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

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Abstract

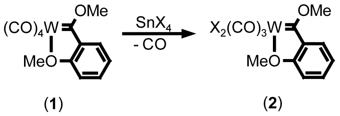
The carbene-*C*,*N* chelate tetracarbonyl tungsten complex $[(CO)_4\overline{W{=}C(Ph)NHC_5H_4N}\text{-}o]$ (**4**), obtained from $[(CO)_5W{=}C(Ph)OMe]$ (**3**) and *o*-aminopyridine, reacts with iodine by oxidative decarbonylation to give a single isomer of the carbene-*C*,*N* chelate tricarbonyl dihalogeno tungsten(II) complex $[(CO)_3I_2\overline{W{=}C(Ph)NHC_5H_4N}\text{-}o]$ (**5**). The analogous reaction of **4** with bromine affords two interconverting isomers of $[(CO)_3Br_2\overline{W{=}C(Ph)NHC_5H_4N}\text{-}o]$ (**6**). The oxidative decarbonylation of the carbene-*C*,*O* chelate tetracarbonyl tungsten complex $[(CO)_4\overline{W{=}C(OMe)C_6H_4O}Me\text{-}o]$ (**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 $[(CO)_4I_2\overline{W{=}C(OMe)C_6H_4O}Me\text{-}o]$ (**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, $C_6H_4Me\text{-}p$) 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].



(1)

X = Cl (**a**), Br (**b**), I (**c**)

The reaction of non-chelated tetracarbonyl(phosphine)carbene complexes, $[(CO)_4(PR_3)M{=}C(OMe)C_6H_4\text{-}OMe\text{-}o]$, 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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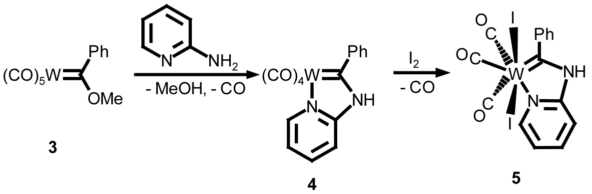
$HNMe_2$ as previously described [8]. When $SnBr_4$ was added to a solution of $[(CO)_5W{=}C(NMe_2)Ph]$ in $CDCl_3$, the color of the solution changed from yellow to orange, however, the spectra remained unchanged. When $SnBr_4$ was replaced by bromine, the solution turned dark brown. From the IR spectrum, it followed that several complexes had been formed. The ^1H-NMR spectrum indicated dissociation of the carbene ligand from the metal. A tungsten(II) carbene complex could not been identified. Obviously, the electron-donating properties of the aminocarbene ligand are insufficient for the oxidative decarbonylation to occur.

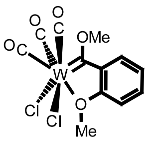
In contrast, the reaction of the *C*,*N*-chelated aminocarbene complex **4** with iodine afforded a tungsten(II) carbene complex. Complex **4** was obtained analogously to the homologous chromium complex [9] by aminolysis of **3** [10] with 2-aminopyridine at low temperature and subsequent decarbonylative chelation at ambient temperature. When an equimolar amount of iodine was slowly added to a solution of **4** in dichloromethane, the evolution of a gas was observed. The solution turned red and an orange precipitate **5** formed (Eq. (2)).



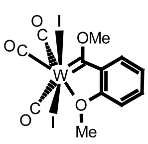
(2)

Complex **5** is readily soluble in tetrahydrofuran, but poorly soluble in dichloromethane. Thus, small amounts of CH_2Cl_2-soluble by-products are easily removed by washing of the precipitate with CH_2Cl_2.

The IR spectrum of complex **5** in THF shows three ν(CO) absorption, indicating the lack of a mirror plane in the complex. The spectrum is similar to that of the carbene-*C*,*O* chelate *diiodo* complex **2c** [6] but the ν(CO) absorptions are at slightly higher energies. In contrast, the related C_s-symmetric *dichloro* complex **2a** [6] exhibits two ν(CO) absorptions only.



2a



2c

On oxidative decarbonylation, the resonance of the *ortho* proton of the pyridyl group in the ^1H-NMR spectrum shifts to lower field ($\delta = 9.38$ ppm) compared to that of **4** ($\delta = 8.97$ ppm) as expected from the change in the oxidation number from 0 to 2. In accord with the conclusions drawn from the ν(CO) spectrum the ^{13}C-NMR spectrum of **5** exhibits three CO resonances ($\delta =$ 213.0, 214.5, and 238.0 ppm). The number and position of these resonances are similar to those of **2c** indicating a similar structure. As expected, the carbene resonance in **5** is at considerably higher field than that in **2c** ($\delta =$ 258.5 ppm in **5** and 293.2 ppm in **2c**).

