

Synthesis and X-ray structure of an unexpected bidentate allene–aminocarbene complex of tungsten

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Abstract

This contribution describes the results obtained from the alkylation reaction upon base-induced of propargyl bromide at nitrogen of Ferrocenyl-*N*-pentylaminocarbene of tungsten, chromium and molybdenum. This led to unexpected highly strained Fischer-type carbene complexes (**5a–c**) containing a bidentate allene–aminocarbene ligand. This is the first report of the η^2 -allene Fischer carbene complexes. The structure of **5a** was confirmed by an X-ray diffraction analysis.

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1. Introduction

The synthesis and applications of ferrocenyl-containing ligands is a rapidly expanding field since it has been found that they can be used in catalytic transformations of organic compounds when associated with a second transition metal. More interestingly, these new ligands provide activities, diastereo- and enantio-selectivities which are very often far beyond all those due to classical organic ligands and as a result, some of them have even reached industrial applications [1]. One way among many others to modify, and possibly introduce chirality in ferrocene complexes, would be to start from ferrocenyl carbene

complexes [2]. As part of a project directed to the synthesis and modifications of ferrocenyl carbene complexes by way of the chemistry developed in our Laboratories, we became involved in the preparation of ferrocenyl aminocarbene complexes tethered to double and triple bonds. Two methods [3] which have been extensively and successfully used in the chemistry of carbene complexes for the introduction of a double or triple bond-containing tether were tested: (1) the direct reaction of a primary or secondary amine with an alkoxycarbene complex; (2) the alkylation at nitrogen of an aminocarbene complex derived from a primary amine by means of an alkyl halide in the presence of a base. The purpose of this communication is to describe the results of the second approach, which however, did not lead to the desired complexes but to original, highly strained Fischer-type carbene complexes containing a bidentate allene–aminocarbene ligand.

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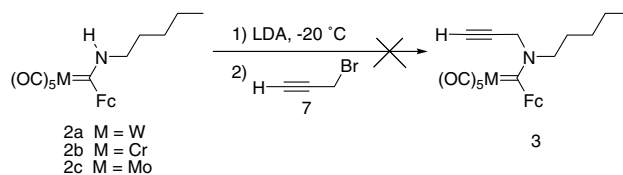
2. Results and discussion

The starting ferrocenylalkoxycarbene complexes **1a–c** (M = W, Cr, Mo) were prepared in good yield (62%, 85%, and 50%) by the use of improved methods [4] related to those already described in the literature [2]. These complexes led to the corresponding aminocarbene complexes **2a–c** in excellent yield (Scheme 1).

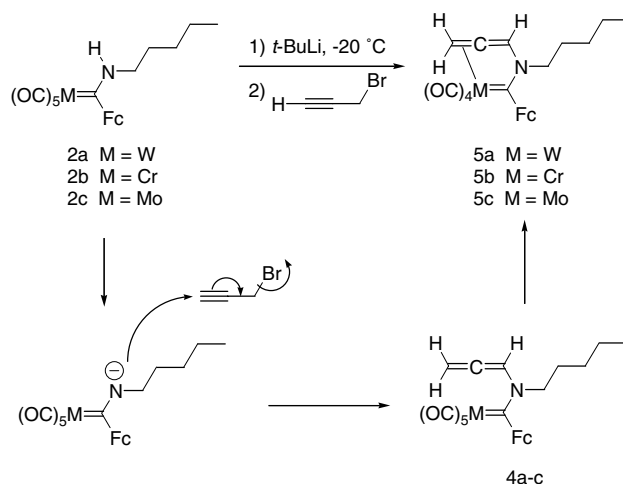
The interaction of complexes **1a–c** with propargylamine led, however, only to decomposition products [5,6]. Similarly, attempts to classically alkylate complexes **2a–c** at nitrogen upon LDA deprotonation followed by addition of propargyl bromide failed: no expected **3a–c** were isolated (Scheme 2).

When, however, *t*BuLi was used as a base, at 0 °C, the addition of propargyl bromide to **2a** led after 2 h at room temperature to a new complex which could be isolated and purified by alumina chromatography (decomposition took place on silica gel) giving a red solid in 39% yield (Scheme 3).

