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Phosphinidene reactivity toward unsaturated phosphorus heterocycles

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Abstract

The transient electrophilic phosphinidene complex $PhPW(CO)_5$ reacts in the presence of CuCl at room temperature with phospholene **2** and phospholes **4a–c** to give the corresponding $W(CO)_5$ complexed products **3** and **5a–c**. The intermediate phosphoranylidene phosphine complexes, formed, from the addition of $PhPW(CO)_5$ to the phosphorus atom of the substrates, are characterized by NMR spectroscopy and by a single crystal X-ray structure determination for the one generated from phospholene **2**. This intermediate **8** is a CuCl-complexed dimer, which speculatively results from dissociating the phosphole–CuCl tetramer on insertion of $PhPW(CO)_5$ into the P–Cu bonds. Reacting $PhPW(CO)_5$ with phospholene **2** at 110°C in the absence of CuCl gives besides the $W(CO)_5$-complexed phospholene **3** also a bisphospholene–$W(CO)_4$ complex **13**. The formation of **13** is attributed to a ligand exchange reaction in the intermediate phosphinidene–phospholene adduct. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphinidene; Reactivity; Unsaturated phosphorus heterocycles

1. Introduction

Since Mathey showed that terminal phosphinidene complexes $RPM(CO)_5$ ($M = W$, Cr, Mo) can be generated in situ from phosphanorbornadienes [1], the carbene-like reactivity of these electrophilic species toward various functional groups has been scrutinized [2]. 1,2-Additions occur with simple C=C and C≡C bonds. With dienes larger five-membered ring structures result from a subsequent 1,3-sigmatropic shift and by direct 1,4-addition [3]. Additions to C=N bonds, via pre-association to the N-atom, have been reported to give heterocycles in which two imines are incorporated [4], but the smaller aza-phosphiranes are known too [5]. Bond insertions of $PhPW(CO)_5$ are also well established. They have been shown to occur for O–H [1,5,6], N–H [6,7], and C–H [8] bonds and even for selected C–C [9] and C–P [10] bonds giving a broad spectrum of phosphine derivatives. Association of the phosphinidene complex to the P-atom of phosphines PR_3 (R = alkyl, phenyl) reportedly gives complexes of phosphoranylidene phosphines ($R_3PP(Ph)W(CO)_5$) [11] which can be applied as phospha-Wittig reagents to generate P=C bonds [11,12]. Interested in expanding the scope of $PhPW(CO)_5$ we decided to study its reactivity toward unsaturated organophosphorus compounds. Our intend was to establish whether addition to a C=C bond can be accomplished in the presence of a P-group. Here we report on the reactions with a phospholene and with various phospholes.

2. Results and discussion

Reaction of the complexed phosphinidene precursor **1** with phospholene **2** at room temperature in the

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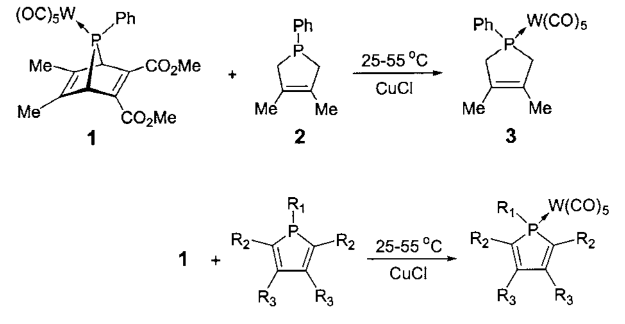
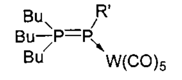
presence of more than one equivalent of CuCl afforded to our surprise the W(CO)$_5$-complexed phospholene **3** in 90% yield as the sole product. Likewise, reaction of **1** with phospholes (**4a**–**c**) resulted only in the W(CO)$_5$-complexed phospholes (**5a**–**c**), also in good yields. These reactions seem perplexingly simple as the substrates are merely complexed with a W(CO)$_5$ group. However, the addition of this transition metal group cannot be a simple transfer from **1**. We wondered about the role of PhPW(CO)$_5$ that must be generated from **1** under the reaction conditions. It is evident that no addition to C=C bonds occur, but does association to the P-atom take place? It also surprised us that more than one equivalent of CuCl is needed for the reactions, whereas only catalytic amounts are used for generating PhPW(CO)$_5$ from **1**. We observed no reaction at room temperature with less than one equivalent.

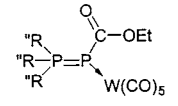


a: R_1 = Ph, R_2 = H, R_3 = Me
b: R_1 = Me, R_2 = H, R_3 = Me
c: R_1 = Ph, R_2 = Ph, R_3 = H

Monitoring the reactions of **1** with **2** and with **4a**,**b** (not **4c**) by ^{31}P-NMR showed the formation of intermediates with PP bonds as evidenced by their ^{1}J(P–P) coupling constants. Executing the reaction of **1** with **2** for a short time (ca. 75 min), to maximize the formation of an intermediate (**8**), enabled its isolation and even its purification using low temperature chromatography on silica gel. The ^{31}P-NMR doublets of **8** at δ − 54.7 and 31.1 ppm suggest a phosphinidene–phospholene complex, although it has a relatively small ^{1}J(P–P) coupling constant of 294 Hz for a P=P bond. The ^{31}P-NMR data for the more reactive and only in situ observed phosphinidene-phosphole complexes **9a** and **9b** are similar.



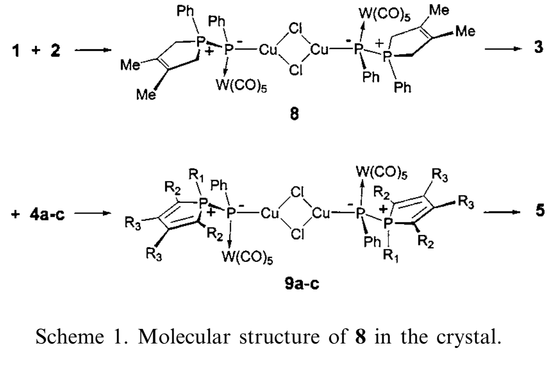
6a R' = Ph
6b R' = Me
6c R' = Allyl



7a R" = Et
7b R" = Bu

It is informative to compare these spectroscopic data with those of phosphoranylidenephosphines. Mathey reported the very reactive, and difficult to purify $Bu_3P{=}PRW(CO)_5$ (**6**, R = Ph, Me, allyl) complexes to have ^{31}P-NMR resonances for the phosphinidene and phosphine phosphorus atoms of − 100 to − 145 and 31–35 ppm, respectively, with ^{1}J(P–P) coupling constants ranging from 430 to 444 Hz [11]. Of the more stable complexes $R_3P{=}P(CO_2Et)W(CO)_5$ (**7**, R = Bu, Et) the Et derivative **7a** (confirmed by a crystal structure determination) has corresponding phosphorus chemical shifts of − 97 and 38 ppm and a smaller coupling constant of 361 Hz. These comparisons do indeed suggest a similar association of PhPW(CO)$_5$ to the phospholene and phospholes of reaction 1 and 2.

To establish unequivocally the structure of the more stable intermediate, we resorted to its single crystal structure analysis. Surprisingly, intermediate **8** is not a regular phosphoranylidene phospholene complex, but rather a CuCl-complexed dimer (Fig. 1, Scheme 1). We suggest that similar CuCl-complexed dimers (**9a**–**c**) are formed in the reaction of complex **1** with phospholes **4a**–**c**. The compound crystallizes with one molecule in the asymmetric unit, which has approximately non-crystallographic inversion symmetry. Selected bond lengths and angles for **8** are given in the caption of Fig. 1. The organophosphorus part of the structure is as expected. The two PP bond lengths of 2.1814(19) and 2.1751(18) Å are slightly longer (ca. 0.02 Å) than those reported for **7a** and the PW bonds of 2.5597(13) and 2.5559(13) Å are correspondingly shorter. The 5–6° larger PPW angles of 115.11(6)° and 116.09(6)° may indicate more congestion in **8**. The PCu bond lengths of 2.1979(14) and 2.1955(14) Å between the organophosphorus parts and the central Cu_2Cl_2 ring are in line with those reported for $[Ar_3PCuCl]_2$ complexes [13]. The bridging Cl atoms of the Cu_2Cl_2 ring are bound asymmetrically, i.e. with Cu(11)Cl(11) and Cu(11)Cl(12) bond lengths of 2.2661(14) and 2.3518(14) Å, respectively, which is in line with related studies on $[(\text{cyclohexyl})_3PCuCl]_2$ and $[(o\text{-tolyl})_3PCuCl]_2$ [13]. The Cu atoms are in distorted trigonal planar environments, Σ angles of 360.0° and 359.9°, with obtuse ClCuCl angles of 99.13(5)° and 99.14(5)°; the angles at the chlorines are acute, i.e. 80.94(4)° and 80.83(4)°. The Cu···Cu distance of 2.9954(9) Å is of similar length as those of related $[R_3P_2Cu_2Cl_2]$ systems [13]. In analogy with these earlier studies we consider this distance to be too long to represent a formal metal–metal bond.



Scheme 1. Molecular structure of **8** in the crystal.

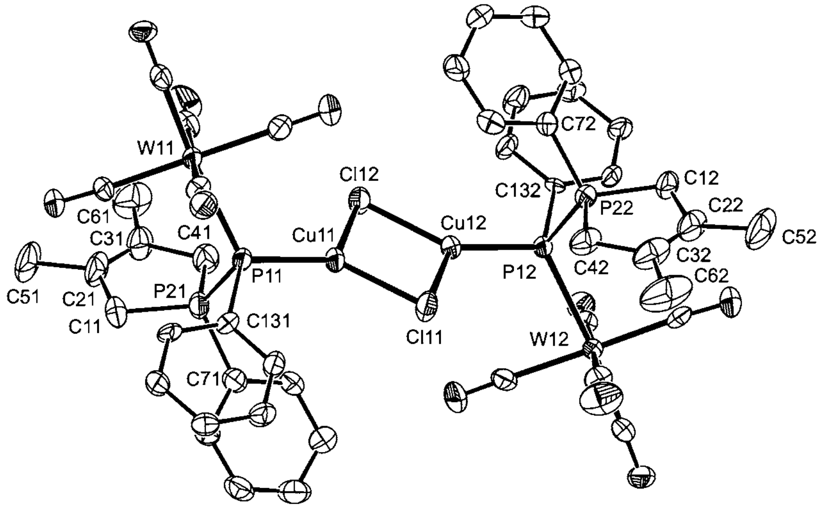
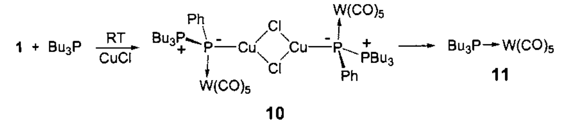


Fig. 1. Displacement ellipsoid plot of **8** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W11–P11 2.5597(13), W12–P12 2.5559(13), Cu11–P11 2.1979(14), Cu12–P12 2.1955(14), P11–P21 2.1814(19), P12–P22 2.1751(18), P11–C131 1.826(5), P12–C132 1.841(4), Cu11–Cl11 2.2661(14), Cu12–Cl12 2.2672(13), Cu11–Cl12 2.3518(14), Cl11–Cu12 2.3501(14); P21–P11–W11 115.11(6), P22–P12–W12 116.09(6), Cu11–P11–W11 119.94(6), Cu12–P12–W12 119.11(5), C131–P11–W11 114.34(16), C132–P12–W12 114.20(16), Cl11–Cu11–Cl12 99.13(5), Cl12–Cu12–Cl11 99.14(5), Cu11–Cl11–Cu12 80.89(4), Cu12–Cl12–Cu11 80.83(4).

The presence of CuCl in the crystal structure of **8** may explain why more than one equivalent is needed in the reactions. Reportedly, **6** and **7** are formed at 25–40°C in THF as solvent without the use of CuCl. No transfer of the $W(CO)_5$ group from the phosphinidene to the phosphine phosphorus was observed in these systems [11]. Interestingly, reaction of complex **1** with tributylphosphine in the presence of more than one equivalent of CuCl does give the $W(CO)_5$ complexed tributylphosphine (**11**). The ^1J(P–P) coupling constant for the intermediate **10** of 286 Hz is 158 Hz smaller than that for **6a**. This relatively small coupling constant, which is similar to those of **8** and **9a–c**, is attributed to the complexation of the phosphoranylidene phosphine complexes to CuCl. We suggest that the $W(CO)_5$ transfer in **8** and **9a–c** to generate **3** and **5**, respectively, proceeds via a π-complex with concurrent elimination of rapidly oligomerizing (Cu-complexed) PhP; π-complexes between transition metal groups and P=P bonds are well established [14].



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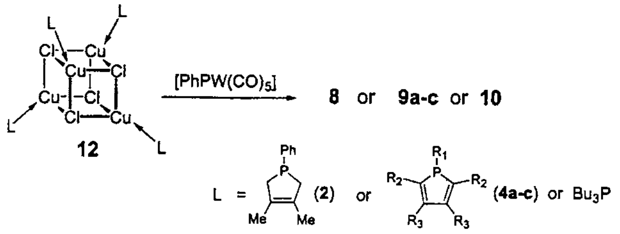
Why is CuCl present in the crystal structure of **8**? It is likely that CuCl coordinates with phospholene **2**, the phospholes **4a–c**, and Bu_3P. In fact, Nelson et al. showed Cu(I) halides to coordinate to 1-phenyl-3,4-dimethylphosphole (L) to form various complexes of the type $[L_nCuX]_m$ ($n = 1, 2, 3$; $m = 4, 2, 1$). They reported a crystal structure for the tetramer [15]. The $P_4Cu_4I_4$ core of this structure has a C_2-distorted cubic form. With bulkier ligands dimers [13,16] and monomers [17] were found. We speculate that reaction of **1** occurs with the $[LCuCl]_4$ tetramer (**12**) of the phospholene (**2**), phospholes (**4a–c**), and Bu_3P with insertion of $PhPW(CO)_5$ into the PCu coordinating bonds to result in the $[L'CuCl]_2$ dimers **8** or **9a–c**, or **10**, respectively. We attribute the cleavage of the tetramer to the more congested nature of the $R_2P(Ph)$=$PPhW(CO)_5$ ligand.



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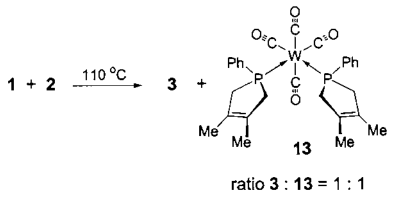
To further inspect the impact of CuCl on the course of the reactions we conducted experiments without this catalyst. Reaction of **1** with phospholene **2** in toluene at 110°C gave again complex **3**, but also bisphospholene complex **13** in a 1:1 ratio (Scheme 2). The formation of **3** illustrates that the $W(CO)_5$-shift in intermediate **8** is independent of CuCl. However, CuCl may facilitate the elimination of PhP and the concurrent transfer of $W(CO)_5$. Because of its rather complicated ^{13}C-NMR spectrum, due to the higher order couplings, we used a single crystal X-ray structure determination (Fig. 2) to establish with confidence the identity of **13** ($\delta(^{31}P) = 1.8$ ppm). Whereas formation of **13** may be rationalized by a simple thermally induced ligand exchange of **3**, heating



Scheme 2.

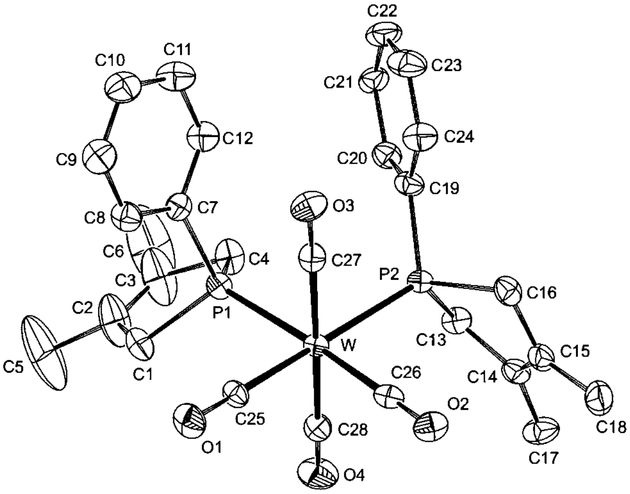


Fig. 2. Displacement ellipsoid plot of **13** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): W–P1 2.4962(10), W–P2 2.5138(11), P1–C7 1.817(4), P2–C19 1.821(4), P1–C1 1.843(5), P2–C13 1.845(4), P1–C4 1.844(4), P2–C16 1.833(4), C2–C3 1.308(9), C14–C15 1.343(6), C1–C2 1.508(7), C13–C14 1.525(6), C3–C4 1.508(7), C15–C16 1.518(6); P1–W–P2 95.23(3), C7–P1–W 113.49(13), C19–P2–W 115.69(14), C25–W–P1 86.63(12), C26–W–P2 88.04(13), C27–W–P1 88.10(11), C27–W–P2 86.63(13), C28–W–P1 87.74(12), C28–W–P2 91.28(13), C1–P1–C4 92.5(2), C16–P2–C13 92.3(2).

of this compound together with phospholene **2** at 110°C for several hours does not give any **13**. It seems then more plausible that ligand exchange occurs in the intermediate phosphinidene–phosphole complex. Indeed, heating a mixture of isolated **8** and **2** at 110°C does result in a mixture of bisphospholene complex **13** and **3**.

Phosphoranylidene-phosphines can be considered phospha-Wittig reagents. In fact, **6**, but not the more stable **7**, are known to react with aldehydes only to form incipient phosphaalkenes, which can subsequently be trapped with, for example, methanol [11,12]. However, we did not observe a reaction of **8** with benzaldehyde nor with isobutyraldehyde, but obtained only **3**. The formal phosphinidene O–H insertion product [(MeO)PHPh]W(CO)$_5$ results in the presence of methanol as trapping reagent.

3. Conclusions

Transient electrophilic phosphinidene complex PhPW(CO)$_5$ adds to the phosphorus center of phospholenes (**2**) and phospholes (**4a**–**c**) instead of reacting with their olefinic bonds. The resulting intermediates convert to the corresponding W(CO)$_5$-complexed products **3** and **5a**–**c** with transfer of the transition metal group and expulsion of PPh. The intermediate phosphoranylidene-phosphine complexes are identified by NMR spectroscopy. A crystal structure of the one generated from phospholene **2** showed it to be a CuCl-complexed dimer (**8**). Generating PhPW(CO)$_5$ in the absence of CuCl and reacting it with phospholene **2** gives besides **3** also bisphospholene complex **13**.

4. Experimental

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuum and liquids were distilled (under N_2) prior to use. Solvents were used as purchased except for toluene, which was distilled over sodium, and $CHCl_3$, which was dried over molecular sieves. NMR spectra were recorded on Bruker AC 200 (^1H, ^{13}C) and WM 250 spectrometers (^{31}P) using $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards, IR spectra on a Mattson-6030 Galaxy FTIR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan Mat 90 spectrometer. 1-Phenyl-3,4-dimethylphospholene (**2**) [18], 1-phenyl-3,4-dimethylphosphole (**4a**) [19], 1,3,4-trimethylphosphole (**4b**) [19] and 1,2,5-triphenylphosphole (**4c**) [20] were prepared according to literature procedures.

*4.1. Reaction of **1** with 1-phenyl-3,4-dimethylphospholene (**2**)*

*4.1.1. Formation of [(Me)$_2$C$_4$H$_4$P(Ph)=PPhW(CO)$_5$CuCl]$_2$ (**8**)*

A mixture of complex **1** (0.62 g, 0.95 mmol), **2** (0.18 g, 0.95 mmol) and CuCl (0.11 g, 1.10 mmol) in 5 ml of $CHCl_3$ was stirred at room temperature (r.t.) for 75 min. Chromatography on activated silica at -15°C with pentane–CH_2Cl_2 (2:1) as eluent and crystallization from a hexane–CH_2Cl_2 mixture gave 0.33 g (47.4% (based on **1**) of complex **8** as yellow crystals: ^{31}P-NMR ($CDCl_3$) $\delta = 31.1$ (d, ^1J(P–P) = 294 Hz, P–P–W), -54.7 (d, ^1J(P–P) = 294 Hz, P–P–W); ^1H-NMR ($CDCl_3$) $\delta = 1.72$ (d, ^4J(P–H) = 5.0 Hz, 12H, CH_3), 3.0–3.5 (m, 8H, CH_2), 7.3–7.7 (m, 20H, Ph); ^{13}C-NMR ($CDCl_3$) $\delta = 199.7$ (d, ^2J(P–C) = 16.1 Hz, *trans*-CO), 197.2 (d, ^2J(P–C) = 3.9 Hz, ^1J(P–W) = 125.4 Hz, *cis*-CO), 137.5 (dd, ^3J(P–C) = 5.1 Hz, ^2J(P–C) = 13.7 Hz, *o*-Ph), 133.1 (d, ^4J(P–C) = 3.0 Hz, *p*-Ph), 131.8 (d, ^3J(P–C) = 8.6 Hz, *m*-Ph), 130.4 (d, ^1J(P–C) = 11.1 Hz, *ipso*-Ph), 130.2 (d, ^4J(P–C) = 3.0 Hz, *p*-Ph), 129.4 (d, ^3J(P–C) = 11.5 Hz, *m*-Ph), 128.8 (dd, ^3J(P–C) = 3.5

Hz, ^{2}J(P–C) = 7.6 Hz, *o*-Ph), 128.6 (d, ^{2}J(P–C) = 4.5 Hz, C=C), 124.9 (d, ^{1}J(P–C) = 59.7 Hz, *ipso*-Ph), 36.5 (d, ^{1}J(P–C) = 42.9 Hz, CH_2), 16.7 (dd, ^{3}J(P–C) = 11.4 Hz, ^{4}J(P–C) = 3.5 Hz, CH_3). IR (CH_2Cl_2, cm^{-1}): ν(CO) = 1934 (s), 2067 (w).

4.1.2. Formation of [1-phenyl-3,4-dimethylphospholene](pentacarbonyl)tungsten (3)

A mixture of complex **1** (0.17 g, 0.25 mmol), **2** (44 mg, 0.23 mmol) and CuCl in $CHCl_3$ was stirred overnight at r.t. Evaporation to dryness and chromatography on silica with pentane–toluene (3:1) gave 117 mg (90%) of **3** as colorless crystals. Spectroscopic data for **3** are in accord with literature data [21].

4.1.3. Formation of 3 and cis-bis-[1-phenyl-3,4-dimethylphospholene]-(pentacarbonyl)tungsten (13)

A solution of complex **1** (0.29 g, 0.45 mmol) and **2** (0.26 g, 1.3 mmol) in 4 ml of toluene was heated at 110°C for 2 h. Evaporation to dryness and chromatography on silica with pentane–toluene (4:1), gave 86 mg (37%) of **3** and 99 mg (32%) of **13**. Colorless crystals of **13** were obtained after recrystallization from pentane–CH_2Cl_2: m.p. 96–97°C; ^{31}P-NMR ($CDCl_3$) $\delta = 1.8$ ($^{1}J(^{31}P-^{183}W) = 224.7$ Hz); ^{1}H-NMR ($CDCl_3$) $\delta = 1.54$ (s, 6H, CH_3), 2.6–2.9 (m, 4H, CH_2), 7.17–7.24 (m, 10H, phenyl); ^{13}C-NMR ($CDCl_3$) $\delta = 206.0$ (m, *trans*-CO), 202.2 (t, ^{2}J(P–C) = 7.7 Hz, *cis*-CO), 138.9 (m, ^{1+3}J(P–C) = 30.8 Hz, *ipso*-Ar), 129.6–128.0 (Ar), 129.6 (s, C=C), 44.6 (m, ^{1+3}J(P–C) = 27.7 Hz, CH_2), 16.0 (s, CH_3). IR (KBr, cm^{-1}): ν(CO) = 2062 (s), 2089 (w); HRMS. Calc. for $C_{28}H_{30}P_2WO_4$: 676.11293; Found: 676.11279.

4.2. Reaction of 1 with phospholes 4a–c

4.2.1. Reaction of 1 with 1-phenyl-3,4-dimethylphosphole (4a)

A solution of complex **1** (0.28 g, 0.42 mmol), **4a** (0.20 g, 1.1 mmol) and CuCl in 5 ml of $CHCl_3$ was stirred overnight at r.t. Filtration, evaporation to dryness and chromatography on silica with pentane–toluene (4:1) gave 0.16 g (74%) of **5a** as a yellow solid. Spectroscopic data for **5a** are in accord with literature data [22]. Monitoring the reaction by ^{31}P-NMR showed the formation of intermediate **9a**: ^{31}P-NMR $\delta = 40.5$ (d, ^{1}J(P–P) = 316 Hz, P–P–W), −53.3 (d, ^{1}J(P–P) = 316 Hz, P–P–W).

4.2.2. Reaction of 1 with 1,3,4-trimethylphosphole (4b)

A solution of complex **1** (0.89 g, 1.35 mmol), **4b** (0.17 g, 1.35 mmol) and CuCl (0.17 g, 0.17 mmol) in $CHCl_3$ was stirred overnight at r.t. Filtration, evaporation to dryness and chromatography on silica with pentane–toluene (4:1) gave 0.25 g (41%) of **5b** as a yellow oil. Spectroscopic data for **5b** were identical to an authentic sample [23]. Monitoring the reaction by ^{31}P-NMR showed the formation of intermediate **9b**: ^{31}P-NMR $\delta = 36.9$ (d, ^{1}J(P–P) = 294 Hz, P–P–W), −72.6 (d, ^{1}J(P–P) = 294 Hz, P–P–W).

4.2.3. Reaction of 1 with 1,2,5-triphenylphosphole (4c)

A solution of complex **1** (0.29 g, 0.45 mmol), **4c** (0.14 g, 0.45 mmol) and CuCl in toluene was heated at 55°C for 2 h. Filtration, evaporation to dryness and chromatography on silica with pentane–toluene (1:1) gave 0.17 g (61%) of **5c** as a yellow solid. Spectroscopic data for **5c** were identical to an authentic sample [24].

4.3. Reaction of 1 with tributylphosphine

A solution of complex **1** (0.14 mg, 0.21 mmol), tributylphosphine (53 µl, 0.21 mmol) and CuCl (22 mg, 0.22 mmol) in 3 ml of $CHCl_3$ was stirred at r.t. for 4.5 h. Evaporation to dryness and chromatography on silica with pentane–dichloromethane (4:1) gave 61 mg of **11** as a light yellow oil. Spectroscopic data for **11** are in accord with literature data [25]. Monitoring the reaction by ^{31}P-NMR showed the formation of intermediate **10**: ^{31}P-NMR $\delta = 23.2$ (d, ^{1}J(P–P) = 286 Hz, P–P–W), −79.7 (d, ^{1}J(P–P) = 286 Hz, P–P–W).

4.4. Attempted reaction of 8 with aldehydes

4.4.1. Reaction in the presence of methanol

A solution of complex **1** (0.24 g, 0.37 mmol), **2** (64 mg, 0.34 mmol) and CuCl in 5 ml of $CHCl_3$ was stirred at r.t. When the conversion of **1** to **8** was complete (as monitored by ^{31}P-NMR), one equivalent of benzaldehyde or isobutyraldehyde was added. After 5 min, 0.16 ml (4.0 mmol) of MeOH was added and stirring was continued for 45 min. Evaporation to dryness and chromatography on silica with pentane–toluene (4:1) afforded 0.10–0.12 g (76–88%) of [(MeO)PHPh]-W$(CO)_5$ as a white solid. Spectroscopic data for [(MeO)PHPh]W$(CO)_5$ are in accord with literature data [1].

4.4.2. Reaction without methanol

Complex **8** was synthesized in situ as described above. Addition of five equivalents of benzaldehyde or isobutyraldehyde and stirring overnight at r.t. yielded quantitatively complex **3** as indicated by ^{31}P-NMR.

4.5. X-ray crystallography

4.5.1. Crystal structure determination of complex 8

$C_{46}H_{40}Cl_2Cu_2O_{10}P_4W_2$ + solvent, Fw = 1442.34[1], yellow block, 0.36 × 0.27 × 0.09 mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 10.7136(8)$, $b = 15.9667(13)$, $c = 20.2435(14)$ Å, $\alpha = 93.161(4)$, $\beta = 103.032(3)$, $\gamma = 93.428(3)°$, $V = 3359.2(4)$

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[1] Derived values do not contain the contribution of the disordered solvent.

Å^3, $Z = 2$, $\rho = 1.426$ g cm^{-3}.[1] A total of 29 905 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 100(2) K. A total of 14 786 reflections were unique ($R_{\text{int}} = 0.051$). The absorption correction was based on multiple measured reflections (program PLATON [26], routine MULABS, $\mu = 4.25$ mm^{-1},[1] 0.54–0.73 transmission). The structure was solved with Patterson methods (DIRDIF-97 [27]) and refined with SHELXL-97 [28] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The crystal structure contains large voids (1087 Å^3/unit cell) filled with disordered dichloromethane and hexane molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON [26], CALC SQUEEZE, 344 e$^-$/unit cell). 599 refined parameters, no restraints. R values $[I > 2\sigma(I)]$: $R_1 = 0.0449$, $wR_2 = 0.1027$. R values [all reflections]: $R_1 = 0.0681$, $wR_2 = 0.1086$. GoF = 1.070. Rest electron density between -2.29 and 2.21 e Å^{-3}. Molecular illustration, structure checking and calculations were performed with the PLATON package [26].

4.5.2. *Crystal structure determination of complex* **13**

$C_{28}H_{30}O_4P_2W$ + solvent, Fw = 676.31[1], colourless block, $0.50 \times 0.25 \times 0.13$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 8.2135(6)$, $b = 9.7430(6)$, $c = 18.8082(11)$ Å, $\alpha = 95.296(5)$, $\beta = 96.453(6)$, $\gamma = 108.070(6)°$, $V = 1408.87(16)$ Å^3, $Z = 2$, $\rho = 1.594$ g cm^{-3}.[1] A total of 12 483 reflections were measured on an Enraf-Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K. A total of 6478 reflections were unique ($R_{\text{int}} = 0.084$). The absorption correction was based on psi-scans (program PLATON [26], routine ABSP, $\mu = 4.24$ mm^{-1},[1] 0.82–0.98 transmission). The structure was solved with Patterson methods (DIRDIF-97 [27]) and refined with SHELXL-97 [28] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The crystal structure contains a void (92 Å^3/unit cell) filled with disordered dichloromethane and hexane molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON [26], CALC SQUEEZE, 29 e$^-$/unit cell). 320 refined parameters, no restraints. R values $[I > 2\sigma(I)]$: $R_1 = 0.0280$, $wR_2 = 0.0724$. R values [all reflections]: $R_1 = 0.0324$, $wR_2 = 0.0751$. GoF = 1.081. Rest electron density between -1.29 and 1.51 e Å^{-3}. Molecular illustration, structure checking and calculations were performed with the PLATON package [26].

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 146323 for compound **8** and CCDC no. 146324 for compound **13**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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