

Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>



Biscarbene complexes from the reactions of *O*-ethyl lactim and 1-alkynyl Fischer carbene complexes of chromium and tungsten

Zhaoyan Zheng^a, Zhengkun Yu^{a,*}, Liandi Wang^a, Wei He^a, Zishuang Liu^a, Xiuwen Han^b

^a Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China

Received 19 June 2006; received in revised form 9 August 2006; accepted 17 August 2006

Available online 30 August 2006

Abstract

Reactions of *O*-ethyl lactim $\sim(\text{CH}_2)_3\text{-N}=\text{C}(\text{OEt})\sim$ with 1-alkynyl Fischer carbene complexes $(\text{OC})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ ($\text{M} = \text{Cr}, \text{W}$) afforded biscarbene complexes with an azabicyclo[3.2.0]heptene core. Under a nitrogen atmosphere, the resultant chromium biscarbene complex gave a SiO_2 -promoted rearrangement complex in 86% yield. Thermal annelation of the rearrangement product followed by hydrolysis over SiO_2 formed a cyclopentenone derivative. A cyclopentadiene derivative was obtained as a rare example of intermediate Fischer carbene species, suggesting a possible reaction pathway for the thermal annelation of the rearrangement complex. Stepwise oxidation of the chromium biscarbene complexes with an azabicyclo[3.2.0]heptene core with pyridine-*N*-oxide (PNO) under mild controlled conditions generated partially and completely demetalated carbonyl products, respectively. The key carbene complexes and demetalated compounds were structurally characterized by X-ray crystallographic studies.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fischer Carbene; *O*-Ethyl lactim; Biscarbene; Chromium; Tungsten

1. Introduction

Fischer monocarbene complexes of group VI have been extensively studied due to their versatile applications in organic synthesis [1] since they were first reported by Fischer and Maasböl [2]. However, Fischer poly- or biscarbene complexes were not paid any attention over a long period [3]. Until recently, limited work has been directed in this aspect [4]. Azabicyclic[4.2.0]octadiene biscarbene complexes of tungsten [5], azabicyclic[n.2.0]alkenyl biscarbene complexes of chromium and tungsten and related reactions of the tungsten biscarbene complexes [6] were reported, respectively. Unusually stable biscarbene complexes were obtained from the reactions of 2-alkenyl-2-oxazoline and 1-alkynyl Fischer carbene complexes of chromium and tungsten from our laboratories [7a]. As

building blocks or versatile reagents in organic synthesis, Fischer chromium monocarbene complexes usually exhibit reactivity higher than their tungsten analogues that they have been employed in a lot of synthetic reactions [1], and Fischer tungsten biscarbene complexes demonstrate reactivity higher than their chromium analogues [4].

Formation of a biscarbene complex is usually attributed to the capability of the newly formed intermediate monocarbene species to proceed a consecutive reaction. In principle, the reactivity of a Fischer biscarbene complex depends on both the metal center and the adjacent electronic and steric environment around the $\text{M}=\text{C}$ bond in the complex. Probing into the formation mechanism of a Fischer biscarbene complex and reactivity of the $\text{M}=\text{C}$ bonds in it are two major aspects in exploration of Fischer biscarbene chemistry. In a previous paper co-authored by Aumann and Yu (one of the authors of this paper), et al. [6], it was reported that reactions of 1-alkynyl Fischer carbene complexes $(\text{OC})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$ (**1**) ($\text{M} = \text{Cr}$ (**a**),

* Corresponding author. Tel./fax: +86 411 84379227.

E-mail address: zkuyu@dicp.ac.cn (Z.K. Yu).

W (**b**)) with *O*-methyl lactims $\sim(\text{CH}_2)_n\text{-N}=\text{C}(\text{OCH}_3)\sim$ ($n = 3, 4$) afforded biscarbene complexes of type **3** (Scheme 1), in which the stability of a tungsten biscarbene complex over silica gel was studied, while further investigation of its chromium analogues failed due to complicated transformations of the chromium biscarbene complex under the same conditions. Thus, a more detailed and controlled study has been expected to probe into the formation and reactivity of complexes of type **3**. Herein, we report synthesis of biscarbene complexes **3a,b** from the reactions of **1** and *O*-ethyl lactim $\sim(\text{CH}_2)_3\text{-N}=\text{C}(\text{OEt})\sim$ (**2**), and reactions of the Fischer chromium biscarbene complex **3a** under controlled conditions. X-ray crystal structures of the key Fischer carbene complexes including a rare intermediate carbene complex were determined.

2. Results and discussion

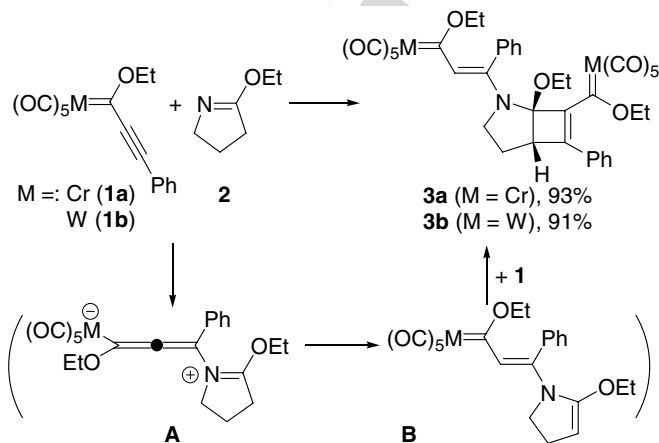
2.1. Synthesis of 2-Azabicyclo[3.2.0]heptene biscarbene complexes **3**

O-Ethyl lactim (**2**) instead of *O*-methyl lactim $\sim(\text{CH}_2)_n\text{-N}=\text{C}(\text{OMe})\sim$ ($n = 3, 4$) was employed to react with 1-alkynyl Fischer carbene complexes in a 1:2 molar ratio in pentane at ambient temperature, affording biscarbene complexes **3** in 91–93% yields (Scheme 1). The biscarbene products were conveniently collected as dark brown precipitates by centrifugation from the reaction mixture. It should be noted that ethyl as a group bulkier than methyl was introduced to the lactim molecule to increase the steric hindrance around the [3.2.0]heptene moiety and expectedly adjust the reactivity of the newly formed complexes. Excess of **2** did not affect the formation of **3**. Monocarbene complexes of type **B** were actually isolated as the major products from the reactions of **1b** and seven- or eight-membered *O*-methyl lactims [6], revealing that the steric parameters from the lactims obviously affect formation of the carbene complex products. The reactions of **1** and **2** presumably proceed *via* the intermediate species **A** and **B** (Scheme 1), suggesting that the [2 + 2] cycloaddition of **B**

