

The first carbene-*C,N* chelate tetracarbonyl dihalogeno and carbene-*C,O* chelate tetracarbonyl benzochinone tungsten complexes

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Received 2 November 2001

Abstract

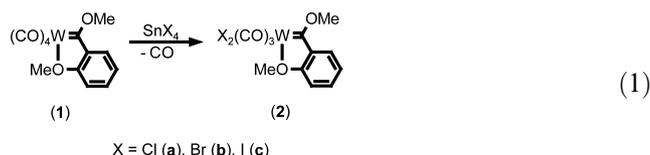
The carbene-*C,N* chelate tetracarbonyl tungsten complex $[(CO)_4\overline{W=C(Ph)NHC_5H_4N^1-o}]$ (**4**), obtained from $[(CO)_5W=C(Ph)OMe]$ (**3**) and *o*-aminopyridine, reacts with iodine by oxidative decarbonylation to give a single isomer of the carbene-*C,N* chelate tricarbonyl dihalogeno tungsten(II) complex $[(CO)_3I_2\overline{W=C(Ph)NHC_5H_4N^1-o}]$ (**5**). The analogous reaction of **4** with bromine affords two interconverting isomers of $[(CO)_3Br_2\overline{W=C(Ph)NHC_5H_4N^1-o}]$ (**6**). The oxidative decarbonylation of the carbene-*C,O* chelate tetracarbonyl tungsten complex $[(CO)_4\overline{W=C(OMe)C_6H_4O^1Me-o}]$ (**1**) with tetrachloro-*o*-benzochinone yields the first carbene-*C,O* chelate tricarbonyl-*o*-benzochinone tungsten(II) complex **8**. The structures of **5** and of $[(CO)_4I_2\overline{W=C(OMe)C_6H_4O^1Me-o}]$ (**2c**) were established by X-ray structural analyses. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; Oxidative decarbonylation; Chelate complexes; Tungsten complexes

1. Introduction

There are only few examples known of Fischer-type molybdenum(II) and tungsten(II) carbene carbonyl complexes not stabilized by aromatic π -ligands [1]. In 1977, Lappert and Pye reported the synthesis of some Lappert-type W(II) complexes with cyclic bisaminocarbene ligands [2] by oxidation of the corresponding W(0) carbene complexes. However, compared to Fischer-type carbene ligands, the back-bonding properties of the *N*-heterocyclic carbene ligands is almost negligible [3]. In addition, a few compounds of the type $[Cl_2(CO)-(PMe_3)_2W=C(R)H]$ ($R = CMe_3, Ph, C_6H_4Me-p$) were prepared by Schrock and coworkers [4] and Mayr et al. [5].

Recently, we reported the synthesis of the first heptacoordinated dihalogeno carbene-*C,O* chelate tricarbonyl molybdenum(II) and tungsten(II) complexes by oxidative decarbonylation of carbene-*C,O* chelate tetracarbonyl complexes with SnX_4 ($X = Cl, Br, I$), $SbCl_5$, or $TiCl_4$, e.g. Eq. (1) [6].



The reaction of non-chelated tetracarbonyl(phosphine)carbene complexes, $[(CO)_4(PR_3)M=C(OMe)C_6H_4-OMe-o]$, with SnX_4 or bromine was found to likewise afford carbene-*C,O* chelate dihalogeno complexes [6,7]. In contrast, the reaction of the non-chelated pentacarbonylcarbene complex $[(CO)_5W=C(OMe)Ph]$ (**3**) with excess $SnCl_4$ did not give a tungsten(II) carbene complex but rather, among other products, a carbyne complex [6]. From these observations and those by Lappert et al., it was concluded that an energetically high-lying HOMO at the metal is required for the oxidative decarbonylation. To determine whether an aminocarbene ligand sufficiently raises the electron density at the metal, the reaction of aminocarbene pentacarbonyl complexes was investigated.

