Preparation, Characterization, and Reactions of the First Parent Acetylene Fischer Carbene Complexes

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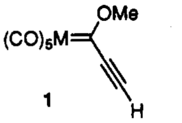
*Summary: The parent acetylenic Fischer carbene complexes of the type 2, $(CO)_5M{=}C(NMe_2)C{\equiv}CH$, are isolated and characterized as both chromium (**2a**) and tungsten (**2b**) derivatives. Their Diels–Alder and Michael addition reactions are described, as well as the deprotonation of their acetylenic hydrogens.*

Due to their potential in Diels–Alder reactions,[1] Michael additions,[2] [2 + 2] cycloadditions,[3] and [3 + 2] cycloadditions,[4] we have long sought to prepare the parent methoxy acetylene Fischer carbene complexes of the type 1. Efforts to prepare either complex **1a** or **1b** by the standard Fischer method has resulted in the generation of unstable materials that cannot be isolated and properly characterized.[5] We now report that the parent acetylene complexes **2a** and **2b** can be easily prepared by the standard Fischer method and are sufficiently stable to complete characterization due to the stabilizing effect of the dimethylamino substituent at the carbene carbon. We also have investigated Diels–Alder and Michael addition reactions of these complexes and demonstrate that these complexes can be deprotonated and alkylated with cyclohexenone.



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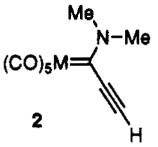

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1a, **2a**: M = Cr
1b, **2b**: M = W

Complexes **2a** and **2b** can both be synthesized in two steps from chromium and tungsten hexacarbonyl, respectively. In a one-pot procedure, the ((trimethylsilyl)ethynyl)(dimethylamino)carbene complexes of type **5** are made by addition of lithium (trimethylsilyl)acetylide to the metal hexacarbonyl followed by methylation with methyl trifluoromethanesulfonate. This produces the known ((trimethylsilyl)ethynyl)(methoxy)carbene complexes **4**,[4a] which, without purification, are directly subjected to aminolysis with dimethylamine at −100 °C, giving a 53% overall yield of **5a** from the metal carbonyl (46% for **5b**).[7] The final step involves cleavage of the trimethylsilyl group at −78 °C in ether with 1 M tetrabutylammonium fluoride in THF. This reaction, after

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(1) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (b) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (d) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (e) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873.

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(3) (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727. (b) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (c) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419. (d) Camps, F.; Llebaría, M. G.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479. (e) de Meijere, A.; Wessjohann, L. *Synlett.* **1990**, 20. (f) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (g) Pipoh, R.; van Eldik, R.; Wulff, W. D.; Wang, S. L. B. *Organometallics* **1992**, *11*, 490.

(4) (a) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229. (b) Camps, F.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1470. (c) Dötz, K. H.; Christoffers, J. *J. Organomet. Chem.* **1992**, *426*, C58. (d) Chan, K. S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2602.

(5) Treatment of tungsten hexacarbonyl with sodium acetylide in THF followed by methylation with Meerwein salt gives a purple solution which most likely contains complex **1b** but which cannot be isolated and characterized without decomposition. Removal of solvent from this solution provides a crude compound having a proton NMR spectrum with two distinct singlets which stood out in a 3:1 integral ratio (δ 4.52 (3 H), δ 4.55 (1 H)).[6]

(6) Faron, K. L.; Wulff, W. D., unpublished results.

