C–O bond activation in carbene-C,O chelate tungsten(II) complexes — MeX elimination in the reaction of
\[ X_2(CO)_3\text{W} = \text{C}(\text{C}_6\text{H}_4\text{OMe}-o)\text{OMe} \] with \( L_2 \) (\( L_2 = \text{dppe}, 2 \text{PMe}_3 \))

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Abstract

The heptacoordinated dihalogeno carbene-C,O chelate carbonyl complexes \[ X_2(CO)_3\text{W} = \text{C}(\text{C}_6\text{H}_4\text{OMe}-o)\text{OMe} \] (3a–c, \( X = \text{Cl} \) (a), \( \text{Br} \) (b), \( \text{I} \) (c)) react with \( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \) (dppe) via CO and MeX elimination to give the aryloxycarbene-C,O chelate complexes \[ X(CO)_2(\text{dppe})\text{W} = \text{C}(\text{C}_6\text{H}_4\text{OMe}-o)\text{OMe} \] (7a–c). The analogous reactions of 3a–c with two equivalents of \( \text{PMe}_3 \) and that of the monophosphine complexes \[ X_2(CO)_2(\text{PMe}_3)\text{W} = \text{C}(\text{C}_6\text{H}_4\text{OMe}-o)\text{OMe} \] (9a–c) with one equivalent of \( \text{PMe}_3 \) likewise afford aryloxycarbene-C,O chelate complexes \[ X(CO)_2(\text{PMe}_3)_2\text{W} = \text{C}(\text{C}_6\text{H}_4\text{OMe}-o)\text{OMe} \] (8a–c). In contrast to 8a and 8b the structure of 8c is dynamic. © 2001 Published by Elsevier Science B.V.

Keywords: Carbene complexes; Substitution; Elimination; Tungsten complexes

1. Introduction

Fischer-type molybdenum(II) and tungsten(II) carbene carbonyl complexes not stabilized by aromatic \( \pi \)-ligands are a rather rare class of carbene complexes [1]. A few compounds of the type \[ \text{Cl}_2(CO)(\text{PMe}_3)_2\text{W} = \text{C}(\text{R})\text{H} \] (\( \text{R} = \text{CMe}_3, \text{Ph}, \text{C}_6\text{H}_4\text{Me}-p \)) were prepared by Schrock and coworkers [2] and Mayr et al. [3]. Recently, we reported on 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 \( \text{SnX}_4 \) (\( X = \text{Cl}, \text{Br}, \text{I}, \text{SbCl}_5 \), or \( \text{TiCl}_4 \) (Eq. 1) [4].

Before, by oxidation of W(0) carbene complexes only a few Lappert-type W(II) complexes with cyclic bisaminocarbene ligands had been obtained [5]. Compared to Fischer-type carbene ligands, the back-bonding properties of the \( N \)-heterocyclic carbene ligands is almost negligible [6]. In addition to the carbene-C,O chelate complexes 1 and 2 non-chelated carbene tungsten(0) complexes such as 5 were also found to react with \( \text{SnX}_4 \) by oxidative decarbonylation to likewise form dihalogeno carbene-C,O chelate phosphine tungsten(II) complexes 6 (Eq. 2) [7].

The corresponding reaction of \([\text{CO}]_4(\text{Bu,P})\text{W} = \text{C}(\text{OMe})\text{C}_6\text{H}_4\text{R}‘-p \) (\( R‘ = \text{H}, \text{OMe} \) with \( \text{SnBr}_4 \) afforded non-chelated carbene W(II) complexes \([\text{Br}_2(\text{CO})_2(\text{Bu,P})\text{W} = \text{C}(\text{OMe})\text{C}_6\text{H}_4\text{R}‘-p \]. An alternative approach to non-chelated carbene W(II) complexes involves the opening of the chelate

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ring in carbene-C,O chelate W(II) complexes. Thus, when 1 was treated with PPh3, the complex [(CO)4(PPh3)W=C(OCH3)C6H4OMe-o] was formed. However, treatment of 3b with one equivalent of PMe3 did not give the corresponding non-chelated carbene W(II) complex but rather, via exchange of a CO ligand by PMe3, the CO substitution product (Eq. 3).

\[
\begin{align*}
\text{Br}_2(CO)_3W=O & \quad \text{PMe}_3 \quad \text{Br}_2(CO)_3(Me)_3W=O \\
\end{align*}
\]

(3)

We now report on another reaction course strongly deviating from those observed so far.

