Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polyhedron 24 (2005) 173–180
POLYHEDRON
www.elsevier.com/locate/poly

Synthesis and structural characterization of (pyrazolyl)alkenyl Fischer carbene complexes of chromium and tungsten

Kai-Chun Gu [a], Jin-Zhu Chen [a], Zhao-Yan Zheng [a], Si-Zhong Wu [a], Xiao-Wei Wu [a], Xiu-Wen Han [b], Zheng-Kun Yu [a,*]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, P.R. China*
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, P.R. China*

Received 11 October 2004; accepted 3 November 2004
Available online 18 December 2004

Abstract

Michael addition of substituted pyrazoles **2** to 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (**1**) (**a**, M = Cr and **b** M = W) afforded (pyrazolyl)alkenyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(CH{=}C(R^1R^2R^3pz)Ph)$ ($R^1R^2R^3pz$ = pyrazolyl) **3** (M = Cr) and **4** (M = W), respectively, with an exclusive (*E*)-configuration in mild to excellent yields. The reaction of **1a** and 3,5-dimethylpyrazole (**2b**) was monitored to demonstrate the formation and decomposition of complex **3b** by ^1H NMR measurements in $CDCl_3$ at 23 °C. Complexes **3** and **4** were characterized with ^1H, $^{13}C\{^1H\}$ NMR, IR spectroscopies and elemental analysis. When the substituted pyrazoles were 3-methylpyrazole (**2a**) and 3,5-di-*tert*-butylpyrazole (**2d**), molecular structures of the corresponding (pyrazolyl)alkenyl Fischer carbene complexes **3a** and **4d** were characterized by X-ray crystallographic study.

Keywords: Fischer carbene; Pyrazole; Michael addition; Chromium; Tungsten

1. Introduction

Fischer carbene complexes were first synthesized by Fischer and Maasböl in 1964 [1,2] and have been paid much attention in the last two decades because they can be rather readily prepared and manipulated to demonstrate diverse reactivity in organic synthesis [3]. Transformations from alkynyl carbene to alkenyl carbene complexes have been extensively investigated. Michael addition of dimethylamine to Fischer alkynylcarbene complexes was reported by Fischer and Kreissl [4] as early as 1972, followed by several other groups [5]. Michael-type addition of amines or N–H bond-containing compounds to α,β-unsaturated Fischer carbene complexes to form β-aminovinyl-substituted products has been considered a useful methodology for certain preparative organic synthesis because the resultant Michael-type adducts are usually reactive intermediates [6–18]. A rich chemistry of pyrazoles [19] and pyrazolato ligands [20–22] has been evolved since pyrazoles were first prepared in 1968 [23], due to the presence of pyrazolyl-containing compounds in nature and potential bioactivity of pyrazole derivatives as well as their good coordination ability as ligands. Pyrazole contains a reactive N–H bond which can be easily deprotonated to proceed a lot of reactions. However, up to date no β-pyrazolyl subsitituted alkenyl Fischer carbene complexes have been synthesized, although 1-methoxy-1-(5-pyrazole) Fischer carbene complexes were reportedly generated in the reactions of 1-alkynyl Fischer carbene

* Corresponding author. Tel./fax: +86 411 8437 9227.
E-mail address: zkyu@dicp.ac.cn (Z.-K. Yu).

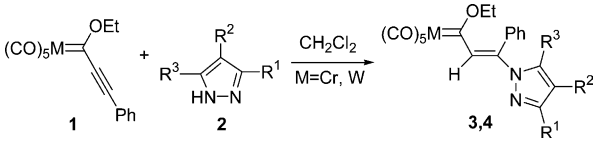
0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.11.012

complexes with Me_3SiCHN_2 [24a] and $(CO)_5W$-C(OEt)(CH=C($C_3H_3N_2$)Ph) was detected by UV spectroscopy [24b]. Herein, we report the synthesis of (pyrazolyl)alkenyl Fischer carbene complexes **3** and **4** by the reactions of substituted pyrazoles **2** with 1-alkynyl Fischer carbene complexes **1a**,**b** (**a**, M = Cr; **b**, M = W) under mild conditions, as well as their structural characterization.

2. Results and discussion

2.1. Synthesis of (pyrazolyl)alkenyl carbene complexes 3 and 4

Treatment of the 1-alkynyl Fischer carbene complexes **1a** and **1b** with an equivalent amount of substituted pyrazole in dichloromethane at ambient temperature afforded (pyrazolyl)alkenyl Fischer carbene complexes **3** and **4** in mild to excellent yields (Eq. (1)). The reaction temperature was elevated to 38 °C due to the poor solubility of 3,5-di-*tert*-butylpyrazole and 3,5-di-phenylpyrazole in CH_2Cl_2. 3-Methylpyrazole exhibited very low reactivity to both complexes **1a** and **1b** and only 32.2% and 17.6% yields of the desired products were achieved over a period of 77–85 h for **1a** and **1b**, respectively.



(1)

2	R^1	R^2	R^3	3 (M = Cr), %	4 (M = W), %
2a	Me	H	H	**3a**, 32.2	**4a**, 17.6
2b	Me	H	Me	**3b**, ~77[a]	**4b**, 99.6
2c	Ph	H	Ph	**3c**, 60.5	**4c**, 90.4
2d	*t*-Bu	H	*t*-Bu	**3d**, 65.8	**4d**, 80.5
2e	Me	Me	Me	**3e**, 65.8	**4e**, 93.0
2f	Me	$PhCH_2$	Me	**3f**, 88.5	**4f**, 93.1

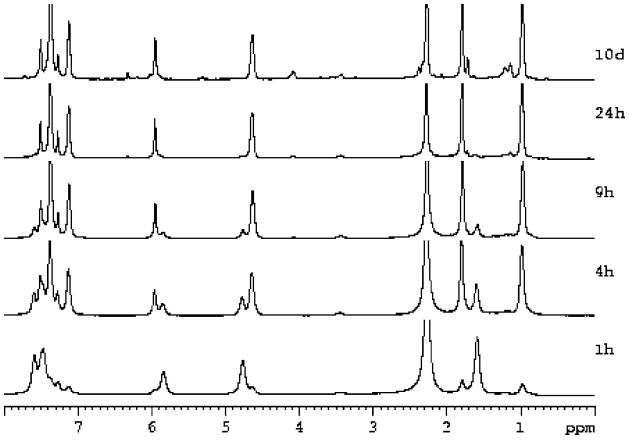
[a] Containing small amounts of decomposition products.

