: Chichester, 2000.

[4] (a) Meyer, S.; Koch, R.; Metzger, J. O. *Angew. Chem., Int. Ed.* **2003**, *42*, 4700. (b) Traeger, J. C. *Int. J. Mass Spectrom.* **2000**, *200*, 387.

[5] Van Berkel, G. J., Electrospray Ionization Mass Spectrometry, Wiley: New York, 1997.

[6] (a) Martínez-Álvarez, R.; Gómez-Gallego, M.; Fernández, I.; Mancheño, M. J.; Sierra, M. A. *Organometallics* **2004**, *26*, 4647. (b) Sierra, M. A.; Gómez-Gallego, M.; Mancheño, M. J.; Martínez-Alvarez, R.; Ramírez-López, P.; Kayali, N.; González, A. *J. Mass. Spectrom.* **2003**, *38*, 151.

10.1021/jo050553y CCC: $30.25

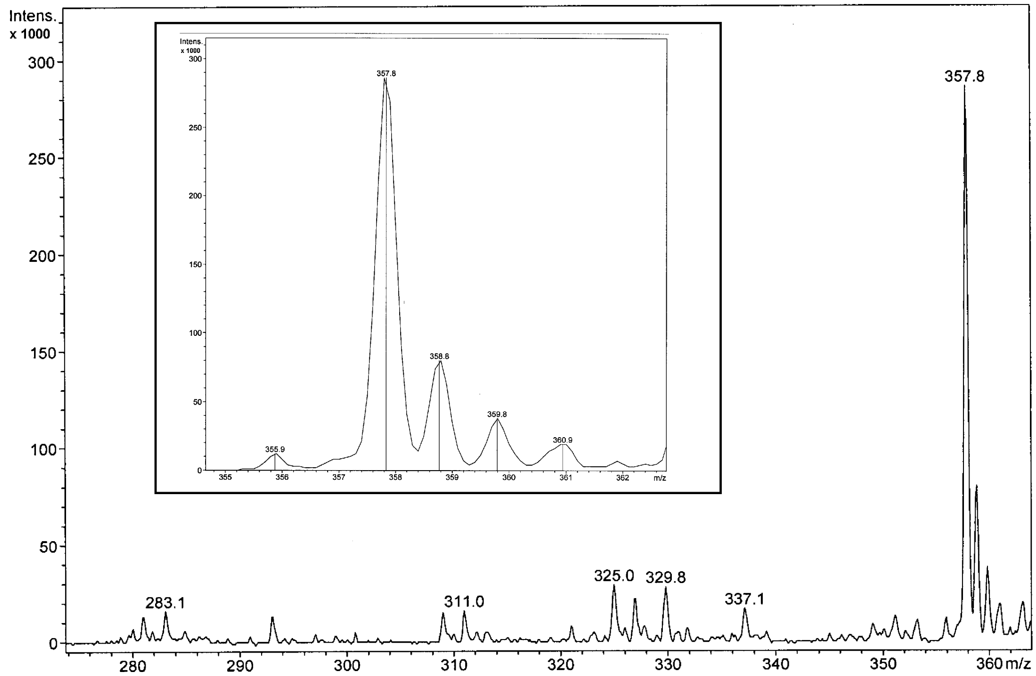
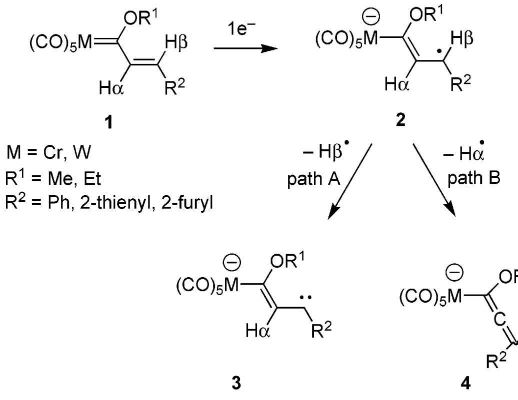


FIGURE 1. ESI mass spectrum of complex **5** showing the pseudomolecular ion $[M - H]^-$ at *m/z* 358. The magnified area corresponds to the isotopic cluster of the $[M - H]^-$ ion.

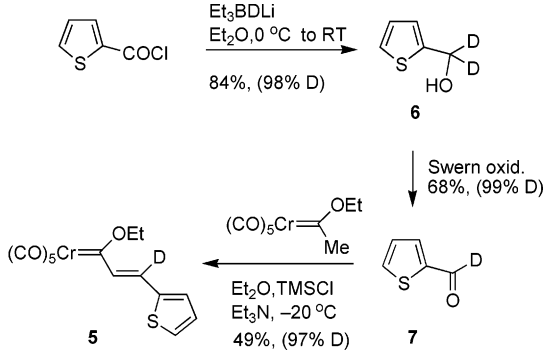
agents such as Na/K alloy,[7] potassium 1-methylnaphthalenide,[8] SmI_2,[9] or potassium graphite (C_8K).[10] Our results have shown that Fischer carbene complexes such as **1** can be ionized under ESI conditions in the presence of additives that act as electron carriers.[6] The process could be interpreted by initial capture of one electron to form intermediate **2** which would evolve to the $[M - H]^-$ detected ion by loss of a hydrogen radical. The nature of the $[M - H]^-$ ion is unknown, and although it could have the structure of a carbene anion **3**[6,11] obtained by breakage of Hβ, the formation of allenyl anion **4** by the alternate Hα breakage should not be discarded (Scheme 1).

SCHEME 1



The aim of this work is to understand the mechanism of ionization of group 6 Fischer carbene complexes mediated by electron carriers under ET-ESI (electron transfer-electrospray ionization) conditions. In this study, we will use labeling experiments combined with DFT calculations to unambiguously determine which of the two proposed mechanistic pathways in Scheme 1 is already occurring during the ESI process. An isotope tracer is one of the traditional mechanistic tools of physical organic chemistry that can also be applied to the investigation of organometallic reaction mechanisms.[12] This is an area of research of growing importance. On the other hand, the use of ESI combined with deuterium-labeling experiments has been employed in the elucidation of fragmentation mechanisms[13] and in the investigation of reactive intermediates in organometallic reactions.[14]

SCHEME 2



Results and Discussion

Monodeuterated complex **5** was prepared from 2-thiophenecarbonyl chloride by reduction with superdeuteride

---

(7) Krusic, P. J.; Klabunde, U.; Casey, C. P.; Block, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 2015.