2. Results

When one equivalent of 1,2-bis(diphenylphosphino)ethane, Ph2PCH2CH2PPh2 (dppe), was added to a solution of 3c in dichloromethane, a rapid gas evolution was observed. From the resulting solution a red powder (7c, yield 86%) was isolated (Eq. 4).

\[
\begin{align*}
X_2(CO)_3W & \quad \text{Ph}_2PCH_2CH_2PPh_2 \quad Ph_2PCH_2CH_2PPh_2 \\
\end{align*}
\]

(4)

Surprisingly, the 1H-NMR spectrum of the new compound 7c showed, apart from the peaks expected for the dppe ligand and the C6H4 group, only one OMe resonance (at δ = 4.47 ppm) indicating loss of one methyl group in the course of the reaction. In accord with the conclusion the 31P-NMR spectrum likewise exhibited only one OMe resonance in addition to signals for two inequivalent CO ligands, the carbene carbon atom and the carbon atoms of the dppe ligand and the C6H4 group. From the positions and the coupling constants of the peaks in the 31P-NMR spectrum it followed that both phosphorus atoms of the dppe ligand were attached to the metal in inequivalent positions.

When the reaction was carried out in a sealed tube in CD2Cl2 and the progress of the reaction was monitored by 1H-NMR spectroscopy, an additional Me resonance was detected. By comparison with the spectrum of an authentic sample the additional peak could be assigned to MeI. These observations indicated the elimination of one iodide ligand and of the Me substituent of the coordinating OMe group in the form of MeI and the addition of dppe to the complex.

The chloro and the bromo complexes 3a and 3b reacted with dppe analogously. In both cases, carbene-C,O chelate complexes with a chelating bisphosphine ligand (Eq. 4: 7a and 7b) and the corresponding methyl halides were formed. Complex 7a was obtained in 78%, 7b in 82% yield. From the NMR and IR spectra it followed that 7a and 7b were structurally related to 7c.

CO and MeX elimination as observed in the reactions of 3a–c with dppe was not confined to reactions with bisphosphine as the substrate. When one equivalent of PMe3 was added to solutions of 3c in dichloromethane, only half of 3c was consumed. Two equivalents of PMe3 were required for the complete conversion of 3c. Again, by 1H-NMR spectroscopy the formation of MeI was detected.

The 1H-NMR spectrum of the new complex 8c (Eq. 5) in CD2Cl2 at −80 °C exhibited, in addition to the peaks for the C6H4 group, a sharp singlet at δ = 4.41 ppm for the OMe group and two well separated doublets at δ = 1.25 and 1.42 (J = 9.5 Hz, each) for the methyl substituents of the PMe3 ligand (intensity ratio 1:3:3) indicating inequivalence of the PMe3 ligands. The 31P-NMR spectrum showed two resonances, both at ambient temperature and at −80 °C, confirming the inequivalence of the phosphine ligands. In accord with that the 13C-NMR spectrum exhibited two doublets for the PMe3 ligands. The resonances of the carbene carbon atom and the two carbonyl ligands were split into two doublets each.

When solutions of 8c in CD2Cl2 were warmed to ambient temperature the two doublets attributed to PMe3 coalesced into a broad singlet at δ = 1.4 ppm indicating a dynamic process that leads to equivalence of the PMe3 ligands on the 1H-NMR time scale at that temperature (see Eq. 5) presumably by a polytopal rearrangement via a pentagonal-bipyramidal transition state.

The chloro and bromo complexes 3a and 3b reacted with PMe3 in excess in a similar way as was deduced from NMR and IR spectroscopic observations. In both cases, carbene-C,O chelate bisphosphine complexes related to 8c (Eq. 6: 8a and 8b) and the corresponding methyl halides were formed. However, in contrast to 8c, 8a and 8b did not show dynamic behavior.
The complexes 8a–c were also formed when PMe₃ was added to solutions of the monophosphine complexes 9a–c, respectively (Eq. 7).