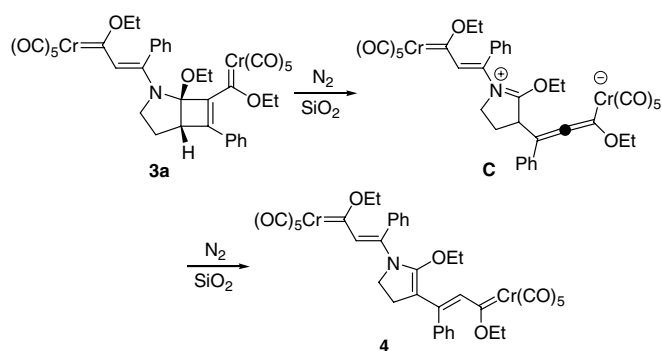
with another molecule of **1** is faster than the first step transformation. Because species **A** could not be isolated under the stated conditions, formation of **B** from **A** *via* 1,5-H shift is considered to be spontaneous. It is noteworthy that the NMR of **3b** was not successfully measured due to the broadening of its NMR signals.

2.2. Rearrangement of chromium biscarbene complex **3a**

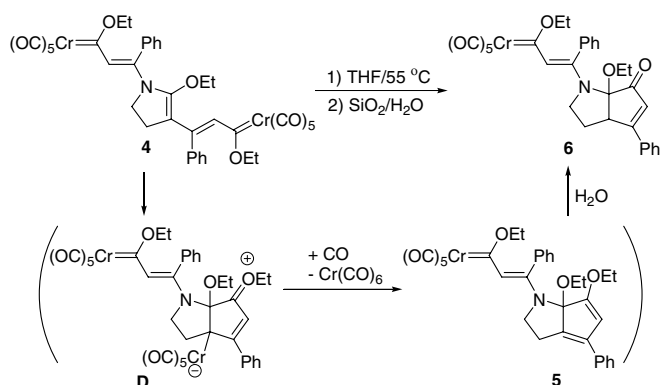
Rearrangement of a tungsten biscarbene complex of type **3** occurred over silica gel to give compound of type **4** in 21% yield [6], and isomerization of another tungsten biscarbene complex was also observed [5]. The chromium biscarbene complex, *i.e.*, **3a**, was applied for a comparison study with its tungsten analogue [6]. Complexes **3a,b** are stable in the solid state. An attempt to separate **3a** from the reaction mixture by flash silica gel column chromatography resulted in a dark blue fraction and some complicated decomposition mixture. It was found that the dark blue fraction, *i.e.*, **4**, is very air-, moisture-, and heat-sensitive. Much effort was made to isolate this dark blue compound under the usual column chromatography conditions, but no success had been achieved. An alternative isolation of this dark blue fraction by flash column chromatography was carried out over a short pad of silica gel under a nitrogen atmosphere in which a receiving flask cooled with an ice-water bath was used (Scheme 2). Eventually, complex **4** was obtained as a dark blue solid in 86% yield. Thus, an inert atmosphere is helpful for isolation of air-, moisture-, and heat-sensitive Fischer carbene complexes, which has not been reported before [1]. Due to the unstability and broadening of its NMR signals, the ^{13}C NMR spectra of **4** was not successfully measured. Recrystallization of **4** at low temperature afforded a decomposition mixture over a period of two weeks and single crystals suitable for its X-ray crystal structure determination were not obtained. In one of many trials a few pieces of single crystals were picked out from the recrystallization residue of complex **4** at -25°C . Unexpectedly, the intermediate complex **5** was structurally revealed from a low precision X-ray crystallographic determination (Scheme 3). Complex **5** is a rare example of cyclopentadiene derivatives activated by two ethoxy groups. It was



Scheme 1. Synthesis of biscarbene complexes **3**.



Scheme 2. Rearrangement of complex **3a**.



Scheme 3. Thermal annelation of complex 4.

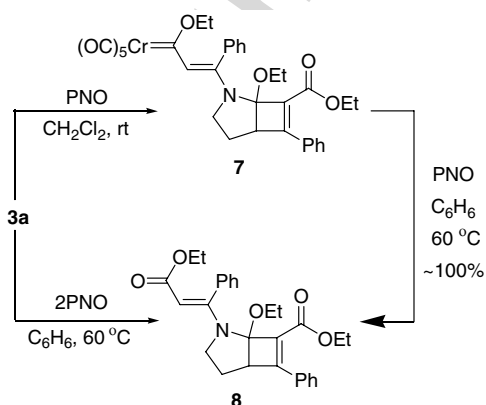
failed to collect enough amount of **5** for its full characterization.

2.3. Thermal annelation of complex 4

In the paper co-authored by Aumann and Yu et al., a tungsten biscarbene complex of type **3** was considered to undergo annelation-hydrolysis, affording a monocarbene product of type **6** (Scheme 3) and a ring-opening hydrolysis biscarbene product *via* an intermediate species of type **4** [6]. In the present paper, a solution of complex **4** in THF was heated at 55 °C until the biscarbene complex was completely consumed, isolation with flash silica gel column chromatography gave the annelation-hydrolysis product, i.e., complex **6**, in 41% yield. Because both the monocarbene complexes **5** and **6** were structurally confirmed, the annelation pathway of complex **4** is reasonably proposed in Scheme 3. Spontaneous monitoring of the annelation reaction in C₆D₆ by NMR determinations failed to give useful information regarding the formation of **6**.

