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C–O bond activation in carbene-*C,O* chelate tungsten(II) complexes — MeX elimination in the reaction of $[X_2(CO)_3W{=}C(C_6H_4OMe\text{-}o)OMe]$ with L_2 (L_2 = dppe, 2 PMe_3)

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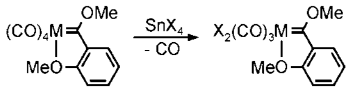
Abstract

The heptacoordinated dihalogeno carbene-*C,O* chelate carbonyl complexes $[X_2(CO)_3W{=}C(C_6H_4OMe\text{-}o)OMe]$ (**3a**–**c**, X = Cl (**a**), Br (**b**), I (**c**)) react with $Ph_2PCH_2CH_2PPh_2$ (dppe) via CO and MeX elimination to give the aryloxycarbene-*C,O* chelate complexes $[X(CO)_2(dppe)W{=}C(C_6H_4O)OMe)OMe]$ (**7a**–**c**). The analogous reactions of **3a**–**c** with *two* equivalents of PMe_3 and that of the monophosphine complexes $[X_2(CO)_2(PMe_3)W{=}C(C_6H_4OMe\text{-}o)OMe]$ (**9a**–**c**) with *one* equivalent of PMe_3 likewise afford aryloxycarbene-*C,O* chelate complexes $[X(CO)_2(PMe_3)_2W{=}C(C_6H_4O)OMe]$ (**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 π-ligands are a rather rare class of carbene complexes [1]. A few compounds of the type $[Cl_2(CO)(PMe_3)_2$-$W{=}C(R)H]$ (R = CMe_3, Ph, C_6H_4Me-*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 SnX_4 (X = Cl, Br, I), $SbCl_5$, or $TiCl_4$ (Eq. 1) [4].

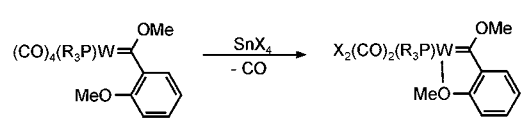


1, 2 **3a - c, 4a, b** (1)

M = W (**1, 3**), Mo (**2, 4**)
X = Cl (**a**), Br (**b**), I (**c**)

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 SnX_4 by oxidative decarbonylation to likewise form dihalogeno carbene-*C,O* chelate phosphine tungsten(II) complexes **6** (Eq. 2) [7].



5 **6** (2)

R = Me, ^{n}Bu; X = Cl, Br, I

The corresponding reaction of $[(CO)_4(^nBu_3P)$-$W{=}C(OMe)C_6H_4R'\text{-}p]$ (R′ = H, OMe) with $SnBr_4$ afforded non-chelated carbene W(II) complexes $[Br_2$-$(CO)_3(^nBu_3P)W{=}C(OMe)C_6H_4R'\text{-}p]$.

An alternative approach to non-chelated carbene W(II) complexes involves the opening of the chelate

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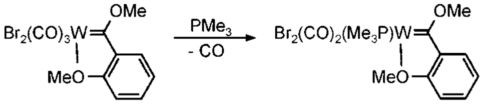
ring in carbene-*C*,*O* chelate W(II) complexes. Thus, when **1** was treated with PPh_3 the complex $[(CO)_4(Ph_3P)W{=}C(OMe)C_6H_4OMe\text{-}o]$ was formed. However, treatment of **3b** with one equivalent of PMe_3 did not give the corresponding non-chelated carbene W(II) complex but rather, via exchange of a CO ligand by PMe_3, the CO substitution product (Eq. 3).



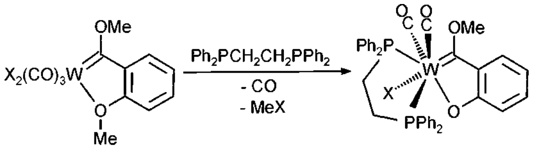
3b

(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, $Ph_2PCH_2CH_2PPh_2$ (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).



3a-c **7a-c**

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

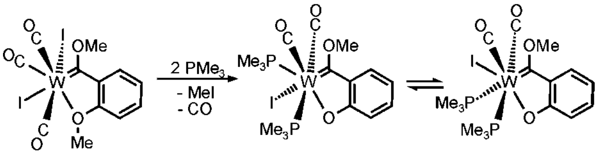
(4)

Surprisingly, the ^1H-NMR spectrum of the new compound **7c** showed, apart from the peaks expected for the dppe ligand and the C_6H_4 group, only one OMe resonance (at $\delta = 4.47$ ppm) indicating loss of one methyl group in the course of the reaction. In accord with the conclusion the ^{13}C-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 C_6H_4 group. From the positions and the J_{PW} coupling constants of the peaks in the ^{31}P-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 CD_2Cl_2 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 PMe_3 was added to solutions of **3c** in dichloromethane, only half of **3c** was consumed. Two equivalents of PMe_3 were required for the complete conversion of **3c**. Again, by ^1H-NMR spectroscopy the formation of MeI was detected.



