Behavior of Group 6 Fischer Aminocarbene Complexes in a Supercharged Medium: A Single Electron Transfer−H Atom Transfer Process

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Received February 27, 2009

The ESI-MS study of the ionization of a series of aryl, alkenyl, and alkynyl (Fischer) aminocarbene complexes is described. The process requires the initial capture of one electron from the ESI source, followed by the transfer of a hydrogen atom to the additive (TTF or Cs_2CO_3). Regardless of their structure, both NH and N,N-disubstituted aminocarbenes can effectively ionize under ESI-MS conditions, as long as they have abstractable H atoms. Overall, the process can be envisaged as a single electron transfer−H atom transfer process. The experimental findings are supported by DFT calculations. The ESI-MS ionization of bis-alkynylaminocarbene complexes follows the same patterns. However, the $[M - H]^-$ ions evolve by arylacetylene extrusion together with the usual sequence of CO loss. The process requires the presence of a free NH group and occurs by intramolecular hydrogen transfer from the NH to the metal center. Bis-aminocarbenes having rigid tethers between the nitrogen atoms or lacking free NH groups do not produce this fragmentation.

Introduction

Single electron transfer (SET)[1] reactions in organic chemistry are well-established, and their synthetic utility has been profusely demonstrated during the last century.[2] However, knowledge of SET processes in organometallic complexes or about the interaction between organometallic complexes and organic or organometallic additives in a nonconventional media (electrospray ionization sources (ESI)) is less extensive.[3] Mechanisms beginning with SET processes followed by H atom transfer (HAT)[4,5] are a subclass of the general proton-coupled electron transfer processes (PCET),[6] which have gained increasing interest in the fields of experimental and theoretical chemistry in the past years.[7] In this context, transition metal Fischer carbene complexes[8] are paramount to study both the chemical and ESI-induced SET processes,[3] since the electron-withdrawing effect of the $M(CO)_5$ moiety in these compounds renders the carbene carbon very electrophilic, and hence an extremely good electron acceptor.[6]

Due to the fact that ESI is a technique[9] that allows the transfer of ions from solution to the gas phase as isolated entities, it is an exceptional media to study SET processes to organometallic compounds in nonconventional media. In this technique, transfer of ions from solution to the gas phase occurs through three main steps: production of charged droplets at the capillary, size-reduction of the charged droplets due to the high voltage applied, and production of very small drops from which ions in the gas phase are generated. During the last years, we have demonstrated[10] that the ESI-reactivity of neutral carbene complexes lacking acidic positions or basic centers can be studied in the presence of additives such as tetrathiafulvalene (TTF) or hydroquinone (HQ). We proposed the term *electron carriers*[10a] for TTF and HQ since, apparently, they efficiently transferred one electron from the ESI source to the carbene, leading to the formation of a radical anion species that evolves in the ESI conditions to the detected $[M - H]^-$ species (Scheme 1).

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[2] (a) Kochi, J. K. *Angew. Chem., Int. Ed.* **1988**, *27*, 1227. (b) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.

[3] Sierra, M. A.; Gómez-Gallego, M.; Martínez-Álvarez, R. *Chem.*−*Eur. J.* **2007**, *13*, 736.

[4] Mayer, J. M.; Hrovat, D. A.; Thomas, J. L.; Borden, W. T. *J. Am. Chem. Soc.* **2002**, *124*, 11142.

[5] In the HAT process both electrons and protons are transferred from the same chemical bond in a concerted manner.

[6] Huynh, M. H. V.; Meyer, T. J. *Chem. Rev.* **2007**, *107*, 5004.

[7] Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363.

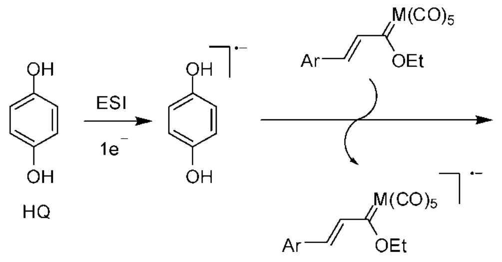
[8] Selected reviews in the chemistry and synthetic applications of Fischer carbene complexes: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1065. (d) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (e) Rudler, H.; Audouin, M.; Chelain, E.; Denise, B.; Goumont, R.; Massoud, A.; Parlier, A.; Pacreau, A.; Rudler, M.; Yefsah, R.; Álvarez, C. F.; Delgado-Reyes, *Chem. Soc. Rev.* **1991**, *20*, 503. (f) Grötjahn, D. B.; Dötz, K. H. *Synlett.* **1991**, 381. (g) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 470. (h) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, p 549. (i) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (j) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (k) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163. (l) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (m) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (n) Gómez-Gallego, M.; Mancheño, M. J.; Sierra, M. A. *Acc. Chem. Res.* **2005**, *38*, 44. (o) Herndon, J. W. *Coord. Chem. Rev.* **2006**, *250*, 1889. (p) Sierra, M. A.; Fernández, I.; Cossío, F. P. *Chem. Commun.* **2008**, 4671.

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

[10] (a) Sierra, M. A.; Gómez-Gallego, M.; Mancheño, M. J.; Martínez-Álvarez, R.; Ramírez-López, P.; Kayali, N.; González, A. *J. Mass Spectrom.* **2003**, *38*, 151. (b) Martínez-Álvarez, R.; Gómez-Gallego, M.; Fernández, I.; Mancheño, M. J.; Sierra, M. A. *Organometallics* **2004**, *26*, 4647. (c) Wulff, W. D.; Korthals, K. A.; Martínez-Álvarez, R.; Gómez-Gallego, M.; Fernández, I.; Sierra, M. A. *J. Org. Chem.* **2005**, *70*, 5269.

10.1021/om900159h CCC: $40.75

Scheme 1. Proposed Mechanism for the SET Process from Hydroquinone (HQ) to α,*β*-Unsaturated Chromium(0) (Fischer) Carbene Complexes[10]



Classical deuterium labeling experiments carried on substrate, solvent, and additive were used to study the different mechanisms for the evolution of the $[M - H]^-$ ions. These experiments were conclusive proof for the suitability of this methodology to study the reactivity of group 6 metal−carbene complexes in supercharged media.[10c]

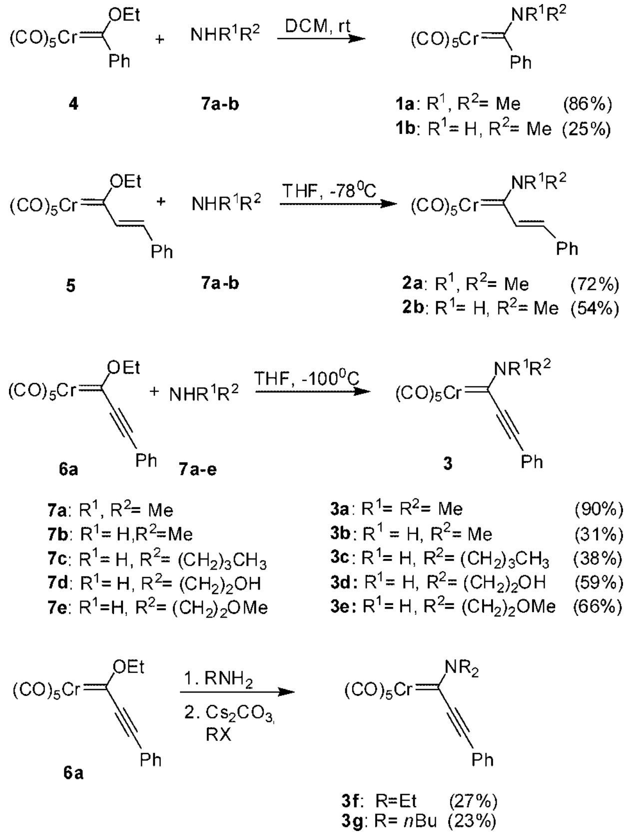
Nevertheless, the interaction between the additive and the complex (that is, the actual mechanism of the ionization process) remains an open matter. In this article we report a detailed study on the ionization process of group 6 mono- and bis-aminocarbene complexes (in which both metal centers are tethered by the amino groups). Unseen reaction pathways for the evolution of the molecular anions will be discussed, and a different mechanism for the interaction between the additive and the complex, involving a HAT process, will be proposed on experimental and computational grounds.