2.4. Stepwise oxidation of complex 3a

Oxidation of complex **3a** with pyridine-*N*-oxide (PNO) under mild conditions afforded stepwise demetalation products, i.e., monocarbene complex **7** and diester **8**,



Scheme 4. Stepwise oxidation of complex 3a.

respectively (Scheme 4). With 1.0 equiv of PNO in CH₂Cl₂ at ambient temperature, the Cr=C unit attached to the cyclobutenyl ring was oxidatively demetalated to form the monocarbene complex **7**, while the Cr=C additionally stabilized by the vinylogous nitrogen stayed unchanged. Under relatively harsh conditions, e.g., 60 °C in benzene, **3a** was completely demetalated to the diester **8** with 2.0 equiv of PNO. Complex **7** can also be quantitatively demetalated to **8**. Oxidation seems to be the most convenient method to transform Fischer carbene complexes to organic products. The present stepwise oxidation protocol provides an alternative route to poly-, bis-, or monocarbene complexes [7].

2.5. X-ray crystal structures of compounds 3b, 6, 7, and 8

The solid-state crystal structures of compounds **3b**, **5**, **6**, **7**, and **8** were determined by X-ray crystallographic study, but only a low-precision X-ray crystal structure was revealed for complex **5**. The crystallographic data are summarized in Table 1, and selected bond distances and angles in Table 2. Both the metal units in **3b** are arranged exo with respect to the envelope-shaped 2-azabicyclo[3.2.0]heptene core (Fig. 1) with the different W–C bond lengths (W(1)–C(6), 2.239(10) Å; W(2)–C(32), 2.159(9) Å). The C(7)–C(8) bond distance (1.406(15) Å) in **3b** is much longer than that (1.357(14) Å) of its tungsten analogue resulted from the reaction of **1b** and *O*-methyl lactim [6] and between a typical C=C bond length and a typical C–C bond length. Lengthening of the C(7)–C(8) bond in **3b** is presumably attributed to the introduction of an ethoxy instead of a methoxy [6] to a bridge carbon atom of the azabicyclo[3.2.0]heptene core, resulting in bigger steric hindrance around this C=C bond. Although the weighted *R*-values are not very good for the crystallographic data of **5** due to the low quality of the single crystal used for X-ray crystal structural determination, the preliminary structural analysis of **5** [8] reveals a very rare example of an unstable Fischer carbene complex. The molecular structure of complex **6** is partially similar to that of **3b** (Figs. 1 and 2), and their corresponding bond distances and angles are very similar (Table 2). The obvious structural difference between **3b** and **6** is the presence of a cyclopentenone moiety in **6**, and the C(7)–C(8) bond distance (1.385(4) Å) in **6** is typical of a C=C bond due to the release of steric hindrance by removal of a Cr(CO)₅ unit from **3a**. The molecular structure of complex **7** is similar to that of its tungsten biscarbene precursor **3b** with bond distances of Cr–C(6) (2.093(4) Å) and C(7)–C(8) (1.380(5) Å), and their structural difference is that the Cr(CO)₅ moiety attached to the cyclobutenyl ring in **3a** was replaced by an oxygen atom in **7** (Fig. 3). Compound **8** is a diester which exhibits a molecular structure similar to that of **7** with two typical C–C double bonds, i.e., C(2)–C(3) (1.359(3) Å) and C(18)–C(19) (1.336(4) Å) (Fig. 4). In all these compounds, the [3.2.0]heptene core keeps unchanged.

Table 1
Crystal data and refinement details for compounds **3b**, **6–8**

	3b	6	7	8
Empirical formula	C ₃₈ H ₃₁ NO ₁₃ W ₂	C ₃₁ H ₂₇ NO ₈ Cr	C ₃₃ H ₃₁ NO ₉ Cr	C ₂₈ H ₃₁ NO ₅
Formula weight	1077.34	593.54	637.59	461.54
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> 2(1)2(1)2(1)
<i>a</i> (Å)	21.2182(18)	9.9064(10)	13.3812(9)	7.9691(6)
<i>b</i> (Å)	11.1149(9)	11.2578(10)	16.3433(11)	10.7420(9)
<i>c</i> (Å)	18.4145(16)	13.9615(14)	29.677(2)	29.440(2)
α (°)	90	84.347(2)	90	90
β (°)	114.8310(10)	76.954(2)	90	90
γ (°)	90	70.678(2)	90	90
<i>V</i> (Å ³)	3941.3(6)	1430.9(2)	6490.1(8)	2520.2(3)
<i>Z</i>	4	2	8	4
<i>D</i> _c (g cm ⁻³)	1.816	1.378	1.305	1.216
μ (mm ⁻¹)	5.896	0.452	0.406	0.083
<i>F</i> (000)	2072	616	2656	984
Crystal size (mm ³)	0.38 × 0.22 × 0.11	0.25 × 0.24 × 0.04	0.52 × 0.14 × 0.06	0.51 × 0.38 × 0.09
θ Limits (°)	2.12–27.50	1.50–27.0 0	2.05–26.00	2.02–27.00
No. of data collected	22945	8541	34041	14922
No. of unique data	8856	6096	6373	5498
<i>R</i> _{int}	0.1964	0.0461	0.1340	0.1001
No. of data observed with <i>I</i> > 2 σ (<i>I</i>)	5184	3279	3216	3743
No. of refined parameters	491	372	400	322
Goodness-of-fit on <i>F</i> ²	0.848	0.879	0.978	0.967
<i>R</i> (obsd. data/all data)	0.0692/0.1010	0.0567/0.1067	0.0718/0.1456	0.0588/0.0854
<i>wR</i> ₂ (obsd. data/all data)	0.1404/0.1540	0.1010/0.1195	0.1669/0.1992	0.1353/0.1488
Residual ρ _{max} (e Å ⁻³)	2.590 (–3.034)	0.309 (–0.292)	0.412 (–0.410)	0.319 (–0.147)

