# FULL PAPER

# *P*-OR Functional Phosphanido and/or Li/OR Phosphinidenoid Complexes?

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*Dedicated to Professor K. Tamao[‡]*

*P*-H,*P*-OR-substituted phosphane complexes **3a–e** have been synthesized by two methods: (1) the thermal reaction of 2*H*-azaphosphirene complex **1** with methanol, *n*-butanol, or ethylene glycol monomethyl ether (**3b,c,e**) or (2) the reaction of *P*-chlorophosphane complex **2** with appropriate sodium phenolate salts (**3a,d**). All the complexes **3a–e** were obtained in good yields and fully characterized by NMR, IR, MS, and elemental analysis. Furthermore, the structures of **3a**, **3d** and **3e** were confirmed unambiguously by X-ray analysis. The de-protonation of complexes **3a–e** by using lithium diisopropylamide in the presence of 12-crown-4 led to phosphinidenoid complexes **4a–e**, which exhibit downfield $^{31}$P resonances and small tungsten–phosphorus coupling constants. Studies on the reactivity of complexes **4a–c,e** revealed a "phosphanido-type" reactivity, and only for complex **4d**, a thermally labile complex, was evidence found for a "phosphinidene-type" reactivity.

## Introduction

Alkali phosphanides[1] **I** and their complexes[2] **II** (Scheme 1) are classes of compounds in which an alkali metal is (most often) bound directly to the phosphorus atom. They can be considered as key reagents in main-group-element and transition-metal chemistry as they are valuable synthons for the formation of P–E bond systems.
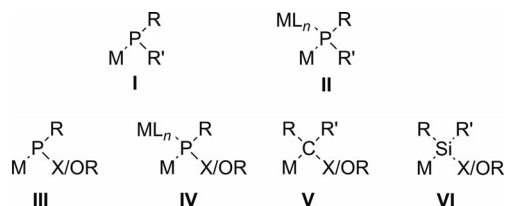


Scheme 1. Phosphanides **I** and their complexes **II**, phosphinidenoids **III** and their complexes **IV**, carbenoids **V**, and silylenoids **VI** (R, R′ = organic substituent; M = alkali metal, such as Li, Na, K; X = halogen; ML$_n$ = transition-metal fragment).

In 1987, Mathey and co-workers reported the synthesis of the first monometalated terminal (phosphanido)transition-metal complex (**II**) [(CO)$_5$W(LiPH$_2$)],[2a] which was obtained by treating the (phosphane)tungsten complex with *n*BuLi at low temperature. The complex, identified by $^{31}$P NMR spectroscopy ($\delta$ = –273 ppm, $^1J_{W,P}$ = 68 Hz, $^1J_{P,H}$ = 320 Hz), reacted as a nucleophile with alkyl halides to pro-

vide [(CO)$_5$W(RPH$_2$)]; the bonding situation of lithium remained unclear. In 2005, Westerhausen et al. reported the phosphanido complex [Li(thf)$_4$][(CO)$_5$W{P(Si*i*Pr$_3$)$_2$}], revealing a solvent-separated ion-pair structure[2b] and an unusually upfield-shifted $^{31}$P resonance ($\delta$ = –409.2 ppm, $^1J_{W,P}$ = 136.1 Hz). In addition to such examples of ill- and well-defined bonding situations of P–Li compounds are examples in which the lithium ion coordinates within the molecule but not to the phosphorus atom. One recent example may be the phosphanido complex [(CO)$_5$W(RP{CNLi(12-crown-4)})][2c] [R = CH(SiMe$_3$)$_2$; $\delta$ = –152.9, $^1J_{W,P}$ = 100 Hz], in which the lithium ion is bound to the nitrogen atom; this phosphanido complex reacts with electrophiles such as MeI or MeOSO$_2$CF$_3$ exclusively to give the *P*-methylated phosphane complex. Note also that, despite the presence of the cyano functionality, no decomposition to yield LiCN was observed at ambient temperature.

Given this background and the formal similarities between phosphinidenoids[3] **III** and their complexes **IV** on the one hand, and carbenoids[4] **V** and silylenoids[5] **VI** (Scheme 1) on the other, one might wonder why it took so long to establish phosphinidenoid complexes **IV**[6] or why phosphinidenoids **III** have not yet even been fully achieved.[7] This is even more strange given the versatile use of **V** and **VI** in organic synthesis, that is, enabling a plethora of reactions such as electrophilic, nucleophilic, carbene-like, and, to some extent, redox reactions. The chemistry of Ph$_2$Si(Li)O*t*Bu[5b] might be a good case in point for silylenoids **VI**, which have been developed by Tamao et al. It is remarkable that all the Li/X or Li/OR carbenoids and silylenoids known to date show $^{13}$C or $^{29}$Si NMR chemical

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shifts downfield of their non-lithiated precursors. In addition to this important NMR feature, they show markedly elongated C–E or Si–E bonds (E = Cl, O) in solid-state structures compared with their corresponding non-lithiated derivatives.[4g,5h]

