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Halogenation and oxygenation of the metal and oxidation of phosphorus in complexes of the type $M(dppe)_2(N_2)_2$ (M = Mo, W) by reaction with thionylhalides

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Abstract

$M(dppe)_2(N_2)_2$ (M = Mo, W; dppe = 1,2-bis(diphenylphosphino)ethane) is converted by thionylchloride into the chlorinated and oxygenated derivatives $MoCl_4(dppeO_2)$ and $WCl_3(O)(dppeO_2)$, respectively. In contrast, thionylbromide reacts with $W(dppe)_2(N_2)_2$, to give specifically the tetrabromide $WBr_4(dppe)$. The molecular structure of $MoCl_4(dppeO_2)$ has been determined by single crystal X-ray analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oxygenation; Halogenation; Molybdenum; Tungsten; Thionylhalides

1. Introduction

Recently we reported on the possibility of using thionylchloride to oxidize organometallic compounds by oxygenation and chlorination in one step. Thus, $CpV(CO)_4$ (Cp = η^5-cyclopentadienyl) and $\{CpMo(CO)_3\}_2$ react with thionylchloride to form the compounds $CpM(O)Cl_2$ (M = V, Mo) [1], respectively. Even the analogous, electron-richer cobalt complex $Cp^*Co(CO)_2$ (Cp^* = η^5-pentamethylcyclopentadienyl) is halogenated by thionylhalides without formation of an oxygen containing reaction product. However, the product obtained is solvent dependent. Whereas the reaction of $Cp^*Co(CO)_2$ with thionylchloride in polar solvents like THF or CH_2Cl_2 yields the salt $[(Cp^*Co)_2(\mu\text{-}Cl)_3]_2[Co_2Cl_6]$, the neutral dimer $\{Cp^*CoCl(\mu\text{-}Cl)\}_2$ is formed by using the non-polar hexane [2]. The reaction of $Cp^*Co(CO)_2$ with thionylbromide always leads only to the formation of $\{Cp^*CoBr(\mu\text{-}Br)\}_2$, independent of the solvent used.

We have now extended the reaction of thionylhalides to the dppe complexes $M(dppe)_2(N_2)_2$ (M = Mo, W) (**1**, **1′**). In this case quite different reaction products are obtained. With $SOCl_2$, the elimination of one dppe ligand and both N_2 molecules is always observed as well as the oxidation of the remaining dppe ligand and chlorination of both metal centers. Additionally, in the case of tungsten, oxygenation of the metal atom occurs. The formal insertion of oxygen into both the metal–phosphorus bonds of the Mdppe mojety gives, surprisingly, the ligand $dppeO_2$ ($dppeO_2$ = 1,2-bis-(diphenylphosphoryl)ethane).

Hitherto, there are two methods for synthesizing transition metal complexes containing the bidentate $dppeO_2$ ligand. The most common is the reaction of the metal halides MX_2 (M = Mn [3], Fe [4–6], Co [7], Ni [8], Zn [9,10]), with $dppeO_2$, giving 1:1 stoichiometric products for the metal to ligand ratio. The second method is the one-pot reaction between transition metal complexes containing labile ligands, dppe and any oxidizing agent, e.g. molecular oxygen [5]. $DppeO_2$ shows three different ligand functions. The most common is the bidentate one (η^2-O,O′), followed by the two-metal bridging function (μ_2-O,O′) [8,9,11–13] and finally, the monodentate one (η^1-O) [12,14] (see Scheme 1).