Results and Discussion

Complexes **1**−**3** were prepared by reaction of the corresponding alkoxycarbene complexes **4**−**6** with amines **7a**−**e**. For the synthesis of α,*β*-unsaturated aminocarbene complexes, formation of the 1,2-adducts over the 1,4-adducts was achieved at low temperature, according to previously reported procedures (Scheme 2).[11]

Complexes **1** were studied first. Aminocarbene **1a** was solved in $CHCl_3$ (1.5×10^{-5} mol/L) and pumped through a PEEK capillary into the ESI source (5.0 kV). Simultaneously, a 25 mM solution of tetrathiafulvalene (TTF) in MeOH/$CHCl_3$ (1:1) was introduced. No ionization was detected under these conditions. However, when complex **1b** was treated in the same way, a nice $[M - H]^-$ ion at *m*/*z* 310 was obtained. The $[M - H]^-$ ions were isolated and their MS^n spectra[12] were recorded using the collision-induced dissociation (CID) method (He). Together with a sequential CO loss, also observed for alkoxychromium(0) carbene complexes,[13] **1b** produced a new type of fragmentation, extruding methyl isocyanide (detected in MS^3).

Scheme 2. Synthesis of Complexes 1−**3**



Just by comparison of their structures, the different behavior observed for aminocarbenes **1a** and **1b** could suggest that the ionization process requires the presence of an NH group attached to the carbene carbon, which may be involved in an acid−base process. However, the ionization of **1b** takes place in the presence of the scarcely basic TTF as additive, but the use of a stronger base (CO_3^{2-}) did not change the outcome of the process. These results point to a process somewhat more complex than a simple acid−base proton transfer and rule out the alternative role of the additive as an *electron carrier* responsible for the ionization of the complex.[10] It is much more likely to consider the initial formation of radical anions **8a**,**b**, derived from the capture of one electron (from the source) by the aminocarbene complex. Then, in order to produce a detectable molecular ion, the loss of a hydrogen atom is required and, at this point, the additive must be playing a main role. Overall, the ionization of **1b** can be envisaged as a SET-HAT process (Scheme 3). The formation of a $[M - H]^-$ ion is not possible in the case of aminocarbene **1a**, which lacks abstractable H atoms.

Once the $[M - H]^-$ ion **9** is formed from **1b**, it evolves by sequential CO loss to generate the unsaturated species **10**, followed by extrusion of methyl isocyanide, as observed in the MS^2 and MS^3 spectra (Table 1).[13] This process leads to a new species, **11**, in which the moiety formerly attached to the carbene carbon is now joined to the metal center.[14] The coordinatively unsaturated character of the metal should favor this sequence of events (this is further supported by the fact that the evolution of the isocyanide did not occur from the molecular ion, requiring at least extrusion of one of the CO ligands) (Scheme 3).

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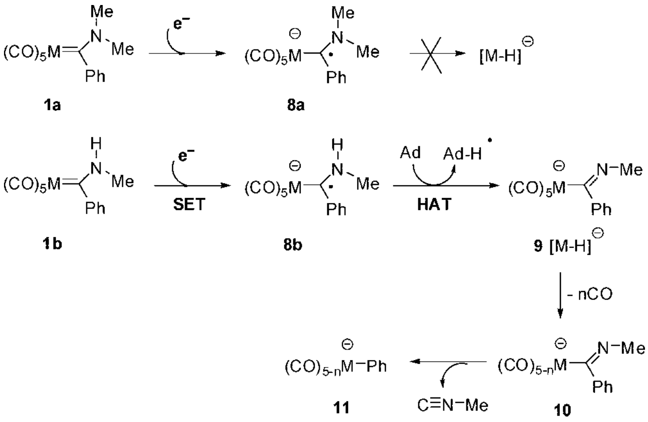
[11] (a) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; De Meijere, A. *Organometallics* **1993**, *12*, 2556. (b) Aumann, R.; Hinterding, P. *Chem. Ber.* **1992**, *125*, 3765. (c) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (d) Hegedus, L. S.; Schwindt, M. A.; De Lombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990**, *112*, 2264. (e) Hegedus, L. S. *Pure Appl. Chem.* **1983**, *55*, 1745. (f) Fischer, E. O.; Kalder, H. J. *J. Organomet. Chem.* **1977**, *131*, 57. (g) Aumann, R.; Hinterding, P. *Chem. Ber.* **1993**, *126*, 421. (h) Moretó, J.; Ricart, S.; Dötz, K. H.; Molins, E. *Organometallics* **2001**, *20*, 62.

[12] Through this work MS^n ($n = 1$) refers to spectra of the molecular ion, while the value of n ($n \neq 1$) denotes the successive collision-induced dissociation of isolated MS^{1}ions.

[13] (a) Müller, J.; Connor, J. A. *Chem. Ber.* **1969**, *102*, 1148. (b) Fischer, E. O.; Leopold, M.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 1150. (c) Careri, A.; Mangia, P.; Manini, P.; Predieri, G.; Licandro, E.; Papagni, A. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 51.

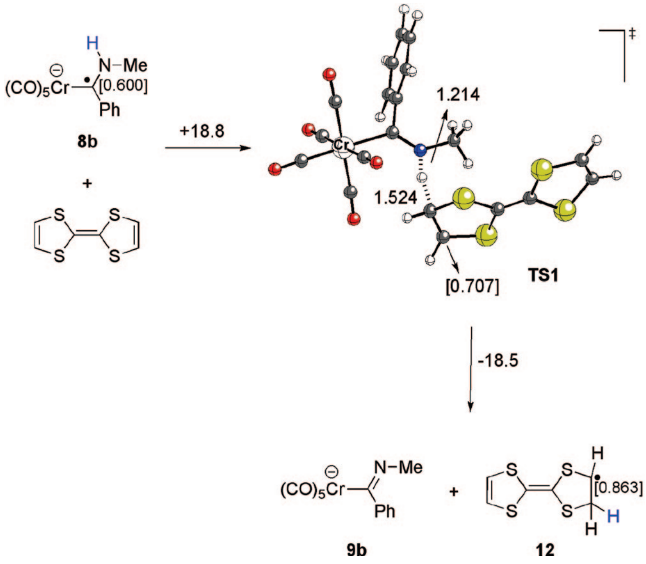
[14] The alternative and simplest way to explain the formation of isocyanide from intermediate **10** is the extrusion of the phenyl moiety as a Ph^- fragment. However, we have not observed this extrusion in the many experiments carried out through this work.

Scheme 3. Proposed Mechanism for Ionization of NH-Substituted Aminocarbene Complexes 1



To support the mechanism of ionization proposed for compound **1b**, DFT calculations were carried out for the HAT process. The reaction of radical anion **8b** and TTF was computed at the uB3LYP/6-31+G(d)&LanL2DZ level. The computed spin-density in **8b** (0.60 au) clearly shows that the former carbene carbon atom acts as the acceptor center of the electron provided by the ESI source. Transfer of the H atom from the N−H group of **8b** to TTF occurs via the transition state **TS1**, which has developed the TTF−H bond at the expense of the TTF C═C double-bond breakage (Scheme 4). The activation barrier of the process is 18.8 kcal/mol. The reaction products are the expected anion **9b** and the radical TTF−H$^•$ **12** (whose spin-density is concentrated in the carbon atom, 0.86 au) through a slightly endothermic process (reaction energy of 0.3 kcal/mol). Therefore, the computational results are compatible with the SET-HAT mechanism proposed in Scheme 3.

Scheme 4. DFT-Computed Mechanism for the Ionization of 8b[a]

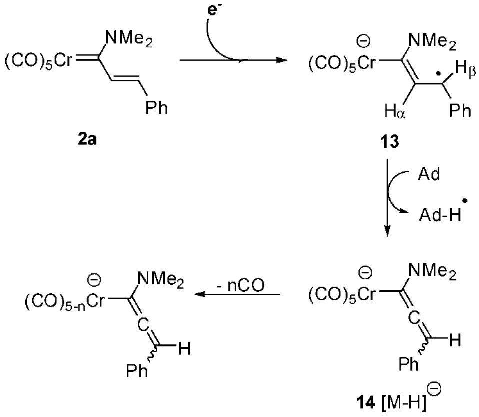


[a] All structures correspond to fully optimized uB3LYP/6-31+G(d)&LanL2DZ geometries. Bond distances and energies are given in Å and kcal/mol, respectively. Numbers close to the arrows correspond to the relative energies between the corresponding structures. Zero-point vibrational energy corrections have been included (kcal/mol). Computed spin-densities (in au) are given in brackets.

Conjugated aminocarbenes **2** and **3** were studied next. Alkenyl and alkynyl complexes **2b**, **3b**, and **3c**, bearing an NH group attached to the carbene carbon, gave nice molecular [M − H]$^-$ ions at *m*/*z* 336, 334, and 376, respectively. A mechanism analogous to that depicted in Scheme 3 could explain their ionization. However, once formed, the molecular ions follow different fragmentation patterns. Thus, for complexes **3b** and **3c** the correspondent isocyanide (methyl or butyl) is observed in the MS^2 and MS^3 spectra, whereas for complex **2b** only the usual CO loss cascade is observed (Table 1).[13] The fragmentation patterns were similar with either TTF or CO_3^{2-} as additive.