Recently, Li/X (phosphinidenoid)tungsten complexes (X = F,[8a] Cl[8b,8c]) were firmly established, and their thf solutions displayed markedly downfield-shifted $^{31}$P NMR resonances and small tungsten–phosphorus coupling constants; information on the solid-state structures of such derivatives is still lacking. Reactivity studies on Li/Cl (phosphinidenoid)tungsten complexes [R = CH(SiMe$_3$)$_2$, C$_5$Me$_5$] revealed nucleophilic reactivity towards organic iodides[9] and acyl chlorides,[10] and phosphinidene-like reactivity towards π-systems such as nitriles, alkynes, and aldehydes.[8b] The high negative charge density at the phosphorus atom also enabled redox reactions, as the initial studies revealed: SET oxidation occurs with tritylium salts, thus leading to transient *P*-X functional phosphanyl complexes that were detected by EPR spectroscopy.[11] The latter not only possess high electron-spin density at the phosphorus atom (70–85%) but also underwent phosphorus-centered reactions thereby providing new perspectives in synthesis[11] as well as new insights into systems possessing very weak P–C bonds.[12]

Recently, we gained further insight into these systems. The use of strong and sterically demanding organic bases enabled the synthesis of *P*-X and *P*-OR (phosphinidenoid) tungsten complexes possessing enhanced thermal stabilities. The first single-crystal structure of a *P*-OPh complex derivative revealed a solvent-separated ion pair by virtue of weakly coordinating cations.[13] In contrast, the first attempts to synthesize Li/OAc (phosphinidenoid)tungsten complexes (OAc = CH$_3$CO$_2$) resulted only in decomposition upon warming to ambient temperature,[14] whereas an Li/OPh (phosphinidenoid)tungsten complex was successfully used in P–C bond-forming reactions with acyl chlorides.[10]

Herein we report the first extensive study on the synthesis and reactions of Li/OR (phosphinidenoid)tungsten complexes.

## Results and Discussion

Potential precursors for Li/OR phosphinidenoid complexes, that is, bifunctional phosphane complexes **3a–e**, were conveniently prepared according to the two routes shown in Scheme 2: (1) by thermal reaction of 2*H*-azaphosphirene complex **1**[15] with methanol, ethylene glycol monomethyl ether, or *n*-butanol in toluene at 75 °C (**3b,c,e**) or (2) by reaction of *P*-chlorophosphane complex **2**[16] and sodium phenolate salts in diethyl ether at –40 °C with NaCl elimination (**3a,d**).

All reactions led selectively and in good yields (51–66%) to the 1,1′-bifunctional phosphane complexes **3a–e**, which were isolated by column chromatography or by washing with *n*-pentane at low temperature. Complexes **3a–e** were
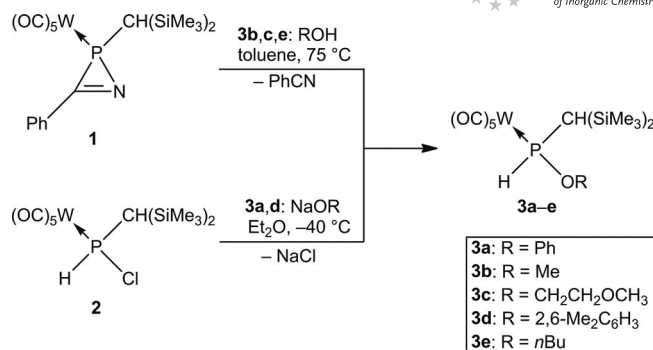


Scheme 2. Synthesis of 1,1′-bifunctional phosphane complexes **3a–e**.

fully characterized by multinuclear NMR, IR, MS, and elemental analysis. Moreover, the structures of **3a**, **3d**, and **3e** were unambiguously confirmed by single-crystal X-ray analysis.

The $^{31}$P NMR resonances of complexes **3a–e** appear in the narrow range of δ = 99.0–109.7 ppm ($^1J_{W,P}$ = 265–275 Hz, $^1J_{P,H}$ = 320–330 Hz), in quite good agreement with the values reported earlier by Mathey and co-workers for 1,1′-bifunctional phosphane complexes, although they demonstrated that the chemical shifts are strongly influenced by the R group on the phosphorus atom. For example, [(CO)$_5$W{ClH$_2$CP(H)OMe}][17] displays a resonance at δ = 104.8 ppm ($^1J_{W,P}$ = 283.2 Hz, $^1J_{P,H}$ = 352 Hz), whereas [(CO)$_5$W{EtO$_2$CP(H)OMe}][18] exhibits a resonance at δ = 78.3 ppm ($^1J_{W,P}$ = 278 Hz, $^1J_{P,H}$ = 365.5 Hz). Selected NMR spectroscopic data for the new complexes **3a–e** are given in Table 1.

Table 1. Selected NMR spectroscopic data (in CDCl$_3$) for complexes **3a–e**.

| Complex | δ [ppm]/*J* [Hz] | | |
|---------|------------------|---|---|
| | δ($^{31}$P)/$^1J_{W,P}$ | δ($^1$H)[a]/$^1J_{P,H}$ | δ($^{13}$C)[b]/$^1J_{P,C}$ |
| **3a** | 106.8/275.9 | 8.41/325.2 | 22.6/13.7 |
| **3b** | 109.7/267.0 | 7.80/320.7 | 21.4/13.6 |
| **3c** | 107.3/267.0 | 7.86/324.1 | 23.5/13.6 |
| **3d** | 99.0/274.7 | 8.47/336.3 | 24.2/9.7 |
| **3e** | 102.5/267.0 | 7.83/319.7 | 30.2/8.4 |

[a] Hydrogen atom directly bound to the phosphorus atom. [b] Carbon atom directly bound to the phosphorus atom.