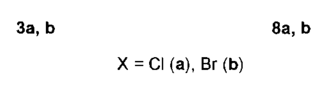
3c **8c**

(5)

The ^1H-NMR spectrum of the new complex **8c** (Eq. 5) in CD_2Cl_2 at −80 °C exhibited, in addition to the peaks for the C_6H_4 group, a sharp singlet at $\delta = 4.41$ ppm for the OMe group and two well separated doublets at $\delta = 1.25$ and 1.42 ($J = 9.5$ Hz, each) for the methyl substituents of the PMe_3 ligand (intensity ratio 1:3:3) indicating inequivalence of the PMe_3 ligands. The ^{31}P-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 ^{13}C-NMR spectrum exhibited two doublets for the PMe_3 ligands. The resonances of the carbene carbon atom and the two carbonyl ligands were split into two doublets each.

When solutions of **8c** in CD_2Cl_2 were warmed to ambient temperature the two doublets attributed to PMe_3 coalesced into a broad singlet at $\delta = 1.4$ ppm indicating a dynamic process that leads to equivalence of the PMe_3 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 PMe_3 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.

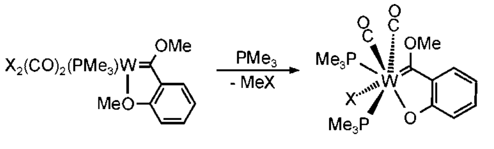


3a, b **8a, b**

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

(6)

The complexes **8a**–**c** were also formed when PMe_3 was added to solutions of the monophosphine complexes **9a**–**c**, respectively (Eq. 7).



(7)

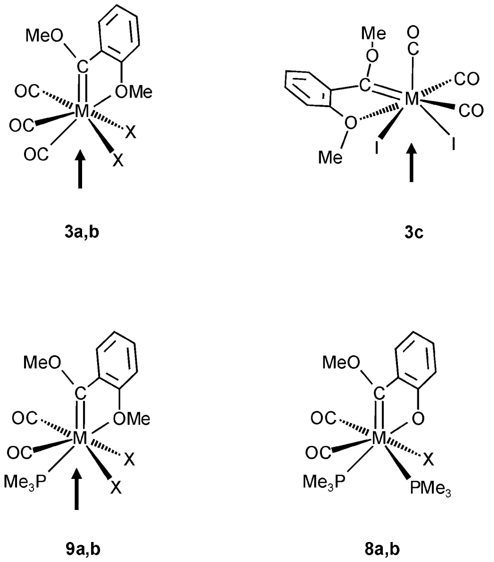
9a-c **8a-c**

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

This indicated that monophosphine complexes might be intermediates in the formation of **8a**–**c** from **3a**–**c** and PMe_3. Therefore, solutions of **3a**–**c** were titrated with PMe_3 solutions and the reactions were monitored by IR spectroscopy. The monophosphine complexes **9a** and **9b** could be clearly identified as intermediates, however, the intermediary formation of the corresponding iodo monophosphine complexes could not be detected. When solutions of equimolar amounts of **3c** and **9c** were titrated with PMe_3 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 PMe_3 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 PMe_3 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.

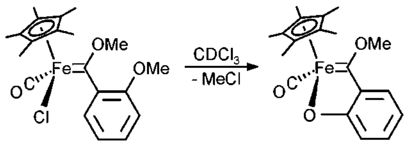


3a,b **3c**

9a,b **8a,b**

Fig. 1. Structures of the heptacoordinated W(II) complexes and presumed direction (arrow) of an attack by nucleophiles.

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 metallacycle 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 PMe_3. A subsequent displacement of a halogeno ligand by the second phosphine (or the second PPh_2 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 $[MoBr_2(CO)(bipy)(dppm)]$ reacted with phosphines and phosphites L to give $[MoBr(CO)(bipy)(dppm)L]^+$ (bipy = 2,2′-bipyridine, dppm = bis(dimethylphosphino)methane) [8]. The phosphine/halide substitution step could then be followed by cleavage of the O–CH_3 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 CH_3 in an S_N2 type fashion. A related reaction has been observed with a cationic iron complex (Eq. 8) [9].



(8)

All dihalogeno carbene-*C*,*O* chelate complexes **3a**–**c** react with excess PMe_3 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 C_s-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 **9c** cannot be prepared by substitution of a CO ligand in **3c** but is accessible only by oxidative decarbonylation of $[(CO)_5W{=}C(C_6H_4OMe\text{-}o)OMe]$ 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 ^{13}C-NMR: Bruker WM 250, Bruker AC 250, JEOL JNX 400. ^{31}P-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 (^{13}C-NMR spectra: $CDCl_3$ $\delta = 77.0$, CD_2Cl_2 $\delta = 53.8$) or to external H_3PO_4 (^{31}P-NMR spectra).