In the other cases, the tungsten carbene complex **1b** demonstrated higher reactivity (shorter reaction time) to the investigated substituted pyrazoles than its chromium analogue, leading to higher yields for the tungsten products (80.5–99.6%) and lower isolated yields for their chromium analogues (60.5–88.5%). It was observed that the chromium products were subject to decomposition on silica gel when the crude products were purified by column chromatography.

It is noteworthy that complex **4b** was obtained in 99.6% isolated yield while its chromium analogue, i.e., complex **3b** underwent decomposition under mild conditions to form some unidentified products when 3,5-dimethyl pyrazole was used. In order to understand the behavior of complex **3b**, Fischer carbene complex **1a** was treated with an equivalent amount of 3,5-dimethyl pyrazole (**2b**) in $CDCl_3$ in a 5-mL NMR tube at ambient temperature and the reaction was monitored by ^1H NMR measurements over a period of ten days (Scheme 1). The ^1H NMR measurements revealed that the reaction exclusively proceeded to form **3b** and the reaction was completed in 24 h at ambient temperature. It was noticed that the product, i.e., **3b**, gradually decomposed when the reaction solution was kept at ambient temperature for a longer time (e.g., 10 days). It was also observed that the reaction of **1a** with an excess of the pyrazole (2.0 equiv.) in $CDCl_3$ at ambient temperature did not lead to any formation of the de-ethoxy product, i.e., the 2,4-dipyrazolyl alkenylcarbene complex. Due to its decomposition at ambient temperature, the full characterization data for complex **3b** could not be collected, but its NMR data was tentatively assigned.

2.2. Spectroscopy of (pyrazolyl)alkenyl carbene complexes 3 and 4

The strong bands in the region 2069–1902 cm^{-1} of the IR spectra are characteristic of the typical patterns expected for a $M(CO)_5$ moiety in Fischer carbene complexes. The proton resonances of HC=C($R^1R^2R^3$pz)Ph in complexes **3** and **4** in $CDCl_3$ are shown in the region 8.20–7.31 ppm as singlets and those of the alkenyl complexes of chromium, **3**, are slightly shifted downfield as compared with their tungsten analogues. The ^{13}C resonances of the carbene carbons, i.e., Cr=C in complexes **3** are at 331.4–338.4 ppm and those of W=C in complexes **4** are at 310.5–304.6 ppm, while the ^{13}C NMR signals of typical β-aminoalkenyl Fischer carbene complexes exhibiting some conjugation between the metal carbene M=C and the alkenyl moiety are in the region ~270–290 ppm [7,10], and those of metal carbene M=C in $(OC)_5M$=



Scheme 1. Formation and decomposition of **3b** from the reaction of **1a** and 3,5-dimethylpyrazole (**2b**) monitored by ^1H NMR measurements in $CDCl_3$ at 23 °C.

C(OMe)Me showing no conjugation between the M=C and methyl moieties are at ~320 ppm (M = Cr) to 361 ppm (M = W) [25]. These results indicate that only little (or even no) π-conjugation is expected to operate within the (pyrazolyl)alkenyl unit and the metal carbene bond M=C. The ^{13}C resonance signals of the $M(CO)_5$ moieties are always shown at about 224 ppm/216 ppm for the chromium complexes **3** and at about 204 ppm/197 ppm for the tungsten complexes **4** with a 1:4 intensity ratio. The proton signals of the 4′-H in the pyrazolyl ring appear at 7.00–5.96 ppm as singlets, and the ^{13}C resonance signals of the C4′ and C3′ (i.e., C=N) carbons are shown in the region 102.8–119.5 and 150.5–161.5 ppm, respectively, corresponding to those of an NH deprotonated pyrazolyl ring [22].

2.3. Crystal structure analyses of complexes *3a* and *4d*

Fig. 1 is a perspective SCHAKAL-97 drawing of complex **3a** showing the labelling scheme. The molecular structure is in line with the assignment by IR and NMR spectra of the complex. The pyrazolyl ring is situated at an (*E*)-configuration with respect to the $(CO)_5Cr$=C moiety. The distances Cr–C6, C6–C7 and C7–C8 are 2.057(3), 1.456(4) and 1.344(4) Å, respectively, corresponding to a typical Cr=C bond in alkenyl Fischer carbene complexes, single and double carbon–carbon bonds, indicating little or even no π-conjugation in the metal butadienyl system. The pyrazolyl ring is bound to C8 atom via the N1 atom of the pyrazolyl moiety and the methyl substituent on the pyrazolyl ring is arranged in a position separated far away from the phenyl group to reduce the steric hindrance. The lengths N2–C19 (1.321(3) Å) and C17–C18 (1.336(4) Å) are in