The $^{13}$C{$^1$H} NMR data shown in Table 1 reveal $^{13}$C resonances in the range δ = 21.4–30.2 ppm with $^1J_{P,C}$ values of 8.4–13.7 Hz; these have been assigned to the carbon atom of the CH(SiMe$_3$)$_2$ group directly bound to the phosphorus atom and are similar to the data of related *P*-X organophosphane complexes [R = CH(SiMe$_3$)$_2$], such as [(CO)$_5$W{RP(H)F}][8a] (δ$_C$ = 28.0 ppm, $^1J_{P,C}$ = 18.8 Hz) and [(CO)$_5$W{RP(H)Cl}][16] (δ$_C$ = 24.6 ppm, $^1J_{P,C}$ = 4.8 Hz).

The IR spectra of the complexes **3a–e** display a ν(P–H) absorption band at 2367 (**3a**), 2264 (**3b**), 2260 (**3c**), 2257 (**3d**), and 2290 (**3e**), which are in the normal range found for P–H absorptions (2200–2400 cm$^{-1}$).[19,20] Typically very

intense absorptions due to CO stretching vibrations of the W(CO)$_5$ group in complexes **3a–e** can be observed in the range 1910–2010 cm$^{-1}$.

The molecular structures of **3a**, **3d**, and **3e** in the solid state were determined by single-crystal X-ray diffraction studies (Figures 1, 2 and 3). The crystal system/space group of **3e** is orthorhombic $P2_12_12_1$, whereas those of **3a** and **3d** are triclinic $P\bar{1}$. These complexes show common molecular structural features; for example, all the phosphorus centers have a trigonal geometry [sum of the bond angles at the phosphorus atom (includes the W(CO)$_5$ moiety but not the P–H group): 342.3 (**3a**), 338.4 (**3d**), 341.1° (**3e**)]. Although measured carefully, the P–H bond lengths of **3a**, **3d**, and **3e** vary significantly: 1.40 (**3a**), 1.27 (**3d**), and 1.34 Å (**3e**).
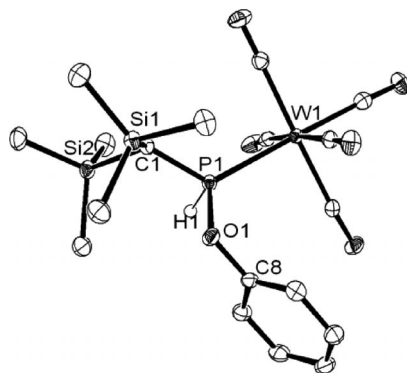


Figure 1. Molecular structure of complex **3a** in the crystal form (ellipsoids drawn at the 50% probability level; except for H1, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–H1 1.40(3), P1–C1 1.811(2), P1–W 2.4791(6), P1–O1 1.6522(17), O1–C8 1.397(3); H1–P1–C1 102.4(12), H1–P1–O1 97.9(12), H1–P1–W1 110.4(11), C1–P1–W1 123.40(8), C1–P1–O1 100.43(10), W1–P1–O1 118.47(7).
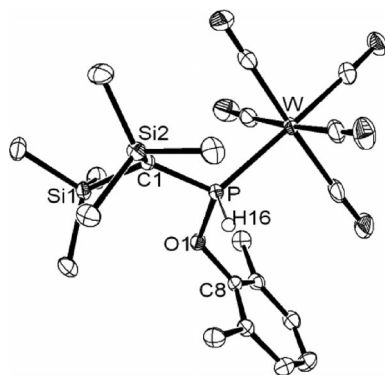


Figure 2. Molecular structure of complex **3d** in the crystal form (ellipsoids drawn at the 50% probability level; except for H16, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P–H16 1.27(3), P–W 2.4918(6), P–C1 1.810(3), P–O1 1.6571(18), O1–C8 1.404(3); H16–P–W 114.9(16), H16–P–C1 103.3(16), H16–P–O1 97.2(16), C1–P–W 117.04(8), C1–P–O1 102.37(10), O1–P–W 119.03(7).

The 1,1′-bifunctional organophosphane complexes **3a–e** were then subjected to deprotonation by using lithium diisopropylamide (LDA) in diethyl ether at –78 °C in the presence of 12-crown-4 (Scheme 3). The $^{31}$P NMR resonances of the resulting Li/OR phosphinidenoid complexes
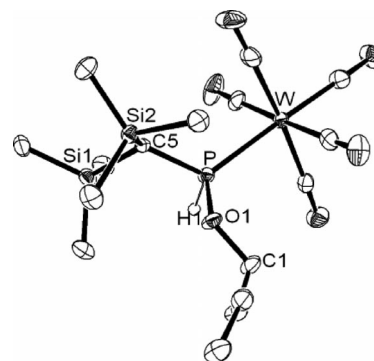


Figure 3. Molecular structure of complex **3e** in the crystal form (ellipsoids drawn at the 50% probability level; except for H1 hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P–H1 1.34(3), P–O1 1.621(2), P–W 2.4750(8), P–C5 1.807(3); H1–P–O1 95.9(13), H1–P–C5 105.2(13), H1–P–W 111.0(12), O1–P–C5 99.33(13), O1–P–W 121.39(9), C5–P–W 120.38(11).