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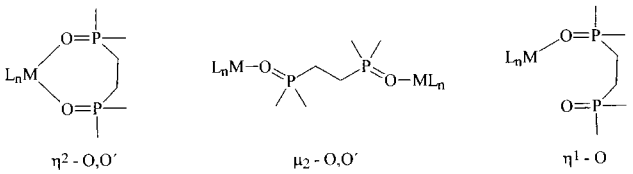
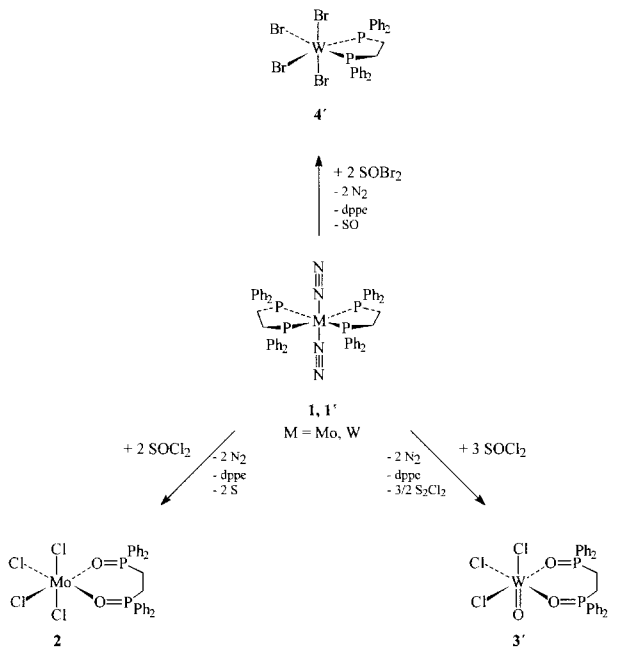


Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Synthesis and NMR characterization

The reaction between the dppe complexes $M(dppe)_2(N_2)_2$ (M = Mo, W) (**1**, **1′**) and thionylhalides (1:1.5 molar ratio) in THF at 0°C affords different products. If $Mo(dppe)_2(N_2)_2$ (**1**) is reacted with $SOCl_2$, the formation of the yellow tetrachloride $MoCl_4(dppeO_2)$ (**2**) is observed. In **2**, the molybdenum center, Mo(0) of **1**, has been oxidized to Mo(IV) and both phosphorus(III) atoms of dppe are oxidized to phosphorus(V) ones. The analogous tungsten complex $W(dppe)_2(N_2)_2$ (**1′**) reacts with $SOCl_2$ to give the colorless $dppeO_2$ complex of tungsten oxide trichloride $W(O)Cl_3(dppeO_2)$ (**3′**), with the oxidation number of +5 for tungsten. This is due to the preference of tungsten for higher oxidation states. The reaction of **1′** with thionylbromide, however, leads only to the bright orange tetrabromide complex $WBr_4(dppe)$ (**4′**). In this case neither oxygenation at the metal center nor at the dppe ligand is observed. The reaction of **1** with thionylbromide was also attempted. However, no evidence could be found for analogous or either products as **2**, **3′** or **4′** (Scheme 2).

In Table 1, the ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR chemical shifts for the compounds **2**, **3′** and **4′** are given. Their ^{1}H-NMR spectra show the typical multiplets of the phenyl ligand in dppe and $dppeO_2$ in the region of $\delta = 7.42$ to 8.23. The chemical shifts of the protons in the C_2H_4-moiety are only observed as broad singlets at $\delta = 2.50$ (**3′**) and 1.98 (**4′**). The protons of the C_2H_4 group in **2** have not been detected; possibly due to some overlap with the THF signals.

The $^{13}C\{^1H\}$-NMR spectra of **2**, **3′** and **4′** only show the chemical shifts of the phenyl-carbon atoms occurring between $\delta = 133$ and 128 as multiplets. Signals for the chemical shifts of the carbon atoms of the C_2H_4 bridge were not observed.

The $^{31}P\{^1H\}$-NMR spectra of **2** and **3′** show only one singlet for the $dppeO_2$ ligand at $\delta = 31.6$ (**2**) and 30.9 (**3′**), while the chemical shift of the non-oxidized dppe ligand in **4′** lies downfield at $\delta = 48.7$ in the expected region.

2.2. Infrared and mass spectra

Typically, the very strong absorption of the $\nu(N_2)$ vibration of the starting material [15] disappears during the reaction with SOX_2. The very strong absorptions at 1173 and 1130 cm^{-1} (**2**) and 1198 and 1158 cm^{-1} (**3′**), respectively, clearly show the presence of P=O doubly-bonded groups in these molecules. No such bands exist in the IR-spectrum of **4′** due to the presence of the non-oxidized dppe. In **3′**, however, there is another strong band in the IR-spectrum at 982 cm^{-1}, belonging to the ν(W=O) absorption. Because of the halogen ligands, the IR-spectra of **2**, **3′** and **4′** show several ν(M–X) absorptions: In the case of **2**, a very strong absorption is found at 327 cm^{-1}, with two shoulders at 349 and 305 cm^{-1}, and a weak one at 367 cm^{-1}, which are in agreement to the C_{2v} symmetry of the molecule. **3′** gives two strong absorptions at 315 and 298 cm^{-1}

