

# New Rearrangement and Fragmentation Processes of Group 6 Alkoxyalkynyl (Fischer) Carbene Complexes Induced by Aromatic Diamines

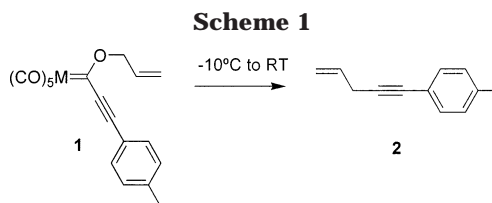
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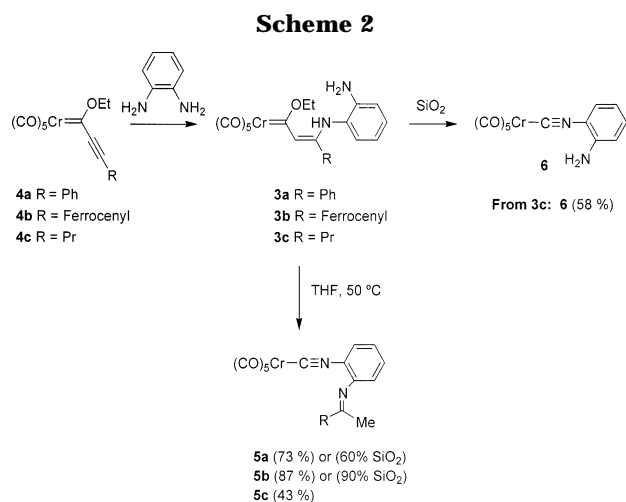
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**Summary:** The rearrangement of chromium(0) carbene complexes **4** to isocyanides **5** occurs either thermally or by SiO<sub>2</sub> catalysis through 1,2-diaminobenzene addition followed by breakage of the bicyclic carbene intermediate **11**. Complexes **4** with 1,8-diaminonaphthalene lead in very smooth conditions to 2-substituted perimidines **9** with good yields through an unprecedented cleavage of the carbon skeleton of the metal complex in a formal retro-Aumann reaction.

Many reactions of  $\alpha,\beta$ -unsaturated group 6 Fischer carbene complexes and nucleophiles are analogous to those experienced by organic esters and amides.<sup>1</sup> However, in many cases, the presence of the metal fragment results in the formation of more sophisticated products than those expected from the standard 1,4- or 1,2-addition of the nucleophile.<sup>2</sup> The chemistry developed therefrom has produced an impressive array of synthetically useful processes.<sup>3</sup> Recently, we and others have demonstrated that the metal fragment of  $\alpha,\beta$ -unsaturated chromium(0) carbene complexes also participates in the addition reactions of simple nucleophiles such as the hydride anion.<sup>4</sup> Despite the number of reactions reported for  $\alpha,\beta$ -unsaturated group 6 metal carbenes, reactions in which the carbon skeleton of the complex is broken are rare. The first example of this class of processes was reported by Dötz in the spontaneous retro-Fischer fragmentation of complex **1** to enyne



**2** (Scheme 1).<sup>5,6</sup> During our ongoing research directed toward the synthesis of cyclophanic bi- and polynuclear group 6 metal carbene complexes,<sup>7</sup> we observed that 1,4-adducts such as **3** derived from the addition of 1,2-diaminobenzene to different alkoxyalkynyl group 6 carbene complexes **4** were reactive either by gently heating or in the presence of SiO<sub>2</sub> (Scheme 2). Reported herein is this novel alkoxyalkynylchromium(0) carbene to chromium(0) isocyanide rearrangement in the Michael adducts **3** derived from the reaction of those complexes with 1,2-diaminobenzene,<sup>6</sup> as well as an unprecedented “retro-Aumann” process<sup>8</sup> in the reaction of alkyne-alkoxy group 6 carbene complexes with 1,8-diaminonaphthalene.



Complexes **3a–c**, obtained from the standard addition of 1,2-diaminobenzene to alkoxyalkynylchromium(0) carbene complexes **4a–c**, evolve to new chromium-

(5) (a) Christoffers, J.; Dötz, K. H. *Organometallics* **1994**, *13*, 4189. The retro-Fischer reaction of (alkylethoxy)carbene complexes (M = Cr, W) induced by a  $\beta$ -imino functionality has been reported while this paper was being considered for publication: (b) Aumann, R.; Fu, X.; Vogt, D.; Fröhlich, R.; Kataeva, O. *Organometallics* **2002**, *21*, 2736.

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(1) This is in agreement with the statement of the isolobal analogy principle. See: (a) Hoffmann, R. *Science*, **1981**, *211*, 995. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(2) Reviews: (a) Barluenga, J.; Flórez, F.; Fañanas, J. J. *Organomet. Chem.* **2001**, *624*, 5. (b) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (c) Aumann, R.; Nienaber, H. *Adv. Organomet. Chem.* **1997**, *41*, 163.

(3) Selected reviews in the chemistry and synthetic applications of Fischer-carbene complexes: (a) Dötz, K. H.; Fischer, H.; Hoffmann, P.; Kreissel, F. 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 Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford 1995; Vol. 12, p 470. (d) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271. (e) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (f) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591.

(4) (a) Gómez-Gallego, M.; Mancheño, M. J.; Ramirez, P.; Piñar, C.; Sierra, M. A. *Tetrahedron* **2000**, *56*, 4893. (b) Mancheño, M. J.; Sierra, M. A.; Gómez-Gallego, M.; Ramirez, P. *Organometallics* **1999**, *18*, 3252. (c) Barluenga, J.; Rubio, E.; López-Pelegrín, J. A.; Tomás, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1091.

containing products by gently heating in THF solution (Scheme 2).<sup>9</sup> These new products lacked the carbene ligand, and their outstanding NMR characteristics were the presence of a signal attributable to a methyl group ( $\delta = 1.77\text{--}2.23$  ppm and  $\delta = 18.0\text{--}20.4$  ppm in  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively), as well as a signal assignable to a quaternary carbon at 214.5 ppm in their  $^{13}\text{C}$  NMR spectra. A single monocrystal of the product derived from complex **3b** was analyzed by X-ray diffraction.<sup>10</sup> The structure of isocyanide complex **5b** was thus established for this compound (Figure 1) and, hence, for compounds **5a** and **5c** obtained from complexes **3a** and **3c**, respectively.<sup>11</sup> The rearrangement alkoxychromium(0) carbene  $\rightarrow$  pentacarbonylchromium(0) isocyanide also occurred in the presence of silica gel, and compounds **5** could be obtained by column chromatography or by stirring a hexane/AcOEt (10:1) solution of complexes **3** in the presence of  $\text{SiO}_2$ . Under these conditions compound **3c** produced complex **6** resulting from the hydrolysis of the imine group in the initially formed isocyanide complex **5c**. This is an expected result since aliphatic imines are considerably more prone to hydrolysis than aromatic imines.

(6) The identification in very low yields of pentacarbonylchromium(0) allylisocyanide in the decomposition mixtures obtained during the reaction of pentacarbonyl[(allylamino)(phenylethynyl)carbene]tungsten(0) and allylamine has been also reported. Moretó, J. M.; Ricart, S. *J. Organomet. Chem.* **2001**, 617–618, 334.

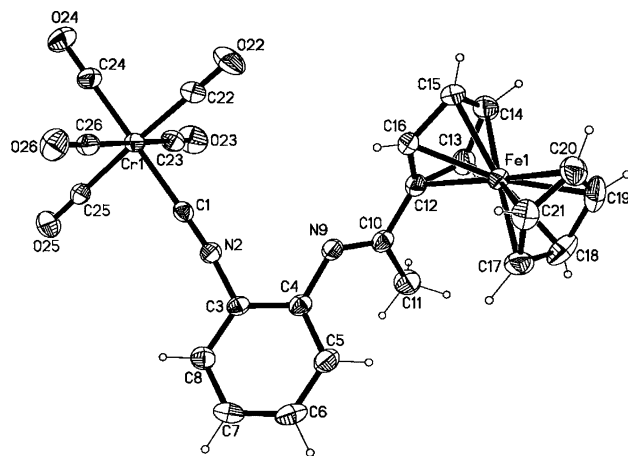
(7) Fernández, I.; Sierra, M. A.; Mancheño, M. J.; Gómez-Gallego, M.; Ricart, S. *Organometallics* **2001**, 20, 4304.

(8) The Aumann reaction, namely, the reaction of an alkoxyalkyl group 6 carbene complex with an aldehyde lacking an  $\alpha$ -hydrogen,  $\text{TMSCl}$ , and  $\text{Et}_3\text{N}$  to yield an  $\alpha,\beta$ -unsaturated complex, is the standard method to prepare this kind of compound. Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, 120, 537.

(9) The experimental procedure for the reaction of complex **3b** to form isocyanide complex **5b** is representative of the methodology followed through this work: In a flame-dried, airless flask containing a magnetic stirring bar, degassed by evacuation/back-filled with argon (3 times), 100 mg (0.18 mmol) of carbene complex **3b** was dissolved in THF (3 mL). The reaction was heated at 50 °C under an argon atmosphere until the disappearance of the starting material (10 h, checked by TLC). The solvent was removed under reduced pressure, and the reaction crude was dissolved into a mixture of hexane/ $\text{Et}_2\text{O}$  (2:1) and filtered through a double pad of Celite and  $\text{SiO}_2$  to yield, after removing the solvent, 80 mg (87%) of isocyanide complex **5b** as an orange solid. When carbene complex **3b** (1.13 g, 2 mmol) was submitted to flash column chromatography on silica gel under argon pressure 935 mg (90%) of the isocyanide complex **5b** was also obtained.  $^1\text{H}$  NMR (300 MHz):  $\delta$  7.32–7.24 (m, 2H, ArH), 7.01 (t,  $J = 7.3$  Hz, 1H, ArH), 6.79 (d,  $J = 7.8$  Hz, 1H, ArH), 4.77 (s, 2H, CH), 4.40 (s, 2H, CH), 4.16 (s, 5H, Cp), 2.08 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz):  $\delta$  216.7 (CO trans), 214.5 (Cr–CN), 214.3 (CO cis), 171.2 (C=N), 148.8, 129.5, 126.2, 123.4, 120.7 (aromatic C), 82.0 (Cq), 71.2 (CH), 69.5 (Cp), 68.8 (CH), 18.6 ( $\text{CH}_3$ ). IR ( $\text{CCl}_4$ ):  $\nu$  2141 (CN), 2056, 1998, 1954, 1626, 1464, 1215  $\text{cm}^{-1}$ . MS (ESI),  $[\text{M} + \text{H}]^+$ : 521.1. Anal. Calcd  $\text{C}_{24}\text{H}_{16}\text{CrFeN}_2\text{O}_5$ : C 55.41, H 3.10, N 5.38. Found: C 55.64, H 3.27, N 5.55.

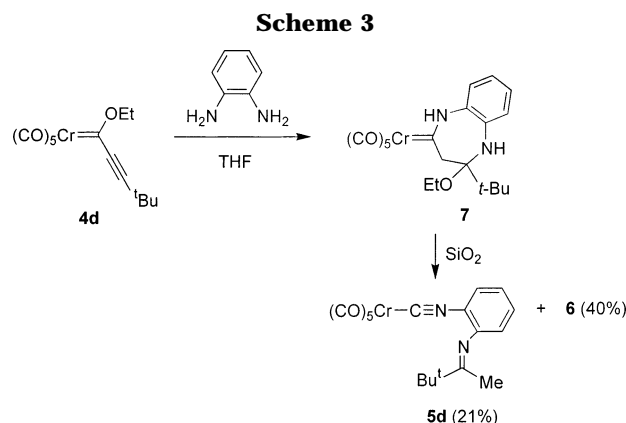
(10) Crystal was monoclinic, space group =  $P2(1)/c$ ,  $a = 9.972(2)$  Å,  $b = 18.104(4)$  Å,  $c = 12.532(3)$  Å,  $\beta = 94.262(4)^\circ$ ;  $V = 2257.0(8)$  Å<sup>3</sup>;  $Z = 4$ ;  $cd = 1.531$   $\text{mg}\cdot\text{m}^{-3}$ ;  $\mu = 1.162$   $\text{mm}^{-1}$ ;  $F(000) = 1056$ . 11 550 measured reflections were collected on a SMART CCD-Bruker diffractometer, 3967 reflections observed ( $I > 3\sigma(I)$ ), 298 refined parameters,  $R = 0.033$ , ( $R_w = 0.0709$ ). The structure was solved by direct methods and Fourier synthesis. The refinement was done by full matrix least-squares procedures on  $F^2$  (SHELXTL version 5.1). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. Further crystallographic details for the structure reported in this paper may be obtained from the Cambridge Crystallographic Data Center, on quoting the depository number CCDC 180603.

(11) Some examples of group 6 isocyanide complexes: (a) Balbo-Block, M.; Bartel, C.; Lentz, D.; Preugschat, D. *Chem. Eur. J.* **2001**, 7, 881. (b) Lentz, D.; Willemsen, S. *J. Organomet. Chem.* **2000**, 612, 96. (c) Liu, C.-Y.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1996**, 15, 1055. (d) Hahn, F. E.; Tamm, M.; Lügger, T. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1356. (e) Kunz, R.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 330. Review: (f) Lentz, D. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1315.



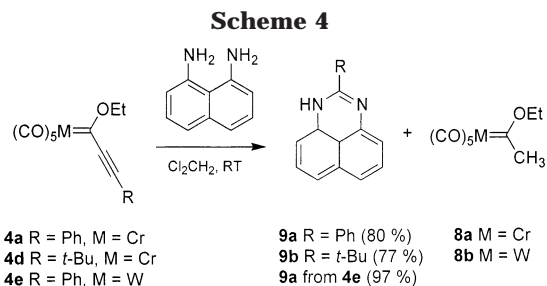
**Figure 1.** ORTEP view of the structure of **3b** showing the atomic numbering with 30% probability ellipsoids. Selected bond lengths [Å] and angles [deg]: Cr1–C24 ( $\text{CO}_{\text{trans}}$ ) 1.867(3) Cr1–( $\text{CO}_{\text{cis}}$ ) (average) 1.893(3), Cr1–C1 1.988(3), C1–N2 1.154(3), N2–C3 1.394(3), N9–C10 1.289(3), Cr1–C1–N2 177.2(2), C24–Cr1–C1 179.0(1).

The reaction of compound **4d** with 1,2-diaminobenzene produced a new chromium carbene complex that quickly evolved after  $\text{SiO}_2$  flash chromatography to the isocyanide complex **5d** and complex **6**. Although this new carbene complex was thermally stable at room temperature, it quickly decomposed to a mixture of unidentified products when heated in THF. The spectroscopic data for this new complex were consistent with the hemiaminal **7**. The hemiaminal structure also explains the thermal stability of **7** and its evolution to **5d** in the presence of acid silica gel, since hemiaminals are not stable in acid media (Scheme 3).

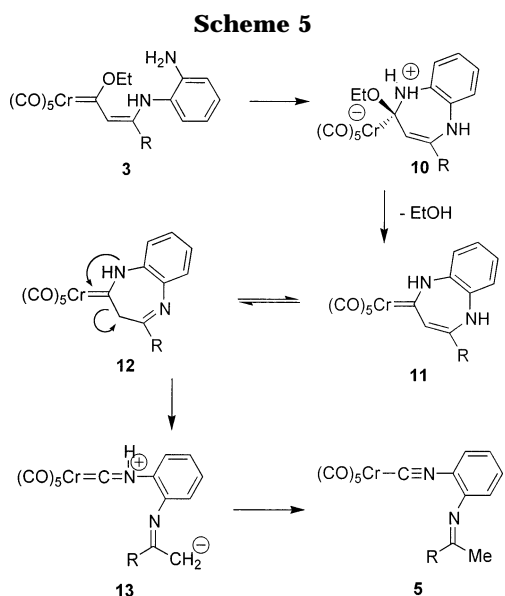


The scenario was totally different when 1,8-diaminonaphthalene was used as the nucleophile. Thus, the reaction of alkynyl alkoxy chromium carbene complexes **4a** and **4d** with 1,8-diaminonaphthalene in  $\text{Cl}_2\text{CH}_2$  at room temperature produced a new complex identified as pentacarbonyl[(ethoxy)(methyl)carbene]chromium(0), **8a**, together with a new organic material lacking any metal moiety. The spectroscopic and analytical data of these organic compounds were fully consistent with a perimidine structure **9**.<sup>12</sup> The reaction is independent of the substituent attached to the triple bond. Thus, phenyl and alkyl substituents are compatible with the fragmentation, producing the heterocyclic compounds **9a,b** in good yields (Scheme 4). Tungsten carbene complex **4e** also reacted with 1,8-naphthalenediamine,

yielding perimidine **9a** and pentacarbonyl[(ethoxy)-(methyl)carbene]tungsten(0), **8b**, in 97% and 91% yields, respectively. Therefore, the use of tungsten instead of chromium carbene complexes exerts no influence on the reactivity observed (Scheme 4).

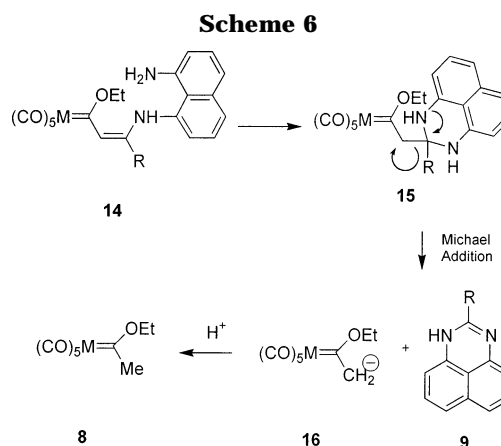


The results obtained in the reactions of complexes **4** with 1,2-diaminobenzene may be rationalized through an initial intramolecular addition of the amino group to the carbene carbon of complexes **3** to form zwitterionic complexes **10**.<sup>13</sup> Compounds **10** should evolve by elimination of EtOH to form intermediates **11**, which produce the final products through their imine tautomers **12** by breakage of the bond  $\alpha$  to the chromium center (Scheme 5). Support for this proposal is found in the isolation of hemiaminal complex **7**, which should be formed by EtOH addition to intermediate **12** (R = *t*-Bu) (Scheme 3).



The particular peri-position of the two amino groups in 1,8-diaminonaphthalene enables the double Michael addition of this reagent to the alkynyl carbene complexes **4** to form the intermediate complexes **15**, through the first 1,4-adducts **14**. Cleavage of **15** would form

perimidines **9** together with enolates **16**, which after protonation would yield carbene complexes **8** (Scheme 6). A similar 1,4-addition of a dinucleophile to an alkynyl carbene complex was earlier reported in the reaction of catechol with pentacarbonyl[ethoxy(2-phenylethenyl)]tungsten(0) carbene complex.<sup>14</sup> In this case the oxygenated Michael adduct was stable. Evidently, in our case the bond breakage is favored by the strong peri-interaction present in intermediate **15**.



In conclusion, we have reported two new fragmentation reactions of alkynyl group 6 carbene complexes: the thermal or SiO<sub>2</sub>-promoted rearrangement of complexes **3** to isocyanides **5** and the unprecedented "retro-Aumann" cleavage of  $\alpha,\beta$ -unsaturated group 6 Fischer carbene complexes **4** by reaction with 1,8-diaminonaphthalene. This latter process leads to 2-substituted perimidines **9** with good yields under smooth conditions. These kind of compounds have great potential as DNA-intercalating agents and play an important role in organic molecule-based magnets and conducting materials.<sup>12</sup> Further work directed toward the application of these new processes to other complexes and dinucleophiles is actively underway in our laboratories.

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**Supporting Information Available:** Text describing the full experimental procedure and characterization of compounds **3a–c**, **4b**, **5a–d**, **6**, **7**, and **9a,b**, as well as crystallographic information for compound **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) For recent articles about the properties of these compounds, see: (a) Bu, X.; Deady, L. W.; Finlay, G. J.; Baguley, B. C.; Denny, W. A. *J. Med. Chem.* **2001**, *44*, 2004. (b) Tkacyk, K.; Tarasiuk, J.; Seksek, O.; Borowski, E.; Garnier-Suillerot, A. *Eur. J. Pharmacol.* **2001**, *413*, 131. (c) Citterio, D.; Minamihashi, T. K.; Kuniyoshi, Y.; Hisamoto, H.; Sasaki, S.; Suzuki, K. *Anal. Chem.* **2001**, *73*, 5339. (d) Morita, Y.; Aoki, T.; Fukui, K.; Nakawaza, S.; Tamaki, K.; Suzuki, S.; Fuyuhiko, A.; Yamamoto, K.; Sato, K.; Shiomi, D.; Naito, A.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1793.

(13) Zwitterionic complexes related to **10** have been isolated in the reactions of alkoxy-pentacarbonylchromium(0) carbene complexes and different amines. See: (a) Rudler, H.; Durand-Revillé, T. *J. Organomet. Chem.* **2001**, *617–618*, 571, and references therein. Other nucleophiles such as tertiary phosphines and hydride anions formed structurally related zwitterionic complexes. See: (b) Aumann, R.; Jaspe, B.; Läge, M.; Krebs, B. *Chem. Ber.* **1994**, *127*, 2475.  
 (14) (a) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *J. Organomet. Chem.* **1991**, *35*, C-17. (b) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Ros, J.; Yáñez, R. *J. Organomet. Chem.* **1992**, *440*, 79.