**4a–e** were observed at low field ($\delta$ = 200–220 ppm) with small tungsten–phosphorus coupling constants of about 76 Hz (Table 2). This matches the data obtained for the related Li/F ($\delta$ = 305.9 ppm, $^1J_{W,P}$ = 71.3 Hz)[8a] and Li/Cl phosphinidenoid complexes ($\delta$ = 212.9 ppm, $^1J_{W,P}$ = 67.4 Hz) with the same substituent on the phosphorus atom.[8b] In particular, the latter set of data are strikingly similar to the NMR spectroscopic data of **4a–e**, which in turn means that the Li/X phosphinidenoid complexes are largely determined by the specific bonding situation of the phosphorus center and to a minor extent by the nature of the substituent X. Even more important is the observation that these data are also almost identical to those reported for the solvent-separated ion pairs [cation: *N,N*-di-*tert*-butylimidazolium, X = OPh: $\delta$ = 208.6 ppm, $^1J_{W,P}$ = 75.5 Hz; cation: *t*Bu-P$_4$-phosphazene, X = OPh: $\delta$ =
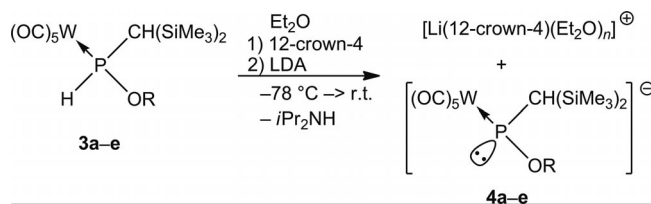


Scheme 3. Synthesis of Li/OR organophosphinidenoid complexes **4a–e**.

Table 2. Selected NMR spectroscopic data (in [D$_8$]thf) for complexes **4a–e**.

| Complex | $\delta$ [ppm]/$J$ [Hz] | |
| --- | --- | --- |
| | $\delta$($^{31}$P)/$^1J_{W,P}$ | $\delta$($^{13}$C)[a]/$^1J_{P,C}$ |
| **4a** | 209.1/76.2 | 25.4/75.0 |
| **4b** | 209.6/68.7 | 25.8/66.6 |
| **4c** | 208.8/69.0 | 24.3/68.5 |
| **4d** | 220.7/78.5 | 22.7/78.8 |
| **4e** | 201.3/68.6 | –/–[b] |

[a] Carbon atom directly bound to the phosphorus atom. [b] Could not be clearly assigned.

209.7 ppm, $^1J_{W,P}$ = 76.3 Hz], which led us to the conclusion that complexes **4a–e** have separated ion pairs as well; phosphorus–lithium coupling was not observed.[13]

In contrast to the former report on Li/OAc phosphinidenoid complexes,[14] the Li/OR complexes **4a–c,e** (not **4d**) are stable at ambient temperature and could be fully characterized by multinuclear NMR spectroscopy in [D$_8$]thf. The $^{13}$C{$^1$H} NMR spectra of complexes **4a–e** display resonances for the carbon atom of the CH(SiMe$_3$)$_2$ group directly bound to the phosphorus atom at $\delta \approx$ 23–25 ppm. The increase in the phosphorus–carbon coupling constants is remarkable relative to the precursors **3a–d** [75.0 (**4a**), 66.0 (**4b**), 68.5 (**4c**), and 78.8 Hz (**4d**)] and parallel the finding for the Li/F and Li/Cl phosphinidenoid complexes (87.4 and 80.5 Hz).

In addition to the already noted significantly enhanced thermal stabilities of the Li/OR phosphinidenoid complexes compared with their halogen analogues, one more aspect deserves mention: None of the derivatives underwent decomposition to give diphosphene complexes; however, in the case of complex **4d**, the presence of cyclotriphosphane[21] was observed in the NMR spectra (after ca. 1 h). Although the pathway for its formation is unclear at this point, the latter provides some evidence of decomposition by a phosphinidene-like pathway. Having now accessed Li/OR phosphinidenoid complexes and given the increased lability of **4d**, the reactivities of **4a–d** towards different substrates, such as methyl iodide, deuterated chloroform (**4a**), benzoyl chloride (**4a–c**), phenylacetylene (**4a,b**), and benzaldehyde (**4a,b**), were studied; the results are shown in Scheme 4.
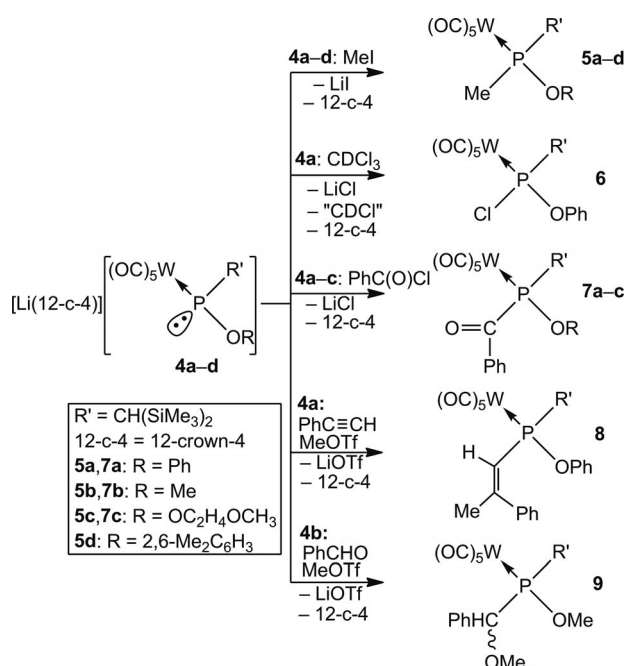
All the products **5a–d**, **6**, **7a–c**,[10] **8**, and **9** were fully characterized by multinuclear NMR, IR, MS, and elemental analysis. In addition, the structures of **5a** (Figure 4) and **6** (Figure 5) were established unequivocally by X-ray crystal analysis.