(7) The following analytical and spectral data were collected for the alkyne carbene complexes. **5a**: orange solid; mp 54–57 °C; ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9H, $Si(CH_3)_3$), 3.63 (s, 3H, N–CH_3), 3.86 (s, 3H, N–CH_3); ^{1}H NMR (C_6D_6) δ 0.26 (s, 9H, $Si(CH_3)_3$), 2.34 (s, 3H, N–CH_3), 2.93 (s, 3H, N–CH_3); ^{13}C NMR ($CDCl_3$) δ −0.83, 47.74, 49.22, 104.27, 137.16, 217.17, 224.13, 250.60; ^{13}C NMR (C_6D_6) δ −0.75, 46.81, 48.48, 104.71, 136.70, 217.83, 224.37, 249.23; IR (thin film) 2962 w, 2856 w, 2055 s, 1980 m, 1918 s, 1912 s, 1522 w, 1402 w, 1252 w, 1046 w, 847 m, 653 m cm^{-1}; mass spectrum *m/z* (% relative intensity) 345 (M^+, 2), 289 (M^+ − 2CO, 8), 261 (M^+ − 3CO, 14), 233 (M^+ − 4CO, 15), 205 (M^+ − 5CO, 100), 190 (9), 175 (7), 149 (20), 134 (26), 117 (8), 97 (14). Anal. Calcd for $C_{13}H_{15}NO_5SiCr$: C, 45.21; H, 4.38; N, 4.06; Cr, 15.06. Found: C, 45.31; H, 4.57; N, 4.01; Cr, 15.49. **5b**: orange solid; mp 39–41 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H, $Si(CH_3)_3$), 3.57 (s, 3H, N–CH_3), 3.74 (s, 3H, N–CH_3); ^{13}C NMR ($CDCl_3$) δ −1.10, 46.37, 51.51, 106.06, 134.16, 198.43 ($^1J_{C,W}$ = 128 Hz), 204.19, 230.85; IR (thin film) 2962 w, 2063 s, 1977 shoulder, 1903 s, 1525 w, 1405 w, 1252 w, 846 m cm^{-1}; mass spectrum *m/z* (% relative intensity) 477 (M^+, 42, ^{184}W), 421 (M^+ − 2CO, 83, ^{184}W), 393 (M^+ − 3CO, 45, ^{184}W), 365 (M^+ − 4CO, 98, ^{184}W), 337 (M^+ − 5CO, 100, ^{184}W), 320 (25, ^{184}W), 277 (33, ^{184}W), 238 (17), 222 (8), 160 (10), 73 (9). Anal. Calcd for $C_{13}H_{15}NO_5SiW$: C, 32.72; H, 3.17; N, 2.94; W, 38.53. Found: C, 32.86; H, 3.20; N, 2.77; W, 38.32. **2a**: yellow solid; mp 49–51 °C; ^{1}H NMR ($CDCl_3$) δ 3.65 (s, 3H, N–CH_3), 3.89 (s, 3H, N–CH_3), 5.91 (s, 1H, C–H); ^{1}H NMR (C_6D_6) δ 2.30 (s, 3H, N–CH_3), 2.87 (s, 3H, N–CH_3), 5.04 (s, 1H, C–H); ^{13}C NMR ($CDCl_3$) δ 47.97 (q), 49.71 (q), 84.16 (d, $^2J_{C,H}$ = 49 Hz), 116.01 (d, $^1J_{C,H}$ = 254 Hz), 216.98 (s), 223.82 (s), 251.46 (s); ^{13}C NMR (C_6D_6) δ 47.17, 49.02, 84.38, 115.69, 217.51, 224.32, 248.85; IR (thin film) 3299 m, 2057 m, 1980 shoulder, 1908 s, 1530 w, 1402 w, 1154 w, 1001 w cm^{-1}; mass spectrum *m/z* (% relative intensity) 273 (M^+, 12), 217 (M^+ − 2CO, 23), 189 (M^+ − 3CO, 33), 161 (M^+ − 4CO, 32), 133 (M^+ − 5CO, 100), 118 (87), 103 (19), 90 (8), 77 (62), 66 (6). Anal. Calcd for $C_{10}H_7NO_5Cr$: C, 43.97; H, 2.58; N, 5.13; Cr, 19.03. Found: C, 44.28; H, 2.59; N, 4.66; Cr, 19.67. **2b**: yellow solid; 60–63 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3H, N–CH_3), 3.78 (s, 3H, N–CH_3), 5.65 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 46.62 (q), 51.93 (q), 85.94 (d, $^2J_{C,H}$ = 48 Hz), 112.88 (d, $^1J_{C,H}$ = 255 Hz), 198.2 ($^1J_{C,W}$ = 128 Hz), 203.92 ($^1J_{C,W}$ = 128 Hz), 231.05 (s); IR (thin film) 3298 w, 2064 m, 1970 shoulder, 1902 s, 1534 w cm^{-1}; mass spectrum *m/z* (% relative intensity) 405 (M^+, 18, ^{184}W), 349 (M^+ − 2CO, 20, ^{184}W), 321 (M^+ − 3CO, 24, ^{184}W), 293 (M^+ − 4CO), 44, ^{184}W), 265 (M^+ − 5CO, 53, ^{184}W), 250 (13, ^{184}W), 238 (11), 221 (18), 211 (11), 179 (7), 165 (8), 149 (23), 137 (14), 125 (23), 111 (40), 97 (60), 85 (66), 71 (100).