(8) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1990**, *112*, 9419.

(9) (a) Fuchibe, K.; Iwasawa, N. *Org. Lett.* **2000**, *2*, 3297. (b) Fuchibe, K.; Iwasawa, N. *Chem. Eur. J.* **2003**, *9*, 905.

(10) Sierra, M. A.; Ramírez-López, P.; Gómez-Gallego, M.; Lejon, T.; Mancheño, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3442.

(11) (a) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771. (b) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584.

(12) See: Blum, S. A.; Tan, K. L.; Bergman, R. G. *J. Org. Chem.* **2003**, *68*, 4127 and references therein.

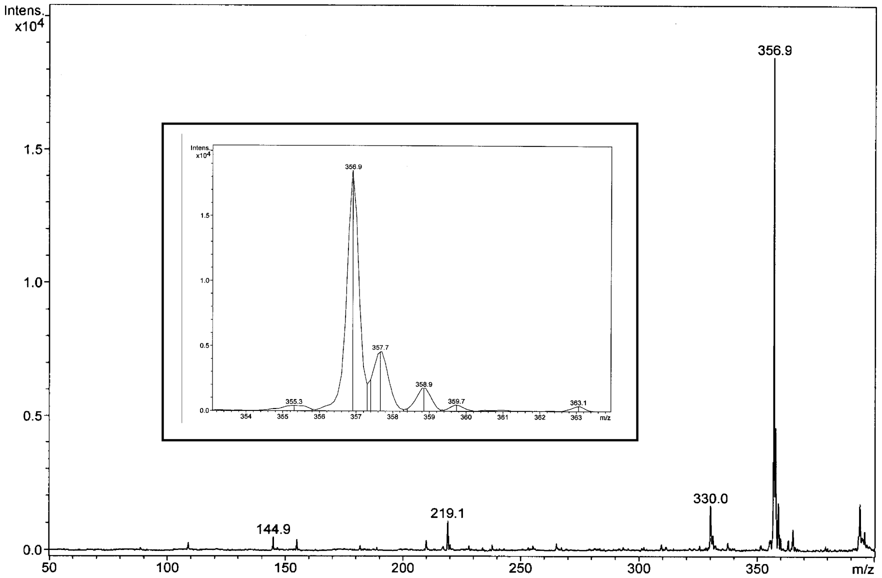
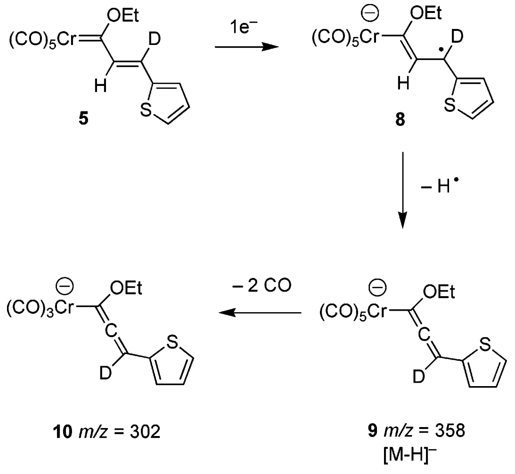


FIGURE 2. ESI mass spectrum of complex **11** showing the pseudomolecular ion [M − D]$^-$ at *m/z* 357. The magnified area corresponds to the isotopic cluster of the [M − D]$^-$ ion.

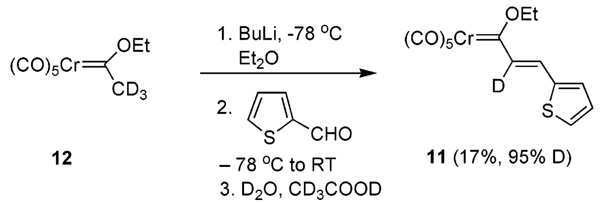
to yield dideuterated alcohol **6**, Swern oxidation to aldehyde **7**, and reaction of this compound with [ethoxymethylpentacarbonyl]chromium(0)carbene under Aumann conditions (Et_3N/TMSCl).[15] Complex **5** was determined to be 97% deuterated at the β-position (Scheme 2).

SCHEME 3



ESI-MS spectra of complex **5** were recorded using an ESQUIRE-LC ion-trap spectrometer in negative mode of detection. To a sample of **5** in chloroform (1.5×10^{-5} mol L^{-1}) a methanolic solution of hydroquinone (HQ, 25 mM) was added following our previously reported methodology.[6] A pseudomolecular ion at *m/z* 358 corresponding to [M − H]$^-$ was observed (Figure 1). The isotopic cluster of this ion (Figure 1) reveals a composition related to $C_{12}H_8DO_6SCr$. Tandem mass spectrometry (MS^n) was used to determine the fragmentation pathway of this ion.

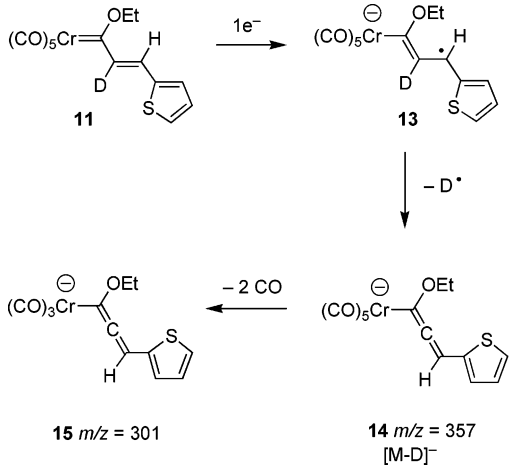
SCHEME 4



Thus, the loss of two CO molecules affords a peak at *m/z* 302 [M − H − (2CO)]$^-$ ($C_{12}H_8DO_4SCr$) corresponding to MS^2, while MS^3 yields a peak at *m/z* 218 which corresponds to the elimination of another three CO molecules. This fragmentation pattern was identical to that observed for the nondeuterated compound **1** (M = Cr).[6b] These results suggested that the evolution of the initially formed radical-anion **8** occurs as proposed in path B in Scheme 1, by loss of the Hα and formation of the allenyl anion **9** detected as [M − H]$^-$. Further extrusion of two CO ligands should provide the ion **10** (*m/z* 302) (Scheme 3).