From the reactions with typical electrophiles such as MeI, CDCl$_3$, and PhC(O)Cl, the nucleophilic reactivity of complexes **4a–d** came to the fore. It is noteworthy that the reaction of **4a** with CDCl$_3$ led to the *P*-chlorophosphane complex **6**, most probably via an intermediate *P*-CDCl$_2$ complex by a C→P chlorine shift; related decompositions have been observed previously.[22]

The outcomes of the reactions of complexes **4a,b** with PhCCH and PhCHO differed from those of the corresponding Li/Cl phosphinidenoid complex. Here, the *P*-vinylphosphane complex **8** (from **4a**) and *P*-(α-methoxybenzyl)phosphane complex **9** (from **4b**) were obtained as the final products after methylation with TfOMe, clearly showing the nucleophilic reactivity of the Li/OR derivatives in the first reaction step. The $^{31}$P NMR signal for complex **8** appears at $\delta$ = 154.1 ppm ($^1J_{W,P}$ = 269.6 Hz), which is downfield of the *P*-vinylphosphane complexes [(CO)$_5$W(Ph)-P(OMe)(ClC=CH$_2$)][23] ($\delta$ = 125.6 ppm, $^1J_{W,P}$ = 289.0 Hz) and [(CO)$_5$W(Ph)P(OMe)(PhC=CHPh)] ($\delta$ = 129.3 ppm, $^1J_{W,P}$ = 278.0 Hz).[24] Comparison of the $^{31}$P NMR spectroscopic data of complex **9** ($\delta$ = 161.8 ppm, $^1J_{W,P}$ = 275.9 Hz) with those of [(CO)$_5$WP(R)(F){CH(OH)Ph}] [R = CH(SiMe$_3$)$_2$; $\delta$ = 198.1 ppm, $^1J_{W,P}$ = 296 Hz][25] lend further support to this assignment. It is also remarkable that the formation of complex **9** was only observed in the case of the methoxy derivative **4b** and not in the case of the phenoxy analogue **4a**, which may be explained by either the higher steric demand of the phenyl group in **4a** and/or by assuming a higher nucleophilicity of complex **4b** compared with **4a**.

The molecular structure of *P*-methylphosphane complex **5a** was confirmed by X-ray analysis (Figure 4); comparison with its precursor **3a** and [(CO)$_5$W{RP(Me)(CN)}] [R = CH(SiMe$_3$)$_2$][3] showed no differences of particular interest.



Scheme 4. Reactions of Li/OR phosphinidenoid complexes **4** with different reagents.
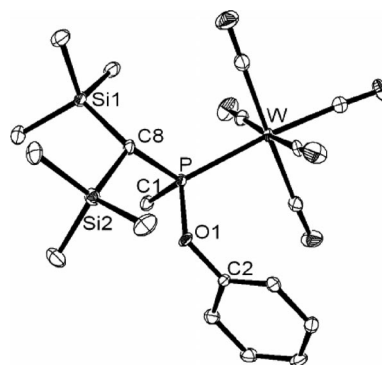


Figure 4. Molecular structure of complex **5a** in the crystal form (ellipsoids are shown at the 50% probability level, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P–O1 1.649(2), P–W 2.5045(7), P–C8 1.819(3), P–C1 1.814(3), O1–C2 1.398(3); C1–P–O1 100.28(12), C1–P–C8 106.89(13), C1–P–W 115.28(10), O1–P–C8 97.66(12), O1–P–W 114.80(8), C8–P–W 119.05(9), P–O1–C2 124.68(17).

*P*-Chlorophosphane complex **6** showed a resonance at $\delta$ = 186.7 ppm in the $^{31}$P NMR spectrum with a large coupling constant ($^{1}J_{W,P}$ = 335.7 Hz). The crystallographic parameters of **6** (Figure 5) are in the normal range as also observed for complex **5a**.
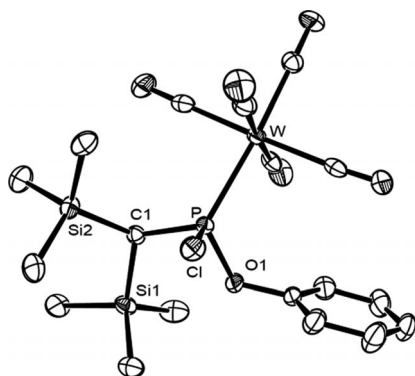


Figure 5. Molecular structure of complex **6** in the crystal form (ellipsoids are shown at the 50 % probability level, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and bond angles [°]: P–O1 1.6187(16), P–C1 1.799(2), P–W 2.4731(6), P–Cl 2.0918(9), O1–C8 1.411(3); W–P–O1 117.48(7), W–P–C1 120.18(8), W–P–Cl 114.08(3), C1–P–O1 99.58(10), Cl–P–O1 99.00(7), P–O1–C8 124.35(16).