A different reaction outcome was observed for conjugated N,N-disubstituted aminocarbenes **2a** and **3a**. In spite of the lack of NH bonds in its structure, alkenyl carbene **2a** ionized to yield the corresponding [M − H]$^-$ ion (*m*/*z* 350), whereas alkynyl carbene **3a** did not ionize at all. These results suggest that for all the alkenyl complexes **2** a different ionization mechanism is operative, as the H$^•$ capture must take place from a CH bond. The proposed pathway for the ionization of **2a** is depicted in Scheme 5.

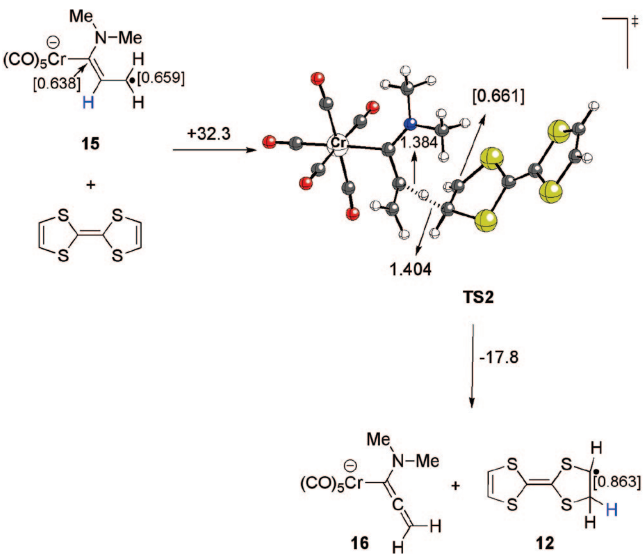
Scheme 5. Proposed Mechanism for Ionization of Complex 2a



Thus, the formation of the radical anion **13** proposed as the first step must be now followed by the H-transfer from the C−Hα bond of the carbene to the additive, leading to the detected molecular ion **14**. The preferential breakage of the C−Hα bond during the ESI-MS ionization of alkenyl alkoxy carbene complexes was previously demonstrated by us.[10c] Clearly, the lack of abstractable hydrogens in the alkynyl aminocarbene **3a** makes the ionization of this compound not possible. To support the proposal in Scheme 5, DFT calculations were made using radical anion **15** as a model for complex **2a**. In this case, the spin-density is shared by the former carbene carbon atom (0.64 au) and the double-bond terminal carbon atom (0.66 au) as a consequence of the electronic π-delocalization. The C−H$_\alpha$ transfer to TTF was analogous to that calculated from a NH group (Scheme 6), but in this case, the energy barrier involved to reach **TS2** was considerably higher (32.3 kcal/mol), as it would be expected considering the well-known higher strength of a C−H bond compared with an N−H bond. Furthermore, the computed NBO-Wiberg bond orders agree with the higher strength of the C−H bond in **15** (0.91 au) compared to the N−H bond in **8b** (0.80 au). After the hydrogen atom transfer, the reaction products will be the anion **16** and the radical TTF−H$^•$ **12** in an endothermic process (reaction energy of 14.5 kcal/mol).

Considering these results, it could be postulated that the ionization of an aminocarbene complex (and the further detection of [M − H]$^-$ ions) does not depend on the substitution of the N atom, but on the presence of any abstractable H atoms in

Scheme 6. DFT-Computed Mechanism for the Ionization of 16[a]

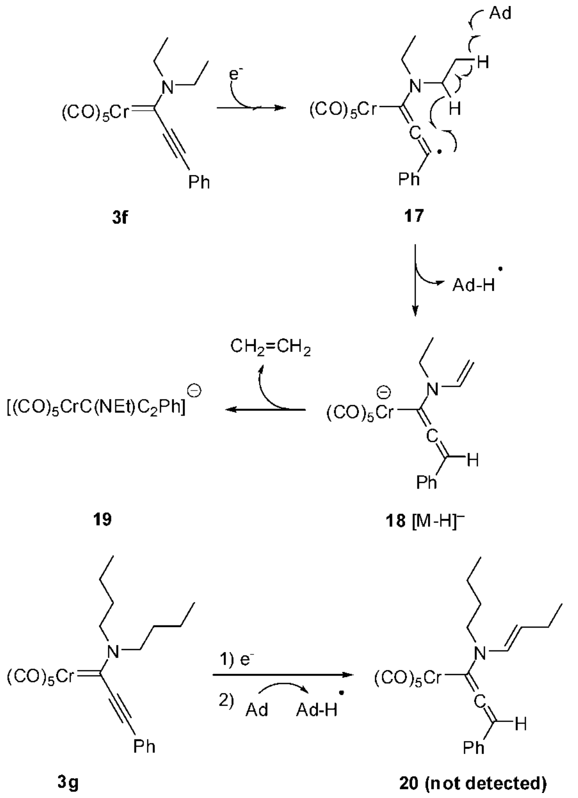


[a] See Scheme 4 for caption details.

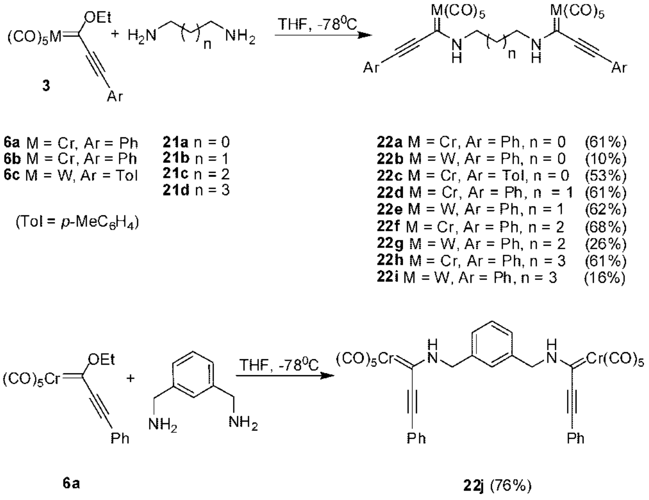
the structure. To check this point, complexes **3f** and **3g** were prepared by reaction of complex **6a** with ethylamine or *n*-butylamine, followed by alkylation with EtI or *n*BuBr, respectively, in the presence of Cs_2CO_3 (see Scheme 2). The study of the ESI ionization in the above conditions revealed that while compound **3f** (R = Et) led to the $[M - H]^-$ ion at *m*/*z* 348, no ionization was observed for **3g** (Table 1). Additionally, the fragmentation for **3f** revealed an additional loss of ethylene together with the expected loss of CO. The formation of ethylene was further confirmed by high-resolution mass spectrometry (HRMS), which discriminates between the extrusion of a CO (27.9951 Da) and a $CH_2{=}CH_2$ (28.0323 Da). In fact, the MS^1 and MS^2 spectra of the $[M - H]^-$ ion showed clear extrusions of fragments at 28.0323 Da ($CH_2{=}CH_2$) and 27.9951 Da (CO), respectively. The detection of ethylene gives valuable information to understand the mechanism of the ionization of **3f**. Thus, once the radical anion **17** is formed, the transference of the H atom to the additive should take place from the ethyl group to form the allenyl anion **18**, detected as $[M - H]^-$ ion (*m*/*z* 348) (Scheme 7). Extrusion of ethylene could take place from **18** leading to anion **19**. This sequence of events is analogous to that proposed for the ionization of alkynyl-ethoxy chromocarbenes.[10c] The analogous allenyl anion **20** derived from *n*-butyl aminocarbene **3g** was not detected. The impossibility of extruding a stable ethylene molecule could be the reason for this behavior (Scheme 7).

Once we had a clearer picture about the factors influencing the ionization of mono- and disubstituted aminocarbene complexes, our next goal was to study the reactivity of bis-alkynyl aminocarbene complexes **22**. In these compounds, the effect of additional factors, such as the structure and length of the tether between the nitrogen atoms and the nature of the metal carbene, can be established. The synthesis of compounds **22** was carried out by reaction of the corresponding alkoxycarbene complexes **6** and diamines **21** (Scheme 8). Both chromium(0) and tungsten(0) bis-carbene complexes **22** efficiently ionized in the presence of TTF, showing intense $[M - H]^-$ ions that extruded arylacetylene (MS^2) in all cases (Table 2). This reactivity pattern was independent both of the length of the tether joining the metal–carbene centers and of the nature of the metals. To study the behavior of mixed bis-aminocarbenes (namely, complexes bearing both a Cr and a W metallic center), aminocarbene **22k** was prepared by reacting equimolecular amounts of complexes **6a** and **6b** with 1,4-diaminobutane. The product was obtained together with the corresponding homometallic bis-carbene complexes **22f** and **22g**. The mixture of the three compounds was submitted to ESI-MS analysis, and the molecular ion $[M - H]^-$ ion corresponding to **22k** at *m*/*z* 827 was detected. Furthermore, the expected loss of phenylacetylene from this molecular ion was clearly observed in the MS^2 spectra of the mixture (Table 2).