Table 1
NMR-spectra of **2**, **3′** and **4′**

Compound	Solvent	^{1}H-NMR [δ]	$^{13}C\{^1H\}$-NMR [δ]	$^{31}P\{^1H\}$-NMR [δ]
2	DMSO-d_6	7.81–7.51 (m, Ph)	133.5–129.2 (m, Ph)	31.6 (s, $dppeO_2$)
3′	DMSO-d_6	7.71–7.42 (m, Ph, 20H) 2.50 (s, CH_2, 4H)	132.3–129.0 (m, Ph)	30.9 (s, $dppeO_2$)
4′	$CDCl_3$	8.23–8.02 (m, Ph, 20H) 1.98 (s, CH_2, 4H)	131.8–128.2 (m, Ph)	48.7 (s, dppe)

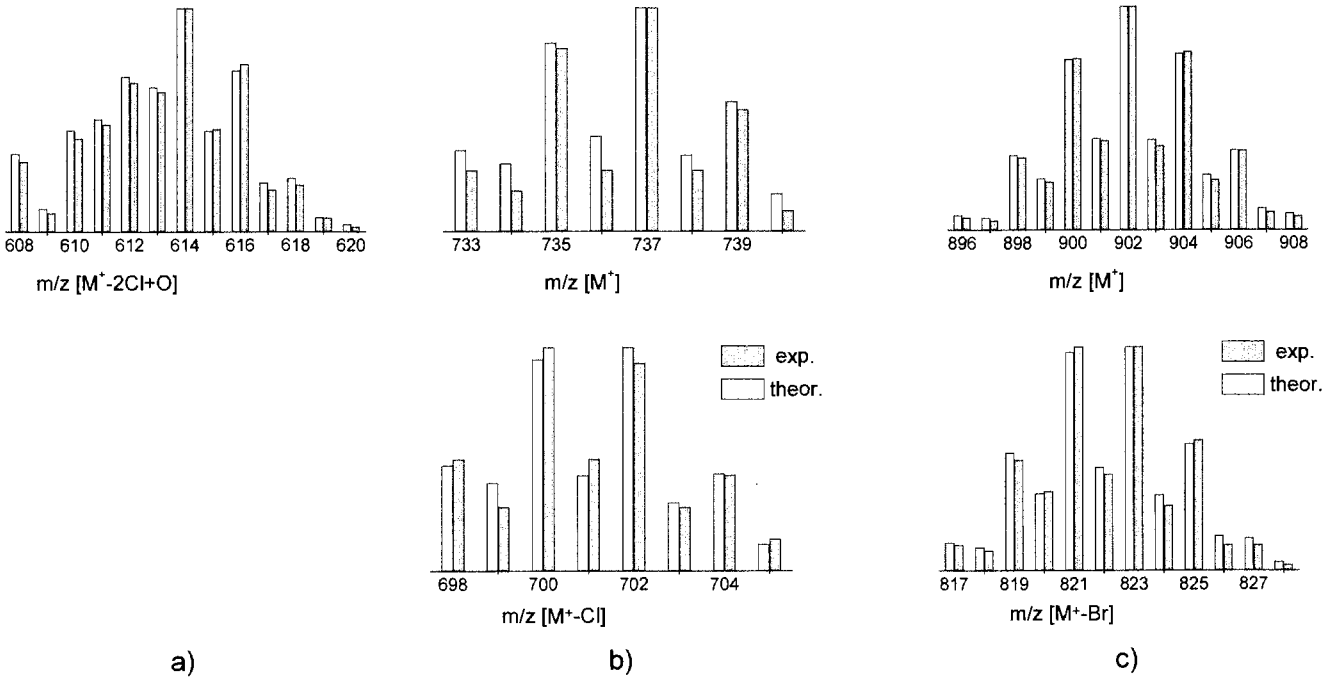


Fig. 1. Experimental (exp.) and theoretical (theor.) isotope distribution of **2** ([M^+–2Cl + O]) (a), **3′** ([M^+], [M^+–Cl] (b) and **4′** ([M^+], [M^+–Br]) (c).

with one shoulder at 284 cm^{-1}. In the IR-spectrum of **4′**, one strong absorption is found at 241 cm^{-1}, with a weak shoulder at 255 cm^{-1}, and two weak absorptions at 272 and 225 cm^{-1}, also confirming the structure proposed with C_{2v} symmetry.