This indicated that monophosphine complexes might be intermediates in the formation of 8a–c from 3a–c and PMe₃. Therefore, solutions of 3a–c were titrated with PMe₃ applying the same reaction conditions, 8c readily formed but 3c was consumed first. From this observation it followed that in the reaction of 3c with PMe₃ to give 8c, the sequence 3c → 9c → 8c is at best of minor importance and 8c is preferentially formed via an intermediate other than 9c. Nonetheless, with PMe₃ in excess, 9c is converted into 8c albeit considerably slower than 3c.

3. Discussion and conclusion

The reactivity of dihalogeno carbene-C,O chelate carbonyl complexes towards phosphines has turned out to be more diverse than originally anticipated. Previously [7], two reaction patterns had been identified: (a) replacement of a CO ligand in these carbene-C,O chelate complexes by a coordinating phosphine to give dihalogeno carbene-C,O chelate carbonyl phosphine complexes and (b) displacement of the chelating methoxy group of the carbene-C,O chelate ligand by the phosphine to give non-chelated dihalogeno carbene carbonyl phosphine complexes.

The reaction mode described in this paper strongly deviates from these reaction patterns although the formation of 7a–c from 3a–c and dppe presumably also is initiated by replacement of the coordinating methoxy ligand by the phosphine. Opening of the metallocycle is then followed by dissociation of a CO ligand and re-chelation. Alternatively, the phosphine could also directly displace a CO ligand to give a dihalogeno carbene-C,O chelate carbonyl phosphine complex as has been observed in the reactions of 3a and 3b with one equivalent of PMe₃. A subsequent displacement of a halogeno ligand by the second phosphine (or the second PPh₂ end group of dppe) could lead to a cationic carbene phosphine complex. A similar formation of a cationic from a neutral complex has already been observed before: the heptacoordinated complex [MoBr₂(CO)(bipy)(dppm)] reacted with phosphines and phosphites L to give [MoBr₂(CO)(bipy)(dppm)L]⁺ (bipy = 2,2’-bipyridine, dppm = bis(dimethylphosphino)methane) [8]. The phosphine/halide substitution step could then be followed by cleavage of the O–CH₃ bond of the aryl methoxy group which is activated by coordination to the cationic metal center. This step presumably proceeds by a nucleophilic attack of the halide at CH₃, in an S_N2 type fashion. A related reaction has been observed with a cationic iron complex (Eq. 8) [9].

All dihalogeno carbene-C,O chelate complexes 3a–c react with excess PMe₃ to give aryloxycarbene-C,O chelate complexes 8a–c, though at different rates. However, while 9a and 9b are intermediates in this reaction, for 9c this could be ruled out by competition experiments and by comparison of the relative reaction rates. The deviating behavior of 3c compared to 3a,b is possibly due to the different structures of 3a–c. The structure of all dihalogeno carbene-C,O chelate tricarbonyl complexes 3a–c is best described by a capped octahedron. The complexes 3a and 3b are C₂-symmetric, the carbene carbon atom occupying the capping position. The mirror plane (formed by the C,O-chelating carbene ligand, the metal, and one CO ligand)
bisects the X–W–X angle (Fig. 1 [4]). The structure of 3c deviates from this arrangement. Instead of the carbene carbon atom, a CO ligand occupies the capping position and the chelating carbene ligand bridges the capped (CO, CO, carbene carbon atom) and the uncapped face (I, I, OMe) of the octahedron (Fig. 1 [4]).