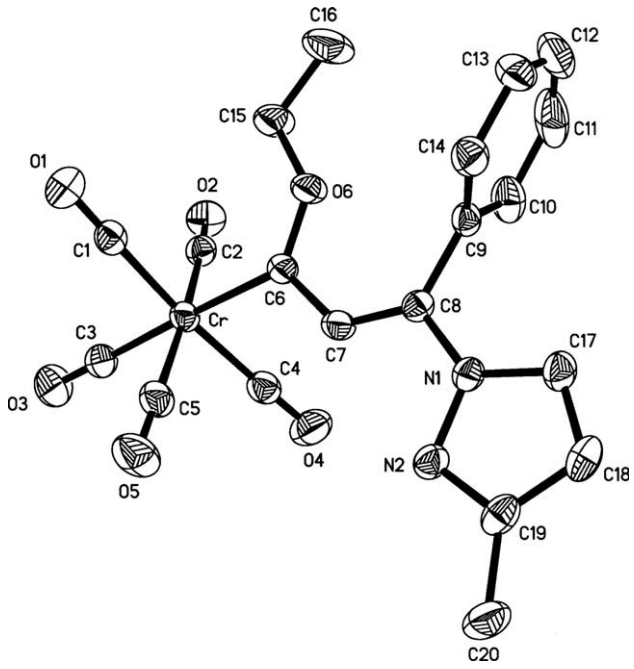


Fig. 1. Molecular structure of complex **3a**.

accordance with C=N and C=C bonds, respectively, revealing no structural change for the pyrazolyl ring. All the structural data confirms a Michael addition product from the 1-alkynylcarbene complex **1a**. No obvious difference is observed between the molecular structures of **3a** and **4d** (Fig. 2). The W–C6 bond length is 2.150(5) Å and C7–C8 bond length in **4d** is 1.342(7) Å. The N1–C8 bond (1.405(6) Å) is longer than its analogue in **3a** (1.395(3) Å), presumably due to bigger steric hindrance from the *tert*-butyl groups. The angle C17–N1–C8 (133.9(4)°) in **4d** is bigger than that in **3a**

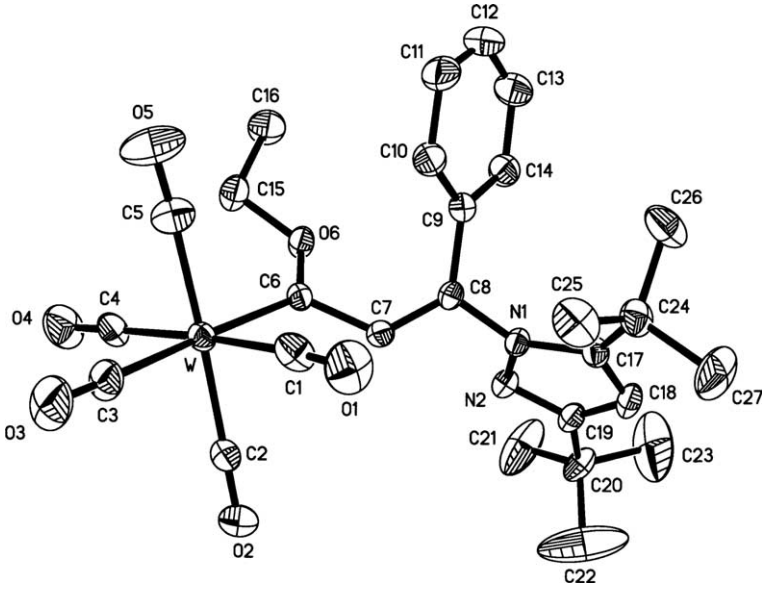


Fig. 2. Molecular structure of complex **4d**.

(127.7(3)°) and N1–C8 (1.405(6) Å) in **4d** is longer than that in **3a** (1.395(3) Å), demonstrating that the 3,5-di-*tert*-butylpyrazolyl ring is separated farther away from the backbone of the alkenyl carbene complex than the less steric ring, i.e., 3-methylpyyrazolyl.

3. Experimental

Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: ^{1}H and ^{13}C NMR spectra were obtained with Bruker DRX-400 spectrometer (chemical shifts refer to $\delta_{TMS} = 0.00$ ppm); IR spectra were obtained on a Bruker Tensor 27 spectrophotometer. Elemental analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Substituted pyrazoles were prepared as reported [23]. 3,4,5-Trimethylpyrazole [26] and 3,5-dimethyl-4-benzyl-pyrazole [27] were synthesized by reported procedures, respectively.

*General procedure for the synthesis of the (pyrazolyl)alkenyl carbene complexes **3** and **4***. A mixture of 1-alkynylcarbene complex **1** (1.0 mmol) and substituted pyrazole (1.0 mmol) in 3 mL of dichloromethane was stirred in a 5-mL screwtop vessel at ambient temperature (23 °C) or elevated temperature as stated. The reaction was monitored by TLC analysis on silica gel. After the reaction was completed, the resultant mixture was subject to column chromatography on silica gel to collect the product **3** or **4**. Recrystallization at −20 °C afforded single crystals suitable for X-ray crystallographic study. The crystal color of complexes **3** and **4** are red and dark red, respectively.

*2-Ethoxy-4-phenyl-4-(3′-methylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3a**):* 23 °C, 85 h, 139 mg (32.2%). M.p. 89–91 °C. Single crystals suitable for X-ray determination were grown in CH_2Cl_2/pentane (v/v, 1/4) at −20 °C. ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 8.20 (br, 1H, 3-H), 7.42 and 7.20 (br each, 3:2 H, 4-Ph), 7.00 (br, 1H, 4′-H), 6.12 (br, 1H, 5′-H), 4.57 (q, 2H, OCH_2), 2.35 (s, 3H, 3′-CH_3), 0.81 (br, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 331.40 (s, Cq, Cr=C), 224.39 and 216.84 (s each, Cq, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 153.49 (s, Cq, C=N, C3′), 134.70 (s, Cq, *i*-C of Ph), 132.70 and 109.32 (s each,1:1 CH, C5′ and C4′), 129.83 and 128.67 (s each, aromatic CH, 4-Ph), 129.54 (s, CH, C4), 129.34 (s, CH, C3), 75.99 (s, OCH_2), 14.15 (s, 4′-CH_3), 13.96 (s, CH_2CH_3); IR (KBr) cm^{-1}: 2050.2 (90), 1924.0 (100), 1903.6 (100) [ν(C≡O)], 1537.2 (80), 1490.9 (60), 1444.6 (50) [ν(C=C, C=N)]. *Anal.* Calc. for $C_{20}H_{16}N_2O_6Cr$: C, 55.56; H, 3.73; N, 6.48. Found: C, 55.51; H, 3.76; N, 6.45%.