Encouraged by our initial success in using NHC and phosphazene derivatives and creating a cation in the process,[13] we carried out a preliminary study on the possibility of replacing the lithium ion by an organic cation by using an already formed Li/OR phosphinidenoid complex. As the reaction of complex **4a** with tetra-*n*-butylammonium fluoride (**10**) with a 1:1 stoichiometry was unselective, we employed an excess of the ammonium fluoride, which led to a selective, albeit surprising outcome. We assume that the anionic phosphane complex **12** is initially formed, which decomposes to give complex **13** as the final product (Scheme 5). One byproduct, compound **11**, was isolated and unambiguously confirmed. As complex **13** possesses a *P*-CH$_3$ substituent instead of the *P*-CH(SiMe$_3$)$_2$, it must have been formed by a desilylation pathway, which is still unknown. Recently, a selective desilylation of this particular substituent was achieved in the case of a diazaphosphole complex by a different proto-
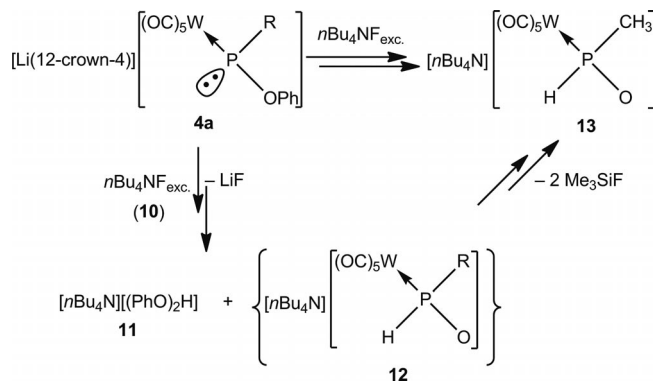


Scheme 5. Proposed mechanism for the reaction of complex **4a** with tetra-*n*-butylammonium fluoride.

col.[26] The NMR spectroscopic data of complex **13** ($\delta$ = 33.2 ppm, $^{1}J_{W,P}$ = 227.6 Hz, $^{1}J_{P,H}$ = 300.1 Hz) are similar to those of the known complex [Li(12-crown-4)][(CO)$_5$WRP(H)O] ($\delta$ = 46.0 ppm, $^{1}J_{W,P}$ = 244.1 Hz, $^{1}J_{P,H}$ = 302.6 Hz),[14] but has a solvent-separated ion-pair structure.

To examine this surprising result further, the reaction of pure [(CO)$_5$WP(R)H{OLi(12-crown-4)}] (**14**)[14] with tetra-*n*-butylammonium fluoride was performed (Scheme 6), but yielded the same result.
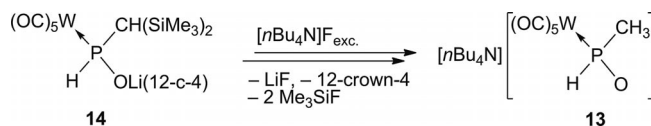


Scheme 6. Selective transformation of complex **14** into complex **13**.

## Conclusions

In this first systematic study on the synthesis, properties, and reactions of Li/OR (phosphinidenoid)tungsten complexes the following results were obtained. *P*-Bifunctional phosphane complexes **3a**–**e**, synthesized by two different routes, are excellent precursors for Li/OR phosphinidenoid complexes **4a**–**e**, which were obtained by the reactions of **3a**–**e** with lithium diisopropylamide (LDA) and 12-crown-4. The $^{31}$P NMR analyses of complexes **4a**–**e** revealed resonances at low field (ca. 200–220 ppm) and small tungsten–phosphorus coupling constants (ca. 68–75 Hz), which is the typical NMR signature.

Complexes **4a**–**c,e** showed a significantly increased thermal stability and hence a more pronounced phosphanido-type reactivity. However, derivative **4d** showed a tendency to decompose to a cyclotriphosphane, but not to a diphosphene complex, as has been observed previously for chloro Li/Cl phosphinidenoid complex.

The nucleophilic reactivity of complexes **4** was examined in reactions with MeI, CDCl$_3$, and PhC(O)Cl, and also with $\pi$-systems such as PhCHO and PhCCH. In the last two cases, quenching with TfOMe allowed the isolation of complexes **8** and **9** and hence confirmed that nucleophilic attack of complex **4** at C–C (**4a**) and C–O double bonds (**4b**) is effective.

Cation exchange in complex **4a** failed, and instead salt **13** was obtained, which shows that a complicated decomposition, including a desilylation of the phosphorus ligand, had taken place.