Table 2
Selected bond lengths (Å) and angles (°) for compounds **3b**, **6–8**

Complex 3b					
W(1)–C(6)	2.239(10)	W(2)–C(32)	2.159(9)	C(6)–C(7)	1.446(14)
C(7)–C(8)	1.406(15)	C(11)–C(12)	1.566(15)	C(13)–C(14)	1.380(14)
C(13)–C(32)	1.432(15)				
W(1)–C(6)–C(7)	120.4(6)	W(2)–C(32)–C(13)	121.9(6)		
C(11)–C(12)–C(13)	86.0(7)	C(11)–C(14)–C(13)	95.9(8)		
Complex 6					
Cr–C(6)	2.102(3)	C(6)–C(7)	1.425(4)	C(7)–C(8)	1.385(4)
C(11)–C(12)	1.544(4)	C(12)–C(13)	1.555(4)	C(11)–C(15)	1.498(4)
C(13)–C(14)	1.443(4)	C(14)–C(15)	1.333(4)		
Cr–C(6)–C(7)	120.2(2)	C(12)–C(11)–C(15)	105.2(2)		
C(12)–C(13)–C(14)	106.8(4)				
Complex 7					
Cr–C(6)	2.093(4)	C(6)–C(7)	1.434(6)	C(7)–C(8)	1.380(5)
C(11)–C(12)	1.565(5)	C(12)–C(13)	1.515(6)	C(13)–C(14)	1.353(5)
C(11)–C(14)	1.526(6)				
Cr–C(6)–C(7)	121.6(3)	C(11)–C(12)–C(13)	86.7(3)		
C(11)–C(14)–C(13)	94.3(3)				
Diester 8					
C(1)–C(2)	1.522(3)	C(2)–C(3)	1.359(3)	C(3)–C(4)	1.506(4)
C(1)–C(4)	1.567(3)	C(2)–C(9)	1.452(4)	C(18)–C(19)	1.336(4)
C(19)–C(20)	1.455(3)				
C(2)–C(1)–C(4)	86.32(17)	C(2)–C(3)–C(4)	94.9(2)		
C(18)–C(19)–C(20)	123.8(3)				

2.6. Summary

In summary, biscarbene complexes were prepared from the reactions of *O*-ethyl lactim $\sim(\text{CH}_2)_3\text{-N}=\text{C}(\text{OEt})\sim$ with

1-alkynyl Fischer carbene complexes $(\text{OC})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CPh}$. Rearrangement, annulation and oxidation of the chromium biscarbene complex were pursued to study its reactivity and reaction mechanism. The present results

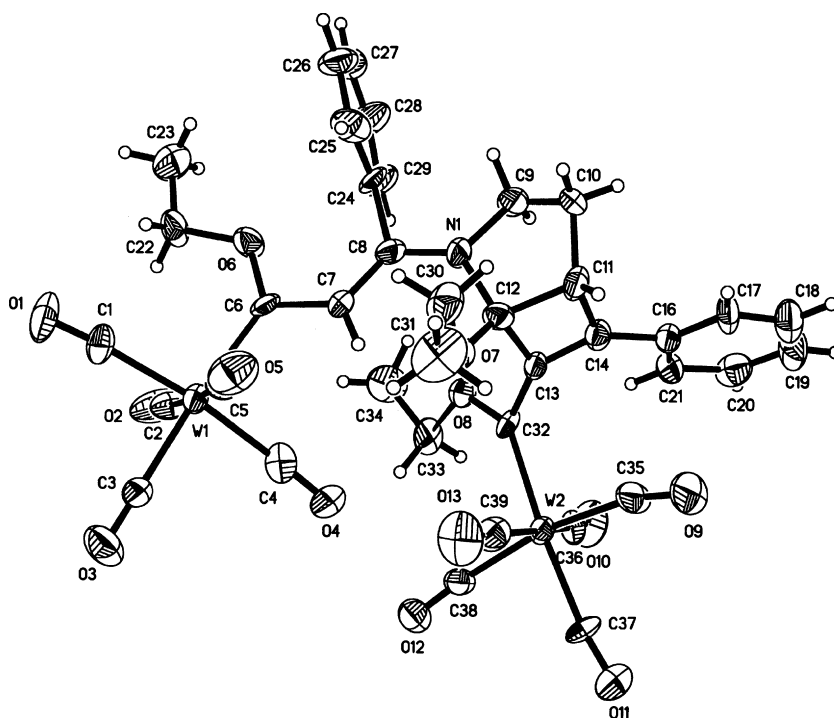


Fig. 1. Perspective view of complex 3b.

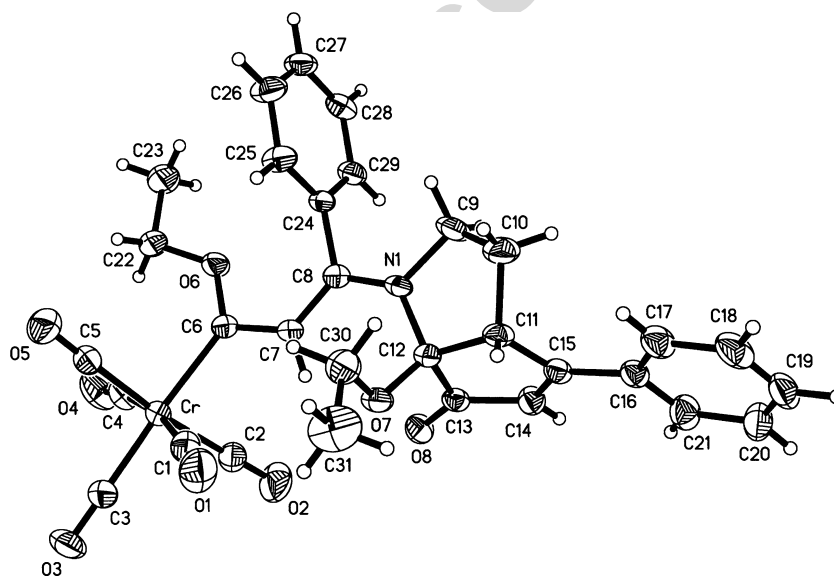


Fig. 2. Perspective view of complex 6.

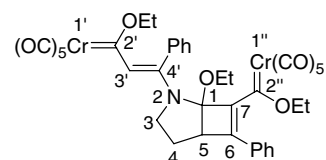
suggest that it is possible to collect reactive or unstable Fischer carbene complexes in decent yields under an inert atmosphere and also possible to isolate intermediate Fischer carbene species under controlled conditions.

3. Experimental

3.1. General considerations

Reaction solvents were dried and distilled prior to use by the literature methods. Chemicals were used as received. ^1H

and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or CDCl_3 ($\delta(^1\text{H})$, 7.26 ppm; $\delta(^{13}\text{C})$, 77.16 ppm). IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer.