*2-Ethoxy-4-phenyl-4-(3′-methylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (**4a**):* 23 °C, 77 h, 99 mg (17.6%). M.p. 121–122 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 8.03 (s, 1H, 3-H), 7.30 and 7.10 (m each, 3:2 H, 4-Ph), 6.86 and 6.00 (dd each, J = 1.9 Hz, 1:1H, 4′- and 5′-H), 4.25 (q, 2H, OCH_2), 2.21 (s, 3H, 3′-CH_3), 0.66 (t, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 304.55 (s, Cq, Cr=C), 204.29 and 198.43 (s each, Cq, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 153.77 (s, Cq, C=N, C3′), 137.59 (s, Cq, C4), 134.90 (s, Cq, *i*-C of Ph), 132.63, 129.65 and 128.64 (aromatic CH, 4-Ph), 129.56 (s, CH, C5′), 109.56 (s, CH, C4′), 78.53 (s, OCH_2), 14.24 (s, 3′-CH_3), 13.80 (s, CH_2CH_3); IR (KBr) cm^{-1}: 2057.9 (90), 1947.0 (100), 1924.0 (100), 1899.8 (100) [ν(C≡O)], 1537.2 (90), 1490.9 (70), 1442.7 (60) (ν(C=C, C=N)). *Anal.* Calc. for $C_{20}H_{16}N_2O_6W$: C, 42.58; H, 2.86; N, 4.96. Found: C, 42.59; H, 2.88; N, 4.93%.

*2-Ethoxy-4-phenyl-4-(3′,5′-di-methylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3b**):* 23 °C, 10 h, 77.0%. Dec. 23 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.58 (s, 1H, 3-H), 7.37 and 7.12 (br each, 3:2 H, 4-Ph), 5.95 (s, 1H, 4′-H), 4.63 (br, 2H, OCH_2), 2.27 and 1.79 (s each, 3:3 H, 3′- and 5′-CH_3), 0.97 (br, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 335.50 (s, Cq, Cr=C), 224.14 and 216.58 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 150.71 and 143.70 (s each, Cq each, C3′ and C5′), 135.85 (s, CH, C3), 134.58 (s, Cq, C4), 132.81 (s, Cq, *i*-C of 4-Ph), 129.65, 129.50 and 128.72 (s each, 1:2:2 CH, 4-Ph), 109.54 (s, CH, C4′), 76.34 (s, OCH_2), 14.13, 13.83 and 12.96 (s each, CH_3).

*2-Ethoxy-4-phenyl-4-(3′,5′-di-methylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (**4b**):* 23 °C, 8 h, 576 mg (99.6%). M.p. 89–90 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.43 (s, 1H, 3-H), 7.37 and 7.16 (m each, 3:2 H, 4-Ph), 5.96 (s, 1H, 4′-H), 4.47 (q, 2H, OCH_2), 2.27 and 1.76 (s each, 3:3 H, 3′- and 5′-CH_3), 0.92 (t, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 307.55 (s, Cq, W=C), 204.06 and 197.45 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 150.89 and 142.50 (s each, Cq each, C=N, C3′ and C5′), 139.22 (s, CH, C3), 137.41 (s, Cq, C4), 135.96 (s, Cq, *i*-C of 4-Ph), 129.61 and 128.61 (3:2 CH, 4-Ph), 109.91 (s, CH, C4′), 78.72 (s, OCH_2), 13.85 and 13.09(s, 3′-CH_3 and 5′-CH_3), 13.10 (s, CH_2CH_3); IR (KBr) cm^{-1} : 2059.8 (30), 1931.3 (70), 1901.7 (70) [ν(C≡ O)], 1533.2 (45), 1477.4 (25) [ν(C=C, C=N)]. *Anal.* Calc. for $C_{21}H_{18}N_2O_6W$: C, 43.62; H, 3.14; N, 4.84. Found: C, 43.70; H, 3.16; N, 4.80%.

*2-Ethoxy-4-phenyl-4-(3′,5′-di-phenylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3c**):* 38 °C, 48h, 345 mg (60.5%). M.p. 106–107 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.92 and 7.41 (m each, 2:3 H, 4-Ph), 7.72 (s, 1H, 3-H), 7.38–6.90 (m, 10H, 3′- and 5′-Ph), 6.76 (s, 1H, 4′-H), 4.64 (br, 2H, OCH_2), 0.96 (br, 3H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$,

23 °C, 400 MHz): δ 335.72 (s, Cq, Cr=C), 224.08 and 216.45 (s each, Cq, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 152.72 and 146.97 (s each, Cq, C=N, C3′ and C5′), 137.52 (s, CH, C3), 135.48 (s, Cq, C4), 134.57, 132.58 and 130.40 (s each, Cq each, *i*-C of Ph), 129.60, 129.10, 128.84, 128.73, 128.61, 128.45, 128.16, 127.97 and 126.20 (aromatic CH of 4-, 5′-, and 3′-Ph), 106.72 (s, CH, C4′), 76.45 (s, O*C*H_2), 14.06 (s, *C*H_3); IR (KBr) cm^{-1}: 2057.9 (100), 1986.7 (100), 1911.3 (100) [ν(C≡O)], 1548.7 (80), 1487.0 (70), 1446.5 (60) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{31}H_{22}N_2O_6Cr$: C, 65.26; H, 3.89; N, 4.91. Found: C, 65.26; H, 3.88; N, 4.88%.