## Experimental Section

**General:** All operations were performed under purified and dried argon. Solvents were distilled from sodium wire/benzophenone. NMR spectroscopic data were recorded with a Bruker Avance 300 spectrometer at 25 °C. Shifts are given relative to tetramethylsilane ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz) and 85 % H$_3$PO$_4$ ($^{31}$P: 121.5 MHz) in ppm. MS data were recorded with a Kratos MS 50 spectrometer (EI, 70 eV). IR spectra were recorded with an FT-IR Nicolet 380 spectrometer. Melting points were obtained with a Büchi 535 capil-

lary apparatus. Elemental analyses were performed by using an Elementa (Vario EL) analytical gas chromatograph.

**Synthesis of 3a:** Phosphane complex **2** (551 mg, 1 mmol) in Et$_2$O (10 mL) was added to a solution of sodium phenolate (150 mg, 1.2 mmol) in Et$_2$O (10 mL) at low temperature. Then the reaction mixture was stirred overnight, while gently warming to ambient temperature. The mixture was filtered, the solvent removed in vacuo (10$^{-2}$ mbar), and the raw product was purified by washing with *n*-pentane at low temperature (ca. –50 °C); yellow crystals were obtained from *n*-pentane. Yield: 378 mg (0.62 mmol), 62%; m.p. 78 °C (decomp.). $^1$H NMR (CDCl$_3$): $\delta$ = 0.28 [d, $^4J_{H,H}$ = 0.6 Hz, 9 H, Si(CH$_3$)$_3$], 0.38 [s, 9 H, Si(CH$_3$)$_3$], 1.10 [dd, $^3J_{P,H}$ = 1.9, $^2J_{P,H}$ = 2.8 Hz, 1 H, PCH], 7.08 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, *o*-Ph-*H*), 7.17 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, *p*-Ph-*H*), 7.36 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, *m*-Ph-*H*), 8.41 (d, $^1J_{P,H}$ = 325.2, $^3J_{P,H}$ = 1.7 Hz, 1 H, P-*H*) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 0.3 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 2.2 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 22.9 (d, $^1J_{P,C}$ = 13.7 Hz, PCH), 120.2 (d, $^4J_{P,C}$ = 6.5 Hz, *m*-Ph*C*), 124.1 (d, $^5J_{P,C}$ = 1.3 Hz, *p*-Ph*C*), 129.7 (s, *o*-Ph*C*), 153.7 (d, $^2J_{P,C}$ = 6.5 Hz, PO*C*), 195.8 (d, $^2J_{P,C}$ = 7.8 Hz, *cis*-CO), 198.3 (d, $^2J_{P,C}$ = 27.2 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 106.8 (s$_{sat}$, $^1J_{W,P}$ = 275.9, $^1J_{P,H}$ = 325.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1910 [vs, $\nu$(CO)], 1920 [vs, $\nu$(CO)], 1957 [s, $\nu$(CO)], 1979 [m, $\nu$(CO)], 2073 [m, $\nu$(CO)], 2290 [w, $\nu$(PH)] cm$^{-1}$. MS: *m/z* (%) = 608.0 (51) [M]$^{+\cdot}$, 524.0 (80) [M – 3 CO]$^+$, 496.0 (45) [M – 4 CO]$^+$, 468.0 (40) [M – 5 CO]$^+$, 73.0 (100) [SiMe$_3$]$^+$. C$_{18}$H$_{25}$O$_6$PSi$_2$W (608.39): calcd. C 35.54, H 4.14; found C 35.57, H 4.27.

**Synthesis of 3b:** Methanol (41 μL, 1 mmol) was added to a solution of 2*H*-azaphosphirene complex **1** (1 mmol, 617 mg) in toluene (30 mL), and the solution was stirred at 75 °C for 3 h. All volatiles were then removed in vacuo (ca. 0.01 mbar), and the product was purified by column chromatography (SiO$_2$, –20 °C, eluent: petroleum ether) and obtained as the first fraction. Yield: 290 mg (0.53 mmol), 53%; m.p. 64 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 0.12 (s, 9 H, SiMe$_3$), 0.18 (s, 9 H, SiMe$_3$), 0.86 (d, $^3J_{H,H}$ = 1.5 Hz, 1 H, PC*H*), 3.43 (d, $^3J_{P,H}$ = 14.7 Hz, 3 H, POC*H$_3$*), 7.8 (d, $^1J_{P,H}$ = 320.7, $^3J_{H,H}$ = 1.5 Hz, 1 H, POC*H$_3$*) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = –1.9 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 0.0 [d, $^3J_{P,C}$ = 3.2 Hz, Si(CH$_3$)$_3$], 21.4 [d, $^1J_{P,C}$ = 13.6 Hz, *C*H(SiMe$_3$)$_2$], 54.1 (d, $^2J_{P,C}$ = 3.9 Hz, PO*C*H$_3$), 194.6 (d, $^2J_{P,C}$ = 7.1, $^1J_{W,C}$ = 125.4 Hz, *cis*-CO), 197.3 (d, $^2J_{P,C}$ = 24.6 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 109.7 (s$_{sat}$, $^1J_{W,P}$ = 267.0, $^1J_{P,H}$ = 320.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1917 [s, $\nu$(CO)], 1941 [s, $\nu$(CO)], 1994 [m, $\nu$(CO)], 2071 [m, $\nu$(CO)], 2257 [w, $\nu$(PH)] cm$^{-1}$. MS: *m/z* (%) = 546.0 (64) [M]$^+$, 518.0 (42) [M – CO]$^+$, 490.0 (72) [M – 2 CO]$^+$, 462.0 (41) [M – 3 CO]$^+$, 406.0 (65) [M – 5 CO]$^+$, 73.0 (100) [SiMe$_3$]$^+$. C$_{13}$H$_{23}$O$_6$PSi$_2$W (546.32): calcd. C 28.58, H 4.24; found C 28.74, H 4.31.

