

Novel hepta-coordinated molybdenum(II) and tungsten(II) carbene complexes by oxidative decarbonylation of Mo(0) and W(0) carbene complexes

Monika Jaeger, Rüdiger Stumpf, Carsten Troll and Helmut Fischer*

Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany.
E-mail: hfischer@dg6.chemie.uni-konstanz.de

Received (in Basel, Switzerland) 16th March 2000, Accepted 17th April 2000

C,O-Chelated tetracarbonyl[*o*-methoxyphenyl(methoxy)carbene] complexes of molybdenum(0) and tungsten(0) react with tin tetrahalides SnX₄ (X = Cl, Br, I) by oxidative decarbonylation and incorporation of two halides to form novel chelated hepta-coordinated Fischer-type tricarbonyl-(bishalogeno)carbene molybdenum(II) and tungsten(II) complexes

Heteroatom-stabilized Fischer-type transition-metal carbene complexes are important stoichiometric or catalytic reagents for the transformation of organic substrates and for the synthesis of organometallic compounds.¹ For instance, the carbene complexes [(CO)₅M=C(OR)R'] (M = Cr, Mo, W; R = Me, Et; R' = alkyl, aryl, ...) react with boron trihalides BX₃ by abstraction of OR⁻ and substitution of a halide ion for a CO ligand to give carbyne complexes, *trans*-[X(CO)₄M≡CR'] (Scheme 1).² Apart from boron trihalides, other Lewis acids such as aluminium or gallium trihalides^{3,4} or ethyl aluminium dichloride⁴ have also been employed in the synthesis of carbyne complexes.⁵

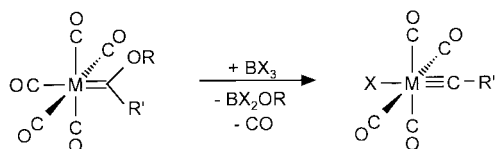
We now observed that the reactions of chelated alkoxy-carbene complexes of molybdenum and tungsten with the Lewis acids SnX₄ deviate from this carbene → carbyne transformation pattern and report (i) on the facile oxidation of the central metal in these complexes and (ii) on the formation of novel hepta-coordinated group 6 metal(II) carbene complexes.

Addition of a solution of SnCl₄ to the C,O carbene chelate complex **1a**⁶ in CH₂Cl₂ led to an immediate gas evolution. The originally brown solution turned red and a white precipitate formed. From the position and the intensity ratio of the ν(CO) absorptions (2049s and 1974vs cm⁻¹) in the IR spectrum[†] of the reaction solution it followed that very likely a carbyne complex⁷ had not been formed. The conclusion was confirmed by the ¹H NMR spectrum of the new complex (Scheme 2, **2a**). The spectrum exhibited, in addition to signals for four aromatic protons, two singlets at δ 4.49 and 4.94 (ratio 4:3:3) indicating that both MeO groups of **1a** were still present in the new complex. The mass spectrum indicated that two chloride atoms had been incorporated into the complex.

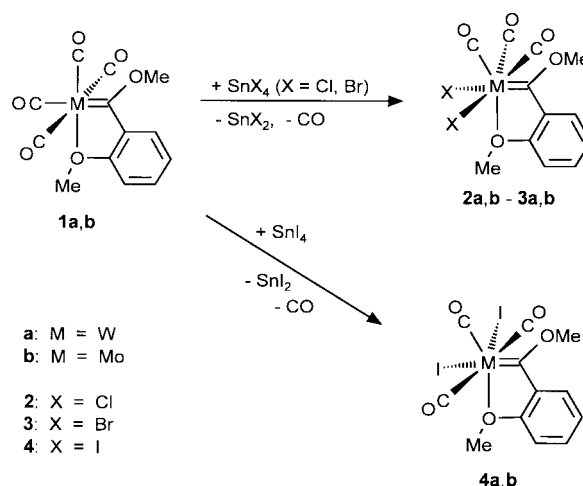
Finally, from pentane-CH₂Cl₂, crystals suitable for an X-ray analysis were grown.‡ The structure of **2a** is shown in Fig. 1. The metal is hepta-coordinated and the complex is C_s-symmetric. The mirror plane formed by the C,O-chelating carbene ligand, the tungsten atom and one CO ligand bisects the Cl-W-Cl angle and one OC-W-CO angle.