To discard the possibility of isotopic scrambling with the electron-transfer reagent or the solvent within the

SCHEME 5



---

[13] See, for example: (a) Gatlin, C. J.; Turecek, F.; Vaisar, T. *J. Mass Spectrom.* **1995**, *30*, 1617, 1636. (b) Goodwin, L.; Startin, J. R.; Goodall, D. M.; Keely, B. J. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 37. (c) Shoeib, T.; Hopkinson, A. C.; Siu, K. W. M. *J. Phys. Chem. B* **2001**, *105*, 12399. (d) Shoeib, T.; Cunje, A.; Hopkinson, A. C.; Siu, K. W. M. *J. Am. Chem. Soc., Mass Spectrom.* **2002**, *13*, 408.

[14] Plattner, D. A. *Int. J. Mass Spectrom.* **2001**, *207*, 125.

[15] Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537.

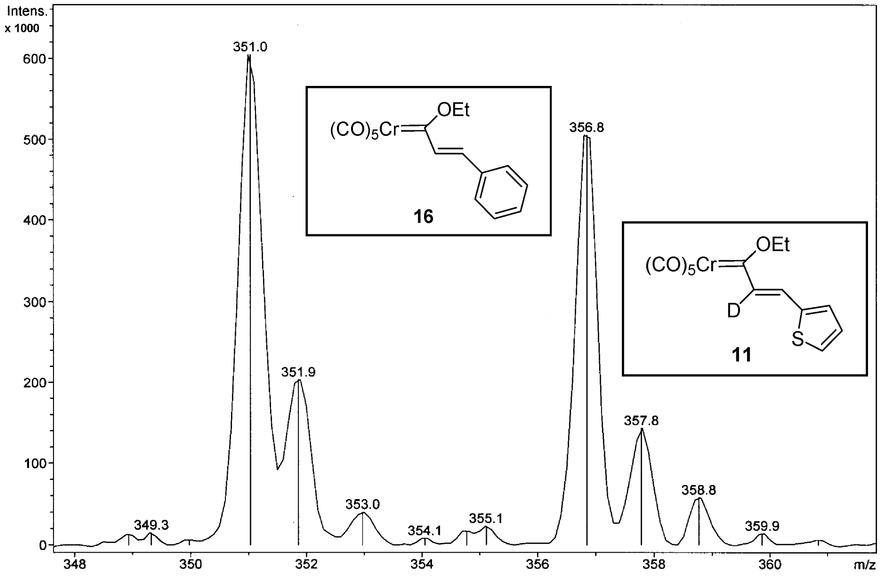


FIGURE 3. Pseudomolecular ion region of the ESI mass spectrum of the mixture of complexes **11** and **16**. The ion at *m/z* 351 corresponds to the $[M - H]^-$ of **16** while the ion at *m/z* 357 corresponds to the $[M - D]^-$ of **11**.

droplet during the ionization process, an experiment with complex **5**, perdeuterated hydroquinone (HQ-d_6), and CD_3OD was carried out. Under these conditions, only the pseudomolecular $[M - H]^-$ ion **9** at *m/z* 358 was observed, which indicates that the possible H/D interchange does not take place in any position of the complex (ESI-MS included as Supporting Information).

To unambiguously confirm the proposed ionization pattern, α-monodeuterated complex **11** was prepared. In this case, perdeuterated methyl chromium(0)carbene