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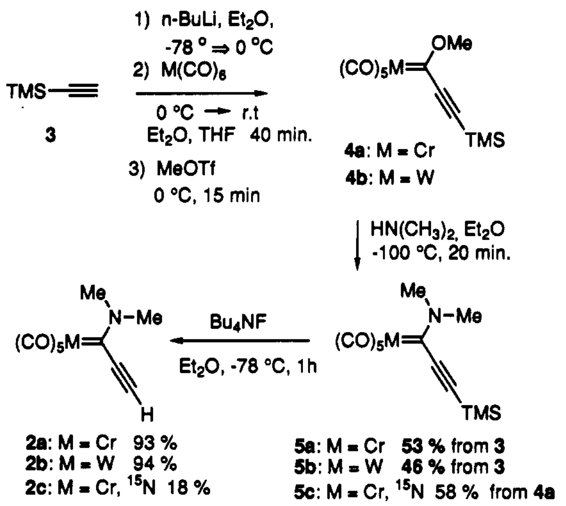
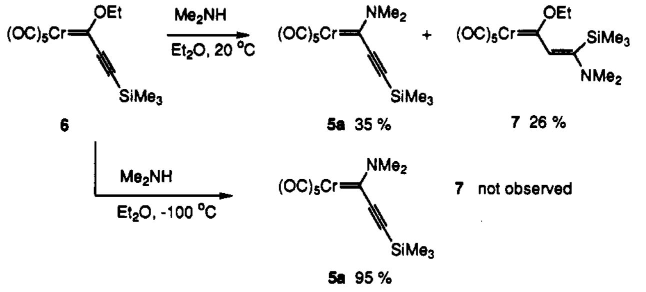
Scheme I



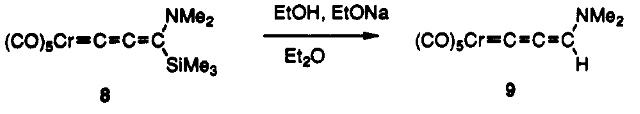
Scheme II



quenching with water at −78 °C, provides complexes **2a** and **2b** in 93% and 94% yields, respectively.

The parent acetylene complexes **2a** and **2b** were fully characterized by the normal spectroscopic methods[7] and can be handled in air and purified by silica gel chromatography without special precautions. As is characteristic of other terminal acetylenes, the C–H stretches for complexes **2a** and **2b** were observed at 3299 and 3298 cm^{-1}, respectively, and the carbon–hydrogen coupling constants were $J_{CH} = 254$ Hz and $J_{CH} = 255$ Hz, respectively. It was surprising to find that the acetylene protons of complexes **2a** and **2b** were located at δ 5.91 ppm (Cr) and δ 5.65 ppm (W). To the best of our knowledge, no acetylene protons have been previously observed to be deshielded to this extent. One reasonable explanation for this phenomenon is that it is the result of an anisotropic distortion by the metal carbene function of the cylindrical π symmetry normally observed for acetylenes.

Concern over the assignment of the structures of the complexes **2** and **5** was raised by a recent report in which the major product of the aminolysis of the (trimethylsilyl)acetylene ethoxy complex **6** with dimethylamine at room temperature was assigned as the allenylidene complex **8** rather than the acetylene complex **5a**.[2g] Furthermore, it was reported that the base cleavage of this product led to a compound characterized as the proto-desilylated allenylidene complex **9** rather than the parent acetylene complex **2a**. To address this issue, we repeated the reaction of **6** with dimethylamine at room temperature and found the major product to be identical in all respects with the compound that is obtained at low temperature and that was assigned the structure **5a**.[8] This is also consistent with the early observations by Fischer, who found that 1,2-addition of amines to acetylene carbene complexes is predominant over 1,4-addition at low temperatures.[2a,b] Suitable single crystals could be grown for the tungsten complex **5b**, and the results of an X-ray analysis of these crystals (Figure 1) provide support for the assignment of the acetylene structure to the trimethylsilyl derivatives **5**.[9] In order to verify this finding in the chromium case and also to establish that the proto-desilylation did not occur with amine migration, we prepared the ^{15}N-labeled derivatives **5c** and **2c** from 99% ^{15}N-labeled dimethylamine (Icon Services, Inc.) according to the procedure outlined in Scheme I.[19] The ^{13}C NMR spectrum of **5c** revealed that the nitrogen was coupled to the carbene carbon (δ 250.60, $J_{NC} = 5.5$ Hz) and not to either of the acetylene carbons (≡*C*—Si, δ 137.16; ≡*C*—C_{carb}, δ 104.27).[10] More informative was the ^{13}C NMR spectrum of the ^{15}N-labeled parent alkyne complex **2c**, from which it was learned that the nitrogen was coupled ($J_{NC} = 6.6$ Hz) only to the carbon at δ 251.46 and not to either of the carbons at δ 116.01 or δ 84.16. Since the proton in this molecule is coupled only to the carbons at δ 116.01 ($J_{CH} = 254$ Hz) and δ 84.16 ($^2J_{CH} = 49$ Hz), it is clear that the nitrogen and proton are on different carbons and thus the data are inconsistent with the assignment of this molecule as the structure **9**.[11,12]