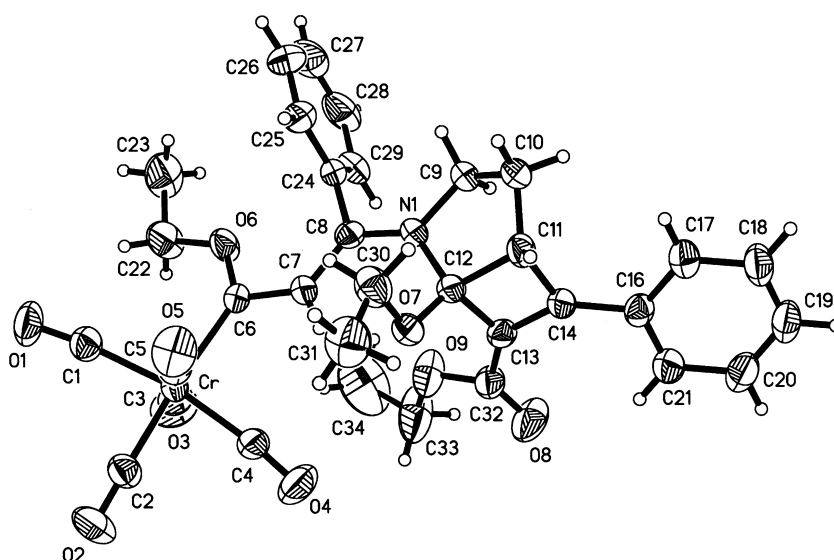


Fig. 3. Perspective view of complex 7.

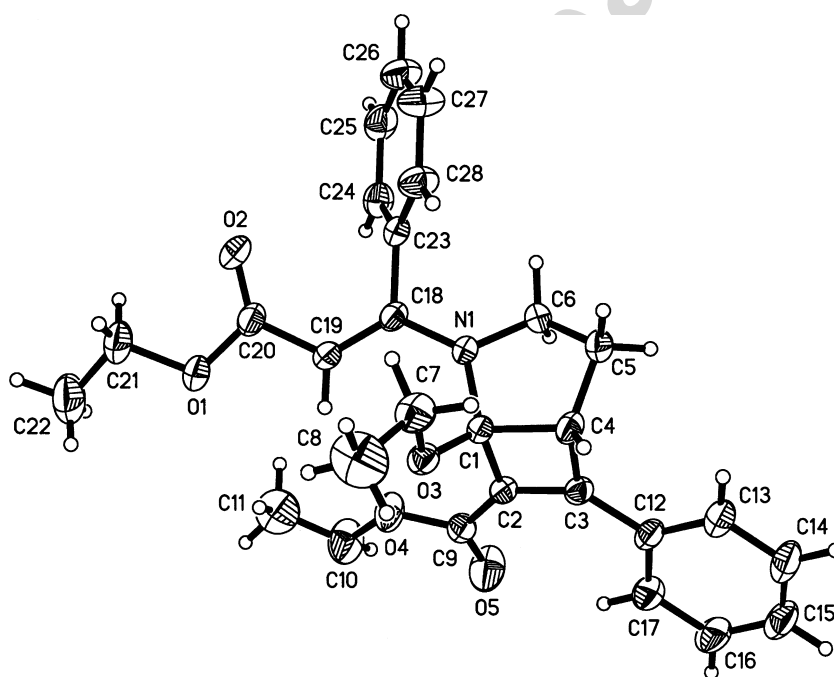


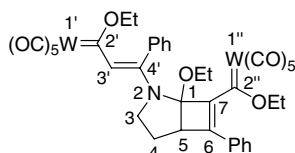
Fig. 4. Perspective view of diester 8.

3.1.1. 7-(1,1,1,1-Pentacarbonyl-2-ethoxy-1-chroma-1-ethen-2-yl)-2-(1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dienyl)-1-ethoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene (**3a**)

Pentacarbonyl (1-ethoxy-3-phenyl-2-propyn-1-ylidene) chromium **1a** (350 mg, 1.00 mmol) and 5-ethoxy-3,4-dihydro-2*H*-pyrrole (**2**) (57 mg, 0.50 mmol) were reacted in 3 mL of pentane in a 5-mL screwtop vessel at ambient temperature. The reaction was monitored by TLC analysis on silica gel. After \approx 3 h, the brown precipitate was collected by centrifugation and washed with pentane (**3a**, 379 mg, 93%, brown crystals from recrystallization in 1:5 dichloro-

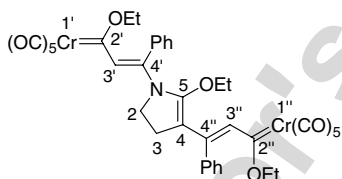
methane/pentane at $-20\text{ }^\circ\text{C}$). M.p.: $>113\text{ }^\circ\text{C}$, dec. ^1H ($\text{CDCl}_3/\text{CS}_2$, 4:1) δ 7.37 (s and br, 1 H, 3'-H), 7.37, 7.18 and 7.04 (m and br, 6:2:2 H, 2 \times Ph), 5.02 and 4.86 (m and br, 1:1 H, 2''-OCH₂), 4.34 and 4.17 (m and br, 1:1 H, 2'-OCH₂), 3.90 (m and br, 1 H, 5-H), 3.81 and 3.65 (m, 1:1 H, 1-OCH₂), 3.20 (m and br, 2 H, 3-H₂), 1.81 (m and br, 2 H, 4-H₂), 1.70 (t, 3 H, 2''-OCH₂CH₃), 1.36 (t and br, 3 H, 1-OCH₂CH₃), 0.65 (t, 3 H, 2'-OCH₂CH₃). ^{13}C $\{^1\text{H}\}$ NMR ($\text{CDCl}_3/\text{CS}_2$, 4:1) δ 346.50 (Cq, Cr=C, C2''), 307.96 (Cq, Cr=C, C2'), 224.36 and 215.57 (Cq, 1:4, *trans*- and *cis*-CO, 2'-Cr(CO)₅), 224.12 and 218.40 (Cq, 1:4, *trans*- and *cis*-CO, 2''-Cr(CO)₅), 149.67