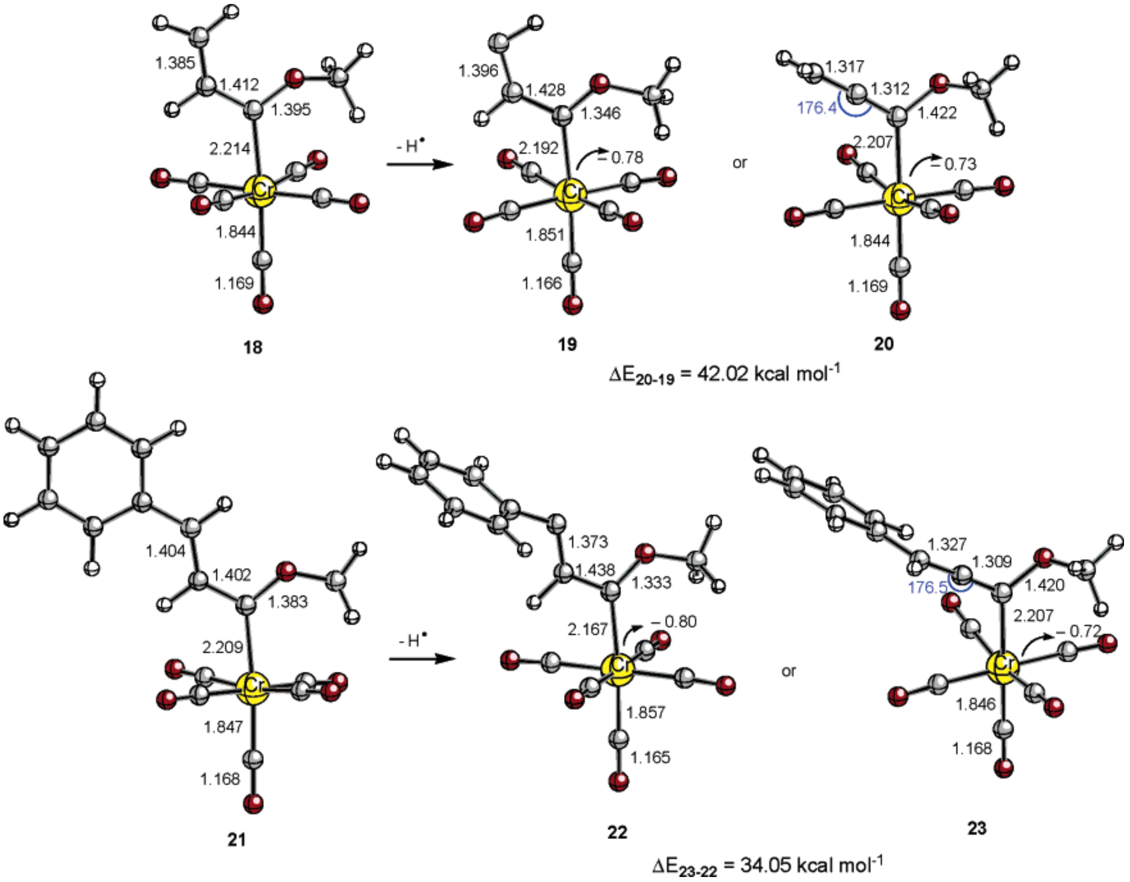


FIGURE 4. Optimized S_0 geometries (B3LYP/LANL2DZ&6-31+G(d)) of radical anions **18** and **21**, carbene anions **19** and **22**, and allenylchromium anions **20** and **23**.

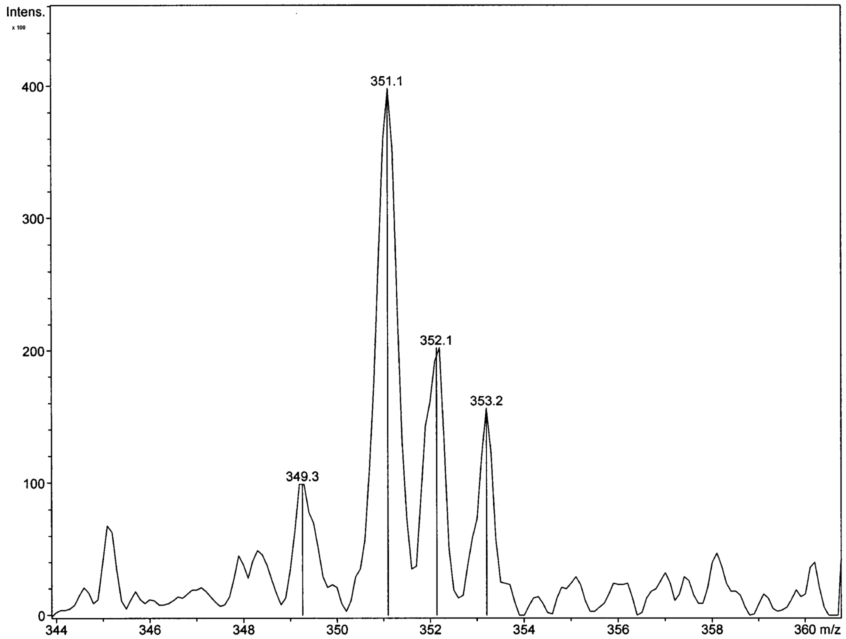


FIGURE 5. Pseudomolecular peaks region of the ESI-MS of complex **24** recorded with HQ-d_6 and CD_3OD.

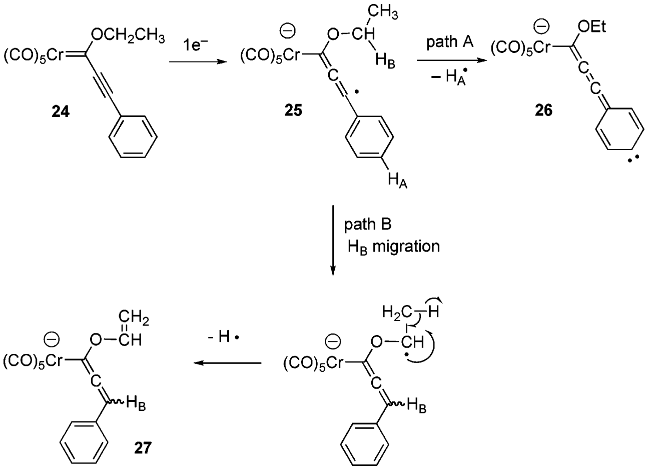
complex **12** (obtained from [ethoxymethylpentacarbonyl]-chromium(0)carbene by treatment with NaOEt/EtOD, followed by quenching with $HCl_{(gas)}$/EtOD) was deprotonated with BuLi and condensed with 2-thiophene carboxaldehyde to yield **11** in 17% yield. The degree of deuteration of this carbene complex in the α-position was 95% (Scheme 4).

Submission of complex **11** to the ESI-MS conditions used above resulted in a pseudomolecular $[M - D]^-$ ion **14** at *m/z* 357 (Figure 2). No pseudomolecular $[M - H]^-$ ion (*m/z* 358) was observed in this case. The fragmentation of the $[M - D]^-$ ion (*m/z* 357) shows again the double simultaneous decarbonylation process characteristic of these compounds, affording exclusively an ion **15** at *m/z* 301 (see the Supporting Information). By analogy with the reaction pattern depicted in Scheme 3, after the initial ET to **11**, the formation of radical anion **13** should lead to allenyl anion **14** by C−D bond breakage. Finally, the double elimination of CO would form **15** (Scheme 5).

The possibility of deuterium scrambling with the HQ and/or with the solvent was rejected again by recording the ESI-MS of complex **11** with HQ-d_6 and CD_3OD. Only the pseudomolecular peak at *m/z* 357 was detected in the experiment (ESI-MS included as Supporting Information).

As an additional confirmation of these results, and to discard any possibility of intermolecular H/D exchange among carbene complex molecules during the experiment, the ESI-MS of an equimolar mixture of labeled complex **11** and compound **16** was recorded under the conditions used through this work. The resulting mass spectrum showed the expected peak $[M - D]^-$ **14** (*m/z* 357) of complex **11**, together with a $[M - H]^-$ pseudomolecular ion (*m/z* 351) corresponding to complex **16** (Figure 3). In both cases, the intensities and the isotopic distribution of the peaks were identical to those observed for the single complexes, which discards any significant H/D scrambling in the process. Therefore, it can be concluded that the results obtained in the ESI-MS ionization of deuterated carbene complexes **5** and **11** indicate that the process occurs by the transfer of $1e^-$ to the organometallic compound, followed by extrusion of the α-hydrogen to form an allenyl anion which is the $[M - H]^-$ species detected in the MS spectra.