*2-Ethoxy-4-phenyl-4-(3′,5′-di-phenylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (**4c**):* 38 °C, 27 h, 635 mg (90.4%). M.p. 132 °C; ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.92, 7.45 and 7.38 (m each, 2:2:1 H, 4-Ph), 7.60 (s, 1H, 3-H), 7.22, 7.15, 7.08 and 6.92 (m each, 2:3:3:2 H, 3′- and 5′-Ph), 6.76 (s, 1H, 4′-H), 4.49 (q, 2H, O*C*H_2), 0.92 (t, 3H, C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, 400 MHz): δ 308.14 (s, Cq, W=C), 204.00 and 197.29 (s each, Cq, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 152.78 and 146.98 (s each, Cq each, C=N, C3′ and C5′), 141.14 (s, CH, C3), 137.18, 132.56 and 130.44 (s each, Cq each, *i*-C of Ph), 135.62 (s, Cq, C4), 129.78, 129.09, 128.87, 128.75, 128.65, 128.45, 128.17, 127.86, and 126.21 (aromatic CH of 4-, 3′- and 5′-Ph), 106.96 (s, CH, C4′), 78.87 (s, O*C*H_2), 13.82 (s, *C*H_3); IR (KBr) cm^{-1}: 2065.6 (60), 1986.7 (55), 1903.6 (80) [ν(C≡O)], 1548.7 (40), 1485.1 (40), 1444.6 (40) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{31}H_{22}N_2O_6W$: C, 53.01; H, 3.16; N, 3.99. Found: C, 53.07; H, 3.18; N, 3.96%.

*2-Ethoxy-4-phenyl-4-(3′,5′-di-tert-butylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3d**):* 38 °C, 24 h, 349 mg (65.8%). M.p. 118-119 °C; ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.40 (s, 1H, 3-H), 7.30 and 6.94 (m each, 3:2 H, 4-Ph), 6.03 (s, 1H, 4′-H), 4.72 (br, 2H, O*C*H_2), 1.33 (9H, s, 5′-C(C*H*$_3$)$_3$), 1.10 (t, 3H, CH_2CH_3), 1.08 (s, 9H, 3′-C(C*H*$_3$)$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, 400 MHz): δ 338.41 (s, Cq, Cr=C), 224.02 and 216.22 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 161.46 and 153.77 (s each, Cq each, C=N, C3′ and C5′), 140.21 (s, CH, C3), 137.14 (s, Cq, C4), 136.36 (s, Cq, *i*-C of 4-Ph), 129.58, 129.40 and 128.41 (1:2:2 CH, 4-Ph), 102.80 (s, CH, C4′), 76.71 (s, O*C*H_2), 32.13 (s, Cq, *C* $(CH_3)_3$), 30.82 and 30.64 (s each, 3′- and 5′-C(*C*H_3)$_3$), 14.22 (s, CH_2CH_3); IR (KBr) cm^{-1}: 2057.9 (60), 1951.8 (60) [ν(C≡O)], 1571.9 (20) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{27}H_{30}N_2O_6Cr$: C, 61.12; H, 5.70; N, 5.28. Found: C, 61.14; H, 5.74; N, 5.18%.

*2-Ethoxy-4-phenyl-4-(3′,5′-di-tert-butylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (**4d**):* 38 °C, 22 h, 533 mg (80.5%). M.p. 132–133 °C. Single crystals suitable for X-ray study were obtained by recrystallization in pentane at −20 °C. ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.31 (s, 1H, 3-H), 7.29 and 7.00 (m each, 3:2 H, 4-Ph), 6.04 (s, 1H, 4′-H), 4.61 (q, 2H, O*C*H_2), 1.34 and 1.08 (s each, 9:9 H, 3′- and 5′-C(C*H*$_3$)$_3$), 1.07 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, 400 MHz): δ 310.50 (s, Cq, W=C), 203.77 and 197.05 (s each, Cq, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 161.52 and 153.82 (s each, Cq, C=N, C3′ and C5′), 144.08 (s, CH, C3), 139.04 (s, Cq, *i*-C of 4-Ph), 137.19 (s, Cq, C4), 129.74, 129.58 and 128.26 (s each, 2:1:2 CH, 4-Ph), 102.97 (s, CH, C4′), 76.12 (s, O*C*H_2), 32.17 (s, Cq, *C* $(CH_3)_3$), 30.83 and 30.65 (s each, 3′- and 5′-C(*C*H_3)$_3$), 13.92 (s, CH_2CH_3); IR (KBr) cm^{-1}: 2065.6 (50), 1953.8 (80), 1908.0 (70) [ν(C≡O)], 1566.1 (40), 1541.0 (40), 1490.9 (30), 1446.5 (30) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{27}H_{30}N_2O_6W$: C, 48.96; H, 4.56; N, 4.23. Found: C, 48.92; H, 4.57; N, 4.18%.