Scheme 7. Proposed Mechanism for Ionization of Complexes 3f and 3g

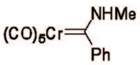
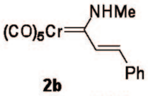
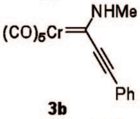
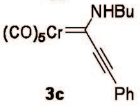
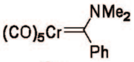
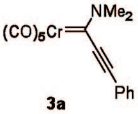
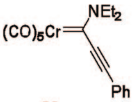


Scheme 8. Synthesis of Bis-aminocarbene Complexes 22



Being structurally related as they are, the differences in reactivity of the molecular ions $[M - H]^-$ derived from alkynyl aminocarbenes **3b**,**c** and bis-aminocarbenes **22** should arise from the presence of a second NH group in the molecule, possibly involved in an interaction with the metallic fragment once the

Table 1. ESI-MS Experiments of Complexes 1−3

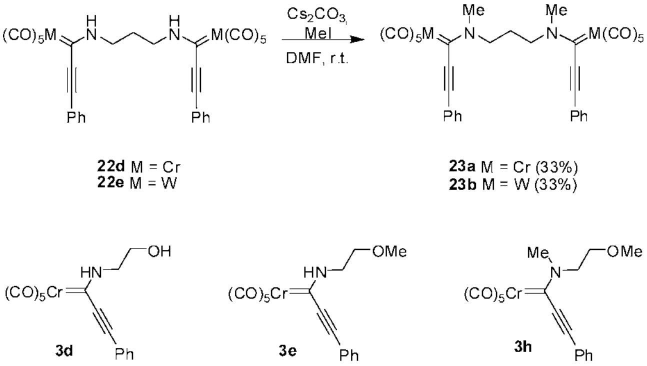
Complex	$[M-H]^-$ *(MS^1)*	*Additive*	*MS^2*	*MS^3*	*MS^4*
 **1b**	310	TTF $Cs_2(CO)_3$	282 [MS^1-CO] 254 [MS^1-2CO]	226 [MS^2-CO] 213 [MS^2-**41**] (MS^2 = *254*) **41: $CH_3N{\equiv}C$**	185 [MS^3-CO] 157 [MS^3-2CO] (MS^3 = *213*)
 **2b**	336	TTF $Cs_2(CO)_3$	308 [MS^1-CO] 280 [MS^1-2CO]	280 [MS^2-CO] (MS^2= *308*)	252 [MS^3-CO]
 **3b**	334	TTF $Cs_2(CO)_3$	306 [MS^1-CO] 278 [MS^1-2CO] 265 [*306*-**41**] **41: $CH_3N{\equiv}C$**	237 [MS^2-**41**] (MS^2 = *278*) **41: $CH_3N{\equiv}C$**	209 [MS^3-CO] 181 [MS^3-2CO]
 **3c**	376	TTF	348 [MS^1-CO] 320 [MS^1-CO]	237 [MS^2-**83**] **83: $CH_3(CH_2)_2N{\equiv}C$** (MS^2 = *320*)	209 [MS^3-CO] 181 [MS^3-2CO]
 **1a**	NID[a]	TTF			
 **2a**	350	TTF $Cs_2(CO)_3$	322 [MS^1-CO] 294 [MS^1-2CO]	266 [MS^2-CO] 238 [MS^2-2CO] 210 [MS^2-3CO] (MS^2 = *294*)	
 **3a**	NID[a]	TTF			
 **3f**	347.9952 ***[M-H-28.0323]⁻*** **28.0323: $CH_2{=}CH_2$**	TTF	292.0064[MS^1-**55.9888**] 236.9640[*264.9591* -**27.9951**] **55.9888: 2xCO** **27.9951: CO**		

[a] No ionization detected.

$[M - H]^-$ ion is formed. The involvement of an NH group was established with complexes **23a**,**b** prepared by alkylation of complexes **22d**,**e** with Cs_2CO_3/MeI (Scheme 9). These complexes did not ionize under the conditions used for aminocarbenes **22** ($CHCl_3$/MeOH), which suggests some kind of intramolecular H-transfer from the free NH group to the metal once the $[M - H]^-$ ion is formed. Furthermore, the extrusion of arylacetylene does not depend on the nature of the metal (Cr, W) and is detected in bis-aminocarbenes having tethers of different lengths (up to five CH_2). To establish the intramolecular nature of the process and to evaluate the need of a flexible chain between the nitrogen atoms, complex **22j**, bearing a rigid *m*-xylylidene tether, was ionized under the same conditions. In this case, only the cascade of CO fragmentations was observed, and no extrusion of phenylacetylene was detected.

An additional evidence for the involvement of an intramolecular H-transfer came from the study of aminocarbenes **3d**, **3e**, and **3h** (Scheme 9). Aminocarbene **3h** was prepared by alkylation of **3e** with Cs_2CO_3/MeI in the above conditions. Complex **3d** incorporates an additional OH group in the structure, and hence an abstractable hydrogen atom, whereas this possibility has been precluded in complex **3e**, structurally related but bearing a OMe group. Finally, complex **3h** has no abstractable H atoms, since both the OH and the NH groups are blocked by a methyl substituent. The study of the ESI-MS ionization revealed that complexes **3d** and **3e** both ionized showing the usual CO cascade, as well as the corresponding isocyanide formation, but only **3d** extruded phenylacetylene in the MS^n experiments, which is in agreement with the proposed H-transfer from the free NH group in bis-aminocarbenes **22** (Table 3).

Scheme 9. Synthesis of Complexes 23, and Complexes 3d, 3e, and 3h



Considering the experimental evidence, a reasonable explanation for the formation of arylacetylenes in the

Table 2. ESI-MS Experiments of Bis-aminocarbene Complexes 22 and 23

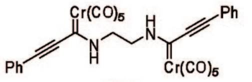
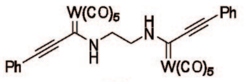
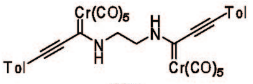
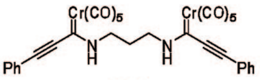
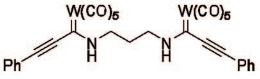
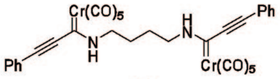
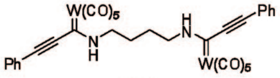
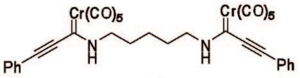
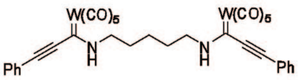
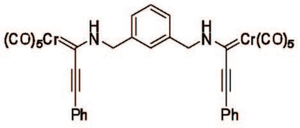
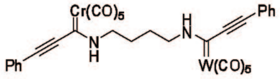
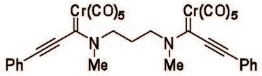
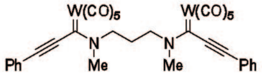
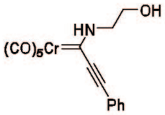
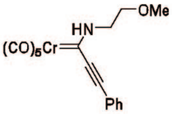
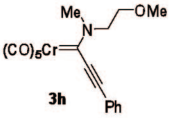
Complex	**[M-H]$^-$**	***Additive***	***MS^2***	***MS^3***
 **22a**	667	TTF	611 [MS^1-2CO] 583 [MS^1-3CO] 555 [MS^1-4CO] 527 [MS^1-5CO] 509 [*611*-**102**] **102: PhC≡CH**	555, 527, 499, 443 [MS^2-nCO] (MS^2=*583*); 453, 425 [MS^2-nCO] (MS^2 = *509*)
 **22b**	931	TTF	875 [MS^1-2CO] 791 [MS^1-5CO] 773 [*875*-**102**] 717 [773- CO] **102: PhC≡CH**	
 **22c**	695	TTF	639 [MS^1-2CO] 611 [MS^1-3CO] 583 [MS^1-4CO] 555 [MS^1-5CO] 527 [MS^1-6CO] 499 [MS^1-6CO] 523 [MS^1-**116**] **116: TolC≡CH**	583 [MS^2-2CO] 523 [MS^2-**116**] (MS^2= 639) **116: TolC≡CH** 467 [MS^3-2CO] 439 [MS^3-3CO] (MS^2 = *523*)
 **22d**	681	TTF	579 [MS^1-**102**] **102: PhC≡CH**	523, 495, 467, 439, 411, 383, 354.5, 326.6, 298.5 [MS^2-nCO] (MS^2 = *579*)
 **22e**	945	TTF	843 [MS^1-**102**] **102: PhC≡CH**	815 [MS^2-CO] 731 [MS^2-4CO] 703 [MS^2-5CO]
 **22f**	695	TTF	667, 639, 611, 583, 555, 499 [MS^1-nCO] 593 [MS^1-**102**] **102: PhC≡CH** 537, 509, 481, 453 [*593*-nCO]	509 [MS^2-CO] 481 [MS^2-2CO] (MS^2 = *537*)
 **22g**	959	TTF	857 [MS^1-**102**] 801 [*857*-2CO] 745 [*857*-2CO] **102: PhC≡CH**	717 [MS^2-CO] (MS^2 = *745*)
 **22h**	709	TTF	681 [MS^1-CO] 653 [MS^1-2CO] 625 [MS^1-3CO] 597 [MS^1-4CO] 569 [MS^1-5CO] 541 [MS^1-6CO] 513 [MS^1-7CO] 607 [MS^1-**102**] 579, 551, 523, 495, 467 [*607*-nCO] **102: PhC≡CH**	541 [MS^2-CO] 513 [MS^2-2CO] 485 [MS^2-3CO] (MS^2 = *569*)
 **22i**	973	TTF	871 [MS^1-**102**], 843, 815, 759, 731 [*871*-nCO] **102: PhC≡CH**	843 [MS^2-CO] 759 [MS^2-4CO] 731 [MS^2-5CO] (MS^2 = *871*)
 **22j**	743	TTF	687 [MS^1-2CO] 631 [MS^1-4CO] 603 [MS^1-5CO] 575 [MS^1-6CO] 547 [MS^1-7CO] 519 [MS^1-8CO] 491 [MS^1-8CO]	631 [MS^1-2CO] 603 [MS^1-3CO] 575 [MS^1-4CO]