SCHEME 6



It has been well stated that in kinetically controlled reactions the most exothermic pathway requires a lower energy of activation.[16] Thus, we have rationalized the preference for the Hα breakage in the ionization process (path B, Scheme 1) by comparing the stability of allenyl anion **4** and carbene anion **3**, the product that would result from the alternative Hβ fragmentation pathway (path A, Scheme 1). DFT calculations were carried out in the model complex $[(CO)_5Cr(OMe)CH{=}CH_2]$, **17**. The S_0 geometries of radical anion **18**, carbene anion **19**, and

---

(16) The Bell−Evans−Polanyi principle states the linear relation observed between energy of activation (E_a) and enthalpy of reaction (ΔH_r) within a series of closely related reactions. *IUPAC Compendium of Chemical Terminology*, 2nd ed., Pergamon Press: New York, 1997. See also: Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.

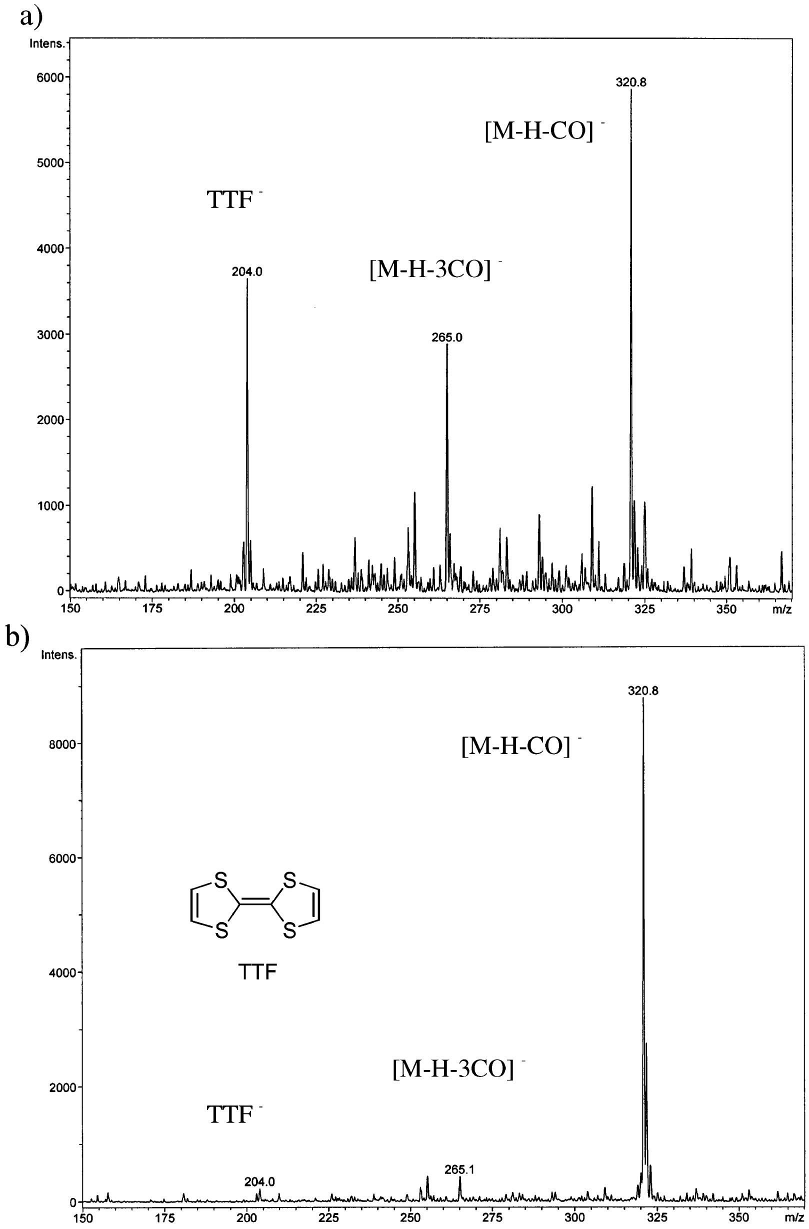


FIGURE 6. (a) ESI mass spectrum of complex **24** with TTF and MeOH. (b) ESI mass spectrum of complex **24** with TTF and CD_3OD.

allenylchromium anion **20** were optimized at the B3LYP/LANL2DZ&6-31+G(d) level and are represented in Figure 4. Our results showed that allenyl anion **20** was considerably more stable (42.02 kcal mol^{-1}) than carbene anion **19**. Being aware that these results could be oversimplified by the fact that model complex **17** lacked an aromatic ring in the β-position, additional calculations were carried out in phenyl-substituted radical anion **21** (formed from carbene complex [$(CO)_5Cr(OMe)CH{=}CHPh$]), carbene anion **22** and allenylchromium anion **23**. Again, the allenyl anion **23** resulted to be more stable than the carbene anion **22** (34.05 kcal mol^{-1}), even though this latter species benefits from the additional conjugative stabilization caused by the phenyl group. Nevertheless, it should be noticed that the difference in energies between these species is very high. As a matter of fact, the value of 34.05 kcal mol^{-1} is an estimation of the stabilization of an allenyl-metal species compared to a vinylmetal species (Figure 4). Furthermore, the charge on the chromium atom is nearly identical in species **21**–**23**, which points to the small effect of the metal in the evolution of the radical anion formed after the initial electron-transfer reaction.