*2-Ethoxy-4-phenyl-4-(3′,4′,5′-trimethylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3e**):* 23 °C, 5 h, 406 mg (88.2%). M.p. 78–79 °C; ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.49 (s, 1H, 3-H), 7.37 and 7.11 (br each, 3:2 H, 4-Ph), 4.60 (br, 2H, O*C*H_2), 2.21, 1.89 and 1.70 (s each, 3:3:3 H, 3′-, 4′- and 5′-C*H*$_3$), 0.94 (br, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, 400 MHz): δ 334.47 (s, Cq, Cr=C), 224.76 and 217.24 (s each, Cq, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 151.03 and 139.15 (s each, Cq each, C=N, C3′ and C5′), 136.65 (s, Cq, C4), 135.94 (s, Cq, *i*-C of 4-Ph), 135.71 (s, CH, C3), 130.18 and 129.18 (each, 3:2 CH, 4-Ph), 116.71 (s, CH, C4′), 76.70 (s, O*C*H_2), 14.62 (s, 5′-*C*H_3), 12.85 (s, 3′-*C*H_3), 12.08 (s, CH_2CH_3), 8.84 (s, 4′-*C*H_3); IR (KBr) cm^{-1}: 2054.1 (80), 1982.0 (70), 1938.4 (100) [ν(C≡O)], 1608.5 (40), 1529.5 (80), 1481.2 (60) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{22}H_{20}N_2O_6Cr$ (460.4): C, 57.39; H, 4.38; N, 6.08. Found: C, 55.89; H, 4.65; N, 6.08%.

*2-Ethoxy-4-phenyl-4-(3′,4′,5′-trimethylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene (**4e**):* 23 °C, 2 h, 551 mg (93.0%). M.p. 104 °C; ^1H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.43 (s, 1H, 3-H), 7.36 and 7.16 (m each, 3:2 H, 4-Ph), 4.45 (q, 2H, O*C*H_2), 2.21, 1.90 and 1.69 (s each, 3:3:3 H, 3′-, 4′- and 5′-C*H*$_3$), 0.89 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, 400 MHz): δ 306.69 (s, Cq, W=C), 204.11 and 197.56 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 151.72 and 138.62 (s each, Cq, C=N, C3′ and C5′), 138.44 (s, CH, C3), 138.29 (s, Cq, C4), 136.23 (s, Cq, *i*-C of 4-Ph), 129.70, 129.56 and 128.53 (2:1:2, CH, 4-Ph), 116.52 (s, CH, C4′), 78.55 (s, O*C*H_2), 13.82 (s, 5′-*C*H_3), 12.33 (s, 3′-*C*H_3), 11.66 (s, CH_2CH_3), 8.30 (s, 4′-*C*H_3); IR (KBr) cm^{-1}: 2059.8 (40), 1939.3 (60), 1913.3 (70) [ν(C≡O)], 1604.7 (30), 1529.5 (40), 1481.2 (30) [ν(C=C, C=N)]. *Anal*. Calc. for $C_{22}H_{20}N_2O_6W$:

C, 44.62; H, 3.40; N, 4.73. Found: C, 44.72; H, 3.42; N, 4.67%.

*2-Ethoxy-4-phenyl-4-(3′,5′-dimethyl-4′-benzylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene (**3f**):* 23 °C, 10 h, 475 mg (88.5%). M.p. 97–98 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.59 (s, 1H, 3-H), 7.44 and 7.35 (br each, 3:2 H, 4-Ph), 7.26 and 7.19 (br each, 2:3 H, 4′-CH_2Ph), 4.70 (br, 2H, OCH_2), 3.78 (br, 2H, 4′-CH_2Ph), 2.23 and 1.81 (s each, 3:3 H, 3′- and 5′-CH_3), 1.03 (br, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 334.57 (s, Cq, Cr=C), 224.18 and 216.64 (s each, Cq, 1:4, *trans*- and *cis*-CO, $Cr(CO)_5$), 150.52 and 140.07 (s each, Cq, C=N, C3′ and C5′), 139.43 (s, Cq, C4), 136.04 and 135.09 (s each, Cq each, *i*-C of Ph), 135.58 (s, CH, C3), 129.57, 128.71, 128.18 and 126.23 (aromatic CH of Ph), 119.14 (s, C4′), 76.25 (s, OCH_2), 29.51 (4′-CH_2Ph), 14.11 (s, 5′-CH_3), 12.54 (s, 3′-CH_3), 11.64 (s, CH_2CH_3); IR (KBr) cm^{-1}: 2059.8 (60), 1986.7 (60), 1939.3 (80), 1915.2 (90) [ν(C≡O)], 1560.3 (40), 1490.9 (30) [ν(C=C, C=N)]. *Anal.* Calc. for $C_{28}H_{24}N_2O_6Cr$: C, 62.68; H, 4.51; N, 5.22. Found: C, 62.37; H, 4.52; N, 5.14%.

*2-Ethoxy-4-phenyl-4-(3′,5′-dimethyl-4′-benzylpyrazol-1′-yl)-1,1,1,1,1-pentacar-bonyl-1-tungsta-1,3-butadiene (**4f**):* 23 °C, 4 h, 622 mg (93.1%). M.p. 110 °C; ^{1}H NMR ($CDCl_3$, 23 °C, 400 MHz): δ 7.52 (s, 1H, 3-H), 7.44 and 7.34 (m each, 3:2 H, 4-Ph), 7.24 and 7.16 (m each, 3:2 H, 4′-CH_2Ph), 4.53 (q, 2H, OCH_2), 3.77 (s, 2H, 4′-CH_2Ph), 2.20 and 1.76 (s each, 3:3 H, 3′- and 5′-CH_3), 0.97 (t, 3H, CH_2CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C, 400 MHz): δ 307.00 (s, Cq, W=C), 204.12 and 197.55 (s each, Cq each, 1:4, *trans*- and *cis*-CO, $W(CO)_5$), 150.77 and 140.00 (s each, Cq each, C=N, C3′ and C5′), 139.48 (s, Cq, C4), 138.90 (s, CH, C3), 137.96 and 136.20 (s each, Cq, *i*-C of Ph), 129.66, 128.64, 128.18 and 126.26 (aromatic CH of Ph), 119.52 (s, C4′), 78.66 (s, OCH_2), 29.51 (4′-CH_2Ph), 13.87 (s, 5′-CH_3), 12.59 (s, 3′-CH_3), 11.79 (s, CH_2CH_3); IR (KBr) cm^{-1} : 2069.5 (80), 1986.7 (80), 1909.4 (100) [ν(C≡O)], 1560.3 (50), 1490.9 (40), 1446.5 (40) [ν(C=C, C=N)]. *Anal.* Calc. for $C_{28}H_{24}N_2O_6W$ (668.3): C, 50.32; H, 3.62; N, 4.19. Found: C, 50.37; H, 3.71; N, 4.17%.