The mass spectrum agreed with the molecular formula of the expected complex **3a** having lost one CO group. The ¹³C NMR spectrum confirmed the presence of the carbene function, giving a signal at 246.4 ppm and of four signals at low field, 210.9, 209.7, 196.3 (2 C) and 189.7 for quaternary carbons (CO groups and quaternary carbon) and the absence of signals for the terminal triple bond. Particularly diagnostic were DEPT and HETCOR experiments since they confirmed the presence of a single N–CH₂ group, and signals for a methylene group at 8.03 (30.07) ppm. It appears therefore that an isomerization of the triple bond to an allene took place, and that this new functionality was coordinated to the metal as in **5a**. This structure could be assessed through single-crystal X-ray diffractometry (Fig. 1). The carbene carbon–tungsten bond, 2.207(7) Å is typical for aminocarbene complexes. So is the value of the C(5)–N(1) bond distance, being between a carbon–nitrogen single and double bond (1.358(8) Å). That the allene group is strongly bonded to the metal appears clearly in these data: the distances W(1)–C(17) and W(1)–C(18) are indeed significantly shorter in this complex than in related aminocarbene complexes bearing a coordinated double bond (2.187(12) vs. 2.431(5) Å [3d,e]. Since W(1)–C(16) is >3 Å there is, however, no interaction between the internal double bond of the allene with the



Scheme 2.



Scheme 3.

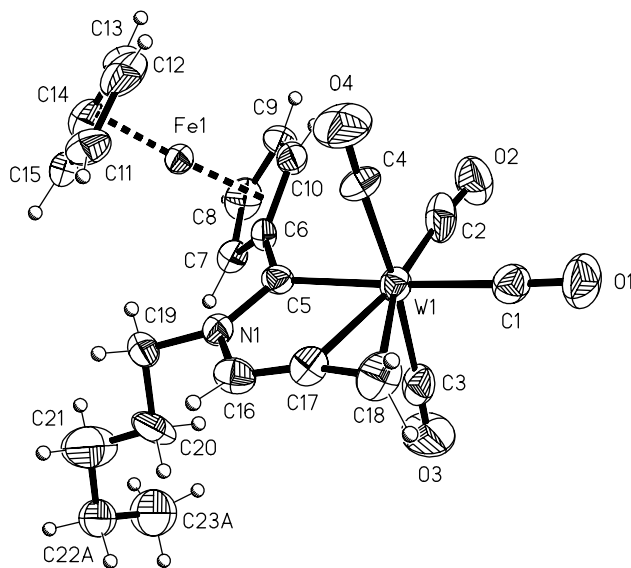
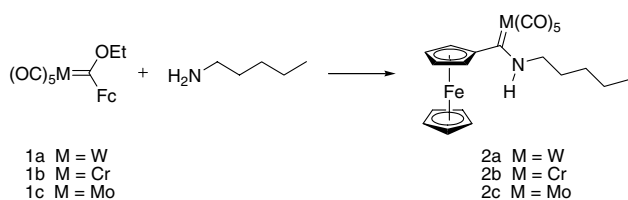


Fig. 1. X-ray crystal structure of complex **5a**. Ellipsoids are shown at the 30% probability level.



Scheme 1.

metal. As far as the geometry of the allenyl group is concerned, it deviates significantly from linearity since C(16)–C(17)–C(18) equals 161.5(12)°. Additionally, the alkyl chain presents disorder generating two conformers in 67/33 ratio, only the major contributors are shown in Fig. 1. The geometry of the ligand, and especially of the carbene function and the coordinated allene nicely

confirm the ^1H NMR data: since the nitrogen atom bears a partial positive charge, both the signals of the NCH_2 and NCH protons must be differently affected when compared to a free *N*-dialkylaminoallene: whereas the NCH_2 and the NCH protons are deshielded, due to the partial positive charge on nitrogen (8.02 and 4.62 vs. 6.06 and 2.88 ppm), the methylene protons of the terminal double bond are shielded (4.07 vs. 5.23 ppm). Complexes **2b,c** behaved similarly and led to the allene aminocarbene complexes **5b,c** in, respectively, 31% and 28% as red solids.

As far as the mechanism of the formation of **5a–c** from **2a–c** is concerned, it is obvious that *t*BuLi can promote both the direct alkylation and the alkyne to allene rearrangement, the coordination to the metal in **4a** being then concomitant with the isomerization [7].

To the best of our knowledge, complexes **5a–c** constitute original allene–carbene complexes of the Fischer-type, although the preparation and structure of special allenyl carbene complexes of ruthenium in which the allene group is directly conjugated with the carbene function have recently been disclosed [8]. Alkene–carbene complexes as well as alkyne–carbene complexes of the Fischer-type are well documented [9]. The present complexes **5a–c** fill thus the gap between these two types of structures. Applications of these highly strained complexes as initiators for alkene and alkyne insertion reactions are in progress.