(Cq, C4'), 131.28 (Cq, *i*-C of 4'-Ph), 126.60 (Cq, *i*-C of 6-Ph), 129.55, 128.88, 128.15, 127.91, 127.15 (CH of 2 × Ph), 127.15 (CH, C3'), 121.33 (Cq, C6), 121.19 (Cq, C7), 99.25 (Cq, C1), 74.01 (2'-OCH₂ and 2''OCH₂), 61.51 (1-OCH₂), 50.50 (CH₂, C3), 48.96 (CH, C5), 22.92 (CH₂, C4), 15.10 (1-OCH₂CH₃), 14.98 (2''-OCH₂CH₃), 14.16 (2'-OCH₂CH₃). IR (KBr), cm⁻¹: ν 2058.9 (80), 1962.2 (100) [(C≡O)]. Anal. Calcd for C₃₈H₃₁Cr₂NO₁₃: C, 56.09; H, 3.84; N, 1.72; Found: C, 55.96; H, 3.88; N, 1.65%.



3.1.2. 7-(1,1,1,1-Pentacarbonyl-2-ethoxy-1-tungsta-1-ethen-2-yl)-2-(1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dienyl)-1-ethoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene (3b)

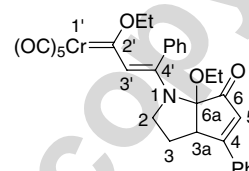
Pentacarbonyl(1-ethoxy-3-phenyl-2-propyn-1-ylidene) tungsten **1b** (482 mg, 1.00 mmol) and 5-ethoxy-3,4-dihydro-2H-pyrrole **2** (57 mg, 0.50 mmol) were reacted in 3 mL of pentane at ambient temperature. The reaction was monitored by TLC on silica gel. After ≈2.5 h, the red brown precipitate was collected by centrifugation and washed with pentane (**3b**, 490 mg, 91%). Single crystals suitable for X-ray crystallographic determination were obtained from recrystallization in dichloromethane and pentane (v/v, 1:4) at -20 °C. M.p.: >127 °C, dec. IR (KBr), cm⁻¹: ν 2073.4 (88), 2056.0 (85), 2005.9 (85), 1903.6 (100), 1882.4 (95) [(C≡O)]. Anal. Calcd for C₃₈H₃₁W₂NO₁₃: C, 42.36; H, 2.90; N, 1.30; Found: C, 42.58; H, 3.17; N, 1.28%.



3.1.3. 1,4-Bis(1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-buta-1,3-dien-4-yl)-5-ethoxy-2,3-dihdropyrrole (4)

A flash column chromatography procedure was carried out under a nitrogen atmosphere as follows. Complex **1a** (204 mg, 0.25 mmol) was dissolved in 2 mL of dry dichloromethane and immediately loaded on the top of a pad of 6 g silica gel, and eluted with using 4:1 mixture of petroleum ether (30–60 °C) and dichloromethane under nitrogen. A dark-blue fraction (air- and temperature-sensitive compound) was collected using a receiving flask cooled at 0 °C under nitrogen. Dark-blue compound **4** was obtained after evaporation of the volatiles under reduced pressure (172 mg, 86%). Recrystallization of **4** was carried out in dichloromethane/petroleum ether (30–60 °C) (v/v, 1:5) at -30 °C in a drybox. ¹H NMR (CDCl₃) δ 7.46, 7.34 and 7.04(m each, 10 H, 2 × Ph), 7.15 (s, 1 H, 3''-H), 6.94 (s, 1

H, 3'-H), 5.00 and 4.47 (m and br, 1:1 H, 2''-OCH₂), 4.47 and 4.34 (m and br, 1:1 H, 2'-OCH₂), 3.78 and 3.63 (m and br, 1:1 H, 5-OCH₂), 3.40 and 3.19 (m and br, 1:1 H, 2-H₂), 2.81 (br, 2 H, 3-H₂), 1.57 (m and br, 6 H, 2'-OCH₂CH₃ and 2''-OCH₂CH₃), 0.77 (m and br, 3 H, 5-OCH₂CH₃). IR (KBr), cm⁻¹: ν 2048.9 (30), 1920.2 (75) [(C≡O)]. Anal. Calcd for C₃₈H₃₁Cr₂NO₁₃: C, 56.09; H, 3.84; N, 1.72; Found: C, 55.39; H, 4.03; N, 1.60%.



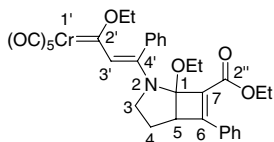
3.1.4. 1-(1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-buta-1,3-dien-4-yl)-6a-ethoxy-2,3,3a,6a-tetrahydro-1H-cyclopenta[b]pyrrol-6-one (6)

1,4-Bis(1,1,1,1-pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-buta-1,3-dien-4-yl)-5-ethoxy-2, 3-dihdropyrrole **4** (108 mg, 0.13 mmol) in 6 mL THF was stirred at 55 °C for 1.5 h until all the biscarbene complex was consumed by TLC analysis. All the volatiles were removed under reduced pressure. The resultant residue was subject to flash silica gel column chromatography with petroleum ether (30–60 °C)/dichloromethane (v/v, 2:1) as the eluent, affording **6** as a yellow solid (32 mg, 41%). Single crystals suitable for X-ray crystallographic study were obtained from recrystallization in dichloromethane/petroleum ether (30–60 °C) (v/v, 1:5) at -20 °C. M.p.: >120 °C, dec. ¹H NMR (CDCl₃) δ 8.14 (s, 1 H, 3'-H), 7.58 and 7.48 (m each, 2:3 H, 4-Ph), 7.32 and 7.05 (m and br, 3:2 H, 4'-Ph), 6.56 (s, 1 H, 5-H), 4.35 and 4.24 (m each, 1:1 H, 2'-OCH₂), 4.00 (t, 1 H, 3a-H), 3.77(m, 2 H, 6a-OCH₂), 3.09 and 2.86 (m each, 1:1 H, 2-H₂), 2.15 and 1.84 (m each, 1:1 H, 3-H₂), 1.44 (t, 3 H, 6a-OCH₂CH₃), 0.59 (t, 3 H, 2'-OCH₂CH₃). ¹³C {¹H} NMR (CDCl₃): δ 310.22 (Cq, Cr=C, C2'), 224.90 and 218.33 (Cq, 1:4, *trans*- and *cis*-CO, Cr(CO)₅), 194.21 (Cq, C=O, C6), 168.41 (Cq, C4'), 146.28 (Cq, C4), 139.44 (Cq, *i*-C of 4'-Ph), 132.17 (Cq, *i*-C of 4-Ph), 131.85 (CH, C3), 129.39, 128.59, 128.02, 127.58, 127.20 and 126.65 (2:1:2:2:1:2, CH, 2 × Ph), 123.57 (CH, C5), 98.16 (Cq, C6a), 74.08 (2'-OCH₂), 60.81 (6a-OCH₂), 50.79 (CH, C3a), 50.25 (CH₂, C2), 25.81 (CH₂, C3), 15.40 (6a-OCH₂CH₃), 14.03 (2-OCH₂CH₃). IR (KBr), cm⁻¹: ν 2048.2 (30), 1909.6 (90) [(C≡O)], 1705.5 (40) [(C=O)]. Anal. Calcd for C₃₁H₂₇CrNO₈: C, 62.73; H, 4.58; N, 2.36; Found: C, 62.16; H, 4.56; N, 2.24%.