*Crystallographic study of complexes **3a** and **4d**.* Single crystals were mounted on a glass fiber and sealed with epoxy glue. Diffraction measurements were made on a Bruker Smart diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 293 K. The crystal structures were solved by means of the program SHELXS-86 and refined by a full-matrix least-squares procedure on F^2 with the program SHELXL-97. Table 1 lists the crystal data and refinement details for complexes **3a** and **4d**. The selected bond lengths and angles are summarized in Tables 2 and 3. The molecular structures of **3a** and **4d** are given in Figs. 1 and 2.

Table 1
Crystal data and refinement details for complexes **3a** and **4d**

Complex	**3a**	**4d**
Empirical formula	$C_{20}H_{16}N_2O_6Cr$	$C_{27}H_{30}N_2O_6W$
Formula weight	432.35	662.38
T (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*C*2/*c*
a (Å)	9.255(1)	30.960(2)
b (Å)	13.542(1)	10.715(1)
c (Å)	16.563(1)	22.558(2)
α (°)	90	90
β (°)	103.3(2)	129.9(1)
γ (°)	90	90
V (Å^3)	2020.2(3)	5744.0(7)
Z	4	8
D_{calc} (g cm^{-3})	1.422	1.532
μ (mm^{-1})	0.605	4.062
F(000)	888	2624
Crystal size (mm)	0.37 × 0.37 × 0.27	0.51 × 0.50 × 0.27
θ limits (°)	1.96–28.30	1.71–28.31
Number of data collected	12127	16958
Number of unique data	4693	6657
R_{int}	0.0464	0.0839
Number of data observed [$I > 2\sigma(I)$]	4693	6657
Number of refined parameters	280	323
Goodness-of-fit	0.902	0.960
R (all data/observed data)	0.080/0.047	0.056/0.044
wR_2 (all data/observed data)	0.129/0.105	0.107/0.103
Residual ρ_{max} (ρ_{min}) (e Å^{-3})	0.357 (−0.254)	3.121 (−1.334)

Table 2
Selected bond lengths (Å) and angles (°) for complex **3a**

Cr–C(6)	2.057(3)
O(6)–C(6)	1.313(3)
C(6)–C(7)	1.456(4)
C(7)–C(8)	1.344(4)
C(8)–C(9)	1.474(4)
N(1)–C(8)	1.395(3)
N(1)–N(2)	1.375(3)
N(1)–C(17)	1.363(3)
N(2)–C(19)	1.321(3)
C(17)–C(18)	1.336(4)
C(18)–C(19)	1.418(4)
O(6)–C(6)–Cr	129.8(2)
C(7)–C(6)–Cr	121.4(2)
O(6)–C(6)–C(7)	108.8(2)
C(8)–C(7)–C(6)	128.6(3)
C(7)–C(8)–C(9)	127.0(2)
N(1)–C(8)–C(9)	113.1(2)
C(7)–C(8)–N(1)	119.8(2)
N(2)–N(1)–C(8)	121.1(2)
C(17)–N(1)–C(8)	127.7(3)
C(17)–N(1)–N(2)	111.1(2)
O(6)–C(6)–C(7)–C(8)	−12.1(4)
Cr–C(6)–C(7)–C(8)	169.4(2)
C(6)–C(7)–C(8)–N(1)	−178.9(3)
C(6)–C(7)–C(8)–C(9)	−1.3(5)
N(1)–C(17)–C(18)–C(19)	0.1(3)
N(1)–N(2)–C(19)–C(18)	0.0(3)
C(17)–C(18)–C(19)–N(2)	−0.1(3)

Table 3
Selected bond lengths (Å) and angles (°) for complex **4d**

W–C(6)	2.150(5)
O(6)–C(6)	1.332(6)
C(6)–C(7)	1.468(7)
C(7)–C(8)	1.342(7)
C(8)–C(9)	1.470(7)
N(1)–C(8)	1.405(6)
N(1)–N(2)	1.375(6)
N(1)–C(17)	1.374(6)
N(2)–C(19)	1.320(6)
C(17)–C(18)	1.358(8)
C(18)–C(19)	1.393(8)
O(6)–C(6)–W	132.2(3)
C(7)–C(6)–W	122.2(3)
O(6)–C(6)–C(7)	105.5(4)
C(8)–C(7)–C(6)	126.9(5)
C(7)–C(8)–C(9)	124.9(4)
N(1)–C(8)–C(9)	117.9(4)
C(7)–C(8)–N(1)	117.2(4)
N(2)–N(1)–C(8)	114.9(4)
C(17)–N(1)–C(8)	133.9(4)
C(17)–N(1)–N(2)	111.2(4)
O(6)–C(6)–C(7)–C(8)	44.0(6)
W–C(6)–C(7)–C(8)	−136.4(5)
C(6)–C(7)–C(8)–N(1)	−166.5(4)
C(6)–C(7)–C(8)–C(9)	10.1(8)
N(1)–C(17)–C(18)–C(19)	−0.2(6)
N(1)–N(2)–C(19)–C(18)	0.6(6)
C(17)–C(18)–C(19)–N(2)	−0.2(7)

4. Conclusion

(Pyrazolyl)alkenyl Fischer carbene complexes were synthesized from the reactions of 1-alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (M = Cr, W) with substituted pyrazoles under mild conditions. Transformation of these complexes into organic heterocyclic compounds are under way.