Table 2. Continued

Complex	$[M\text{-}H]^-$	***Additive***	MS^2	MS^3
 **22k**	827	TTF	725 [MS^1-102] 697 [*725*-CO], 669 [*697*-CO], 613 [*667*-CO], 585 [*613*-CO] **102: $PhC\equiv CH$**	
 **23a**	NID[a]	TTF		
 **23b**	NID[a]	TTF		

[a] No ionization detected.

Table 3. ESI-MS Experiments of Complexes 3d, 3e, and 3h

Complex	$[M\text{-}H]^-$ (MS^1)	***Additive***	MS^2	MS^3
 **3d**	364	TTF	336 [MS^1-CO] 308 [MS^1-2CO]	280 [MS^2-CO] 206 [MS^2-102] **102: $PhC\equiv CH$** 237 [MS^2-71] **71: $OH(CH_2)_2N\equiv C$** (MS^2 = *308*)
 **3e**	378	TTF	350 [MS^1-CO] 322 [MS^1-2CO] 266 [MS^1-4C0]	237 [MS^2-85] **85:$MeO(CH_2)_2N\equiv CH$** (MS^2 = *322*) 209 [MS^3-CO] 181 [MS^2-2CO]
 **3h**	NID[a]	TTF		

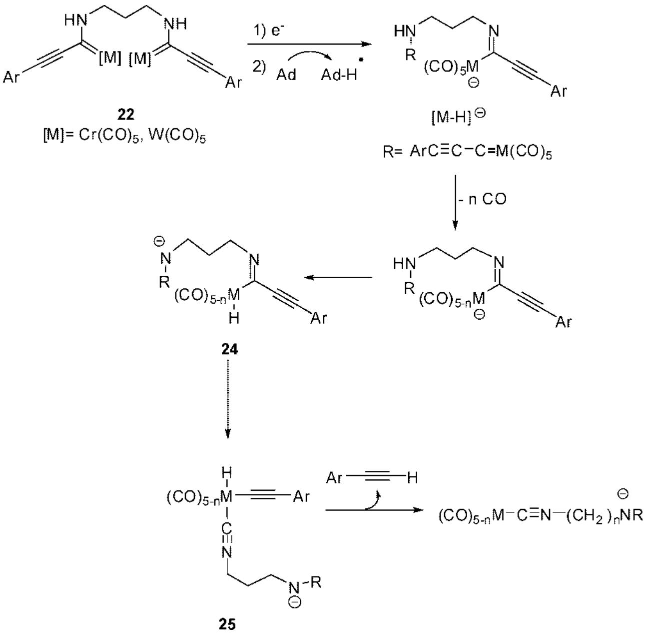
[a] No ionization detected.

fragmentation of the $[M - H]^-$ ions derived from bis-aminocarbenes **22** is depicted in Scheme 10. Thus, after the nCO loss, an intramolecular H-transfer from the free NH group to the metal could take place, leading to a new metal hydride **24**. This species experiences a reductive elimination upon arylacetylene migration, leading to the observed loss of neutral arylacetylene. The absence of the additional NH center (**23a**,**b**) or geometrical restraints (**22j**) are able to inhibit the process.

Conclusions

The ESI-MS ionization of aminocarbene (Fischer) complexes requires the initial capture of one electron (from the ESI source) by the aminocarbene, with subsequent formation of a radical anion. Then, to produce a detectable molecular ion, the capture of a hydrogen atom by the additive is required. Overall, the ionization can be envisaged as a SET-HAT process. Both NH and N,N-disubstituted aminocarbenes can effectively ionize under ESI-MS conditions, as long as they have abstractable H atoms in their structures. The experimental findings are supported by DFT calculations, and the evolution of the $[M - H]^-$ species has been studied by isolation and determination of their MS^n spectra. On the other hand, the ESI-MS ionization of bis-alkynylaminocarbene complexes follows the same patterns. However, the evolution of the $[M - H]^-$ ions is by arylacetylene extrusion together with the usual sequence of CO loss. The process requires the presence of a free NH group and occurs by intramolecular hydrogen transfer from the NH to the metal center. Bis-aminocarbenes having rigid tethers between the nitrogen atoms or lacking free NH groups do not produce this fragmentation. Further computational and experimental work to understand the mechanisms of evolution of metal−carbene and bis-carbene complexes in the supercharged ESI droplets is currently underway in our laboratories.

Scheme 10. Proposed Mechanism for the Ionization of Complexes 22



Experimental Section

General Procedures. All reactions were carried under an argon atmosphere. All solvents used in this work were purified by distillation and were freshly distilled immediately before use. Tetrahydrofuran (THF) was distilled from sodium/benzophenone and dichloromethane (DCM) from calcium hydride. Flame-dried glassware and standard Schlenk techniques were used for moisture-sensitive reactions. Silica gel for flash column chromatography purification of crude mixtures was purchased from Merck (230−400 mesh), and the identification of products was made by thin-layer chromatography (Kiesegel 60F-254). UV light ($\lambda = 254$ nm) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates. NMR spectra were recorded at 22 °C in $CDCl_3$, on Bruker Avance 300 (300 MHz for ^1H, 75 MHz for ^{13}C) or Bruker AM-500 (500 MHz for ^1H, 125 MHz for ^{13}C). 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 Bruker Tensor 27 (MIR 8000−400 cm^{-1}) spectrometer in $CHCl_3$ solution. All commercially available products were used without further purification. Compounds **1a**,[11c] **2a**,[11d] **2b**,[11e] **3a**,[11f] **3b**,[11g] **4**,[15] **5**,[16] **6a**,[11g] **6b**,[11g] **22a**,[11h] and **22b**[11h] were prepared and identified by procedures previously reported in the literature.

ESI-MS Experiments. All ESI-MS experiments were carried out using an ESQUIRE-LC (Bruker Daltonik, Bremen, Germany) ion trap spectrometer in the negative mode of detection. A syringe pump (model 74900, Cole-Parmer, 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 PEEK tubing of 254 μm i.d. (Upchurch Scientific, Oak Harbor, WA) with a flow rate of 3 $\mu L\ min^{-1}$. The stainless steel capillary was held at a potential of 5.0 kV. Nitrogen was used as nebulizer gas with 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 tetrathiafulvalene (TTF)/cesium carbonate (Cs_2CO_3) were used. The spectra reported are the averages of 15 scans using 450 ms as the accumulation time. MS^n spectra were carried out using collision-induced dissociation (CID) with helium after isolation of the appropriate precursor ions. An isolation width of 4.0 *m/z* was used, and the fragmentation voltage amplitude was maintained at 0.60 V with a fragmentation time of 40 ms. The HRMS spectra for compound **3f** were carried out using a QSTAR pulsar i spectrometer (Applied Bisosystems) with a QTOF hybrid analyzer in the negative mode of detection, using the same dilution and potentials as those used for the other ESI-MS experiments. The tables summarize the results obtained for carbene complexes in the presence of different additives.