*4.2. Dicarbonyl[1,2-bis(diphenylphosphino)ethane-κ²P,P′]chloro[methoxy(2-phenoxy)-carbene-κ²C,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_2Cl_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_2Cl_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_2Cl_2, cm^{-1}) ν(CO): 1933 vs, 1850 s — ^1H-NMR ($CDCl_3$): $\delta = 1.96$–2.11 (m, 1H, PCH_2CH_2P), 2.21–2.63 (m, 2H, PCH_2CH_2P) 3.05–3.16 (m, 1H, PCH_2CH_2P), 4.55 (s, 3H, Me), 6.34–6.42 (m, 2H, C_6H_4), 6.92–8.02 (m, 22H, C_6H_4 and Ph) — ^{13}C-NMR ($CDCl_3$): $\delta = 25.1$ (dd, $J_{PC} = 13.4$ and 24.6 Hz, PCH_2CH_2P), 28.4 (dd, $J_{PC} = 18.7$ and 28.1 Hz, PCH_2CH_2P), 65.6 (s, Me), 115.2, 120.7, 121.7 (3s, aryl), 127.9–136.2 (m, C_6H_4 and Ph), 181.8 (2s, C_6H_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) — ^{31}P-NMR ($CDCl_3$): $\delta = 61.9$ (d, $J_{PP} = 22.5$ Hz and dd, $J_{PP} = 22.5$ Hz, $J_{PW} = 220$ Hz), 20.5 (d, $J_{PP} = 22.5$ Hz and dd, $J_{PP} = 22.5$ Hz, $J_{PW} = 138$ Hz). Anal. Found: C, 52.96, H, 3.64. Calc. for $C_{36}H_{31}ClO_4P_2W$ (808.9): C, 53.46, H, 3.86%.

*4.3. Bromodicarbonyl[1,2-bis(diphenylphosphino)ethane-κ²P,P′][methoxy(2-phenoxy)-carbene-κ²C,O]-tungsten(II) (**7b**)*

The synthesis of **7b** from 0.93 g (1.6 mmol) of **3b** and 0.64 g (1.6 mmol) of dppe in 50 ml of CH_2Cl_2 and the purification were carried out analogously to **7a**. Red powder — Yield: 1.12 g (82%) — M.p. 192 °C (dec.) — IR (CH_2Cl_2, cm^{-1}) ν(CO): 1933 vs, 1850 s — ^1H-NMR ($CDCl_3$): $\delta = 1.90$–2.10 (m, 1H, PCH_2CH_2P), 2.23–2.71 (m, 2H, PCH_2CH_2P) 3.05–3.22 (m, 1H, PCH_2CH_2P), 4.55 (s, 3H, Me), 6.34–6.42 (m, 2H, C_6H_4), 6.91–8.02 (m, 22H, C_6H_4 and Ph) — ^{13}C-NMR ($CDCl_3$): $\delta = 25.1$ (dd, $J_{PC} = 13.5$ Hz, $J_{PC} = 24.4$ Hz, PCH_2CH_2P), 28.3 (dd, $J_{PC} = 18.7$ Hz, $J_{PC} = 28.6$ Hz, PCH_2CH_2P), 65.6 (s, Me), 115.2, 120.7, 121.7 (3s, C_6H_4), 127.9–136.2 (m, C_6H_4, Ph), 181.7, 181.8 (2s, C_6H_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) — ^{31}P-NMR ($CDCl_3$): $\delta = 61.7$ (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 $C_{36}H_{31}BrO_4P_2W$ (853.3): C, 50.67, H, 3.66%.

4.4. Dicarbonyl[1,2-bis(diphenylphosphino)ethane-κ^2P,P']iodo[methoxy(2-phenoxy)carbene-κ^2C,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 CH_2Cl_2 and the purification were carried out analogously to **7a**. Red powder — Yield: 0.54 g (86%) — M.p. 212 °C (dec.) — IR (CH_2Cl_2, cm^{-1}) ν(CO): 1932 vs, 1853 s — ^{1}H-NMR ($CDCl_3$): $\delta = 1.89$–2.09 (m, 1H, PCH_2CH_2P), 2.23–2.65 (m, 2H, PCH_2CH_2P) 3.01–3.17 (m, 1H, PCH_2CH_2P), 4.47 (s, 3H, Me), 6.37–6.45 (m, 2H, Aryl-H), 6.90–8.19 (m, 22H, Aryl-H and Ph) — ^{13}C-NMR (CH_2Cl_2, -80 °C): $\delta = 25.1$ (m, PCH_2CH_2P), 27.1 (m, PCH_2CH_2P), 65.8 (s, Me), 114.2, 120.3 (2s, C_6H_4), 126.8–135.5 (m, C_6H_4 and Ph), 180.3 (s, C_6H_4), 208.7 (CO), 251.3 (CO), 284.9 (carbene-C) — ^{31}P-NMR (CH_2Cl_2): $\delta = 60.0$ (d, $J_{PP} = 22.5$ Hz and dd, $J_{PP} = 22.5$ Hz, $J_{PW} = 222$ Hz), 17.3 (d, $J_{PP} = 22.5$ Hz and dd, $J_{PP} = 22.5$ Hz, $J_{PW} = 135$ Hz). Anal. Found: C, 47.68, H, 3.56. Calc. for $C_{36}H_{31}IO_4P_2W$ (900.3): C, 48.03, H, 3.47%.