5. Supplementary material

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers: CCDC 243529 for **3a** and CCDC 243528 for **4d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are grateful for financial support from the Innovation Funding and the "Hundred Talented Program" Funding of the Chinese Academy of Sciences, P.R. China.

References

[1] E.O. Fischer, A. Maasböl, Angew. Chem. 76 (1964) 645.
[2] E.O. Fischer, A. Maasböl, Angew. Chem., Int. Ed. Engl. 3 (1964) 58.
[3] (a) For selected recent reviews, see J. Barluenga, J. Santamaría, M. Tomás, Chem. Rev. 104 (2004) 2259;
(b) J.W. Herndon, Coord. Chem. Rev. 243 (2003) 3;
(c) K.H. Dötz, C. Jakel, W.C. Haase, J. Organomet. Chem. 617–618 (2001) 119;
(d) J. Barluenga, J. Flórez, F.J. Fañanás, J. Organomet. Chem. 624 (2001) 5;
(e) M.A. Sierra, Chem. Rev. 100 (2000) 3591;
(f) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem. Int. Ed. 39 (2000) 3964;
(g) J. Barluenga, F.J. Fañanás, Tetrahedron 56 (2000) 4597;
(h) J.W. Herndon, Tetrahedron 56 (2000) 1257;
(i) R. Aumann, Eur. J. Org. Chem. (2000) 17;
(j) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187;
(k) W.D. Wulff, Organometallics 17 (1998) 3116;
(l) B. Alcaide, L. Casarrubios, G. Domínguez, M.A. Sierra, Curr. Org. Chem. 2 (1998) 551;
(m) L.S. Hegedus, Tetrahedron 53 (1997) 4105;
(n) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163.
[4] E.O. Fischer, F.R. Kreissl, J. Organomet. Chem. 35 (1972) C47.
[5] (a) E.O. Fischer, H.J. Kalder, J. Organomet. Chem. 131 (1977) 57;
(b) L. Lattuda, E. Licandro, A. Papagni, S. Maiorana, A.C. Villa, C. Guastini, J. Chem. Soc., Chem. Commun. (1988) 1092;
(c) R. Aumann, P. Hinterding, Chem. Ber. 123 (1990) 611, 2047;
(d) R. Aumann, P. Hinterding, C. Krüger, P. Betz, Chem. Ber. 123 (1990) 1847;
(e) M. Duetsch, R. Lackmann, F. Stein, A. de Meijere, Synlett (1991) 324.
[6] F. Stein, M. Duetsch, R. Lackmann, M. Noltemeyer, A. de Meijere, Angew. Chem., Int. Ed. Engl. 30 (1991) 1658.
[7] M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 125 (1992) 2051.
[8] F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, Organometallics 12 (1993) 2556.
[9] R. Pipoh, R. van Eldik, G. Henkel, Organometallics 12 (1993) 2236.
[10] R. Aumann, P. Hinterding, Chem. Ber. 126 (1993) 421.
[11] R. Pipoh, R. van Eldik, Organometallics 12 (1993) 2668.
[12] A. Rahm, W.D. Wulff, Organometallics 12 (1993) 597.
[13] F. Funke, M. Duetsch, F. Stein, M. Noltemeyer, A. de Meijere, Chem. Ber. 127 (1994) 911.
[14] R. Aumann, Chem. Ber. 127 (1994) 725.
[15] R. Aumann, B. Jasper, M. Läge, B. Krebs, Organometallics 13 (1994) 3502.
[16] J. Barluenga, M. Tomás, E. Rubio, J.A. López-Pelegrín, S. García-Granda, M.P. Priede, J. Am. Chem. Soc. 121 (1999) 3065.
[17] I. Fernández, M.A. Sierra, M.J. Mancheño, M. Gómez-Gallego, S. Ricart, Organometallics 20 (2001) 4304.
[18] A. Spinella, T. Caruso, U. Pastore, S. Ricart, J. Organomet. Chem. 684 (2003) 266.
[19] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus, Tetrahedron 60 (2004) 939, and references therein.
[20] For selected recent reviews, see G. La Monica, G.A. Ardizzoia, Prog. Inorg. Chem. 46 (1997) 151.
[21] J.E. Cosgriff, G.B. Deacon, Angew. Chem., Int. Ed. Engl. 37 (1998) 286.
[22] C.T. Sirimanne, J.E. Knox, M.J. Heeg, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 125 (2003) 11152.

[23] J. Elguero, E. Gonzalez, R. Jacquier, Bull. Soc. Chim. Fr. (1968) 707.
[24] (a) K.S. Chan, W.D. Wulff, J. Am. Chem. Soc. 108 (1986) 5229; (b) R. Pipoh, P.P. Martinez, R. van Eldik, Ber. Bunsen-Ges. Phys. Chem. 97 (1993) 1435.
[25] (a) A. Hafner, L.S. Hegedus, G. de Weck, B. Hawkins, K.H. Dötz, J. Am. Chem. Soc. 110 (1988) 8413; (b) R. Aumann, Z.K. Yu, R. Fröhlich, F. Zippel, Eur. J. Inorg. Chem. (1998) 1623.
[26] D. Chamber, W.A. Denny, J. Org. Chem. 50 (1985) 4736.
[27] J.C. Jeffery, S.S. Kurek, J.A. McCleverty, E. Psillakis, R.M. Richardson, M.D. Ward, A. Wlodarczyk, J. Chem. Soc., Dalton Trans. (1994) 2559.