Obviously, SnCl₄ had not induced the abstraction of the methoxide substituent from the carbene carbon atom to give a tungsten(0) carbyne complex but rather acted as an oxidizing agent to give a tungsten(II) carbene complex.

The conversion of **1a** into **2a** is quantitative as could be shown by following the reaction of **1a** with SnCl₄ in CDCl₃ by



Scheme 1



Scheme 2

¹H NMR spectroscopy. Analogously to SnCl₄, treatment of **1a** with SbCl₅ or TiCl₄ also afforded complex **2a**. In contrast, when AlCl₃ was added to a solution of **1a** only rapid decomposition of the complex was observed.

The related tungsten(II) dibromo carbene chelate complex **3a** and the corresponding molybdenum(II) complexes **2b** and **3b** (Scheme 2) were obtained by reaction of **1a** with SnBr₄ and of **1b**⁵ with SnCl₄ and SnBr₄, respectively. The IR spectra of the resulting complexes were similar to that of **2a** indicating a similar structure.

In contrast, the diiodo carbene chelate complex **4a** (Scheme 2), formed when **1a** was treated with SnI₄, exhibited three rather than two ν(CO) absorptions and three CO resonances in the ¹³C NMR spectrum, as compared to two for **2a,b** and **3a,b**. These observations indicated that the structure of **4a,b** deviates from

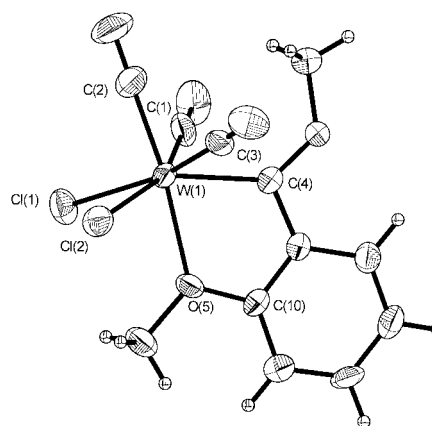
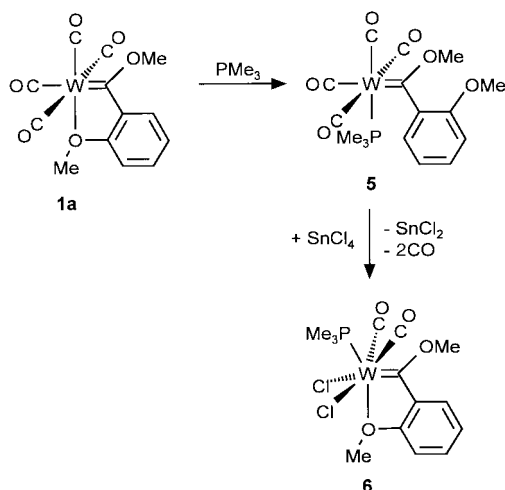


Fig. 1 Molecular structure of **2a**. Selected bond distances (Å) and angles (°): W(1)–C(1) 2.483(2), W(1)–Cl(2) 2.480(2), W(1)–C(1) 2.008(8), W(1)–C(2) 1.983(8), W(1)–C(4) 2.133(8), W(1)–O(5) 2.261(5); Cl(1)–W(1)–Cl(2) 85.1(1), Cl(1)–W(1)–C(4) 130.1(2), Cl(2)–W(1)–C(4) 131.5(2), Cl(1)–W(1)–C(1) 77.1(2), Cl(2)–W(1)–C(3) 78.8(2), C(1)–W(1)–C(3) 115.7(3), C(4)–W(1)–O(5) 73.6(2), W(1)–O(5)–C(10) 117.8(4).



that of **2a**. Presumably, the structure of **4a** is derived from that of **2a** by a mutual halide/CO exchange of two ligands outside the mirror-plane. The reaction of the molybdenum complex also proceeded rapidly, however, the resulting compound **4b** turned out to be very labile and could not be isolated. Its formation could only be established by IR spectroscopy.

Deviating from the tungsten and molybdenum complexes **1a,b** the corresponding chromium complex did not react with SnCl_4 . Within several hours in solution in the presence of SnCl_4 , as well as in its absence, only a slow decomposition of the carbene complex and formation of $[\text{Cr}(\text{CO})_6]$ was observed.

From these observations it was concluded that an energetically high-lying HOMO at the metal is required for the oxidative decarbonylation of **1a,b** by SnX_4 . The assumption is supported by the absence of a reaction between SnCl_4 and the non-chelated *o*-anisylcarbene(pentacarbonyl) complex $[(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{OMe-}o]$. After several hours at room temperature in CH_2Cl_2 only small amounts of **2a** could be detected, presumably formed *via* CO elimination to form **1a** which then rapidly reacts with SnCl_4 . In contrast, the reaction of the phenylcarbene complex $[(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}]$ with excess SnCl_4 afforded among other compounds a carbyne complex.

However, chelation of the carbene ligand is not a prerequisite for the oxidative decarbonylation as is shown by the reaction of **1a** with PMe_3 . Ring-opening of the metallacycle in **1a** by PMe_3 afforded the *cis*-carbene(tetracarbonyl)phosphine complex **5** which subsequently was transformed by SnCl_4 into the chelated tungsten(II) carbene complex **6** (Scheme 3).

Tungsten(II) complexes of the type $(\text{CO})_3(\text{L})_2(\text{X})_2\text{W}$ have been shown to catalyze the ring-opening polymerization of norbornene.⁸ Likewise, complexes **2–4** are active ROMP catalysts for norbornene even at room temperature. The highest catalytic activity was observed with the molybdenum complex **2b** which even at room temperature readily induces without a cocatalyst (i) the ring-opening polymerization of norbornene and norbornadiene and (albeit slowly) of cyclopentene, (ii) the polymerization of phenylacetylene, and (iii) the isomerization of pent-1-ene into pent-2-ene.

Hepta-coordinated Fischer-type Mo(II) and W(II) carbene complexes are exceedingly rare. Usually, Fischer-type carbene complexes react with oxidizing agents by oxidative decarbonylation of the carbene ligand.^{1a} Until now, the oxidative decarbonylation of group 6 carbonyl-carbene complexes has only been observed in the reactions of Br_2 with some Lappert-type carbene complexes in which the electron density at the central metal is increased by cyclic strongly electron-donating bisaminocarbene ligands $=\text{C}[\text{N}(\text{R})-\text{CH}_2-]_2$.⁹ Our results indicate that Fischer-type Mo(II) and W(II) carbene complexes are readily accessible by oxidation of Mo(0) and W(0) carbene complexes as soon as their oxidation potential is reduced by substitution of a suitable strong donor for a CO ligand.

Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Notes and references

† Selected spectroscopic data: IR (CH_2Cl_2): $\nu(\text{CO})$: 2049s, 1974vs (**2a**), 2056, 1989vs (**2b**), 2048s, 1973vs (**3a**), 2052s, 1986vs (**3b**), 2040vs, 1975s, 1922m (**4a**), 2046vs, 1985s, 1936 cm^{-1} (**4b**); ^1H NMR (CDCl_3 , room temp., rel. TMS): $\delta(\text{OMe})$ 4.49, 4.95 (**2a**), 4.53, 4.85 (**2b**), 4.51 (86%), 4.74 (14%), 5.06 (**3a**), 4.55, 4.96 (**3b**), 4.60, 5.16 (**4a**); ^{13}C NMR (CDCl_3 , room temp., rel. TMS): $\delta(\text{C}_{\text{Carbene}})$ 285.2 (**2a**), 295.6 (**2b**), 282.5 (**3a**), 293.2 (**3b**), 293.2 (**4a**); $\delta(\text{CO})$ 210.8, 214.6 (**2a**), 216.3, 220.4 (**2b**), 208.1, 213.3 (**3a**), 214.0, 219.8 (**3b**), 211.4, 213.7, 231.3 (**4a**).

‡ Crystal data for **2a** (from pentane- CH_2Cl_2 , 1:1): $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{O}_5\text{W}\cdot\text{CH}_2\text{Cl}_2$, $M = 573.9$, monoclinic, space group $P2_1/c$, $a = 9.567(6)$, $b = 11.994(6)$, $c = 15.986(5)$ Å, $\beta = 100.57(4)^\circ$, $V = 1803.3(15)$ Å³, $T = 246$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å. 3949 Unique reflections were collected of which 2782 were observed with $F > 4.0\sigma(F)$ (ω -scan). $R(R_w) = 0.035$ (0.037) (observed data). The structure was solved by Patterson methods using the SHELXTL PLUS (VMS) program package.

CCDC 182/1608. See <http://www.rsc.org/suppdata/cc/b0/b002228o/> for crystallographic files in .cif format.

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