$$(CO)_5Cr{=}C{=}C{=}C(NMe_2)(SiMe_3) \xrightarrow[Et_2O]{EtOH,\ EtONa} (CO)_5Cr{=}C{=}C{=}C(NMe_2)(H)$$

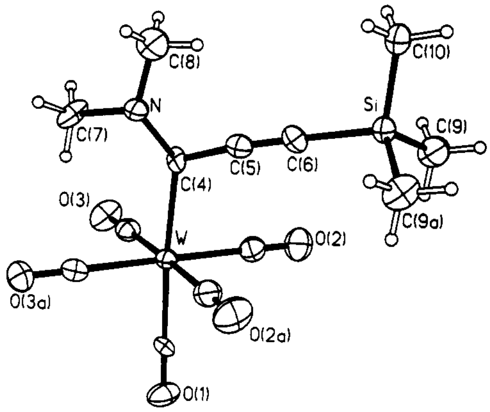


Figure 1. ORTEP drawing of **5b**.

All attempts at effecting Diels–Alder reactions of substituted acetylenic aminocarbene complexes have failed, but for steric reasons it was anticipated that the

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[8] The two major products from the reactions at 20 and −100 °C were identical by ^{1}H NMR and ^{13}C NMR; no depression was observed for a mixed melting point (53–56 °C), and a ^{13}C NMR spectrum of a mixture was homogeneous.

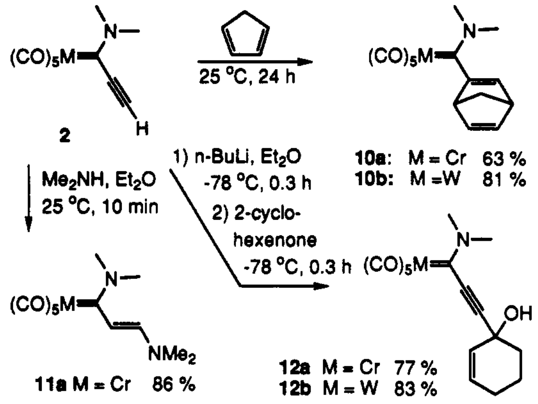
[9] Crystal data for **5b**: $C_{13}H_{15}NO_5SiW$, yellow block, fw 477.2, orthorhombic, *Pnma*, $a = 11.718$ (2) Å, $b = 10.404$ (2) Å, $c = 14.571$ (3) Å, $V = 1776.4$ (6) Å^{-3}, $Z = 4$, $D_{exptl} = 1.784$ g cm^{-3}, μ (Mo Kα) = 67.24 cm^{-1}, 2693 data collected, yielding 2484 independent and 1789 observed ($5\sigma F_o$) data, 2θ range 4–58°, $R(F) = 2.87\%$ $R(wF) = 3.58\%$, highest (and lowest) difference peaks 0.77 (−0.88) e Å^{-3}. Eleven of the sixteen independent non-hydrogen atoms reside on a crystallographic mirror plane without apparent disorder; this indicates that the assignment of the centrosymmetric space group is appropriate.

[10] The $^1J_{NC}$ values observed for **2c** and **5c** are similar to those reported for other aminocarbene complexes: Kreissl, F. R.; Meineke, E. W.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *108*, C29.