Having established the viability of the use of labeling experiments in the study of the behavior of Fischer carbene complexes under ESI conditions, we decided to employ this methodology to confirm the ionization pattern previously proposed by us for alkynyl carbene complexes **24**.[6b] In this case, the anion radical **25** is formed after the capture of an electron, and this initial ionization is followed by the loss of a hydrogen radical to form the $[M - H]^-$ ion (*m/z* 349) detected in the mass spectrum. We postulated[6b] that the cleavage of the aromatic C–H_A bond to yield allene anion carbene complex **26** was the most likely fragmentation pathway (path A, Scheme 6). However, the intramolecular H_B

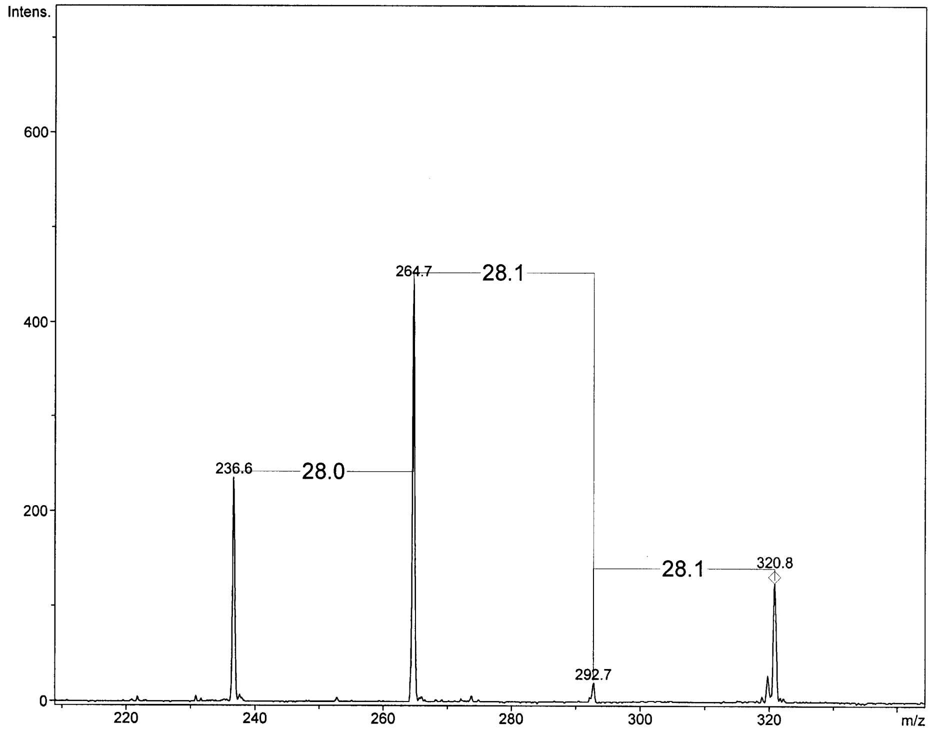


FIGURE 7. Tandem mass spectrum of the pseudomolecular ion of **24** at *m/z* 321 showing the characteristic loss of CO molecules.

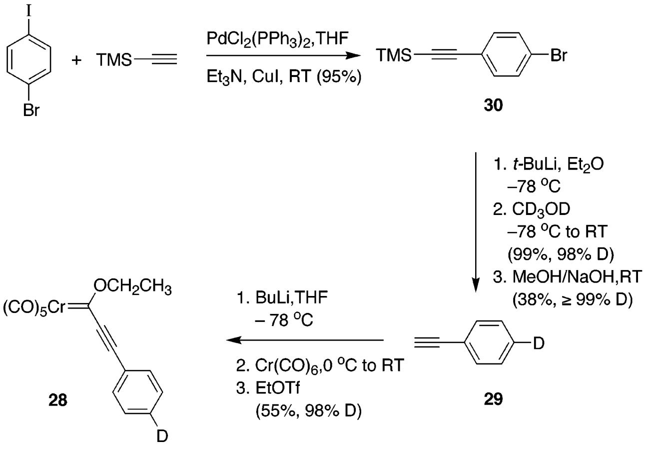
transfer from the ethoxy group in **25**, followed by the loss of a hydrogen radical to form allenyl anion **27**, cannot be discarded (path B, Scheme 6). If this species was formed, it will be also detected as the $[M - H]^-$ ion (*m/z* 349) in the ESI-MS spectrum.

Prior to working with a labeled substrate, we checked the possible proton interchange between the aromatic hydrogens of **24** and the HQ or the solvent (MeOH) during the experiment. The ESI-MS spectrum of **24** was recorded in the presence of HQ-d_6 and CD_3OD. The isotopic cluster of the pseudomolecular ion is displayed in Figure 5. The presence of peaks at *m/z* 351, 352, and 353 only can be explained assuming H/D scrambling in the aromatic ring. The most intense peak (*m/z* 351) could correspond to both the $[M - D]^-$ ion obtained from a trideuterated complex **24** and the $[M - H]^-$ ion obtained from this complex bisdeuraterated in the aromatic ring.

Assuming the proton exchange between alkynyl carbene complex **24** and the HQ/MeOH employed in the ESI-MS experiments, we decided to change the additive, using tetrathiafulvalene (TTF) instead of hydroquinone. Previous work by our research group has demonstrated that TTF can be also used as an efficient electron carrier in ESI-MS experiments with Fischer carbene complexes.[6] The ESI-MS spectra of **24** with TTF (25 mM) in both MeOH and CD_3OD are displayed in Figure 6. The mass spectra show identical pseudomolecular ions corresponding to $[M - H - CO]^-$ (*m/z* 321), which indicate that the exchange H/D of **24** with TTF or solvent does not take place. The TTF appears in both cases at *m/z* 204 as $TTF^{\bullet -}$. Tandem mass spectrometry of the $[M - H - CO]^-$ ion showed the successive loss of CO molecules displayed in Figure 7.

Once the ESI ionization conditions were established, monodeuterated complex **28** was prepared from *p*-D-ethynylbenzene **29** following the standard procedure for the synthesis of Fischer carbene complexes ($Cr(CO)_6$/M−C≡C−Ph/EtOTf). *p*-D-Ethynylbenzene **29** was made from **30** by Sonogashira coupling, D−halogen interchange, and TMS group removal. The desired complex **28** was prepared in 55% yield and ≥98 D-incorporation (Scheme 7).

SCHEME 7



The ionization of complex **28** was carried with TTF in either in MeOH or in CD_3OD (ESI-MS spectra are shown in the Supporting Information). A pseudomolecular $[M - H - CO]^-$ ion (*m/z* 322, $C_{15}H_8DCrO_5$) was observed in both cases. The possibility of scrambling was excluded in the previous experiments and no other peaks due to the fragmentation of the C−D bond could be detected. These experimental results suggest that the ionization of alkynyl carbene complexes **24** and **28** occurs as suggested in path B of Scheme 6. Once the radical anion

25 is formed, H-transfer from the ethoxy group, and sucessive loss of a hydrogen radical give allenyl anion **27**. This species losses a CO molecule to form the $[M - H - CO]^-$ ion detected in the ESI-MS spectra. Tandem MS of complex **28** also affords the typical sequence of CO loss (see the Supporting Information).