3.2. Stepwise oxidation of the chromium biscarbene complex 3a

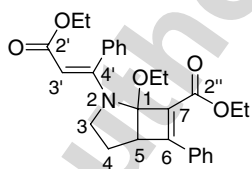
(a) *Partial oxidation*: A solution of pyridine *N*-oxide (24 mg, 0.25 mmol) in 2 mL of CH₂Cl₂ was added dropwise to a solution of **3a** (203 mg, 0.25 mmol) in 2 mL of CH₂Cl₂ in a 5-mL screwtop vessel at room temperature. The

mixture was further stirred for 5 h until all the biscarbene complex was consumed by TLC analysis. Purification by flash silica gel column chromatography with petroleum ether (30–60 °C)/CH₂Cl₂ (v/v, 2:1) afforded **7** as orange crystals (118 mg, 74%). (b) *Complete oxidation*: A mixture of pyridine *N*-oxide (95 mg, 1 mmol) and complex **3a** (407 mg, 0.5 mmol) in 6 mL benzene was stirred at 60 °C for 6 h. Work-up as mentioned above gave diester **8** as colorless crystals (199 mg, 86%).



3.2.1. 2-(1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dienyl)-1-ethoxy-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene-7-carboxylic acid ethyl ester (**7**)

Single crystals suitable for X-ray crystallographic study were obtained from recrystallization in dichloromethane/petroleum ether (30–60 °C) (v/v, 1:5) at –20 °C. M.p.: >100 °C, dec. ¹H NMR (CDCl₃): δ 7.96 (s, 1 H, 3'-H), 7.97, 7.45, 7.34 and 7.08 (m each, 2:3:3:2 H, 2 × Ph), 4.42 and 4.32 (m each, 1:1 H, 2''-OCH₂), 4.32 and 4.20 (m each, 1:1 H, 2'-OCH₂), 3.94 (t, 1 H, 5-H), 3.73 (q, 2 H, 1-OCH₂), 3.11 (m, 2 H, 3-H₂), 1.80 (m, 2 H, 4-H₂), 1.45 (t, 3 H, 1-OCH₂CH₃), 1.33 (t, 3 H, 2''-OCH₂CH₃), 0.62 (t, 3 H, 2'-OCH₂CH₃). ¹³C {¹H} NMR (CDCl₃): δ 305.76 (Cq, Cr=C, C2'), 224.81 and 218.75 (Cq each, 1:4, *trans*- and *cis*-CO, Cr(CO)₅), 162.14 (Cq, C=O, C2''), 154.53 (Cq, C6), 149.68 (Cq, C4'), 139.66 (Cq, *i*-C of 4'-Ph), 130.72 (Cq, *i*-C of 6-Ph), 131.44, 129.71, 128.81, 128.49, 128.02 (CH of 2 × Ph), 127.48 (Cq, C7), 123.38 (CH, C3'), 96.44 (Cq, C1), 73.81 (2'-OCH₂), 61.44 (1-OCH₂), 61.13 (2''-OCH₂), 50.38 (CH₂, C3), 49.93 (CH, C5), 23.29 (CH₂, C4), 15.37 (1-OCH₂CH₃), 14.41 (2''-OCH₂CH₃), 14.19 (2'-OCH₂CH₃). IR (KBr), cm⁻¹: ν 2045.0 (20), 1904.3 (100) [(C≡O)], 1700.5 (20) [(C=O)]. Anal. Calcd for C₃₃H₃₁CrNO₉: C, 62.16; H, 4.90; N, 2.20; Found: C, 62.10; H, 4.85; N, 2.07%.



3.2.2. 1-Ethoxy-2-(2-ethoxycarbonyl-4-phenyl-vinyl)-6-phenyl-2-azabicyclo[3.2.0]hept-6-ene-2,7-dicarboxylic acid ethyl ester (**8**)

Single crystals suitable for X-ray crystallographic study were obtained from recrystallization diethyl ether/petroleum ether (30–60 °C) (v/v, 1:5) at –20 °C. M.p.: 137 °C. ¹H NMR (CDCl₃): δ 7.95, 7.43, 7.37 and 7.19 (m each, 2:3:3:2 H, 2Ph), 6.26 (s, 1 H, 3'-H), 4.34 (q, 2 H, 2''-OCH₂), 3.92 (m, 2 H, 2'-OCH₂), 3.88, (m, 1 H, 5-H), 3.68 (m, 2 H, 1-OCH₂), 3.15 and 2.93 (m each, 1:1 H, 3-

H₂), 1.77 and 1.71 (m each, 1:1 H, 4-H₂), 1.43 (t, 3 H, 1-OCH₂CH₃), 1.37 (t, 3 H, 2''-OCH₂CH₃), 1.09 (t, 3 H, 2'-OCH₂CH₃). ¹³C {¹H} NMR (CDCl₃): δ 168.14 (Cq, C=O, C2'), 163.23 (Cq, C=O, C2''), 158.17 (Cq, C4'), 154.50 (Cq, C6), 138.36 and 128.15 (Cq, *i*-C of 2 × Ph), 131.06, 129.55, 128.73, 128.28, 128.02 (CH of 2 × Ph), 127.62 (Cq, C7), 95.10 (Cq, C1), 93.99 (CH, C3'), 61.21 (2''-OCH₂), 60.48 (1-OCH₂), 58.56 (2'-OCH₂), 50.71 (CH₂, C3), 49.25 (CH, C5), 23.16 (CH₂, C4), 15.59 (1-OCH₂CH₃), 14.46 (2''-OCH₂CH₃), 14.07 (2'-OCH₂CH₃). IR (KBr), cm⁻¹: ν 1695.5 (50) [(C=O)]. Anal. Calcd for C₂₈H₃₁NO₃: C, 72.86; H, 6.77; N, 3.03; Found: C, 72.93; H, 6.73; N, 2.88%.