Computational Details. All the calculations reported in this paper were obtained with the GAUSSIAN 03 suite of programs.[17] Electron correlation was partially taken into account using the unrestricted (u)B3LYP[18] functional in combination with the 6-31G(d)[19] and LanL2dz for Cr.[20] Zero-point vibrational energy (ZPVE) corrections were computed at the B3LYP/def2-SVP level and were not scaled. Reactants and products were characterized by frequency calculations[21] and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate (IRC) method.[22] Bond orders have been computed using the natural bond orbital (NBO) method.[23]

Pentacarbonyl[(*N*-methyl)(phenyl)carbene]chromium(0), 1b. To a solution of complex **4** (500 mg, 1.53 mmol) in THF (20 mL) was added dropwise a solution of methylamine in THF (0.76 mL, 1.53 mmol). The reaction mixture was stirred under argon for 48 h, after which the solvent was evaporated under vacuum and the crude purified (SiO_2, hexanes/ethyl acetate, 8:1) to give **1b** (119 mg, 25%) as a yellow solid. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): δ 2.97 (d, $J = 5.1$ Hz, 3H; CH_3), 6.82 (d, $J = 7.2$ Hz, 2H; ArH), 7.26 (t, $J = 7.2$ Hz, 1H, ArH), 7.44 (t, $J = 7.7$ Hz, 2H, ArH); 9.10 ppm (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 37.8 (CH_3), 118.9, 126.9, 128.7, 149.4 (C_{Ar}), 217.1 (CO cis), 223.2 (CO trans), 283.7 ppm (C═Cr). IR ($CHCl_3$): ν 1923, 2054, 2177, 3385 cm^{-1}. Anal. (%) Calcd for $C_{13}H_9CrNO_5$ (311.21): C 50.17, H 2.91, N 4.50. Found: C 50.47, H 3.11, N 4.70.

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General Procedure for the Preparation of Compounds 3c−e. To a solution of complex **6a** (1 equiv) in THF was added dropwise a solution of the correspondent amine (1 equiv) at −100 °C. The reaction mixture was stirred under argon at this temperature until total consumption of the starting material. The solvent was then evaporated *in vacuo* and the resulting crude reactions purified by flash column chromatography (SiO_2) under argon pressure using the mixture of solvents indicated in each case as eluent.

Pentacarbonyl[1-(*N*-butylamine)-3-phenyl-2-propinylidinecarbene]chromium(0), 3c. According to the general procedure, complex **6a** (100 mg, 0.28 mmol) (solution in 5 mL of THF) was reacted with butylamine (20.9 mg, 0.28 mmol in 5 mL of THF) for 18 h. Purification by flash chromatography (hexanes/ethyl acetate, 8:1) gave an orange solid identified as compound **3c** (40.8 mg, 38%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.03 (d, J = 7.1 Hz, 3H; CH_3), 1.48 (sex, J = 6.9 Hz, 2H; CH_2), 1.76 (q, J = 6.8 Hz, 2H; CH_2), 3.82 (c, J = 6.04 Hz, 2H; CH_2), 7.46 (m, 3H; ArH), 7.55 (m, 2H; ArH), 8.76 ppm (s, 1H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 13.6 (CH_3), 19.7, 31.4, 52.9 (CH_2), 88.9 (C≡$\underline{\mathrm{C}}$-Ar), 121.7 ($\underline{\mathrm{C}}$≡C-Ar), 128.7, 130.7, 131.2, 132.1 (C_{Ar}), 217.2 (CO cis), 223.4 (CO trans), 254.9 ppm (C=Cr). IR ($CHCl_3$): ν 1912, 1929, 2055, 2169, 3375 cm^{-1}. Anal. (%) Calcd for $C_{18}H_{15}CrNO_5$ (377.31): C 57.03, H 4.01, N 3.71. Found: C 57.43, H 3.90, N 3.74.

Pentacarbonyl[1-(*N*-ethanolamine)-3-phenyl-2-propinylidinecarbene]chromium(0), 3d. According to the general procedure, complex **6a** (100 mg, 0.28 mmol, in 5 mL of THF) was reacted with ethanolamine (17 mg, 0.28 mmol in 5 mL of THF). The reaction mixture was stirred under argon for 1 h 30 min, and the solvent was then removed *in vacuo*. After purification by flash column chromatography (hexanes/ethyl acetate, 2:1), compound **3d** was obtained as an orange solid (62 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 3.96−3.77 (m, 4H; CH_2), 7.45 (m, 3H; ArH), 7.53 (m, 2H; ArH), 9.38 ppm (s, 1H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 54.3 (CH_2), 60.6 (CH_2), 89.0 (C≡$\underline{\mathrm{C}}$-Ar), 121.6 ($\underline{\mathrm{C}}$≡C-Ar), 128.7, 130.7, 131.5, 132.0 (C_{Ar}), 217.2 (CO cis), 223.5 (CO trans), 256.1 ppm (C=Cr). IR ($CHCl_3$): ν 1913, 2055, 2172, 3396 cm^{-1}. Anal. (%) Calcd for $C_{16}H_{11}CrNO_6$ (365.26): C 52.61, H 3.04, N 3.83. Found: C 52.20, H 2.86, N 3.80.

Pentacarbonyl[1-(*N*-(2-methoxyethylamine))-3-phenyl-2-propenylidinecarbene]chromium(0), 3e. Following the general procedure described above, complex **6a** (200 mg, 0.57 mmol) was reacted with 2-methoxyethylamine (42.8 mg, 0.57 mmmol) for 6 h. The crude thus obtained was purified by flash column chromatography (4:1 hexanes/ethyl acetate) to give compound **3e** as an orange solid (143 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 3.47 (s, 3H; CH_3), 3.65 (t, ^3J(H,H) = 5.19 Hz, 2H; CH_2), 3.96 (c, ^3J(H,H) = 5.20 Hz, 2H; CH_2), 7.43 (m, 3H; ArH), 7.54 (m, 2H; ArH), 9.10 ppm (s, 1H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 52.2 (CH_2), 59.2 (CH_3), 70.1 (CH_2), 88.9 (C≡$\underline{\mathrm{C}}$-Ar), 121.5 ($\underline{\mathrm{C}}$≡C-Ar), 128.7, 130.7, 131.4, 132.0 (C_{Ar}), 217.1 (CO cis), 223.6 (CO trans), 255.8 ppm (C=Cr). IR ($CHCl_3$): ν 1907, 2055, 2172, 3382 cm^{-1}. Anal. (%) Calcd for $C_{17}H_{13}CrNO_6$ (379.28): C 53.83, H 3.45, N 3.69. Found: C 53.49, H 3.40, N 3.72.

General Procedure for the Preparation of Bis-aminocarbene Complexes 22. To a solution of the correspondent alkoxycarbene complex **6a**−**c** (1 equiv) in THF (5 mL/mmol carbene) at −78 °C was added dropwise a solution of the corresponding diamine (0.5 equiv) in THF (2.5 mL/mmol amine). The reaction mixture was stirred under argon at this temperature until total consumption of the starting material. The solvent was evaporated *in vacuo* and the crude products purified by flash column chromatography (SiO_2) under argon pressure using the mixture of eluents indicated for each complex.

Bis-carbene Complex 22c. Complex **6c** (947 mg, 0.26 mmol) and ethylenediamine (7.8 mg, 0.13 mmol) were reacted according to general procedure described above. The reaction mixture was stirred overnight, and the crude product thus obtained purified using a mixture hexanes/ethyl acetate (10:1) as eluent. After evaporation of the solvent, compound **22c** was obtained as an unstable red solid (48.1 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 2.43 (s, 6H; CH_3), 4.27−4.13 (m, 4H; CH_2), 7.21 (d, J = 7.9 Hz, 4H; ArH), 7.41 (d, J = 7.9 Hz, 4H; ArH), 8.88 ppm (s, 2H; NH). IR: ν 1934, 1981, 2054, 2160, 3387, 3447 cm^{-1}.

Bis-carbene Complex 22d. Following the general procedure, complex **6a** (200 mg, 0.57 mmol) was reacted with 1,3-diaminopropane (21.5 mg, 0.29 mmol). After 36 h, the crude was purified (hexanes/ethyl acetate, 8:1) to yield compound **22d** as an orange-red solid (121 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 2.15 (m, 2H; CH_2), 3.86 (m, 4H; CH_2), 7.49−7.29 (m, 10H; ArH), 8.84 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 29.6 (CH_2), 49.6 (NCH_2), 88.6 (C≡$\underline{\mathrm{C}}$-Ar), 121.2 ($\underline{\mathrm{C}}$≡C-Ar), 128.8, 131.0, 132.1, 133.8 (C_{Ar}), 217.0 (CO cis), 223.3 (CO trans), 259.2 ppm (C=Cr). IR ($CHCl_3$): ν 1919, 2058, 2162, 3354 cm^{-1}. Anal. (%) Calcd for $C_{31}H_{18}Cr_2N_2O_{10}$ (682.47): C 54.56, H 2.66, N 4.10. Found: C 54.16, H 2.48, N 4.30.