In conclusion, through this study we have combined deuterium labeling in substrate, additive, and solvent to establish the mechanism of ionization of conjugated Fisher carbene complexes under ESI conditions. The results indicate that in the ESI source, in the presence of HQ or TTF, an anion-radical is formed. For alkenyl carbene complexes, this species evolves by extrusion of a radical hydrogen to form an allenylchromium anion that is detected in the mass spectrum as $[M - H]^-$ ion. The rationalization based on the higher stability of the allenylchromium anion species compared to the carbene-anion species previously postulated by us in these processes has been extracted from DFT calculations. From the comparison of the energy values it can also be concluded that the presence of the metal has little influence in the evolution of the radical anion formed after the initial electron transfer reaction. In the case of alkynyl carbene complexes, our results demonstrate that the previously proposed allene-anion carbene complex is not formed. Instead, H-transfer from the ethoxy group and successive loss of a hydrogen radical gives an allenyl anion that is detected in the ESI-MS spectra as $[M - H - CO]^-$ ion. To avoid undesirable proton interchange during the experiments, TTF instead of HQ was used in these cases.

Experimental Section

For General Procedures see the Supporting Information.

Preparation of Perdeuterated Hydroquinone (HQ-*d*$_6$). To a solution of hydroquinone (0.11 g, 1 mmol) in 5 mL of diethyl ether was added sodium (0.07 g, 3 mmol). The reaction mixture was stirred at rt for 2 h. The solution was carefully quenched with 1 mL of DCl (95% deuteration). After addition of 2 mL of D_2O, the organic layer was separated and the solvent removed under reduced pressure. The deuterium incorporation was checked by mass spectrometry (see the Supporting Information). ESI-MS ($C_6D_6O_2$): *m*/*z* 114 $[M - D]^-$ (negative mode) and *m*/*z* 139 $[M + Na]^+$ (positive mode).

Preparation of 5. In a 50 mL round-bottom flask where the 14/20 glass joint was replaced with a threaded high-vacuum Teflon stopcock were added 30 mL of diethyl ether, compound **7** (0.59 g, 5.22 mmol), [ethoxymethylpentacarbonyl]-chromium(0)carbene[19] (1.35 g, 5.11 mmol), triethylamine (3.0 mL, 21.5 mmol), and TMSCl (2.0 mL, 15.8 mmol).[15] Three freeze−thaw cycles were done to remove oxygen. The solution was stirred for 23 h at rt and then stored 24 h at −20 °C. The contents of the flask were poured onto silica gel and the solvent removed under reduced pressure. Column chromatography (24.5 cm × 4 cm, silica gel) with 30% dichloromethane/hexane gave 0.89 g of **5** as a black solid, $R_f = 0.51$ (30% CH_2Cl_2/hexane), mp 86−87 °C (49% yield, 97% deuterium incorporation), along with 0.44 g (33%) of recovered [ethoxymethylpentacarbonyl]chromium(0) carbene. The deuterium incorporation was determined by ^{1}H NMR by comparison of the integration of the signals at 7.16 ppm (d) and 7.08 ppm (dd). Spectral data for compound **5**: ^{1}H NMR ($CDCl_3$) δ 1.67 (t, 3 H, $J = 7.1$ Hz), 5.07 (q, 2 H, $J = 7.1$ Hz), 7.08 (dd, 1 H, $J = 3.7$, $J = 5.1$ Hz), 7.38 (dd, 1 H, $J = 1.0$, $J = 3.7$ Hz), 7.47 (dd, $J = 1$, $J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ: 15.1, 75.8, 123.5 (t, $^{1}J = 22.5$ Hz, very weak) 128.7, 130.4, 133.5, 138.3, 139.9, 216.8, 224.4, 328.6; IR (thin film) 3080w, 3026w, 2963m, 2901w, 2108s, 1480m cm^{-1}. Anal. Calcd for $C_{14}H_9DCrO_6S$: C, 46.80; H, 3.09. Found; C, 46.72; H, 2.81.

Preparation of 12. To [ethoxymethylpentacarbonyl]chromium(0) carbene[19] (4.57 g, 17.3 mmol) was added 10 mL of ethanol-*d*$_1$ with predissolved sodium metal (<4 mg). The solution was stirred for 15 min and acidified with concd HCl/ethanol-*d*$_1$ (1:3, v/v). The solution was then taken up in Et_2O and filtered through Celite 503. The organic solvent was removed under reduced pressure. This procedure was repeated four times, resulting in 2.94 g of **12** as orange oil at rt, yellow solid at −20 °C, $R_f = 0.42$ (9:1 hexane/EtOAc) (64% yield, 96% deuterium incorporation). The spectral data were consistent with the known literature compound.[20] The deuterium incorporation was determined by ^{1}H NMR by comparison of the integration of the signals at 2.88 and 1.65 ppm. Spectral data for **12**: ^{1}H NMR ($CDCl_3$) δ 1.64 (t, 3 H, $J = 7.1$ Hz), 2.88 (br s, 0.15 H, from nondeuterated compound), 5.01 (bs, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.9, 49.3 (broad and weak), 216.5, 223.4, 357.8 (deuterated carbon missing due to the relaxation time of C−D); IR (thin film) 2991.97m, 2945.68m, 2905.17w, 2064.10vs, 1917.49vs, 1469.94m, 1367.76s, 1250.03vs, 1128.50s, 1030.12s, 978.03s 812.13m, 640.45vs cm^{-1}.

