The first carbene-\(\text{C},\text{N}\) chelate tetracarbonyl dihalogeno and carbene-\(\text{C},\text{O}\) chelate tetracarbonyl benzochinone tungsten complexes

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Abstract

The carbene-\(\text{C},\text{N}\) chelate tetracarbonyl tungsten complex \([(\text{CO})_4\text{W}(\text{Ph})\text{NHC}_5\text{H}_4\text{N}-\text{o})]\) (4), obtained from \([(\text{CO})_5\text{W}(\text{OMe})]\) (3) and \(\text{o}-\text{aminopyridine}\), reacts with iodine by oxidative decarbonylation to give a single isomer of the carbene-\(\text{C},\text{N}\) chelate tricarbonyl dihalogeno tungsten(II) complex \([(\text{CO})_3\text{I}_2\text{W}(\text{Ph})\text{NHC}_5\text{H}_4\text{N}-\text{o})]\) (5). The analogous reaction of 4 with bromine affords two interconverting isomers of \([(\text{CO})_3\text{Br}_2\text{W}(\text{Ph})\text{NHC}_5\text{H}_4\text{N}-\text{o})]\) (6). The oxidative decarbonylation of the carbene-\(\text{C},\text{O}\) chelate tetracarbonyl tungsten complex \([(\text{CO})_4\text{W}(\text{OMe})\text{C}_6\text{H}_4\text{O}-\text{Me}-\text{o})]\) (1) with tetrachloro-\(\text{o}\)-benzochinone yields the first carbene-\(\text{C},\text{O}\) chelate tricarbonyl-\(\text{o}\)-benzochinone tungsten(II) complex 8. The structures of 5 and of \([(\text{CO})_4\text{I}_2\text{W}(\text{OMe})\text{C}_6\text{H}_4\text{O}-\text{Me}-\text{o})]\) (2c) were established by X-ray structural analyses.

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 \(\pi\)-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 \(\text{N}\)-heterocyclic carbene ligands is almost negligible [3]. In addition, a few compounds of the type \([\text{Cl}_3(\text{CO})-(\text{PMe}_3)_2\text{W}=\text{C}(\text{R})\text{H}]\) (\(\text{R}=\text{CMMe}_2,\ \text{Ph, C}_6\text{H}_4\text{Me-p}\)) were prepared by Schrock and coworkers [4] and Mayr et al. [5].

Recently, we reported the synthesis of the first heptacoordinated dihalogeno carbene-\(\text{C},\text{O}\) chelate tricarbonyl molybdenum(II) and tungsten(II) complexes by oxidative decarbonylation of carbene-\(\text{C},\text{O}\) chelate tetracarbonyl complexes with SnX\(_4\) (\(\text{X}=\text{Cl, Br, I}\)), SbCl\(_5\), or TiCl\(_4\), e.g. Eq. (1) [6].

\[
\text{(CO)}_4\text{W}(\text{OMe})\text{C}_6\text{H}_4\text{O}-\text{Me}-\text{o} + \text{SnCl}_4 \rightarrow \text{(CO)}_4\text{W}(\text{OMe})\text{C}_6\text{H}_4\text{O}-\text{Me}-\text{o} + \text{SnCl}_3 \text{Cl} + \text{CO}.
\]

The reaction of non-chelated tetracarbonyl(phosphine)carbene complexes, \([(\text{CO})_4(\text{PR}_3)\text{M}=\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{O}-\text{OMe}-\text{o})]\), with SnX\(_4\) or bromine was found to likewise afford carbene-\(\text{C},\text{O}\) chelate dihalogeno complexes [6,7]. In contrast, the reaction of the non-chelated pentacarbonylcarbene complex \([(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}]\) (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 \([(\text{CO})_5\text{W}=\text{C}(\text{NMe}_2)\text{Ph}]\) was prepared from \([(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}]\) (3) and
HNMe₂ as previously described [8]. When SnBr₄ was added to a solution of [(CO)₃W=C(NMe₂)Ph] in CDCl₃, the color of the solution changed from yellow to orange, however, the spectra remained unchanged. When SnBr₄ 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 be identified. Obviously, the electron-donating properties of the amino carbene ligand are insufficient for the oxidative decarbonylation to occur.

In contrast, the reaction of the C,N-chelated amino carbene 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)).

\[
\text{(CO)₃W} \text{Ph} \text{NHMe}_2 \rightarrow \text{(CO)₃W} \text{Ph} \text{NH} \rightarrow \text{I} \rightarrow \text{CO} \\
\]

Complex 5 is readily soluble in tetrahydrofuran, but poorly soluble in dichloromethane. Thus, small amounts of CH₂Cl₂-soluble by-products are easily removed by washing of the precipitate with CH₂Cl₂.

The IR spectrum of complex 5 in THF shows three ν(CO) absorptions, indicating the lack of a mirror plane in the complex. The spectrum is similar to that of the carbene-C,O chelate diiodo complex 2e [6] but the ν(CO) absorptions are at slightly higher energies. In contrast, the related C₄-symmetric dichloro complex 2a [6] exhibits two ν(CO) absorptions only.