The molecules **2**, **3′** and **4′** were also identified by their EI-mass spectra. Experimental and theoretical distribution for the peaks and fragments considering the isotopes for Mo, Cl and Br are shown in Fig. 1. They are in good agreement. Instead of the parent peak of **2**, the fragment for [M^+–2Cl + O] with $m/z = 614$ is observed as the highest mass. For the compounds **3′** and **4′**, the parent peaks [M^+], as well as the fragments [M^+–X] (X = Cl, Br) at $m/z = 737$ (**3**: [M^+]), 702 (**3**: [M^+–Cl]), 902 (**4**: [M^+]) and 823 (**4**: [M^+–Br]) are observed.

2.3. Crystal structure analysis of 2

The molecular structure of **2** is shown in Fig. 2. Relevant bond angles and lengths are listed in Table 2 and the crystallographic data are summarized in Table 3. The molecule possesses a crystallographically imposed twofold symmetry, the twofold axis running through the Mo1 atom and through the center of the C13–C14 bond. In **2**, the molybdenum center is nearly octahedrally coordinated with four Cl and two cis oxygen atoms. The oxygen atoms belong to the bidentate $dppeO_2$ ligand which forms a seven-membered ring with Mo1. All bond angles between the molybdenum atom and cisoid ligands lie between 80 and 100°, while all bond angles between the molybdenum and two transoid ligands are about 170°.

The equatorial bond lengths, Mo–Cl1 and Mo–Cl1A = 2.186(4) Å, are significantly shorter than both the axial ones, Mo–Cl2 = 2.365(3)Å and Mo–Cl3 = 2.398(2)Å. The two molybdenum to oxygen bond lengths Mo–O1 and Mo–O1A are equal (2.180(4)Å), and can be considered as Mo–O single bonds. Likewise, the two phosphorus to oxygen bond lengths, P1–O1 and P1A–O1A are also equal by symmetry (1.500(4)Å) and have P=O double bond character. Whereas the equatorial angle Cl1–Mo–Cl1A is 100.9(2)°, the angle O1–Mo–O1A is much smaller (81.5(3)°). Both phosphorus atoms show distorted tetrahedral coordination. While three of the six bond angles are close to the classic tetrahedral angle (O1–P1–C13 and O1A–P1A–C13A: 112.8(4)°; O1–P1–C7 and O1A–P1A–C7A:

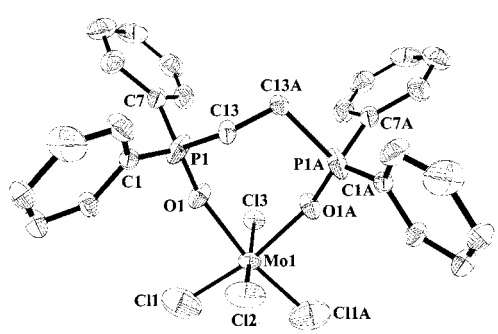


Fig. 2. Molecular structure of **2**; thermal ellipsoids are plotted with 25% probability.

108.1(3)°; C1–P1–C7 and C1A–P1A–C7A: 108.9(5)°) the other three angles vary significantly (O1–P1–C1 and O1A–P1A–C1A: 120.7(4)°; C1–P1–C13 and C1A–P1A–C13A: 84.4(5)°; C7–P1–C13 and C7A–P1A–C13A: 121.2(5)°). Both phosphorus and oxygen atoms form a horizontal plane, out from which the molybdenum atom is bent by about 25°. This seven-membered ring of **2** is not comparable to that of heptasulfur, S_7, which possesses a 'chair' conformation, in fact, the seven-membered ring of **2** shows a 'twist' conformation.

3. Conclusions

While $SOCl_2$ reacts with **1** as a metal-chlorinating, P-oxidizing agent and with **1′** additionally as a metal-oxygenating agent, $SOBr_2$ acts only as a metal-brominating agent on **1′**. Thionylchloride causes a higher oxidation state for tungsten than for molybdenum (V in **3′** and IV in **2**). While the tungsten complex, **3′**, has an oxo ligand, the molybdenum center in **2** has not been oxygenated. The starting material, **1**, however, can be oxidized by *m*-CPBA (*meta*-chloroperbenzoic acid) or by sulfur (of thiirane) to give the dioxo or dithio complexes $(dppe)_2Mo(E)_2$ (E = O, S) [16]. In the case of $SOCl_2$, the formation of Mo–Cl and P=O bonds is obviously preferred over the formation of Mo=O and P–Cl bonds. The weaker oxidizing agent, thionylbromide, reacts only with the tungsten compound, **1′**, to give the tetrabromide **4′**. This means that no metal- or P-oxygenation occurs. No reaction is observed of the molybdenum complex **1** with $SOBr_2$.