3. Experimental

3.1. Chemical and methods

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL 300 spectrometer, using CDCl_3 as solvent and TMS as internal reference. IR spectra were performed on a Perkin–Elmer 283 B or 1420 spectrometer. The FAB spectra were obtained on a JEOL JMS SX 102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using a 6 keV Xenon atoms. The electronic impact (EI) ionization mass spectra were acquired on a JEOL JMS-AX505 HA Mass spectrometer operated in the positive ion mode. The acquisition conditions were ion source temperature 230 °C, ionization energy 70 eV, emission current 0.14 μA and ionization current 100 μA . Mass measurements in FAB are performed at 10,000 resolution using electrical field scans and the polyethylene glycol ions as reference material. Melting points were measured using a Mel-Temp II apparatus and are uncorrected. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under nitrogen atmosphere in carefully dried glassware. THF was distilled from sodium–benzophenone under argon or nitrogen atmosphere. Column

chromatography was performed with Merck silica gel (70–230 mesh) using ethyl acetate:hexane in different ratios as eluent.

3.1.1. Preparation of ferrocenylated group 6 metal Fischer-type carbenes

The preparation of ferrocenylated group 6 metal Fischer-type carbenes were carried out using the methodology previously described elsewhere [4].

3.1.2. Preparation of pentylaminocarbenes

3.1.2.1. [(Ferrocenyl)(pentylamine)methylidene]pentacarbonyltungsten (0) (**2a**). To a solution of **1a** (1 g, 2.29 mmol) in anhydrous ether was added at room temperature 0.4 ml of pentylamine (5.17 mmol), then the reaction was stirred for overnight. The solvent was evaporated under vacuum and then the product was purified by chromatography on alumina using hexane as the eluent to give 1.00 g of a orange solid (94%). ^1H NMR (CDCl_3): δ 9.02 (s, 1H, NH), 4.54 (br s, 2H, subst Cp), 4.50 (br s, 2H, subst Cp), 4.20 (s, 5H, Cp), 3.92 (m, 2H, NCH_2), 1.83 (m, 2H, NCH_2CH_2), 1.49 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.99 (m, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 249.6 (C=W), 203.4 (WCO), 198.7 (WCO), 97.3 (C_{ipso} , fc), 70.9 (CH, subst Cp), 69.7 (Cp), 69.6 (CH, subst Cp), 55.2 (NCH_2), 29.6 (NCH_2CH_2), 29.0 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.5 (CH_2CH_3), 14.0 (CH_3). IR (CHCl_3): ν/cm^{-1} 2053 (CO), 1961 (CO). MS (EI $^+$): m/z 607 (M^+). HR-MS FAB $^+$ $\text{C}_{21}\text{H}_{21}\text{FeNO}_5\text{W}$: Calc. 607.0279. Found: 607.0296%.

3.1.2.2. [(Ferrocenyl)(pentylamine)methylidene]pentacarbonylchromium (0) (**2b**). The complex **2b** was obtained by a similar procedure, like a orange solid (93%). ^1H NMR (CDCl_3): δ 9.50 (s, 1H, NH), 4.45 (br s, 4H, subst Cp), 4.19 (s, 5H, Cp), 4.05 (m, 2H, NCH_2), 1.88 (m, 2H, NCH_2CH_2), 1.51 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.0 (m, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 270.5 (C=Cr), 223.6 (CrCO), 217.8 (CrCO), 99.4 (C_{ipso} , fc), 70.1 (C H, subst Cp), 69.4 (Cp), 68.4 (CH, subst Cp), 52.9 (NCH_2), 29.6 (NCH_2CH_2), 29.1 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.5 (CH_2CH_3), 14.0 (CH_3). IR (KBr): ν/cm^{-1} 2053 (CO), 1927 (CO). MS (FAB $^+$): m/z 475 (M^+). HR-MS FAB $^+$ $\text{C}_{21}\text{H}_{21}\text{CrFeNO}_5$: Calc. 475.0174. Found: 475.0191%.