2. Results and discussion

The aminocarbene complex $[(CO)_5W=C(NMe_2)Ph]$ was prepared from $[(CO)_5W=C(OMe)Ph]$ (**3**) and

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Table 1
Crystallographic data for **2c**·1/4CH₂Cl₂ and **5**·2THF

	2c ·1/4CH ₂ Cl ₂	5 ·2THF
Empirical formula	C ₁₂ H ₁₀ I ₂ O ₅ W·1/4CH ₂ Cl ₂	C ₁₅ H ₁₀ I ₂ N ₂ O ₃ W·2THF
<i>M_r</i> (g mol ⁻¹) (including solvent)	682.2	848.1
Temperature (K)	240(2)	245(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	16.550(4)	11.857(1)
<i>b</i> (Å)	15.630(5)	12.842(1)
<i>c</i> (Å)	28.029(5)	18.429(2)
β (°)	102.62(2)	90.50(1)
Cell volume (Å ³)	7075(2)	2806.1(4)
<i>Z</i>	8	4
<i>D</i> _{calc} (g cm ⁻³)	2.603	2.008
μ (Mo–K α) (mm ⁻¹)	10.110	6.350
<i>F</i> (000)	5000	1592
Crystal size (mm)	0.25 × 0.20 × 0.15	0.4 × 0.3 × 0.2
Scan rate (° min ⁻¹ in ω)	2–29.3	4–30
Scan range $\Delta\omega$ (°)	1.4	1.5
Observed reflections	4598 [<i>F</i> > 4.0 σ (<i>F</i>)]	5148 [<i>F</i> > 4.0 σ (<i>F</i>)]
Independent reflections	7702	6134
Min/max transmission	0.2690/0.5872	0.0396/0.0797
Parameters refined	375	298
<i>R</i> ₁ (%)	5.29	4.97
<i>wR</i> ₂ (%)	10.00	12.38
Res. electron density (e Å ⁻³)	1.578 and –1.446	0.983 and –0.967

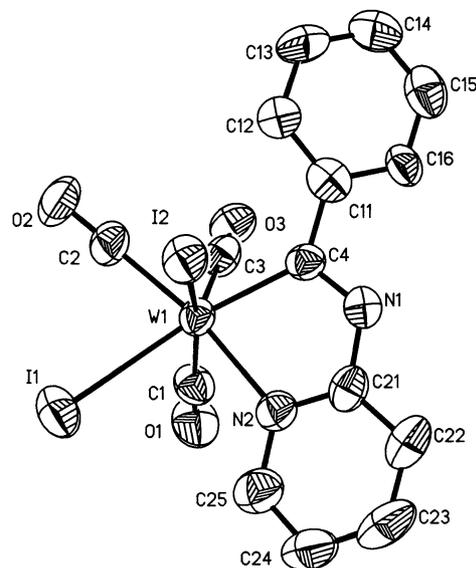
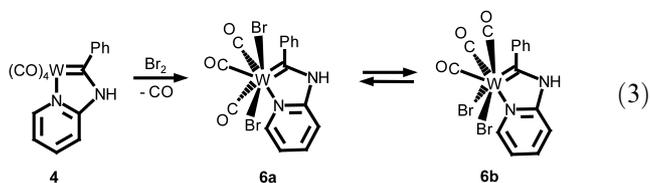


Fig. 2. Molecular structure of **5**. Selected bond distances (Å) and angles (°): W(1)–I(1) 2.8846(8), W(1)–I(2) 2.8438(7), W(1)–C(1) 1.986(9), W(1)–C(2) 2.008(10), W(1)–C(3) 1.972(10), W(1)–C(4) 2.135(8), W(1)–N(2) 2.225(7), C(4)–N(1) 1.326(10), N(1)–C(21) 1.391(12), C(21)–N(2) 1.326(11); I(1)–W(1)–I(2) 86.78(2), C(1)–W(1)–C(2) 106.8(4), C(1)–W(1)–C(3) 74.4(4), I(1)–W(1)–C(4) 155.3(2), I(2)–W(1)–C(4) 73.4(2), I(1)–W(1)–N(2) 91.7(2), I(2)–W(1)–N(2) 85.9(2), C(4)–W(1)–N(2) 72.7(3), W(1)–C(4)–N(1) 116.4(6), C(4)–N(1)–C(21) 120.4(7), N(1)–C(21)–N(2) 113.2(8), W(1)–N(2)–C(21) 117.0(6).

deviates from planarity. The iodo ligands are *cis* and occupy positions on the same side of the chelate plane. In contrast, the dichloro complex **2a** is *C_s*-symmetric and the mirror plane (formed by the chelate ring and one CO ligand) bisects the Cl–W–Cl angle and one OC–W–CO angle [6]. The I–W–I angle, the OC–W–CO and the OC–W–C (carbene) angles in both complexes, **2c** and **5**, are similar. The phenyl ring in **5** is tilted against the chelate plane by 33.9°. In **2c**, the methyl group lies within the chelate plane and is oriented towards the metal–ligand fragment (*Z* conformation). This conformation is usually observed also with non-chelated alkoxy-carbene complexes [11].

The reaction of **4** with bromine proceeded analogously to that with iodine. However, two interconverting isomers (**6a** and **6b**, Eq. (3)) were formed.



The ¹H-NMR spectrum of **6a/6b** is temperature-dependent. At –80 °C, two sharp resonances are observed for the *ortho* proton of the pyridyl group. On warming, these resonances broaden to give two

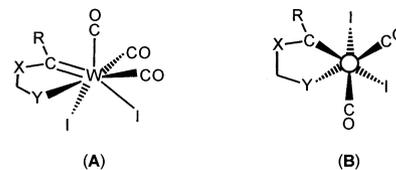
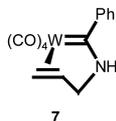


Fig. 3. Structure of **2c** and **5** shown in two different perspectives: (A) side view; and (B) view along the capping OC–W axis.

broad signals at ambient temperature. Based on the observation of two resonances for the carbene carbon atom, five CO signals, and 18 peaks in the aromatic region of the ¹³C-NMR spectrum at –80 °C and on the IR spectrum, the two isomers **6a** and **6b** were assigned structures corresponding to **2c–5** and **2a**. At –80 °C the ratio **6a–6b** is 1:3. The formation of a mixture of isomers in the oxidative decarbonylation of carbene chelate tetracarbonyl complexes has not been observed before. Oxidation of carbene *C,O*-chelate tetracarbonyl complexes gave either *C_s*-symmetric complexes such as **2a** and **2b** or *C₁*-symmetric complexes like the more electron-rich compounds **2c** and **5**. Obviously, increasing electron-donating power of the ligands in these metal(II) complexes increasingly disfavors the *C_s*-symmetric structure (**2a** and **6b**) and favors the *C₁*-symmetric structure as in **2c**, **5** and **6a**. For the interconversion of **6a** and **6b**, several different mechanisms are conceivable. The most likely one involves a series of rearrangements via a capped trigonal prism.

The difference in energy between the different structures for heptacoordinated complexes is small. Complexes with a structure intermediate between a capped octahedron and a -trigonal prism are known, for example $[(\text{CO})_3\text{Br}(\text{Br}_3\text{Ge})\text{W}(\text{bipy})]$ [12] or $[(\text{CO})_2\text{Cl}_2\text{Mo}(\text{P-Me}_2\text{Ph})_3]$ [13]. Compound in which the coordinating heteroatom of the chelating ligand determines whether the complex adopts a capped octahedral or a -trigonal prismatic structure have also been reported [14]. The structure of $[(\text{CO})_2\text{Cl}_2\text{Mo}(\eta^2\text{-Ph}_2\text{X-CH}_2\text{-XPh}_2)(\eta^1\text{-Ph}_2\text{X-CH}_2\text{-XPh}_2)]$ is that of a capped octahedron for $\text{X} = \text{As}$ and that of a distorted capped trigonal prism for $\text{X} = \text{P}$. In the crystal $[(\text{CO})_3\text{I}_2\text{W}(\text{NCPh})_2]$ is a capped octahedron, one of the three CO ligand assuming the capping position. In solution all carbonyl ligands are equivalent in the $^{13}\text{C-NMR}$ spectrum even at $-70\text{ }^\circ\text{C}$ [15].

Next the reaction of bromine with the C,C=C -chelating complex **7** [16] was investigated.



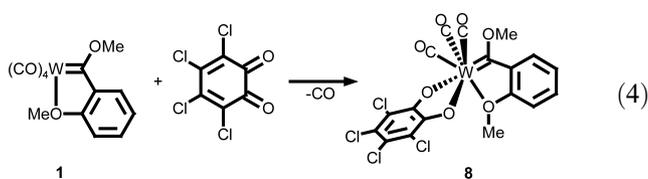
The electron-donating properties of chelating ‘ $\text{C}(\text{Ph})\text{-NH-CH}_2\text{-CH=CH}_2$ ’ are less than those of carbene- C,O or -C,N chelating ligands but intermediate between a carbene- C,O chelate ligand and the combination of an aminocarbene ligand and CO as in $[(\text{CO})_5\text{W}=\text{C}(\text{Ph})\text{NMe}_2]$. Complex **7** reacted in acetonitrile with bromine even at $-30\text{ }^\circ\text{C}$. The similarity of the IR spectrum of the reaction solution with that of **5** or **6a** indicated the formation of a new complex with a structure similar to that of **5** and **6a**. However, it was not possible to isolate and completely characterize the complex since already above $-30\text{ }^\circ\text{C}$ it ‘decomposed’ via subsequent reactions.

Until now, only chlorine, bromine or metal halides were used as the oxidizing agent in the oxidative decarbonylation. All attempts to subsequently replace the halide ligands in the resulting heptacoordinated dihalogeno carbene chelate tricarbonyl metal(II) complexes by other simple nucleophiles such as $[\text{OR}]^-$ or $[\text{SR}]^-$ failed. The reactions of **2b** or **2c** with NaOEt or $\text{LiO-}t\text{-Bu}$ led to dissociation of the carbene ligand. Likewise, no substitution product could be isolated from the reactions of **2b** with $\text{Na}[\text{SC}_6\text{H}_4\text{Me-}p]$ and sodium hydridotris(3,5-dimethylpyrazolyl)borate (NaTp), respectively, although in all of these experiments an alkali metal halide was formed. Similarly, the reaction of **2b** with AgOTf or TlBF_4 in the presence of oxalate did not give an isolable substitution product but only led to decomposition of the complex.

These observations seemed to indicate that anionic ligands other than halides have to be introduced in close connection with the oxidation reaction. Therefore,

oxidizing agents whose reduced form also can function as ligands were investigated next and *o*-benzoquinone was chosen for that.

When a solution of tetrachloro-*o*-benzoquinone in dichloromethane was added to a solution of **3** in CH_2Cl_2 at $-10\text{ }^\circ\text{C}$, the evolution of a gas was observed. Chromatography of the reaction mixture with pentane-dichloromethane at $-50\text{ }^\circ\text{C}$ yielded the dark-green complex **8** as the major product (isolated yield: 62%) and a red compound. The red compound turned out to be a decomposition product of **8** since it was also formed when solutions of **8** were kept for prolonged periods of time at ambient temperature. The compound was not further characterized.



Two signals for OMe groups in the $^1\text{H-NMR}$ spectrum of **8** indicated that the carbene ligand was still coordinated to the metal. From the observation of two $\nu(\text{CO})$ absorptions in the IR spectrum and of two carbonyl resonances (ratio ca. 1:2) in the $^{13}\text{C-NMR}$ spectrum a C_s -symmetric structure as shown in Eq. (4) and similar to that of **2a** was assigned. Compared with the chloro and bromo complexes **2a** and **2b**, the resonances for the carbene carbon atom and the carbonyl ligands are at lower field.

Complex **8** is less stable than its dihalogeno analogues **2a-c**. At ambient temperature in solution, **8** decomposes slowly, but can be stored under nitrogen at $-30\text{ }^\circ\text{C}$ for prolonged periods of time.

In contrast to the reaction of **3** with tetrachloro-*o*-benzoquinone that with 3,5-di-*tert*-butyl-*o*-benzoquinone proceeded only slowly at room temperature. When one equivalent of the quinone was added, the two new $\nu(\text{CO})$ absorptions in the IR spectrum indicated the formation of a new complex, however, the reaction was still incomplete. When benzoquinone was added in excess until all absorptions of **3** had disappeared, no chelate carbene tungsten(II) complex could be isolated from the reaction mixture. Presumably a tungsten(II) complex related to **8** had been formed in the reaction of **3** with 3,5-di-*tert*-butyl-*o*-benzoquinone albeit slowly but quickly decomposed again either by reaction with the quinone or by another pathway. Further oxidation of the tungsten(II) complex seems possible since $[\text{Mo}(\text{CO})_6]$ was found to react with tetrachloro-*o*-benzoquinone or 3,5-di-*tert*-butyl-*o*-benzoquinone to give molybdenum(VI) complexes [17].

Nevertheless, these observations demonstrate that anionic ligands other than halides can be introduced into chelate carbene tungsten(II) complex.

3. Experimental

3.1. General

All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over Na–benzophenone ketyl or CaH₂ and were freshly distilled prior to use. The yields refer to analytically pure compounds and were not optimized. The complexes **1** [18], **2c** [6], **3** [10], **7** [12] were prepared according to literature procedures. IR: FTIR spectrophotometer, Bio.-Rad. — ¹H-NMR and ¹³C-NMR: Bruker WM 250, Bruker AC 250, JEOL JNX 400. Unless specifically mentioned, spectra were recorded at room temperature. Chemical shifts are reported relative to Me₄Si (¹H-NMR spectra) or to the residual solvent peaks (¹³C-NMR spectra: CDCl₃ δ = 77.0 ppm, CD₂Cl₂ δ = 53.8 ppm, C₃H₆O-*d*₆ = 206.6 ppm).

3.2. Tricarbonyldiiodo[phenyl(2-pyridylamino)carbene-κ²C,N]tungsten(II) (**5**)

Iodine (0.51 g, 2.0 mmol) was added in small portions to a solution of 0.96 g (2.0 mmol) of complex **2** in 50 ml of CH₂Cl₂. The solution was stirred for 20 min. With evolution of a gas, the color of the solution turned red and an orange precipitate formed. The precipitate was decanted and twice washed with 50 ml of C₅H₁₂ each. Recrystallization of the residue from THF afforded red crystals, which decomposed in vacuo to give an orange powder. Yield: 1.26 g (89%). — M.p. 235 °C (dec.). — IR (THF, cm⁻¹): ν(CO) 2033 s, 1964 vs, 1921 m. — ¹H-NMR (C₃H₆O-*d*₆): δ 6.99–7.14 (m, 4H, Ph), 7.38–7.42 (m, 2H, pyridyl), 7.58–7.62 (m, 1H, pyridyl), 7.71–7.77 (m, 1H), 9.38 (d, *J*_{HH} = 5.3 Hz, pyridyl-*o*-H). — ¹³C-NMR (C₃H₆O-*d*₆): δ 117.8, 122.6, 129.5, 130.2, 133.9, 142.3, 146.0, 154.5, 158.2 (aryl), 213.0 (CO), 214.5 (CO), 238.0, 258.5 (carbene-C). — Anal. Found: C, 25.41; H, 1.67; N, 4.16. Calc. for C₁₅H₁₀I₂N₂O₃W (703.9): C, 25.59; H, 1.43; N, 3.98%.

3.3. Dibromotricarbonyl[phenyl(2-pyridylamino)carbene-κ²C,N]tungsten(II) (**6**)

Bromine (0.404 g, 2.5 mmol) was added dropwise to a solution of 1.25 g (2.5 mmol) of complex **2** in 50 ml of CH₂Cl₂. The solution was stirred for 20 min. With evolution of a gas, the color of the solution turned red and a red–brown precipitate formed. The precipitate was decanted and twice washed with 50 ml of C₅H₁₂ each. Recrystallization of the residue from THF afforded a brown powder. Yield: 1.10 g (72%). — IR (THF, cm⁻¹): ν(CO) 2037 m, 1967 vs, 1945 m, 1917 w. — ¹H-NMR (C₃H₆O-*d*₆, –80 °C): δ 6.90–8.31

(m, br, 7H, Ph and pyridyl), 9.58 (d, *J*_{HH} = 4.5 Hz, pyridyl-*o*-H of **6b**), 9.83 (s, br, pyridyl-*o*-H of **6a**). — ¹³C-NMR (C₃H₆O-*d*₆, –80 °C): **6a**: δ 112.7, 113.4, 116.8, 121.9, 132.8, 140.6, 143.4, 150.0, 153.2 (aryl), 214.5, 216.0, 243.4 (CO), 256.2 (carbene-C); **6b**: δ 115.6, 120.0, 128.4, 128.6, 129.2, 133.9, 143.6, 151.6, 156.1 (aryl), 210.0, 216.7 (CO), 240.1 (carbene-C).

3.4. Tricarbonyl[methoxy(*o*-methoxyphenyl)carbene-κ²C,O](tetrachloro-*o*-chinolato-κ²C^{1,2})tungsten(II) (**8**)

At –10 °C, a solution of 0.77 g (3.13 mmol) of tetrachloro-*o*-benzochinone in 50 ml of CH₂Cl₂ was added within 30 min to a solution of 1.47 g (3.3 mmol) of **1** in 50 ml of CH₂Cl₂. The solvent was removed in vacuo. The residue was chromatographed at –50 °C with C₅H₁₂–CH₂Cl₂ (ratio slowly changing from 10:1 to 1:20) on silica gel. Four fractions were eluted. The first orange fraction contained [(CO)₅W=C(OMe)C₆H₄OMe-*o*], the second yellow–brown unreacted **1**, and the third red one a decomposition product of **8**. Finally, a green band containing the product **8** was eluted. Removal of the solvent in vacuo gave **8** as fine, dark-green almost black, metallic shiny crystals. Yield: 1.28 g (62% relative to tetrachloro-*o*-benzochinone). — M.p. 169 °C (dec.). — IR (CH₂Cl₂, cm⁻¹): ν(CO) 2043 s, 1958 vs. — ¹H-NMR (C₃H₆O-*d*₆): δ 4.03 (s, 3H, carbene-OMe), 4.70 (s, 3H, aryl-OMe), 7.42 (t, *J* = 7.5 Hz, 1H, aryl), 7.64 (d, *J* = 8.6 Hz, 1H, aryl), 7.84 (d, *J* = 7.9 Hz, 1H, aryl), 7.87 (t, *J* = 7.3 Hz, 1H, aryl). — ¹H-NMR (CDCl₃): δ 3.95 (s, 3H, carbene-OMe), 4.52 (s, 3H, aryl-OMe), 7.20–7.35 (m, 2H, aryl), 7.67–7.72 (m, 2H, aryl). — ¹³C-NMR (CD₂Cl₂, –80 °C): δ 59.4 (s, carbene-OMe), 67.3 (s, aryl-OMe) 111.8, 117.1, 118.0, 122.5, 123.4, 132.4, 138.1, 153.8, 163.9 (9s, aryl), 216.7 (CO), 221.5 (*J*_{WC} = 115 Hz, 2CO), 287.5 (carbene-C). Anal. Found: C, 32.17; H, 1.86. Calc. for C₁₈H₁₀Cl₄O₇W (663.9): C, 32.56; H, 1.52%.

3.5. X-ray structural analyses of **2c** and **5**

Single crystals of **2c** suitable for an X-ray structural analysis were obtained by slow diffusion of C₅H₁₂ into a solution of **2c** in CH₂Cl₂ at –30 °C and from THF (**5**), respectively.

The measurements were performed with a crystal mounted in a glass capillary on a Siemens R3m/V (**2c**) and P4 diffractometer (**5**) (graphite monochromator, Mo–K_α radiation, λ = 0.71073 Å). For the data collection, the Wykoff technique was used (4.0 < 2θ < 54.0°). With both complexes a semiempirical absorption correction (*ψ* scan with 10 reflections) was performed. The structures were solved by Patterson methods using the SHELXTL PLUS (VMS) program package. The positions

of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as ‘riding model’. The positions of all other atoms were refined anisotropically by the full-matrix least-square methods. The crystal of **2c** consisted of two independent molecules.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 173231, 173232 for compounds **2c** and **5**. Copies of the data may be obtained free of charge on application to 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>).

Acknowledgements

Support of these investigations by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

- [1] Early reports on the synthesis of chromium(II), molybdenum(II), and tungsten(II) carbene complexes with a stabilizing aromatic π -donor ligand include: (a) N.A. Bailey, P.L. Chell, A. Mukhopadhyay, H.E. Tabbron, M.J. Winter, *J. Chem. Soc. Chem. Commun.* (1982) 215; (b) F.R. Kreissl, W.J. Sieber, M. Wolfgruber, *J. Organomet. Chem.* 270 (1984) C45; (c) J.A.K. Howard, J.C. Jeffery, J.C.V. Laurie, F.G.A. Stone, A. Stringer, *Inorg. Chim. Acta* 100 (1985) 23; (d) V.A. Osborne, M.J. Winter, *J. Chem. Soc. Chem. Commun.* (1985) 1744; (e) B. Lungwitz, A.C. Filippou, *NATO ASI Ser. Ser. C* 392 (1993) 249; (f) A.C. Filippou, D. Wössner, B. Lungwitz, G. Kociok-Köhn, *Angew. Chem.* 108 (1996) 981; *Angew. Chem. Int. Ed. Engl.* 35 (1996) 876.
- [2] (a) M.F. Lappert, P.L. Pye, *Chem. Soc. Dalton Trans.* (1977) 1283; (b) M.F. Lappert, P.L. Pye, *J. Chem. Soc. Dalton Trans.* (1977) 2172.
- [3] For a recent review on complexes with cyclic bisaminocarbene ligands see: W.A. Herrmann, C. Köcher, *Angew. Chem.* 109 (1997) 2256; *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2162.
- [4] J.H. Wengrovius, R.R. Schrock, M.R. Churchill, H.J. Wasserman, *J. Am. Chem. Soc.* 104 (1982) 1739.
- [5] A. Mayr, M.F. Asaro, M.A. Kjelsberg, K.S. Lee, D. Van Engen, *Organometallics* 6 (1987) 432.
- [6] M. Jaeger, R. Stumpf, C. Troll, H. Fischer, *Chem. Commun.* (2000) 931.
- [7] R. Stumpf, M. Jaeger, H. Fischer, *Organometallics* 20 (2001) 4040.
- [8] E.O. Fischer, K.R. Schmid, W. Kalbfus, C.G. Kreiter, *Chem. Ber.* 106 (1973) 3893.
- [9] K.H. Dötz, A. Rau, K. Harms, *Chem. Ber.* 125 (1992) 2137.
- [10] (a) E.O. Fischer, A. Maasböl, *Angew. Chem.* 76 (1964) 645; (b) E.O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.* 3 (1964) 580.
- [11] U. Schubert, in: K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss (Eds.), *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, p. 73 ff.
- [12] E.M. Cradwick, D. Hall, *J. Organomet. Chem.* 25 (1970) 91.
- [13] A.J. Mawby, G.E. Pringle, *J. Inorg. Nucl. Chem.* 34 (1972) 917.
- [14] M.G.B. Drew, A.P. Wolters, I.B. Tomkins, *J. Chem. Soc. Dalton Trans.* (1977) 974.
- [15] P.K. Baker, D.J. Muldoon, M.B. Hursthouse, S.J. Coles, A.J. Lavery, A. Shawcross, *Z. Naturforsch.* 51B (1996) 263.
- [16] (a) K.H. Dötz, H.-G. Erben, K. Harms, *J. Chem. Soc. Chem. Commun.* (1989) 692; (b) K.H. Dötz, R. Noack, K. Harms, G. Müller, *Tetrahedron* 46 (1990) 1235.
- [17] C.G. Pierpont, H.H. Downs, *J. Am. Chem. Soc.* 97 (1975) 2123.
- [18] K.H. Dötz, H.-G. Erben, W. Staudacher, K. Harms, G. Müller, J. Riede, *J. Organomet. Chem.* 355 (1988) 177.