Table 2
Relevant bond lengths (Å) and angles (°) of **2**

Atoms	Length	Atoms	Angle
Mo1–Cl1	2.186(4)	Cl1–Mo1–Cl1A	100.9(2)
Mo1–Cl2	2.365(3)	Cl1–Mo1–Cl2	95.39(9)
Mo1–Cl3	2.398(2)	Cl1–Mo1–Cl3	90.51(9)
Mo1–O1	2.108(4)	Cl1A–Mo1–Cl2	95.39(9)
P1–O1	1.500(4)	Cl1A–Mo1–Cl3	90.5(9)
		Cl2–Mo1–Cl3	170.71(9)
		Cl1–Mo1–O1A	169.8(2)
		Mo1–O1–P1	149.5(3)
		O1–P1–C13	112.8(4)
		O1–P1–C7	108.1(3)
		C1–P1–C7	108.9(5)
		O1–P1–C1	120.7(4)
		C7–P1–C13	121.2(5)
		C1–P1–C13	84.4(5)

4. Experimental

4.1. General

All reactions were carried out in an argon atmosphere using standard Schlenk techniques. Solvents were distilled over appropriate drying agents and saturated with argon prior to use. IR spectra were recorded with a Nicolet 520 FT-IR spectrometer. NMR spectra were recorded with a JEOL GSX and JEOL EX 400 spectrometer. The spectra were referenced by using the resonance of residual protons in the deuterated solvents. EI-mass spectra were measured with a MAT 90 sectorfield spectrometer at the Institute of Organic Chemistry. Microanalytical data were obtained with the Heraeus Elementar EL in Munich (C, H, N: Institute of Inorganic Chemistry; C, H, Cl, Br: Institute of Organic Chemistry).

Table 3
Crystallographic data of **2**

	2
Empirical formula	$C_{34}H_{40}Cl_4MoO_4P_2$
Crystal color and habit	Yellow, square prism
Formula weight	812.34
Diffractometer used	Siemens CCD area-detector
Temperature (K)	183(3)
Wavelength (Å)	0.71073
Crystal size (mm^3)	$0.3 \times 0.3 \times 0.2$
Crystal system	Monoclinic
Space group	$P2(1)/m$
Unit cell dimensions	
a (Å)	8.6501(2)
b (Å)	15.8878(3)
c (Å)	13.4051(2)
α (°)	90.00
β (°)	100.591(1)
γ (°)	90.00
Volume ($Å^3$)	1810.96(4)
Z	2
D_{calc} (Mg m^{-3})	1.490
Absorption coefficient (mm^{-1})	0.782
$F(000)$	832
2θ-Range of data collection (°)	8.04–49.42
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 18$, $-15 \le l \le 15$
Reflections collected	8736
Independent reflections	3031 ($R_{int} = 0.0407$)
Absorption correction	Semi-empirical (SADABS)
Max. and min. transmission	0.682 and 0.660
Refinement method	Full-matrix least-squares on F^2
GoF (F^2)	1.140
Final R indices [$F > 4\sigma(F)$]	$R_1 = 0.0735$, $wR_2 = 0.1400$
R-indices (all data)	$R_1 = 0.0904$, $wR_2 = 0.1487$
Largest different peak (e $Å^{-3}$)	0.675
Largest different hole (e $Å^{-3}$)	−0.753

$SOCl_2$ was freshly distilled prior to use, $SOBr_2$ (Aldrich) was used as received. $M(dppe)_2(N_2)_2$ (M = Mo, W) (**1**, **1′**) were prepared according to the literature [15].

4.2. Tetrachloro-1,2-bis(diphenylphosphoryl)-ethane-molybdenum(IV) (2)

To the light orange solution of 337 mg (0.38 mmol) of **1** in 40 ml of THF, cooled at 0°C, a solution of 0.04 ml (0.57 mmol) of $SOCl_2$ in 10 ml of THF was added dropwise. The color changed from orange to red. After stirring at 0°C for 12 h, the now yellow solution was filtered, reduced to half its volume in vacuo and stored at 8°C. After 24 h, yellow crystals were formed, isolated by filtration and washed with hexane and dried under argon. Yield: 99 mg (32%), m.p. 208°C (dec.). Anal. Found: C, 51.21; H, 4.94; Cl, 16.60. $C_{26}H_{24}Cl_4MoO_2P_2 \times 2THF$ requires: C, 50.21; H, 5.08; Cl, 17.43%. IR (KBr): ν(P=O) 1172s, 1130 s cm^{-1}. IR (PE): ν(MoCl) 349 sh, 327 s, 305 sh cm^{-1}. NMR (DMSO-d_6): ^1H, δ 7.81–7.51 (m, Ph); $^{13}C\{^1H\}$, δ 133.5–129.2 (m, Ph); $^{31}P\{^1H\}$, δ 31.6 (s, $dppeO_2$). EI-MS: $m/z = 614$ [M^+–2Cl + O].

4.3. Trichloro-oxo-1,2-bis(diphenylphosphoryl)-ethane-tungsten(V) (3′)

A solution of 0.01 ml (0.18 mmol) of $SOCl_2$ in 10 ml of THF was added dropwise at 0°C to the orange solution of 115 mg (0.12 mmol) of **1′** in 40 ml of THF. After stirring the mixture at 0°C for 12 h, the yellow–green precipitate formed was filtered off, washed with hexane and dried in vacuo. Yield: 40 mg (45%), m.p. 185°C (dec.). Anal. Found: C, 45.87; H, 3.64. $C_{26}H_{24}Cl_3O_3P_2W \times 2THF$ requires: C, 45.87; H, 4.58%. IR (KBr): ν(P=O) 1198 s, 1158 s, ν(W=O) 982 s cm^{-1}. IR (PE): ν(WCl) 315 sh, 304 s, 298 s, 284 sh cm^{-1}. NMR (DMSO-d_6): ^1H, δ 7.71–7.41 (m, 20H, Ph), 2.50 (s, 4H, CH_2); $^{13}C\{^1H\}$, δ 132.2–129.0 (m, Ph); $^{31}P\{^1H\}$, δ 30.9 (s, $dppeO_2$). EI-MS: $m/z = 737$ [M^+], 702 [M^+–Cl].

4.4. Tetrabromo-1,2-bis(diphenylphosphino)-ethane-tungsten(IV) (4′)

The orange solution of 151 mg (0.15 mmol) of **1′** in 50 ml of THF was mixed at 0°C with a solution of 0.02 ml (0.23 mmol) of $SOCl_2$ in 10 ml of THF. After stirring the mixture at 0°C for 12 h, the bright orange precipitate formed was filtered, washed with hexane and dried in vacuo. Yield: 111 mg (82%), m.p. 148°C. Anal. Found: C, 43.79; H, 3.83; Br, 24.76. $C_{26}H_{24}Br_4P_2W \times 5THF$ requires: C, 43.77; H, 5.11; Br 25.32%. IR (PE): ν(WBr) 255 sh, 241 s, 225 w cm^{-1}. NMR ($CDCl_3$): ^1H, δ 8.23–8.02 (m, 20H, Ph), 1.98 (s, 4H, CH_2); $^{13}C\{^1H\}$, δ 131.8–128.2 (m, Ph); $^{31}P\{^1H\}$, δ 48.7 (s, dppe). EI-MS: $m/z = 902$ [M^+], 823 [M^+–Br].

4.5. X-ray structure determination of 2

Crystals of **2** were covered with perfluoroethene oil. The selected crystal was mounted on a glass fiber, fitted to the goniometer head which was cooled with a LTP2 device to 193 K. The cell dimensions were determined from the reflexions collected on four sets of 15 frames with four different orientations of the crystal by rotation of the crystal by 0.3° steps using the program SMART. Data collection was performed in the HEMISPHERE mode by collecting data on 1380 frames with two different X settings. The speed was 10 s per frame. After data reduction with the program SAINT an empirical absorption correction was employed (SADABS). The structure was solved by the heavy atom method followed by standard difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated and included in the final refinement by the riding model with $U_i(H) = 1.2\ U_i(C)$.

5. Supplementary material

Crystallographic data for the structural analysis of **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134984. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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