[11] Allylidene complexes of the type **8** are known: (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Hutter, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (b) Köhler, F. H.; Kalder, H. J.; Fischer, E. O. *J. Organomet. Chem.* **1976**, *113*, 11.

[12] After the review of this paper we learned that the structure of **5a** has been confirmed as the alkyne complex: Duetsch, M.; de Meijere, A.; personnal communication.

Scheme III



parent complexes may be more reactive.[1b,13] The Diels–Alder reactions of **2a** and **2b** with cyclopentadiene (neat) afforded after stirring for 24 h the expected carbene complexes in 63% yield for **10a** and 81% for **10b**. The same reaction of the TMS acetylene complex **5b** with cyclopentadiene gave no reaction even after stirring for 48 h at 25 °C. In other failed attempts, the chromium carbene complex derived from dimethylamine and propyne fails to react with Danishefsky's diene at room temperature for 5 days[13] and the tungsten complex derived from dimethylamine and phenylacetylene failed to react with cyclopentadiene at 130 °C.[1b] Like other terminal acetylenes, the alkyne complexes **2** were expected to be acidic, and in fact as the alkylation reactions with cyclohexenone demonstrate, the acetylenic anions can be generated without affecting the carbene complex functional group.[14] Unlike the anions of other aminocarbene complexes, the anions of **2** give only 1,2-addition products with cyclohexenone.[15] The ^{1}H NMR spectra of the crude reaction mixtures from these reactions indicate the presence of a substantial amount of the starting complex **2a** or **2b** (recovery of **2b** was 14% for a total mass balance of 97%). This was shown not to be the result of a reversible aldol reaction occurring during isolation in an experiment where complex **12a** was treated with 1 equiv of *n*-butyllithium at −78 °C and warmed to room temperature and quenched. None of the parent acetylene complex **2a** could be detected in the crude reaction mixture, and **12a** was recovered in 72% yield (99% recovery if the quench is at −78 °C). The possibility that the enone is deprotonated by the acetylene complex cannot be ruled out. Like other alkynylcarbene complexes, the complexes **2** will undergo Michael addition with dimethylamine, as illustrated for the reaction of **2a**.[2] The assignment of trans stereochemistry to the adduct **11a** is made on the basis of the comparison of the J_{HH} value of the vinyl group (J = 12.3 Hz) with those known for *cis*- and *trans*-enamines.[16]

The parent alkyne complexes **2** may be valuable as synthons for propriolic amides. For example, to our knowledge the Diels–Alder reactions of cyclopentadiene and simple propriolic amides are unknown and it has been reported that the diamide of acetylenedicarboxylic acid fails to condense with cyclopentadiene.[17] Furthermore, methods have been developed for the oxidative cleavage of aminocarbene complexes to the corresponding amides.[18] An evaluation of the potential of these parent acetylenic carbene complexes in synthetic strategic analysis is underway.

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Supplementary Material Available: Text giving experimental procedures and spectral data for compounds **2a**, **2b**, **5a**, **5b**, **10a**, **10b**, **11a**, **12a**, and **12b** and tables of X-ray data for compound **5b**, including fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and bond angles (14 pages). Ordering information is given on any current masthead page.

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[13] Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.*, in press.

[14] Certain propriolic esters can be deprotonated without self-condensation: Midland, M.; Tramontano, A.; Cable, J. R. *J. Org. Chem.* **1980**, *45*, 28.

[15] Anderson, B. A.; Wulff, W. D.; Rahm, A. *J. Am. Chem. Soc.*, submitted for publication.

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[17] Blomquist, A. T.; Winslow, E. C. *J. Org. Chem.* **1945**, *10*, 149.

[18] (a) Lukehart, C. M.; Zeile, J. V. *Inorg. Chim. Acta* **1976**, *17*, L7. (b) Anderson, B. A.; Toole, A. J.; Wulff, W. D. *J. Am. Chem. Soc.* **1989**, *111*, 5485. (c) Lluch, A.-M.; Jordi, L.; Sánchez-Baeza, F.; Ricart, S.; Camps, F.; Messeguer, A.; Moretó, J. M. *Tetrahedron Lett.* **1992**, *33*, 3021.

[19] The low yield of [^{15}N]-**2c** is a consequence of an incomplete reaction, since [^{15}N]-**5c** is recovered in 70% yield from the protodesilylation.