3.1.2.3. [(Ferrocenyl)(pentylamine)methylidene]pentacarbonylmolybdenum (0) (**2c**). The complex **2c** was obtained by a similar procedure, like a orange solid (94%). ^1H NMR (CDCl_3): δ 9.10 (s, 1H, NH), 4.53 (br s, 2H, subst Cp), 4.50 (br s, 2H, subst Cp), 4.20 (s, 5H, Cp), 4.0 (m, 2H, NCH_2), 1.82 (m, 2H, NCH_2CH_2), 1.48 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.0 (m, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 261.5 (C=Mo), 213.6 (MoCO), 207.0 (MoCO), 96.0 (C_{ipso} , fc), 70.8 (CH, subst Cp), 69.6 (Cp), 69.2 (CH, subst Cp), 54.5 (NCH_2), 29.6 (NCH_2CH_2),

Table 1
Selected bond lengths [Å] and selected bond angles [°] for **5a**

Selected bond lengths [Å]	
W1–C17	1.979(9)
N1–C16	1.429(10)
W1–C18	2.374(10)
C5–C6	1.455(9)
W1–C5	2.207(7)
C16–C17	1.301(15)
N1–C5	1.358(8)
C17–C18	1.353(15)
Selected bond angles [°]	
C2–W1–C17	161.9(4)
C17–W1–C18	34.2(4)
C5–N1–C19	130.4(7)
C18–C17–W1	80.5(7)
C4–W1–C17	161.9(4)
C5–W1–C18	106.7(3)
N1–C5–W1	116.9(5)
C17–C18–W1	65.3(6)
C17–W1–C5	72.5(4)
C5–N1–C16	114.2(7)
C16–C17–18	161.5(12)
C2–W1–C18	163.4(4)
C5–N1–C16	114.2(7)
C16–C17–W1	117.9(9)

Table 2
Crystal data and structure refinement for **5a**

5a	
Formula	C ₂₃ H ₂₃ FeNO ₄ W
Formula weight (g mol ⁻¹)	617.12
Crystal size (mm)	0.338 × 0.098 × 0.036
Color	Red
Crystal system	Monoclinic
Space group	P2 ₁
Unit cell dimensions	
<i>a</i> (Å)	10.0468(7)
<i>b</i> (Å)	11.5523(8)
<i>c</i> (Å)	10.6413(7)
α (°)	90
β (°)	112.463(1)
γ (°)	90
<i>V</i> (Å ³)	1141.36(13)
<i>Z</i>	2
<i>D</i> _{calc.} (g cm ⁻³)	1.796
Number of collected reflections	9865
Number of independent reflections (<i>R</i> _{int})	5125 unique, <i>R</i> _{int} = 0.063
Absorption correction method	Analytical: Face-indexes
Maximum and minimum transmission	0.8082 and 0.3091
Data/parameters	5125/280
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.0646
<i>R</i> Indices (all data)	<i>R</i> ₁ = 0.0542, <i>wR</i> ₂ = 0.0667
Goodness-of-fit on <i>F</i> ²	0.960

29.0 (CH₂CH₂CH₃), 22.5 (CH₂CH₃), 14.0 (CH₃). IR (CHCl₃): ν/cm⁻¹ 2061 (CO), 1977 (CO), 1931 (CO). MS (FAB⁺): *m/z* 521 (M⁺). HR-MS FAB⁺ C₂₁H₂₁FeMoNO₅: Calc. 520.9823. Found: 520.9812%.

3.1.3. Preparation of allenylaminocarbenes

3.1.3.1. [(Ferrocenyl)(*N*-allenyl-*N*-pentylamine)methylidene]pentacarbonylchromium (0) (**5a**). To a solution of **2a** (0.3 g, 0.63 mmol) in anhydrous THF was added at 0 °C 0.5 ml of a 1.7 M solution of *t*-butyllithium in pentane (0.85 mmol), the mixture was stirred 15 min. at this temperature then a solution of propargyl bromide (0.1 ml, 1.12 mmol in 10 ml of THF) was added by canula. The solution was stirred 3 h at room temperature. The solvent was removed under vacuum; the mixture was purified by chromatography on alumina using hexane as eluent to give 117 mg of a red solid (39%) and 120 mg of recovered starting material. ¹H NMR (CDCl₃): δ 8.03 (t, *J* = 2.76 Hz, 1H, NCH=C), 4.62 (t, 2H, NCH₂), 4.56 (br s, 4H, subst Cp), 4.23 (s, 5H, Cp), 4.07 (d, *J* = 2.76 Hz, 2H, C=CH₂) 1.87 (m, 2H, NCH₂CH₂), 1.44 (m, 4H, CH₂CH₂CH₃), 0.97 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 246.4 (C=W), 210.9 (WCO), 209.7 (WCO), 196.3 (WCO), 189.7 (C=CH₂), 123.4 (NCH=C), 93.3 (C_{ipso}, fc), 72.8 (CH, subst Cp), 70.0 (Cp), 53.2 (NCH₂), 31.4 (NCH₂CH₂), 30.1 (C=CH₂), 29.2 (CH₂CH₂CH₃), 22.6 (CH₂CH₃), 14.1 (CH₃). IR (KBr): ν/cm⁻¹ 2053 (CO), 1927 (CO). MS (FAB⁺): *m/z* 617 (M⁺). HR-MS FAB⁺ C₂₃H₂₃FeNO₄W: Calc. 617.0486. Found: 617.0466%.