Bis-carbene Complex 22e. Complex **6b** (800 mg, 1.70 mmol) was reacted with 1,3-diaminopropane (63.1 mg, 0.85 mmol) following the general procedure. After 24 h, the solvent was evaporated under vacuum and the crude product purified (hexanes/ethyl acetate, 10:1). Evaporation of the solvent yielded compound **22e** as an unstable reddish-orange solid (500 mg, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 2.33−2.20 (m, 2H, CH_2), 3.96−3.84 (m, 4H, NCH_2), 7.59−7.36 (m, 10H, ArH), 8.74 ppm (s, 2H, NH).

Bis-carbene Complex 22f. Complex **6a** (504 mg, 1.44 mmol) and 1,4-diaminobutane (63.5 mg, 0.72 mmol) were stirred under argon for 48 h according to the general procedure. After purification of the crude (hexanes/ethyl acetate, 4:1), compound **22f** was obtained as an orange solid (343 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.88 (m, 4H; CH_2), 3.91−3.89 (m, 4H; CH_2), 7.53−7.38 (m, 10H; ArH), 8.80 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 26.6 (CH_2), 52.1 (NCH_2), 88.8 (C≡$\underline{\mathrm{C}}$-Ar), 121.3, ($\underline{\mathrm{C}}$≡C-Ar), 128.8, 131.0, 132.1, 132.6 (C_{Ar}), 217.1 (CO cis), 223.4 (CO trans), 257.4 ppm (C=Cr). IR ($CHCl_3$): ν 1923, 1985, 2054, 2166, 3391 cm^{-1}. Anal. (%) Calcd for $C_{32}H_{20}Cr_2N_2O_{10}$ (696.5): C 55.18, H 2.89, N 4.02. Found: C 55.54, H 3.08, N 4.20.

Bis-carbene Complex 22g. Following the general procedure, complex **6b** (489 mg, 1.04 mmol) was reacted with 1,4-diaminobutane (45.8 mg, 0.52 mmol) over 24 h. The crude obtained was purified by flash chromatography (hexanes/ethyl acetate, 5:1) to give an orange solid identified as compound **22g** (130 mg, 26%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 2.06−1.82 (m, 4H; CH_2), 3.88−3.77 (m, 4H; CH_2), 7.57−7.37 (m, 10 H; ArH), 8.70 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 26.3 (CH_2), 43.6 (NCH_2), 91.3 (C≡$\underline{\mathrm{C}}$-Ar), 121.2 ($\underline{\mathrm{C}}$≡C-Ar), 128.9, 131.0, 132.0, 144.6 (C_{Ar}), 194.2 (CO cis), 198.4 (CO trans), 234.2 ppm (C=W). IR ($CHCl_3$): ν 1906, 2067, 2174, 3390 cm^{-1}. Anal. (%) Calcd for $C_{32}H_{20}N_2O_{10}W_2$ (960.19): C 40.03; H 2.10; N 2.92. Found: C 40.40, H 2.30, N 3.04.

Bis-carbene Complex 22h. Complex **6a** (493 mg, 1.41 mmol) was reacted with 1,5-diaminopentane (71.9 mg, 0.70 mmol) over 5 days, after which the crude product was purified by flash chromatography (hexanes/ethyl acetate, 4:1) to yield compound **22h** as an orange solid (301 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.57−1.55 (m, 2H; CH_2), 1.88−1.84 (m, 4H; CH_2), 3.85−3.83 (m, 4H; CH_2), 7.54−7.43 (m, 10H; ArH), 8.76 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 23.5 (CH_2), 29.0 (CH_2), 52.6 (NCH_2), 88.8 (C≡$\underline{\mathrm{C}}$-Ar), 121.4 ($\underline{\mathrm{C}}$≡C-Ar), 128.8, 130.8, 131.9, 132.0 (C_{Ar}), 217.2 (CO cis), 223.5 (CO trans), 255.9 ppm (C=Cr). IR ($CHCl_3$): ν 1933, 1979, 2055, 2167, 3375 cm^{-1}. Anal. (%) Calcd for $C_{33}H_{22}Cr_2N_2O_{10}$ (710.53): 55.78, H 3.12, N 3.94. Found: C 56.16, H 3.32, N 4.04.

Bis-carbene Complex 22i. Following the general procedure, complex **6b** (484 mg, 1.03 mmol) was reacted with 1,5-diaminopentane (52.1 mg, 0.51 mmol) for 24 h. The crude product thus obtained was purified by flash column chromatography (hexanes/ethyl acetate, 5:1) to yield compound **22i** as an orange solid (80 mg, 16%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.30−1.23 (m, 2H; CH_2), 1.92 (m, 4H; CH_2), 3.8 (m, 4H; CH_2), 7.57−7.39 (m, 10H; ArH), 8.64 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 23.7 (CH_2), 29.7 (CH_2), 52.4 (NCH_2), 91.3 ($C\equiv\underline{C}$-Ar), 121.3 ($\underline{C}\equiv C$-Ar), 128.3, 128.8, 131.0, 132.3 (C_{Ar}), 198.4 (CO cis), 203.5 (CO trans), 233.0 (C=W). IR ($CHCl_3$): ν 1905, 1984, 2062, 2171, 3375 cm^{-1}. Anal. (%) Calcd for $C_{33}H_{22}N_2O_{10}W_2$ (974.22): C 40.68, H 2.28, N 2.88. Found: C 40.94, H 2.40, N 2.69.

Bis-carbene Complex 22j. Complex **6a** (200 mg, 0.57 mmol) was reacted with *m*-xylylendiamine (40 mg, 0.29 mmol) following the general procedure described above. After purification of the crude reaction by flash chromatography (hexanes/ethyl acetate, 6:1), an orange solid was isolated and identified as compound **22j** (164 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 5.01 (m, 4H; CH_2), 7.70−7.39 (m, 14 H; ArH), 8.93 ppm (s, 2H; NH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 56.8 (CH_2), 89.6 ($C\equiv\underline{C}$-Ar), 121.8 ($\underline{C}\equiv C$-Ar), 129.5, 131.1, 132.0, 135.8 (C_{Ar}), 217.5 (CO cis), 223.7 (CO trans), 258.4 ppm (C=Cr). IR ($CHCl_3$): ν 1915, 1942, 1980, 2056, 2167, 3382 cm^{-1}. Anal. (%) Calcd for $C_{36}H_{20}Cr_2N_2O_{10}$ (744.54): C 58.07, H 2.71, N 3.76. Found: C 58.44, H 2.90, N 3.60.

Bis-carbene Complex 22k. To a solution of complex **6a** (50 mg, 0.14 mmol) and complex **6b** (65.8 mg, 0.14 mmol) in THF at −78 °C was added dropwise a solution of 1,4-diaminobutane (12.3 mg, 0.14 mmol), and the mixture was stirred under argon at −78 °C for 24 h. The solvent was then evaporated *in vacuo* and the crude purified (hexanes/ethyl acetate, 6:1). The product thus obtained was identified as a mixture of complexes **22f**, **22g**, and **22k**, and spectral data for complex **22k** were identified by comparison of the spectra of the mixture to those of complexes **22f** and **22g**. ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ 1.94−1.91 (m, 4H; CH_2), 3.90−3.67 (m, 4H; CH_2), 7.53−7.39 (m, 10H; ArH), 8.65 (s, 1H; NH), 8.75 ppm (s, 1H; NH). ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C): δ 26.6 (CH_2), 29.8 (CH_2), 43.9 (NCH_2), 51.6 (NCH_2), 88.8 ($C\equiv\underline{C}$-Ar), 91.3 ($\underline{C}\equiv C$-Ar), 121.2, 128.8, 130.2, 132.5, 144.5 (C_{Ar}), 194.2, 195.9, 198.3, 203.4 (CO_W), 215.9, 223.3 (CO_{Cr}), 234.5 (C=W), 258.7 ppm (C=Cr). IR ($CHCl_3$): ν 1906, 2067, 2172, 3370 cm^{-1}.

General Procedures for the N-Alkylation of NH-Carbene Complexes. Method A (compounds 3f, 3g). To a solution of compound **6a** (1 equiv) in THF (10 mL/mmol compound) was added dropwise a solution of the corresponding amine (ethylamine/butylamine) (1 equiv) in THF (5 mL/mmol of amine) at −100 °C, and the reaction mixtures were stirred under argon until total consumption of starting material. The solvent was then evaporated *in vacuo*, and the crudes thus obtained were solved in DMF (10 mL/mmol of complex) and Cs_2CO_3 (3 equiv). The corresponding halide (ethyl iodide, butyl bromide) (2.5 equiv) was added. The crudes were stirred until completion and then extracted in ethyl acetate, the organic extracts were washed with brine and water and dried over magnesium sulfate, the solvent was evaporated *in vacuo*, and the products were purified by flash column chromatography under argon pressure.