Preparation of 11. To a solution of **12** (1.0 g, 3.8 mmol) in Et_2O (25 mL) at −78 °C was added 2.4 mL of *n*-butyllithium (1.6 M in hexanes, 3.8 mmol). The solution was stirred for 20 min, and then 2-thiophenecarbaldehyde (0.7 mL, 7.7 mmol) was added at −78 °C. The solution was stirred for 45 min at −78 °C, warmed to rt, and stirred for an additional 4 h. The reaction was extracted with 10 mL of D_2O, and the D_2O layer was adjusted to pH < 7 with acetic acid-*d*$_4$. The D_2O layer was extracted with CH_2Cl_2 (3 × 50 mL), the organic extracts were combined and dried over sodium sulfate, and the solvent was removed under reduced pressure. Column chromatography (2.8 cm × 26 cm, silica gel) with 5% CH_2Cl_2 to 10% CH_2Cl_2/hexane gave 0.24 g of **11** as red solid, mp 86−88 °C,[13] $R_f = 0.30$ (hexane) (17% yield, 95% deuterium incorporation). The deuterium incorporation was determined by ^{1}H NMR by comparison of the integration of the signals at 7.70 ppm (d) and 7.36 ppm (d). Spectral data for **11**: ^{1}H NMR ($CDCl_3$) δ 1.66 (t, 3 H, $J = 7.0$ Hz), 5.04 (q, 1 H, $J = 7.2$ Hz), 7.08 (dd, 1 H, $J = 3.8$, $J = 5.0$ Hz), 7.11 (s, 1 H), 7.36 (d, 1 H, $J = 3.8$ Hz), 7.47 (d, 1 H, $J = 5.0$ Hz), 7.70 (d, 0.05 H, $J = 15.0$ Hz, from nondeuterated compound); ^{13}C NMR ($CDCl_3$) δ 15.2, 75.9, 123.0, 128.7, 130.5, 133.6, 137.9 (t, $^{1}J = 23.7$ Hz, weak), 139.9, 216.8, 224.4, 328.3; IR (thin film) 3112w, 2994m, 2056s, 1916s, 1561s cm^{-1}. Anal. Calcd for $C_{14}H_9DCrO_6S$: C, 46.80; H, 3.09. Found; C, 46.86; H, 2.82.

Preparation of 28. To a solution of **29** (0.37 g, 3.6 mmol) at −78 °C in 20 mL of THF was added *n*-butyllithium (1.6 M in pentane, 2.25 mL, 3.6 mmol). The solution was warmed to 0 °C and stirred for 45 min, which gave a yellow-brown solution. At this point, chromium hexacarbonyl (0.80 g, 3.6 mmol) was added at 0 °C, and the orange solution was allowed to warm to rt over 45 min. The solution was cooled to 0 °C, and ethyl triflate (0.94 mL, 7.3 mmol) was added. The solution was stirred for 35 min, which resulted in a blood-red solution. The contents of the flask were poured onto brine (50 mL) and extracted with three portions of Et_2O (20 mL, 2 × 75 mL). The organic layers were combined and dried with sodium sulfate.

---

[17] (a) Fetizon, M.; Henry, Y.; Moreau, N.; Moreau, G.; Golfier, M.; Prange, T. *Tetrahedron* **1973**, *29*, 1011. (b) Macco, A. A.; Brouwer, R. J. D.; Nossin, P. M. M.; Godefroi, E. F.; Buck, H. M. *J. Org. Chem.* **1978**, *43*, 1591.

[18] (a) Hoskovec, M.; Luxova, A.; Svatos, A.; Boland, W. *Tetrahedron* **2002**, *58*, 9193. (b) Chadwick, D. J.; Chambers, J.; Hargrave, He; Meakins, G. D.; Snowden, R. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2327. (c) Chadwick, D. J.; Chambers, J.; Meakins, G. D.; Snowden, R. L. *J. Chem. Soc., Perkin Trans. 2* **1975**, 604.

[19] Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15.

[20] Chelain, E.; Parlier, A.; Audouin, M.; Rudler, H.; Daran, J. C.; Vaissermann, J. *J. Am. Chem. Soc.* **1993**, *115*, 10568.

The solvent was removed under reduced pressure with care taken to maintain a temperature of 0−10 °C for the water bath. Column chromatography (30 cm × 3.8 cm, silica gel) first with hexane and then with 5% EtOAc/hexane resulted in 0.69 g of **28** as a black solid (hexane), mp 61−63 °C, $R_f = 0.18$ (hexane), $R_f = 0.34$ (5% EtOAc/hexane)[21] (55% yield, ≥98% deuterium incorporation). Again, care was take to maintain a temperature of 0 to 10 °C of the water bath when the solvent was removed. The deuterium incorporation was determined by ^{1}H NMR by setting the region of integration of 7.58 ppm (d) to 2 and noting the difference of the integration of the region of 7.45 ppm (d). This difference was calibrated to the undeuterated compound. Spectral data for **28**: ^{1}H NMR ($CDCl_3$) δ 1.58 (t, 3 H, $J = 7.1$ Hz), 4.74 (q, 2 H, $J = 6.9$ Hz), 7.45 (d, 2 H, $J = 7.8$ Hz), 7.58 (d, 2 H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 15.0, 75.8, 91.8, 121.0, 128.8, 131.3 (t, $^1J = 22.8$ Hz, weak), 132.7, 135.7 (weak), 216.3, 225.7, 313.8; IR (thin film) 2999wb, 2155m, 2060s, 1935s, 1294m, 1196m, 1146w, 1109w, 1036m, 862m, 681m, 650m, 608m, 594m cm^{-1}. Anal. Calcd for $C_{16}H_9DCrO_6$: C, 54.71; H, 3.16. Found: C, 54.40; H, 3.00. Attempts to make compound **28** by treatment of **4-D-trimethylsilylethynylbenzene** with MeLi−LiBr complex were unsuccessful at producing yields greater than 0.1% of the carbene complex.

Acknowledgment. Financial support by the Spanish Ministerio de Ciencia y Tecnología (Grant Nos. CTQ2004-06250-CO2-01 and BQU2002-00406) are gratefully acknowledged. I.F. thanks the Ministerio de Educación y Ciencia for a predoctoral fellowship.

Supporting Information Available: General experimental procedures; synthesis and full characterization of compounds **6**, **7**, **29**, and **30**; MS^2 spectra of complexes **5**, **11**, and **28**; ESI-MS spectra of **5** and **11** with HQ-d_6 in CD_3OD; ESI-MS spectra of HQ-d_6; ESI-MS spectra of **28** with TTF. Cartesian coordinates (Å) and total energies (in au, noncorrected zero-point vibrational energies included) of all stationary points discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050553Y

---

[21] Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47.