If we assume that the incoming ligand attacks the metal at the uncapped face of the octahedron opposite to the capping position (the most accessible site in a capped octahedron) the intermediates resulting from 3a and 3b, on the one hand, and from 3c, on the other hand, would have different structures. In 9a and 9b, the substitution products of the reaction of 3a and 3b with PMe 3, the distribution of the ligands to the various coordination sites in the polyhedron (see Fig. 1 [4]) is sterically and electronically favorable. A similar attack of PMe 3 at 3c (arrow in Fig. 1) would lead to an unfavorable distribution and thus to a labile complex. Please note that, in contrast to 9a and 9b, complex 3c cannot be prepared by substitution of a CO ligand in 3c but is accessible only by oxidative decarbonylation of [(CO)2W=C(C6H4OMe-0)OMe] with SnI 4 [7]. Addition of a phosphine to 9a,b, again to the uncapped face (arrow, Fig. 1), and elimination of MeX finally gives 8a,b. Until now, it was not possible to establish the detailed structure of 8a,b by X-ray crystallography. The most likely structure of 8a,b is shown in Fig. 1 and Eq. 6.

Complex 8c is presumably formed from 9c and PMe 3 by an analogous pathway. However, the pathway leading from 3c to 8c deviates from that leading from 3a,b to 8a,b since 3c does not react with PMe 3 to give 9c. In addition, the reaction of 3c with PMe 3 to form 8c is faster than that of 9c with PMe 3. At present, the detailed pathway of Eq. 5 is unknown.

4. Experimental

4.1. General

All operations were carried out under nitrogen by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium/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 3a–c [4] and 9a–c [7] were prepared according to literature procedures. IR: FT-IR spectrophotometer, Bio.-Rad. 1H-NMR and 31P-NMR: Bruker WM 250, Bruker AC 250, JEOL JNX 400. 31P-NMR: JEOL JNX 400. Unless specifically mentioned, spectra were recorded at room temperature (r.t.) and chemical shifts relative to TMS (1H-NMR spectra), to the residual solvent peaks (31P-NMR spectra: CDCl 3 δ = 77.0, CD 2 Cl 2 δ = 53.8) or to external H 3 PO 4 (31P-NMR spectra).

4.2. Dicarbonyl[1,2-bis(diphenylphosphino)ethane-κ2-P,P′]chloro[meta(2-phenoxy)-carbene-κ2-C,O]-tungsten(II) (7a)

While stirring 0.51 g (1.3 mmol) of 1,2-bis(diphenylphosphino)ethane was added in small portions to a solution of 0.63 g (1.3 mmol) of 3a in 25 ml of CH 2 Cl 2. Stirring was continued for 15 min. The solvent was removed in vacuo. The residue was washed twice with 10 ml of pentane each, dissolved in 10 ml of CH 2 Cl 2. Then, a layer of 10 ml of pentane was carefully placed on top of this solution. When cooled overnight to −30 °C a fine red powder formed which was collected and dried in vacuo. Yield: 0.82 g (78%) — M.p. 205 °C (dec.) — IR (CH 2 Cl 2, cm −1 ) ν(CO): 1933 vs. 1850 s — 1H-NMR (CDCl 3): δ = 1.96–2.11 (m, 1H, PCH 2 CH 2 P), 2.21–2.63 (m, 2H, PCH 2 CH 2 P) 3.05–3.16 (m, 1H, PCH 2 CH 2 P), 4.55 (s, 3H, Me), 6.34–6.42 (m, 2H, C 6 H 4), 6.92–8.02 (m, 2H, C 6 H 4 and Ph) — 31P-NMR (CDCl 3): δ = 25.1 (dd, J PC = 13.4 and 24.6 Hz, PCH 2 CH 2 P), 28.4 (dd, J PC = 18.7 and 28.1 Hz, PCH 2 CH 2 P), 65.6 (s, Me), 115.2, 120.7, 121.7 (3s, aryl), 127.9–136.2 (m, C 6 H 4 and Ph), 181.8 (2s, C 6 H 4), 230.8 (d, J PC = 6.5 Hz, CO), 254.2 (dd, J PC = 6.6 and 34.5 Hz, CO), 293.4 (J PC n.o., carbene-C) — 31P-NMR (CDCl 3): δ = 61.9 (d, J pp = 22.5 Hz and dd, J pp = 22.5 Hz, J pw = 220 Hz), 20.5 (s, J pp = 22.5 Hz and dd, J pp = 22.5 Hz, J pw = 138 Hz). Anal. Found: C, 52.96, H, 3.64. Calc. for C 38 H 31 BrO 4 P 2 W: C, 50.46, H, 3.86%.