![Image](image.png)

On oxidative decarbonylation, the resonance of the ortho proton of the pyridyl group in the ¹H-NMR spectrum shifts to lower field (δ = 9.38 ppm) compared to that of 4 (δ = 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 ¹³C-NMR spectrum of 5 exhibits three CO resonances (δ = 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 (δ = 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 CH₂Cl₂. 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, carbonbene 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 (°): molecular 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) 2.839(1), W(1A)–I(2A) 2.829(1), W(1′)–C(1′A) 2.005(15), W(1′)–C(2′A) 1.939(16), W(1′)–C(3′A) 1.938(14), W(1′)–C(4′A) 2.129(13), W(1′)–O(5′A) 2.264(9), C(4′A)–C(5′A) 1.463(17), C(5′A)–C(10′A) 1.371(19), C(10′A)–O(5′A) 1.399(14), I(1′)–W(1′)–I(2′A) 87.11(4), C(1′A)–W(1′)–C(2′A) 103.8(6), C(1′A)–W(1′)–C(3′A) 72.6(6), I(1′)–W(1′)–C(4′A) 157.5(4), I(2′A)–W(1′)–C(4′A) 74.3(3), I(1′)–W(1′)–O(5′A) 93.0(2), I(2′A)–W(1′)–O(5′A) 86.3(2), C(4′A)–W(1′)–O(5′A) 73.7(4), W(1′)–C(4′A)–C(5′A) 116.9(9), C(5′A)–C(10′A)–O(5′A) 114.4(11), W(1′)–O(5′A)–C(10′A) 116.6(8).}
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 C3-symmetric and the mirror plane (formed by the chelate ring and one CO ligand) bisects the Cl–W–CI 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 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,C-O-chelate tetracarbonyl complexes gave either C3-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 C3-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.

![Fig. 2. Molecular structure of 5. Selected bond distances (Å) and angles (°): W(1)–I(1) 2.8848(6), 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) 155.2(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).](Image 3)

![Fig. 3. Structure of 2c and 5 shown in two different perspectives: (A) side view; and (B) view along the capping OC–W axis.](Image 4)

![Table 1 Crystallographic data for and 2c·1/4CH2Cl2 and 5·2THF](Image 5)

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<td>C15H10I2N2O3W·2THF</td>
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<tr>
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<td>wR2 (%)</td>
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<td>0.983 and −0.967</td>
</tr>
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The difference in energy between the different structures for heptacoordinated complexes is small. Complexes with a structure intermediate between a capped octahedron and a prism are known, for example \([(\text{CO})_5\text{Br}(\text{Br}_3\text{Ge})\text{W}(\text{bipy})]\) [12] or \([(\text{CO})_2\text{Cl}_2\text{Mo}(\text{P-Me}_2\text{Ph}_2)]\) [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 \([(\text{CO})_2\text{Cl}_2\text{Mo}(\text{Ph}_2\text{X}\text{CH}_2\text{CH}_2\text{XPH}_3)(\text{Ph}_3\text{P})]\) is of a capped octahedron for \(X = \text{As}\) and of a distorted capped trigonal prism for \(X = \text{P}\). In the crystal \([(\text{CO})_2\text{W}(\text{NCPh})_2]\) 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 \(-70\) °C [15].

Next the reaction of bromine with the \(C,C=\text{C}\)-chelating complex 7 [16] was investigated.

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 \([(\text{CO})_3\text{W} = \text{C(Ph)NMMe}_2]\). 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[\(\text{SC}_{6}\text{H}_4\text{Me-}p\)] 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 TIBF\(_4\) 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 \(\alpha\)-benzochinone was chosen for that.

When a solution of tetrachloro-\(\alpha\)-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.

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 \(v(\text{CO})\) 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 \(-30\) °C for prolonged periods of time.

In contrast to the reaction of 3 with tetrachloro-\(\alpha\)-benzochinone that with 3,5-di-tert-butyl-\(\alpha\)-benzochinone proceeded only slowly at room temperature. When one equivalent of the chinone was added, the two new \(v(\text{CO})\) 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-\(\alpha\)-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 [\(\text{Mo(\text{CO})}_3\)] was found to react with tetrachloro-\(\alpha\)-benzochinone or 3,5-di-tert-butyl-\(\alpha\)-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 CaH₂ and were freshly distilled prior to use. The yields refer to analytically pure compounds and were not optimized. The complexes 1 [18], 2e [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 quoted relative to Me₂Si (¹H-NMR spectra) or to the residual solvent peaks (¹³C-NMR spectra: CDCl₃ δ = 77.0 ppm, CD₂Cl₂ δ = 53.8 ppm, C₆H₆O-d₆ = 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 solution of a gas, the color of the solution turned red. 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

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 (C₆H₆O-d₆, -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 (C₆H₆O-d₆, -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-κ²C₃) 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)₃W(C(O)Me)C₆H₄OMe-]₂, 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 (C₆H₆O-d₆): δ 4.03 (s, 3H, carbene-OMe), 4.70 (s, 3H, aryl-OMe), 7.42 (t, J = 7.5 Hz, 1H, aryl), 7.67 (d, J = 8.6 Hz, 1H, aryl), 7.84 (d, J = 7.9 Hz, 1H, aryl), 8.78 (t, J = 7.3 Hz, 1H, aryl). — ¹³C-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). — ¹⁵N-NMR (CDCl₃, -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 2e and 5

Single crystals of 2e suitable for an X-ray structural analysis were obtained by slow diffusion of C₅H₁₂ into a solution of 2e 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 (2e) and P4 diffractometer (5) (graphite monochromator, Mo–Kα radiation, λ = 0.71073 Å). For the data collection, the Wyckoff 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).

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