4.5. Dicarbonylchloro[methoxy(2-phenoxy)carbene-κ^2C,O]bis(trimethylphosphine)tungsten(II) (**8a**)

An NMR tube was charged with about 50 mg of **3a**, $CDCl_3$, and excess PMe_3. After the gas evolution had ceased, the ^{1}H-NMR spectrum was recorded at r.t. Based on the NMR spectrum, complex **3a** has completely been consumed. The solvent was then removed in vacuo, the residue dissolved in CH_2Cl_2 and the IR spectrum was recorded. IR (CH_2Cl_2, cm^{-1}) ν(CO): 1929 vs, 1851 s — ^{1}H-NMR ($CDCl_3$): $\delta = 1.24$ (d, $J_{PH} = 9.4$ Hz, 9H, PMe_3), 1.43 (d, $J_{PH} = 9.3$ Hz, 9H, PMe_3), 4.35 (s, 3H, Me), 6.56–6.65 (m, 1H, C_6H_4), 6.98–7.17 (m, 1H, C_6H_4), 7.23–7.50 (m, 2H, C_6H_4).

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

The generation and the spectroscopic investigations of **8b** were carried out analogously to **8a**. IR (CH_2Cl_2, cm^{-1}) ν(CO): 1936 vs, 1844 s — ^{1}H-NMR ($CDCl_3$): $\delta = 1.32$ (d, $J_{PH} = 9.3$ Hz, 9H, PMe_3), 1.48 (d, $J_{PH} = 8.2$ Hz, 9H, PMe_3), 4.41 (s, 3H, Me), 6.58–6.64 (m, 1H, C_6H_4), 6.97–7.17 (m, 1H, C_6H_4), 7.31–7.47 (m, 2H, C_6H_4).

4.7. Dicarbonyliodo[methoxy(2-phenoxy)carbene-κ^2C,O]bis(trimethylphosphine)tungsten(II) (**8c**)

While stirring vigorously 6.2 ml (0.90 mmol) of a solution of PMe_3 (0.15 M in CH_2Cl_2, 0.67 g/100 ml) was slowly added to a solution of 0.30 g (0.45 mmol) of **3c** in 25 ml of CH_2Cl_2. 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 (CH_2Cl_2, cm^{-1}) ν(CO): 1932 vs, 1855 s — ^{1}H-NMR (CH_2Cl_2, -80 °C, relative to $CHDCl_2$: δ 5.32): $\delta = 1.25$ (d, $J_{PH} = 9.5$ Hz, 9H, PMe_3), 1.42 (d, $J_{PH} = 9.5$ Hz, 9H, PMe_3), 4.34 (s, 3H, Me), 6.54–6.60 (m, 1H, C_6H_4), 6.93–6.97 (m, 1H, C_6H_4), 7.25–7.39 (m, 2H, C_6H_4) — ^{13}C-NMR (CD_2Cl_2, -80 °C): $\delta = 12.7$ (d, $J_{PC} = 31.2$ Hz, PMe_3), 13.4 (d, $J_{PC} = 32.2$ Hz, PMe_3), 65.3 (s, Carbene-OMe), 115.4, 118.9, 120.0, 134.8, 136.6, 179.0 (6s, Aryl-C), 235.0 (dd, $J_{PC} = 6.1$ and 15.9 Hz, CO), 252.5 (dd, $J_{PC} = 7.1$ and 26.4 Hz, CO), 287.5 (dd, $J_{PC} = 5.7$ and 16.6 Hz, Carbene-C) — ^{31}P-NMR (CD_2Cl_2, -80 °C): $\delta = -32.7$ (d, $J_{PP} = 145$ Hz and dd, $J_{PP} = 145$ Hz and $J_{PW} = 158$ Hz), -19.6 (d, $J_{PP} = 145$ Hz and dd, $J_{PP} = 145$ Hz and $J_{PW} = 200$ Hz).

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