3.3. X-ray crystallographic studies

Single crystal X-ray diffraction studies for compounds **3b**, **5**, **6**, **7**, and **8** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these compounds are summarized in Table 1.

Acknowledgement

We are grateful to the “Hundred Talented Program” Funding of Chinese Academy of Sciences for financial support of this research.

Appendix A. Supplementary data

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers: CCDC 611352 for **3b**, CCDC 611353 for **5**, and CCDC 611354 for **6**, CCDC 611355 for **7**, and CCDC 611356 for **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.056.

References

- [1] For selected recent reviews, see: (a) J. Barluenga, J. Santamaria, M. Tomás, Chem. Rev. 104 (2004) 2259; (b) J.W. Herndon, Coord. Chem. Rev. 243 (2003) 3; (c) M.A. Sierra, Chem. Rev. 100 (2000) 3591;

- (d) K.H. Dötz, C. Jakel, W.C. Haase, *J. Organomet. Chem.* 617/618 (2001) 119;
- (e) J. Barluenga, J. Floréz, F.J. Fañanás, *J. Organomet. Chem.* 624 (2001) 5;
- (f) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem., Int. Ed. Engl.* 39 (2000) 3964;
- (g) J.W. Herndon, *Tetrahedron* 56 (2000) 1257;
- (h) J. Barluenga, F.J. Fañanás, *Tetrahedron* 56 (2000) 4597;
- (i) R. Aumann, *Eur. J. Org. Chem.* 1 (2000) 17.
- [2] E.O. Fischer, A. Maasböl, *Angew. Chem., Int. Ed.* 3 (1964) 580.
- [3] E.O. Fischer, W. Röhl, N.H.T. Huy, K. Ackermann, *Chem. Ber.* 115 (1982) 2951.
- [4] Selected leading references, see: (a) C.A. Toledano, H. Rudler, J.C. Daran, Y. Jeannin, *J. Chem. Soc., Chem. Commun.* (1984) 574;
- (b) C. Alvarez, A. Pacreau, A. Parlier, H. Rudler, J.C. Daran, *Organometallics* 6 (1987) 1057;
- (c) N.H.T. Huy, P. Lefloch, F. Robert, Y. Jeannin, *J. Organomet. Chem.* 327 (1987) 211;
- (d) A. Geisbauer, S. Mihan, W. Beck, *J. Organomet. Chem.* 501 (1995) 61;
- (e) D.W. Macomber, P. Madhukar, *J. Organomet. Chem.* 433 (1992) 279;
- (f) D.W. Macomber, P. Madhukar, R.D. Rogers, *Organometallics* 10 (1991) 2121;
- (g) T. Wynn, L.S. Hegedus, *J. Am. Chem. Soc.* 122 (2000) 5034;
- (h) K. Puntener, M.D. Hellmann, E. Kuester, L.S. Hegedus, *J. Org. Chem.* 65 (2000) 8301;
- (i) J. Bao, W.D. Wulff, M.J. Fumo, E.B. Grant, D.P. Heller, M.C. Whitcomb, S.-M. Yeung, *J. Am. Chem. Soc.* 118 (1996) 2166;
- (j) C. Hartbaum, E. Mauz, G. Roth, K. Weissenbach, H. Fischer, *H. Organometallics* 18 (1999) 2619;
- (k) M.A. Sierra, M.J. Mancheño, E. Sáez, J.C. del Amo, *J. Am. Chem. Soc.* 120 (1998) 6812;
- (l) M.A. Sierra, J.C. del Amo, M.J. Mancheño, M. Gómez-Gallego, *J. Am. Chem. Soc.* 123 (2001) 851;
- (m) L. Quast, M. Nieger, K.H. Dötz, *Organometallics* 19 (2000) 2179;
- (n) I. Fernández, M.A. Sierra, M.J. Mancheño, M. Gómez-Gallego, S. Ricart, *Organometallics* 20 (2001) 4304.
- [5] R. Aumann, B. Hildmann, R. Fröhlich, *Organometallics* 17 (1998) 1197.
- [6] R. Aumann, Z.K. Yu, R. Fröhlich, *Organometallics* 17 (1998) 2897.
- [7] (a) J.Z. Chen, Z.K. Yu, Z.Y. Zheng, K.C. Gu, S.Z. Wu, F.L. Zeng, W.Q. Tan, X.W. Wu, W.-J. Xiao, *Organometallics* 24 (2005) 302;
- (b) Z.Y. Zheng, J.Z. Chen, Z.K. Yu, X.W. Han, *J. Organomet. Chem.* 691 (2006) 3679.
- [8] Crystal data for complex **5**: $C_{33}H_{31}NO_8Cr$, triclinic, $P\bar{1}$, $a = 11.592(3) \text{ \AA}$, $b = 12.187(3) \text{ \AA}$, $c = 12.325(4) \text{ \AA}$, $\alpha = 65.906(5)^\circ$, $\beta = 77.412(5)^\circ$, $\gamma = 77.548(6)^\circ$, $V = 1535.4(8) \text{ \AA}^3$, $Z = 2$, $D_c = 1.344$, $T = 293(2) \text{ K}$, $R(F) = 8.84\%$ for 4216 reflections ($3.64 \leq 2\theta \leq 53.0^\circ$) and $wR_2 = 30.65\%$ for 6167 reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters.