J. Am. Chem. Soc. **1994,** *116,* 11191−11192 11191

Annulation Reaction of Vinylaminocarbenes: Characterization of the Tetracarbonyl Vinylcarbene and Metalahexatriene Intermediates

José Barluenga,*,† Fernando Aznar,† Alfredo Martín,†
Santiago García-Granda,‡ and Enrique Pérez-Carreño‡

*Instituto Universitario de Química Organometálica
"Enrique Moles" and Departamento de Química Física y
Analítica, Campus del Cristo, Universidad de Oviedo
33071 Oviedo, Spain*

Received July 18, 1994

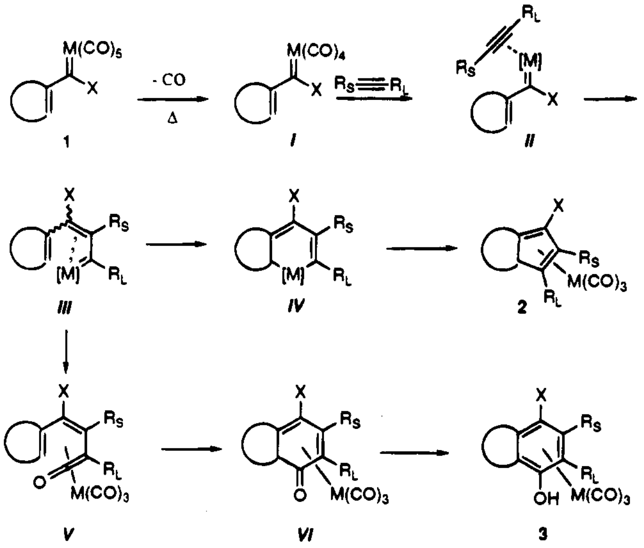
The benzannulation reaction of an unsaturated Fischer carbene complex and an alkyne, initially reported by Dötz,[1] has become in recent years one of the most utilized reactions in natural product synthesis involving an organometallic process.[2] Furthermore, the study of its complex mechanism represents one of the greatest efforts in the field of metal−carbene chemistry.[2] This reaction gives a variety of products depending on the structure and substitution of the carbene, the metal, and the alkyne employed, but typically, cyclopentadiene and phenol derivatives are the main products.

The commonly accepted mechanism for the Dötz reaction is depicted in Scheme 1. The reaction begins with a thermally reversible, rate-limiting CO dissociation of vinylcarbene **1**,[3] followed by alkyne complexation and insertion into the metal carbene bond. It has been proposed that the structure of intermediate **III** determines the partition between products.[4] Thus, intramolecular cyclization and reductive elimination affords the cyclopentadiene products **2**, while, CO insertion, electrocyclic ring closure, and tautomerization yields phenol derivatives **3**.

It should be pointed out that the only intermediate isolated and fully characterized in the mechanism presented, which arises from a reaction between a vinylcarbene and an acetylene, leading to Dötz products, has been the cyclohexadienone derivative **VI**.[2,5] Two other structural analogues have been islolated: an alkynyl π complex similar to **II** coming from the photochemical reaction between an alkyne and a Fischer carbene[6] and an aminovinylketene complex similar to **V** from an intramolecular reaction of a Fischer carbene complex and an alkyne.[7]

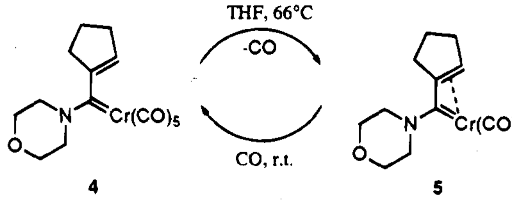
We report here the first isolation and characterization of a η^1:η^3-vinylcarbene complex of a group 6 metal (0),[8,9] which corresponds to the first intermediate (**I**, Scheme 1) of the Dötz reaction, and the first isolation and characterization of a tetracarbonyl metalahexatriene of a group 6 metal(0), which corresponds to the intermediate of the Dötz reaction exemplified as **III** in Scheme 1.

Scheme 1[a]



[a] [M] = M(CO)$_4$; X = NR$_2$, OR, RNCOR′.

Scheme 2



When a solution of carbene **4**[10] in THF (tetrahydrofuran) is heated under reflux, it is observed that the color changes from yellow to bright red. Evaporation of the solvent and further crystallization (hexane−dichloromethane, −20 °C) affords compound **5** in 90% yield (Scheme 2). The structure of **5** was determined from ^{1}H and ^{13}C NMR analysis at 233 K and X-ray analysis.[11] The most remarkable signals in ^{13}C NMR (233 K) are those that show the presence of the carbene carbon (255.5 ppm), four inequivalent CO ligands (222.0, 224.2, 234.9, and 235.8 ppm), and the double-bond high-field signals (85.7 (CH) and 86.9 (C) ppm), which support the η^3 attachment of the metal to the vinylcarbene ligand. The X-ray structural analysis of complex **5** (Figure 1) shows a bond distance between the two alkene carbons bonded to the metal (ca. 1.37 Å) that is only slightly longer than the common distance between two double-bonded carbons (ca. 1.34 Å),[12] and as a consequence, the carbene ligand may therefore be described as an intermediate

---

† Instituto Universitario de Química Organometálica "Enrique Moles".

‡ Departamento de Química Física y Analítica (XR section).

(1) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(2) Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P. *Organometallics* **1994**, *13*, 102 and references cited therein.

(3) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5.

(4) (a) McCallum, J. S.; Kunng, F. A.; Gilbertson, S. R.; Wulff, W. D.; *Organometallics* **1988**, *7*, 2346. (b) Dötz, K. H.; Larbig, H. *Bull. Soc. Chim. Fr.* **1992**, 579.

(5) (a) One complex proposed as a π tetracarbonyl−alkyne−tungsten carbene or as a tetracarbonyl tungstenacyclobutene from a photochemical reaction between a Fischer carbene and diphenylacetylene, that undergoes annulation to yield indene derivatives, has been isolated and characterized by IR and ^{1}H NMR analysis. Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) A tetracarbonyl vinyl chromium carbene complex has been observed by low-temperature IR as an intermediate in the photolysis reaction of pentacarbonyl-[phenylmethoxymethylene] chromium(0) in the presence of alkynes. Knorr, J. R.; Brown, T. L. *Organometallics* **1994**, *13*, 2178.

(6) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236.

(7) Anderson, B. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 8615.

(8) Some examples of η^3-vinylcarbenes of tungsten(II) have been described. (a) Garret, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Goeffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383. (b) Mayr, A.; Asaro, M. F.; Glines, T. J.; Van Engen, D.; Tripp, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 8187.

(9) An iron Fischer carbene complex analogous to **5** has been isolated and characterized. Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413.

(10) Carbene **4** was prepared by the metathesis reaction between an aryloxycarbene and a 2-aminodiene. Submitted for publication.

(11) The structure of C$_{14}$H$_{15}$NO$_5$Cr was determined by X-ray diffraction. M_r = 329.27, monoclinic, space group $P2_1/n$, a = 6.667(1) Å, b = 12.412-(3) Å, c = 17.821(3) Å, β = 94.18(2)°, V = 1470.7(5) Å^3, Z = 4, D_{calcd} = 1.49 g/cm^3. Mo K$_\alpha$ radiation (graphite crystal monochromator, λ = 0.710 73 Å), μ(Mo Kα) = 7.77 cm^{-1}, F(000) = 680, T = 200 K. Final conventional R factor = 0.029 for 1901 "observed" reflections and 250 variables.

(12) *Tables of Interatomic Distances and Configuration of Molecules and Ions*; Sutton, L. E., Ed.; The Chemical Society: London, 1965.

0002-7863/94/1516-11191$04.50/0

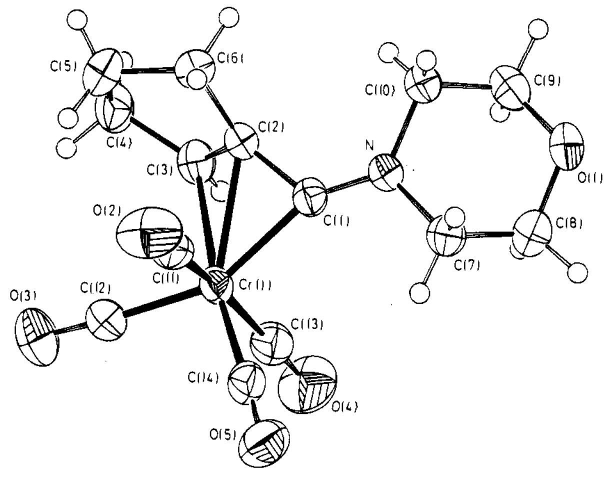
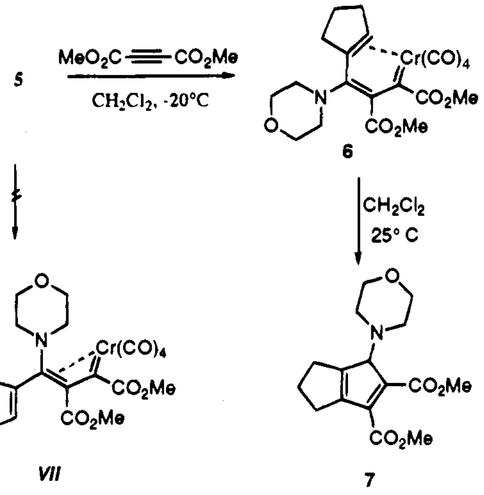


Figure 1. Molecular structure and numbering scheme for **5** [$Cr(CO)_4(C_{10}H_{15}NO)$]. Bond lengths (Å) and angles (°): Cr–C(1), 1.961(2); Cr–C(2), 2.238(2); Cr–C(3), 2.414(3); N–C(1), 1.304(3); C(1)–C(2), 1.441(3); C(2)–C(3), 1.368(4); C(2)–Cr–C(1), 39.4(1); C(3)–Cr(1)–C(2), 33.9(1); C(3)–Cr–C(1), 67.3(1); C(1)–C(2)–C(3), 121.7(2); N–C(1)–Cr, 151.5(2); C(2)–C(1)–N, 126.9(2).

Scheme 3



between a rigorously η^1- and a η^3-bonded system.[13] Two other observations indicated that the π bond between the metal and the alkene is very weak: firstly, when CO was bubbled at room temperature into a solution of **5**, quantitative formation of product **4** resulted within minutes (Scheme 2); secondly, ^{13}C NMR spectroscopy at 293 K shows no CO signal. Similar observations have been reported for tetracarbonyl acylaminocarbene derivatives.[14] It has been proposed that the chelate in these complexes opens rapidly on the NMR time scale and CO ligands exchange because the coordinatively unsaturated resulting species are fluxional.

In view of these results, the ready availability of a formal coordinatively unsaturated 16 e^- complex in solution encouraged us to investigate the possibility of performing the Dötz reaction at low temperatures. It is known that, typically, reactions between Fischer carbenes and alkynes take place at temperatures over 50 °C (25 °C for vinylmolybdenum complexes)[2] as the rate-determining step of the reaction is the formation of an electronically unsaturated intermediate by CO dissociation; nevertheless, reaction of **5** with dimethyl acetylenedicarboxylate takes place at −20 °C in 22 h (Scheme 3) to yield the metalahexatriene **6** (54%) with total *Z* selectivity, since no evidence of the presence of the regioisomer **VII** (Scheme 3) could be observed in the reaction mixture. Compound **6** was isolated by crystallization from the crude reaction mixture (hexane–dichloromethane, −78 °C) and characterized from its ^1H and ^{13}C NMR spectra.[15] The most remarkable data collected from the ^{13}C NMR analysis at 253 K are the four different resonances for CO ligands (220.2, 220.9, 230.0, and 231.1 ppm) and the four olefinic signals, 93.8 (CH) and 102.1 (C) ppm for the complexed double bond and 130.7 (C) and 157.9 (C) ppm for the uncomplexed double bond, which conclusively demonstrate that the C_5–C_6 double bond is in fact the alkenyl ligand attached to the metal.[16]

Compound **6** is not stable in solution at room temperature and decomposes in 6 h to **7** (74%), which is the most common final product in the Dötz reaction with aminocarbenes, after demetalation and a 1,5 hydrogen shift.

In conclusion, the isolation and characterization of two new intermediates in the Dötz reaction is reported. Further studies about their behavior toward other substrates in order to open new possibilities in annulation reactions are under way.

Acknowledgment. This research was supported by Dirección General de Investigación Científica y Técnica (DGICYT) PB92-1005. A MEC fellowship to A.M. is gratefully acnowledged.

Supplementary Material Available: Synthetic procedures and characterization data for **5**–**7** and X-ray crystallographic data for compounds **4** and **5** including tables of atomic coordinates, bond lengths, and bond angles (25 pages); observed and calculated structure factors for **4** and **5** (33 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(13) This result is in agreement with a recent theoretical study (EH-MO). Hofmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769.

(14) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381.

(15) Spectral data for **6**: ^1H NMR (CD_2Cl_2, 253 K) δ 1.61–1.94 (m, 2H), 2.36–2.92 (m, 4H), 3.66 (s, 3H), 3.72–4.20 (m, 8H), 3.90 (s, 3H), 4.81 (s, 1H); ^{13}C NMR (CD_2Cl_2, 253 K) δ 20.7 (CH_2), 34.0 (CH_2), 36.7 (CH_2), 51.4 (CH_3), 52.3 (CH_3), 53.8 (CH_2), 54.2 (CH_2), 66.8 (CH_2), 67.1 (CH_2), 93.8 (CH), 102.1 (C), 130.7 (C), 157.9 (C), 167.5 (C), 178.1 (C), 220.2 (C), 220.9 (C), 230.0 (C), 231.1 (C), 245.9 (C); IR (KBr, cm^{-1}) 1903, 1921, 2015. Spectral data for **5**: ^1H NMR ($CDCl_3$) δ 1.35–1.64 (m, 1H), 1.71–1.88 (m, 1H), 1.96 (d,d, J = 7.8, 14.0 Hz, 1H), 2.20–2.35 (m, 2H), 2.51–2.67 (m, 1H), 3.63–4.01 (m, 8H), 4.67 (s, 1H); ^{13}C NMR (CD_2Cl_2, 233 K) δ 21.0 (CH_2), 31.1 (CH_2), 35.4 (CH_2), 57.0 (CH_2), 58.5 (CH_2), 67.1 (CH_2), 67.5 (CH_2), 85.0 (CH), 86.6 (C), 222.0 (C), 224.2 (C), 234.9 (C), 235.8 (C), 257.6(C) IR (CH_2Cl_2, cm^{-1}) 1879, 1908, 2011, 2045.

(16) Alkene carbene chelates bearing α-heteroatoms (N, O) have been previously synthesized and structurally characterized. As typical examples, see: (a) Dötz, K. H.; Kuhn, W.; Müller, G.; Huber, B.; Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 812. (b) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H. *Organometallics* **1987**, *6*, 1057. (c) Alvarez-Toledano, C.; Parlier, A.; Rudler, M.; Daran, J. C.; Knobler, C.; Jeannin, Y. *J. Organomet. Chem.* **1987**, *328*, 357. (d) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417.