The structure of **5** was additionally established by an X-ray analysis (Fig. 1, Table 1). For comparison, an X-ray structural analysis was also performed on **2c** (Fig. 2, Table 1). The synthesis of complex **2c** (see Eq. (1)) has already been described earlier [6].

Complex **5** crystallizes with two equivalents of THF and complex **2c** with 1/4 equivalent of CH_2Cl_2. The unit cell of **2c** contains two independent molecules. As deduced from the IR and NMR spectra, the structures of **2c** and **5** are similar and are best described by a distorted capped octahedron (Fig. 3).

One CO ligand occupies the capping position. The chelating carbene ligand bridges the capped (CO, CO, carbene carbon atom) and the uncapped face (I, I, N in **5** or OMe in **2c**) of the octahedron. The carbene carbon and one iodide, the heteroatom (O or N) and one CO ligand as well as the second iodide and a CO ligand are mutually ‘trans’. The chelate ring (W1, C4, C5, C10, O5 in **2c** and W1, C4, N1, C21, N2 in **5**) only slightly

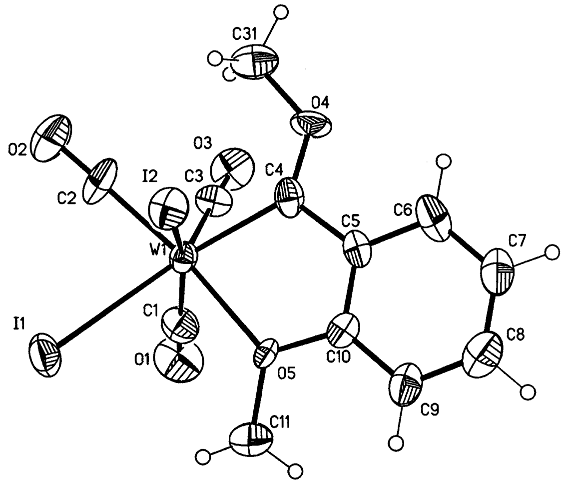


Fig. 1. Molecular structure of **2c**. Selected bond distances (Å) and angles (°): molecule 1: W(1)–I(1) 2.867(1), W(1)–I(2) 2.830(1), W(1)–C(1) 2.037(14), W(1)–C(2) 1.982(13), W(1)–C(3) 1.930(15), W(1)–C(4) 2.130(12), W(1)–O(5) 2.256(7), C(4)–C(5) 1.472(16), C(5)–C(10) 1.375(16), C(10)–O(5) 1.387(14), I(1)–W(1)–I(2) 85.70(4), C(1)–W(1)–C(2) 106.2(6), C(1)–W(1)–C(3) 72.6(5), I(1)–W(1)–C(4) 153.3(3), I(2)–W(1)–C(4) 70.8(3), I(1)–W(1)–O(5) 91.9(2), I(2)–W(1)–O(5) 85.8(2), C(4)–W(1)–O(5) 74.2(4), W(1)–C(4)–C(5) 115.7(9), C(5)–C(10)–O(5) 114.7(10), W(1)–O(5)–C(10) 116.7(6); molecule 2: W(1A)–I(1A) 2.891(1), W(1A)–I(2A) 2.829(1), W(1A)–C(1A) 2.005(15), W(1A)–C(2A) 1.939(16), W(1A)–C(3A) 1.938(14), W(1A)–C(4A) 2.129(13), W(1A)–O(5A) 2.264(9), C(4A)–C(5A) 1.463(17), C(5A)–C(10A) 1.371(19), C(10A)–O(5A) 1.399(14), I(1A)–W(1A)–I(2A) 87.11(4), C(1A)–W(1A)–C(2A) 103.8(6), C(1A)–W(1A)–C(3A) 72.6(6), I(1A)–W(1A)–C(4A) 157.5(4), I(2A)–W(1A)–C(4A) 74.3(3), I(1A)–W(1A)–O(5A) 93.0(2), I(2A)–W(1A)–O(5A) 86.3(2), C(4A)–W(1A)–O(5A) 73.7(4), W(1A)–C(4A)–C(5A) 116.9(9), C(5A)–C(10A)–O(5A) 114.4(11), W(1A)–O(5A)–C(10A) 116.6(8).

Table 1
Crystallographic data for and **2c**·1/4CH_2Cl_2 and **5**·2THF

	2c·1/4CH_2Cl_2	**5**·2THF
Empirical formula	$C_{12}H_{10}I_2O_5W\cdot 1/4CH_2Cl_2$	$C_{15}H_{10}I_2N_2O_3W\cdot 2THF$
M_r (g mol^{-1}) (including solvent)	682.2	848.1
Temperature (K)	240(2)	245(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	16.550(4)	11.857(1)
b (Å)	15.630(5)	12.842(1)
c (Å)	28.029(5)	18.429(2)
β (°)	102.62(2)	90.50(1)
Cell volume (Å^3)	7075(2)	2806.1(4)
Z	8	4
D_{calc} (g cm^{-3})	2.603	2.008
μ(Mo–K_α) (mm^{-1})	10.110	6.350
F(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 [$F > 4.0\sigma(F)$]	5148 [$F > 4.0\sigma(F)$]
Independent reflections	7702	6134
Min/max transmission	0.2690/0.5872	0.0396/0.0797
Parameters refined	375	298
R_1 (%)	5.29	4.97
wR_2 (%)	10.00	12.38
Res. electron density (e Å^{-3})	1.578 and −1.446	0.983 and −0.967

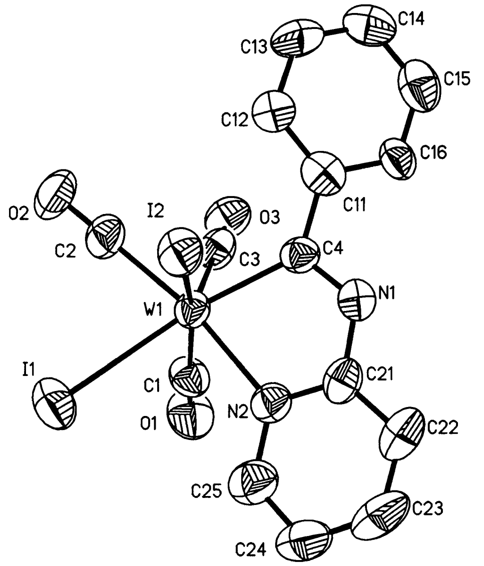


Fig. 2. Molecular structure of **5**. Selected bond distances (Å) and angles (°): W(1)–I(1) 2.8846(8), W(1)–I(2) 2.8438(7), W(1)–C(1) 1.986(9), W(1)–C(2) 2.008(10), W(1)–C(3) 1.972(10), W(1)–C(4) 2.135(8), W(1)–N(2) 2.225(7), C(4)–N(1) 1.326(10), N(1)–C(21) 1.391(12), C(21)–N(2) 1.326(11); I(1)–W(1)–I(2) 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).

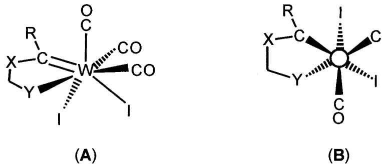
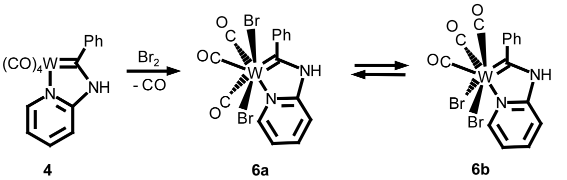


Fig. 3. Structure of **2c** and **5** shown in two different perspectives: (A) side view; and (B) view along the capping OC–W axis.

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 alkoxycarbene 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.

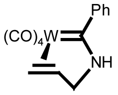


(3)

The ^{1}H-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 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 ^{13}C-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 C_1-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 C_1-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 $[(CO)_3Br(Br_3Ge)W(bipy)]$ [12] or $[(CO)_2Cl_2Mo(PMe_2Ph)_3]$ [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 $[(CO)_2Cl_2Mo(\eta^2\text{-}Ph_2X{-}CH_2{-}XPh_2)(\eta^1\text{-}Ph_2X{-}CH_2{-}XPh_2)]$ is that of a capped octahedron for X = As and that of a distorted capped trigonal prism for X = P. In the crystal $[(CO)_3I_2W(NCPh)_2]$ is a capped octahedron, one of the three CO ligand assuming the capping position. In solution all carbonyl ligands are equivalent in the ^{13}C-NMR spectrum even at −70 °C [15].

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



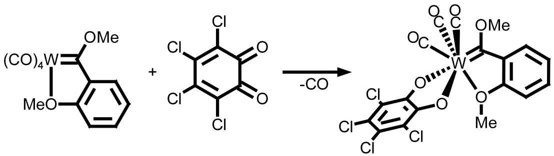
7

The electron-donating properties of chelating ‘C(Ph)–NH–CH$_2$–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 $[(CO)_5W{=}C(Ph)NMe_2]$. Complex **7** reacted in acetonitrile with bromine even at −30 °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 °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 $[OR]^-$ or $[SR]^-$ failed. The reactions of **2b** or **2c** with NaOEt or LiO-*t*-Bu led to dissociation of the carbene ligand. Likewise, no substitution product could be isolated from the reactions of **2b** with Na[SC$_6$H$_4$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*-benzochinone was chosen for that.

When a solution of tetrachloro-*o*-benzochinone in dichloromethane was added to a solution of **3** in CH$_2$Cl$_2$ at −10 °C, the evolution of a gas was observed. Chromatography of the reaction mixture with pentane–dichloromethane at −50 °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.



(4)

Two signals for OMe groups in the ^1H-NMR spectrum of **8** indicated that the carbene ligand was still coordinated to the metal. From the observation of two *ν*(CO) absorptions in the IR spectrum and of two carbonyl resonances (ratio ca. 1:2) in the ^{13}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 °C for prolonged periods of time.

In contrast to the reaction of **3** with tetrachloro-*o*-benzochinone that with 3,5-di-*tert*-butyl-*o*-benzochinone proceeded only slowly at room temperature. When one equivalent of the chinone was added, the two new *ν*(CO) absorptions in the IR spectrum indicated the formation of a new complex, however, the reaction was still incomplete. When benzochinone 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*-benzochinone albeit slowly but quickly decomposed again either by reaction with the chinone or by another pathway. Further oxidation of the tungsten(II) complex seems possible since $[Mo(CO)_6]$ was found to react with tetrachloro-*o*-benzochinone or 3,5-di-*tert*-butyl-*o*-benzochinone 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 CaH_2 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. — ^{1}H-NMR and ^{13}C-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 Me_4Si (^{1}H-NMR spectra) or to the residual solvent peaks (^{13}C-NMR spectra: $CDCl_3$ $\delta=77.0$ ppm, CD_2Cl_2 $\delta=53.8$ ppm, C_3H_6O-$d_6=206.6$ ppm).

3.2. Tricarbonyldiiodo[phenyl(2-pyridylamino)carbene-κ^2C,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 CH_2Cl_2. 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 C_5H_{12} 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. — ^{1}H-NMR (C_3H_6O-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). — ^{13}C-NMR (C_3H_6O-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 $C_{15}H_{10}I_2N_2O_3W$ (703.9): C, 25.59; H, 1.43; N, 3.98%.

3.3. Dibromotricarbonyl[phenyl(2-pyridylamino)carbene-κ^2C,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 CH_2Cl_2. 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 C_5H_{12} 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. — ^{1}H-NMR (C_3H_6O-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**). — ^{13}C-NMR (C_3H_6O-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-κ^2C,O](tetrachloro-*o*-chinolato-$\kappa^2C^{1,2}$)tungsten(II) (**8**)

At −10 °C, a solution of 0.77 g (3.13 mmol) of tetrachloro-*o*-benzochinone in 50 ml of CH_2Cl_2 was added within 30 min to a solution of 1.47 g (3.3 mmol) of **1** in 50 ml of CH_2Cl_2. The solvent was removed in vacuo. The residue was chromatographed at −50 °C with C_5H_{12}–CH_2Cl_2 (ratio slowly changing from 10:1 to 1:20) on silica gel. Four fractions were eluted. The first orange fraction contained $[(CO)_5W{=}C(OMe)C_6H_4OMe$-*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 (CH_2Cl_2, cm^{-1}): ν(CO) 2043 s, 1958 vs. — ^{1}H-NMR (C_3H_6O-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). — ^{1}H-NMR ($CDCl_3$): 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). — ^{13}C-NMR (CD_2Cl_2, −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 $C_{18}H_{10}Cl_4O_7W$ (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 C_5H_{12} into a solution of **2c** in CH_2Cl_2 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, $\lambda=0.71073$ Å). For the data collection, the Wykoff technique was used ($4.0<2\theta<54.0°$). 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).

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