4.3. Bromodicarbonyl[1,2-bis(diphenylphosphino)ethane-κ2-P,P′][methoxy(2-phenoxy)-carbene-κ2-C,O]-tungsten(II) (7b)

The synthesis of 7b from 0.93 g (1.6 mmol) of 3b and 0.64 g (1.6 mol) of dppe and the purification were carried out analogously to 7a. Red powder — Yield: 1.12 g (82%) — M.p. 192 °C (dec.) — IR (CH 2 Cl 2, cm −1 ) ν(CO): 1933 vs. 1850 s — 1H-NMR (CDCl 3): δ = 1.90–2.10 (m, 1H, PCH 2 CH 2 P), 2.23–2.71 (m, 2H, PCH 2 CH 2 P) 3.05–3.22 (m, 1H, PCH 2 CH 2 P), 4.55 (s, 3H, Me), 6.34–6.42 (m, 2H, C 6 H 4), 6.91–8.02 (m, 2H, C 6 H 4 and Ph) — 31C-NMR (CDCl 3): δ = 25.1 (dd, J PC = 13.5 Hz, J PC = 24.4 Hz, PCH 2 CH 2 P), 28.3 (dd, J PC = 18.7 Hz, J PC = 28.6 Hz, PCH 2 CH 2 P), 65.6 (s, Me), 115.2, 120.7, 121.7 (3s, C 6 H 4), 127.9–136.2 (m, C 6 H 4 and Ph), 181.7, 181.8 (2s, C 6 H 4), 230.7 (dd, J PC = 7.6 Hz, J PC n.o., CO), 253.9 (dd, J PC = 6.2 Hz, J PC = 24.5 Hz, CO), 294.9 (carbene-C) — 31P-NMR (CDCl 3): δ = 61.7 (d, J pp = 22.5 Hz and dd, J pp = 22.5 Hz, J pw = 220 Hz), 17.3 (d, J pp = 22.5 Hz and dd, J pp = 22.5 Hz, J pw = 136 Hz). Anal. Found: C, 50.32, H, 3.43. Calc. for C 38 H 31 BrO 4 P 2 W: C, 50.67, H, 3.66%.
4.4. Dicarbonyl[1,2-bis(diphenylphosphino)ethane-κ²,P,P']jodofmethoxy(2-phenoxy)carbene-κ²,C,O]-
tungsten(II) (7c)

The synthesis of 7c from 0.5 g (0.7 mmol) of 3c and 0.3 g (0.7 mmol) of dppe in 20 ml of CH₂Cl₂ and the
purification were carried out analogously to 7a. Red
powder — Yield: 0.54 g (86%) — M.p. 212 °C
(dec.) — IR (CH₂Cl₂, cm⁻¹) ν(CO): 1932 vs, 1855 s — 1H-NMR (CDCl₃): δ = 1.89−2.09 (m, 1H,
PCH₂CH₂P), 2.32−2.65 (m, 2H, PCH₂CH₂P), 3.01−3.17 (m, 1H, PCH₂CH₂P), 4.47 (s, 3H, Me), 6.37−6.45 (m,
2H, Aryl-H), 6.90−8.19 (m, 22H, Aroyl-H and Ph) — 13C-NMR (CH₂Cl₂, −80 °C): δ = 25.1 (m, PCH₂CH₂P), 27.1 (m, PCH₂CH₂P), 65.8 (s, Me), 114.2, 120.3 (2s, C₆H₄), 126.8−135.5 (m, C₆H₄ and Ph), 180.3 (s, C₅H₅), 208.7 (CO), 251.3 (CO), 284.9 (carbene-
C) — 31P-NMR (CD₂Cl₂): δ = 60.0 (d, Jₚₚ = 22.5 Hz and dd, Jₚw = 22.5 Hz, Jw₁ = 135 Hz). Anal.
Found: C, 47.68, H, 3.56. Calc. for C₅₀H₄₁O₆P₄W
(900.3): C, 48.03, H, 3.47%.