Method B (compounds 23a, 23b, 3h). To a solution of the corresponding carbene complex (**22d**/**22e**/**3e**) (1 equiv) in DMF (10 mL/mmol of complex) were added Cs_2CO_3 (6 equiv) and MeI (4 equiv). The reaction mixture was stirred under argon at rt overnight, and then the crude was extracted in ethyl acetate. The organic extracts were washed with brine and water and dried over magnesium sulfate, and the solvent was evaporated *in vacuo*. The products thus obtained were purified by flash column chromatography under argon pressure.

Pentacarbonyl[1-(*N*,*N*′-diethylamine)-3-phenyl-2-propinylidinecarbene]chromium(0), 3f(Method A). Complex **6a** (250 mg, 0.71 mmol) was reacted with ethylamine (45.1 mg, 0.71 mmol) in THF, the product obtained after evaporation of the solvent was immediately solved in DMF, ethyl iodide (280.8 mg, 1.8 mmol) and Cs_2CO_3 (758.6 mg, 2.15 mmol) were added, and the mixture was stirred under argon overnight. After purification by flash chromatography (hexanes/ethyl acetate, 8:1), compound **3f** was obtained as an orange solid (73.4 mg, 27%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.39 (t, $J = 6.59$ Hz, 3H; CH_3), 1.49 (t, $J = 6.62$ Hz, 3H; CH_3), 4.02 (c, $J = 6.93$ Hz, 2H; CH_2), 4.27 (c, $J = 6.78$ Hz, 2H; CH_2), 7.43 (m, 3H; ArH), 7.51 ppm (m, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 14.1, 14.3 (CH_3), 51.5, 54.1 (CH_2), 90.6 ($C\equiv\underline{C}$-Ar), 122.2 ($\underline{C}\equiv C$-Ar), 128.6, 128.9, 130.1, 131.4 (C_{Ar}), 217.2 (CO cis), 224.2 (CO trans), 246.0 ppm (C=Cr). IR ($CHCl_3$): ν 1905, 1977, 2055, 2170 cm^{-1}. Anal. (%) Calcd for $C_{18}H_{15}CrNO_5$ (377.31): C 57.30, H 4.01, N 3.71. Found: C 57.59, H 4.20, N 3.58.

Pentacarbonyl[1-(*N*,*N*′-dibutylamine)-3-phenyl-2-propinylidinecarbene]chromium(0), 3g (Method A). Complex **6a** (400 mg, 1.14 mmol) was reacted with butylamine (83.5 mg, 1.14 mmol) in THF, and the resulting crude product (after evaporation of the solvent) was immediately solved in DMF and mixed with butyl bromide (390.5 mg, 2.85 mmol) and Cs_2CO_3 (1.11 g, 3.42 mmol). Purification of the crude product yielded compound **3g** as an orange solid (115 mg, 23%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 1.02 (m, 6H; CH_3), 1.41 (m, 2H; CH_2), 1.52 (m, 2H; CH_2), 1.81 (m, 4H; CH_2), 4.00 (t, $J = 7.29$ Hz, 2H; CH_2), 4.16 (t, $J = 7.9$ Hz, 2H; CH_2), 7,44 (m, 3H; ArH), 7.51 ppm (m, 2H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 13.1, 13.7 (CH_3), 19.5, 19.9 (CH_2), 30.9, 31.1 (CH_2), 57.1, 59.8 (CH_2), 90.8 ($C\equiv\underline{C}$-Ar), 122.3 ($\underline{C}\equiv C$-Ar), 128.7, 128.9, 130.1, 131.4 (C_{Ar}), 217.3 (CO cis), 224.2 (CO trans), 246.2 ppm (C=Cr). IR ($CHCl_3$): ν 1915, 2055, 2068, 2173 cm^{-1}. Anal. (%) Calcd for $C_{22}H_{23}CrNO_5$ (433.42): C 60.97, H 5.35, N 3.23. Found: C 61.03, H 5.40, N 3,46.

Complex 23a (Method B). Complex **22d** (115 mg, 0.17 mmol) was reacted with MeI (96.5 mg, 0.68 mmol) in the presence of Cs_2CO_3 (332 mg, 1.02 mmol) in DMF for 4 days, yielding (hexanes/ethyl acetate, 6:1) an orange solid identified as compound **23a** (40 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 2.32 (m, 2H; CH_2), 3.96 (s, 6H; CH_3), 4.17 (m, 4H; CH_2), 7.40−7.54 ppm (m, 10H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 26.5 (CH_2), 47.3 (CH_3), 57.7 (CH_2), 90.0 ($C\equiv\underline{C}$-Ar), 121.6 ($\underline{C}\equiv C$-Ar), 128.8, 130.5, 131.3, 131.5 (C_{Ar}), 217.1 (CO cis), 223.8 (CO trans), 252.6 ppm (C=Cr). IR ($CHCl_3$): ν 1906, 1969, 2054, 2168 cm^{-1}. Anal. (%) Calcd for $C_{33}H_{22}Cr_2N_2O_{10}$ (710.53): C 55.78, H 3.12, N 3.94. Found: C 56.10, H 3.30, N 4.10.

Complex 23b (Method B). Complex **22e** (270 mg, 0.28 mmol) was reacted with MeI (161.8, 1.14 mmol) and Cs_2CO_3 (557 mg, 1.71 mmol) in DMF for 48 h. After purification of the crude product (hexanes/ethyl acetate, 6:1), compound **23b** was obtained as an orange solid (90 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 2.34 (m, 2H; CH_2), 3.81 (s, 6H; CH_3), 4.12 (t, $J = 7.64$ Hz, 4H; CH_2), 7.44−7.31 ppm (m, 10H; ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 26.5 (CH_2) 49.6 (CH_3), 56.5 (CH_2), 92.0 ($C\equiv\underline{C}$-Ar), 121.4 ($\underline{C}\equiv C$-Ar), 127.7, 128.8, 130.6, 131.5 (C_{Ar}), 198.3 (CO cis), 203.9 (CO trans), 231.6 ppm (C=W). IR ($CHCl_3$): ν 1897, 1961, 2062, 2169 cm^{-1}. Anal. (%) Calcd for $C_{33}H_{22}N_2O_{10}W_2$ (974.22): C 40.68, H 2.28, N 2.88. Found: C 41.04, H 2.40, N 2.50.

Pentacarbonyl[1-(*N*-methyl,*N*′-(2-methoxyethylamine))-3-phenyl-2-propenylidinecarbene]chromium(0), 3h (Method B). A mixture of complex **3e** (270 mg, 0.71 mmol), MeI (251.2 mg, 1.77 mmol), and Cs_2CO_3 (640 mg, 2.13 mmol) in DMF was stirred under argon for 24 h, after which the crude was worked up following the general procedure and purified (hexanes/ethyl acetate, 8:1) to yield an orange solid identified as compound **3h** (120 mg, 43%) (mixture of isomers syn/anti (m/M) in the ratio 1:2.5). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ 3.41 (s, 3H; OCH_3) (M), 3.50 (s, 3H; OCH_3) (m), 3.63 (m, 2H; CH_2) (M), 3.74 (s, 3H; NCH_3) (M), 3.82 (m, 2H; CH_2) (m), 3.96 (s, 3H; NCH_3) (m), 4.21 (m, 2H; CH_2) (M), 4.42 (m, 2H; CH_2) (m), 7.43 (m, 6H; ArH) (m+M), 7.50 (m, 4H; ArH) (m+M). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C): δ 49.4 (CH_3), 59.1 (CH_3), 60.2, 60.3 (CH_2), 69.7, 70.8 (CH_2), 90.3 ($C\equiv\underline{C}$-Ar), 122.0 ($\underline{C}\equiv C$-Ar), 128.6, 129.8, 130.2, 131.4, 132.3 (C_{Ar}), 217.1 (CO cis), 224.1 (CO trans), 249.6 ppm (C=Cr). IR ($CHCl_3$): ν 1912, 2054, 2067, 2172 cm^{-1}. Anal. (%) Calcd for $C_{18}H_{15}CrNO_6$ (393.31): C 54.97, H 3.84, N 3.56. Found: C 54.67, H 3.80, N 3.18.

Acknowledgment. Support for this work under grants CTQ2007-67730-C02-01/BQU and CSD2007-0006 (Programa Consolider-Ingenio 2010) from the MEC (Spain) and CCG07-UCM/PPQ-2596 from the Comunidad de Madrid is gratefully acknowledged. M.L.L. thanks the MEC (Spain) for a FPU fellowship. I.F. is a Ramón y Cajal fellow.

Supporting Information Available: ^1H and ^{13}C NMR spectra for all complexes, Cartesian coordinates (in Å), and total energies (in au, noncorrected zero-point vibrational energies included) of all the stationary points discussed in the text are available free of charge via the Internet at http://pubs.acs.org.

OM900159H