3.1.3.2. [(Ferrocenyl)(*N*-allenyl-*N*-pentylamine)methylidene]pentacarbonylchromium (0) (**5b**). The complex **5b** was obtained by a similar procedure, like a red solid (31.5%) and 130 mg of starting material. ¹H NMR (CDCl₃): δ 7.68 (br s, 1H, NCH=C), 4.70 (t, 2H, NCH₂), 4.49 (br s, 2H, subst Cp), 4.44 (br s, 2H, subst Cp), 4.15 (s, 5H, Cp), 3.68 (d, 2H, C=CH₂) 1.78 (m, 2H, NCH₂CH₂), 1.40 (m, 4H, CH₂CH₂CH₃), 0.93 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 275.4 (C=Cr), 234.0 (CrCO), 227.4 (CrCO), 214.2 (CrCO), 200.2 (C=CH₂), 122 (NCH=C), 91.8 (C_{ipso}, fc), 71.6 (CH, subst Cp), 70.0 (Cp), 69.8 (CH, subst Cp), 53.4 (NCH₂), 39.4 (C=CH₂), 31.5 (NCH₂CH₂), 29.8 (CH₂CH₂CH₃), 22.6 (CH₂CH₃), 14.1 (CH₃). IR (CHCl₃): ν/cm⁻¹ 2021 (CO), 1918 (CO). MS (FAB⁺): *m/z* 457 (M⁺-28). HR-MS FAB⁺ C₂₃H₂₃CrFeNO₄: Calc. 485.0382. Found: 485.0369%.

3.1.3.3. [(Ferrocenyl)(*N*-allenyl-*N*-pentylamine)methylidene]pentacarbonylmolybdenum (0) (**5c**). The complex **5c** was obtained by a similar procedure, like a red solid (28%) and 80 mg of starting material. ¹H NMR (CDCl₃): δ 7.69 (s, 1H, NCH=C), 4.62 (m, 2H, NCH₂), 4.56 (br s, 4H, subst Cp), 4.23 (s, 5H, Cp), 3.92 (br s, 2H, C=CH₂) 1.87 (m, 2H, NCH₂CH₂), 1.44 (m, 4H, CH₂CH₂CH₃), 0.88 (m, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 265.0 (C=Mo), 221.3 (MoCO), 203.9 (MoCO), 194.4 (C=CH₂), 122.4 (NCH=C), 91.5 (C_{ipso}, fc), 72.5 (CH, subst Cp), 70.1 (CH, subst Cp), 69.9 (Cp), 53.3 (NCH₂), 36.0 (C=CH₂), 31.3

(NCH₂CH₂), 29.1 (CH₂CH₂CH₃), 22.5 (CH₂CH₃), 14.0 (CH₃). IR (KBr): ν/cm^{-1} 2053 (CO), 1927 (CO). MS (FAB⁺): m/z 532 (M⁺). HR-MS FAB⁺ C₂₃H₂₃FeMoNO₄: Calc. 531.0031. Found: 531.0007%.

3.1.3.4. X-ray crystal structure determinations for complex 5a. Data collection and refinement parameters are summarized in Table 2. X-ray crystal data for **5a**: Red single crystals were obtained by slow cooling a saturated solution CH₂Cl₂–hexane solution to –30 °C. A total of 9865 reflections (5125 unique, $R_{\text{int}} = 0.063$) were collected on a Bruker Smart Apex CCD diffractometer with Mo K α radiation, $\lambda = 0.71073$ Å. Data were corrected for Lorentz and polarization effect and analytical absorption corrections based on face index were applied. The structure was solved by direct methods [10] and refined using SHELXL97 [11] software package in full-matrix least squares on F^2 using all data with the all non-hydrogen atoms assigned anisotropic displacement parameters and hydrogens atoms bound to carbon atoms inserted at calculated position with isotropic temperature factor 1.2 times the U_{iso} of the parent carbon atom. Selected bond lengths and bond angles are shown in Table 1.

4. Supporting information available

Crystallographic data or the structural analysis has been deposited with the Cambridge Crystallographic Centre CCDC No. 252452 for complex **5a**. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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