4.5. Dicarbonylchlorofmethoxy(2-phenoxy)carbene-
κ²,C,O]bis(trimethylphosphine)tungsten(II) (8a)

An NMR tube was charged with about 50 mg of 3a,
CDCl₃, and excess PMe₃. After the gas evolution had
ceased, the 1H-NMR spectrum was recorded at r.t.
Based on the NMR spectrum, complex 3a has com-
pletely been consumed. The solvent was then removed in vacuo, the residue dissolved in CH₂Cl₂, and the IR
spectrum was recorded. IR (CH₂Cl₂, cm⁻¹) ν(CO): 1929 vs, 1851 s
— 1H-NMR (CDCl₃): δ = 1.24 (d, Jₚḥ = 9.4 Hz, 9H, PMe₃), 1.43 (d, Jₚḥ = 9.3 Hz, 9H,
PMe₃), 4.35 (s, 3H, Me), 6.36−6.65 (m, 1H, C₆H₅), 6.98−7.17 (m, 1H, C₆H₅), 7.23−7.50 (m, 2H, C₆H₅).

4.6. Bromodicarbonyl[methoxy(2-phenoxy)carbene-
κ²,C,O]bis(trimethylphosphine)tungsten(II) (8b)

The generation and the spectroscopic investigations of 8b were carried out analogously to 8a. IR (CH₂Cl₂,
cm⁻¹) ν(CO): 1936 vs, 1844 s — 1H-NMR (CDCl₃): δ = 1.32 (d, Jₚḥ = 9.3 Hz, 9H, PMe₃), 1.48 (d, Jₚḥ = 8.2
Hz, 9H, PMe₃), 4.41 (s, 3H, Me), 6.58−6.64 (m, 1H, C₆H₅), 6.97−7.17 (m, 1H, C₆H₅), 7.31−7.47 (m, 2H, C₆H₅).

4.7. Dicarboxyliodofmethoxy(2-phenoxy)carbene-
κ²,C,O]bis(trimethylphosphine)tungsten(II) (8c)

While stirring vigorously 6.2 ml (0.90 mmol) of a
solution of PMe₃ (0.15 M in CH₂Cl₂, 0.67 g/100 ml)
was slowly added to a solution of 0.30 g (0.45 mmol) of
3c in 25 ml of CH₂Cl₂. The solution was stirred for 10
min. Its volume was reduced in vacuo to about 10 ml. Then, a layer of 10 ml of pentane was slowly placed on
top of the solution. When cooled overnight to −30 °C
red crystals formed. Yield: 0.13 g (44%) — M.p.
165 °C — IR (CH₂Cl₂, cm⁻¹) ν(CO): 1932 vs, 1855 s
— 1H-NMR (CH₂Cl₂, −80 °C, relative to
CHCl₃): δ = 1.25 (d, Jₚḥ = 9.5 Hz, 9H, PMe₃), 1.42 (d, Jₚḥ = 9.5 Hz, 9H, PMe₃), 4.34 (s, 3H, Me),
6.54−6.60 (m, 1H, C₆H₅), 6.93−6.97 (m, 1H, C₆H₅), 7.25−7.39 (m, 2H, C₆H₅) — 13C-NMR (CD₂Cl₂, −
80 °C): δ = 12.7 (d, Jₚḥ = 31.2 Hz, PMe₃), 13.4 (d,
Jₚḥ = 32.2 Hz, PMe₃), 65.3 (s, Carbene-OMe), 115.4,
118.9, 120.0, 134.8, 136.6, 179.0 (6s, Aryl-C), 235.0 (dd,
Jₚḥ = 6.1 and 15.9 Hz, CO), 252.5 (dd, Jₚḥ = 7.1 and
26.4 Hz, CO), 287.5 (dd, Jₚḥ = 5.7 and 16.6 Hz, Carbe-
ne-C) — 31P-NMR (CD₂Cl₂, −80 °C): δ = −32.7
(d, Jₚḥ = 145 Hz and dd, Jₚw = 145 Hz and Jw₁ = 158
Hz), −19.6 (d, Jₚḥ = 145 Hz and dd, Jₚw = 145 Hz
and Jₚw = 200 Hz).

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