**Synthesis of 3c:** Ethylene glycol monomethyl ether (85 μL, 1 mmol) was added to a solution of 2*H*-azaphosphirene complex **1** (1 mmol, 617 mg) in toluene (30 mL) and then stirred at 75 °C for 3 h. The solvent was then removed in vacuo (ca. 0.01 mbar) and the product purified by column chromatography (SiO$_2$, –20 °C, eluent: petroleum ether) and obtained in the second fraction as a yellow viscous oil after concentration. Yield: 366 mg (0.62 mmol), 62%. $^1$H NMR (CDCl$_3$): $\delta$ = 0.21 [s, 9 H, Si(CH$_3$)$_3$], 0.27 [s, 9 H, Si(CH$_3$)$_3$], 0.93 (d, $^2J_{P,H}$ = 1.8 Hz, 1 H, PC*H*), 3.35 (s, 3 H, OC*H$_3$*), 3.57 (t, $^2J_{H,H}$ = 4.3 Hz, 2 H, *C*H$_2$OCH$_3$), 3.78 (m, $^2J_{H,H}$ = 4.8 Hz, 2 H, OC*H$_2$*CH$_2$), 7.90 (dd, $^1J_{P,H}$ = 324.1, $^4J_{H,H}$ = 1.3 Hz, 1 H, P-*H*) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 0.2 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 2.0 [d, $^3J_{P,C}$ = 3.2 Hz, Si(CH$_3$)$_3$], 23.4 (d, $^1J_{P,C}$ = 13.6 Hz, PCH), 58.7 (s, O*C*H$_3$), 68.0 (d, $^3J_{P,C}$ = 3.9 Hz, *C*H$_2$OCH$_3$), 71.6 (d, $^2J_{P,C}$ = 7.8 Hz, O*C*H$_2$CH$_2$), 196.6 (dd, $^2J_{P,C}$ = 7.1, $^1J_{W,C}$ = 125.4 Hz, *cis*-CO), 199.4 (d, $^2J_{P,C}$ = 24.6 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 107.3 (s$_{sat}$, $^1J_{W,P}$ = 267.0, $^1J_{P,H}$ = 324.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1935 [s, $\nu$(CO)], 1980

[s, $\nu$(CO)], 2072 [s, $\nu$(CO)], 2260 [w, $\nu$(PH)] cm$^{-1}$. MS: *m/z* (%) = 589.9 (40) [M]$^+$, 562.0 (30) [M – CO]$^+$, 534.0 (37) [M – 2 CO]$^+$, 506.0 (85) [M – 3 CO]$^+$, 73.0 (100) [SiMe$_3$]$^+$. C$_{16}$H$_{29}$O$_6$PSi$_2$W (588.40): calcd. C 30.52, H 4.61; found C 30.79, H 4.24.

**Synthesis of 3d:** Complex **2** (551 mg, 1 mmol) in Et$_2$O (10 mL) was added to a solution of sodium 2,6-dimethylphenolate (106 mg, 1.1 mmol) in Et$_2$O (10 mL) at low temperature. Then the reaction mixture was stirred overnight, while gently warming to ambient temperature. It was then filtered, and all the volatiles were removed in vacuo (10$^{-2}$ mbar). The raw product was purified by washing with *n*-pentane at low temperature (ca. –50 °C); pale-yellow crystals were obtained from *n*-pentane. Yield: 420 mg (0.66 mmol), 66%; m.p. 88–90 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 0.35 [d, $^2J_{H,H}$ = 11.1 Hz, 18 H, Si(CH$_3$)$_3$], 1.36 (dd, $^2J_{P,H}$ = 5.1, $^3J_{H,H}$ = 3.1 Hz, 1 H, PC*H*), 2.39 [s, 6 H, 2,6-(CH$_3$)$_2$C$_6$H$_3$], 7.01 (s, 3 H, 2,6-Me$_2$C$_6$H$_3$), 8.47 (dd, $^1J_{P,H}$ = 336.3, $^3J_{H,H}$ = 4.5 Hz, 1 H, P-*H*) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 1.2 [d, $^3J_{P,C}$ = 3.2 Hz, Si(CH$_3$)$_3$], 3.0 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 24.2 (d, $^1J_{P,C}$ = 9.7 Hz, PCH), 124.9 (d, $^5J_{P,C}$ = 1.9 Hz, *p*-Ph*C*), 130.0 (d, $^4J_{P,C}$ = 1.9 Hz, *m*-Ph*C*), 130.6 (d, $^3J_{P,C}$ = 4.5 Hz, *o*-Ph*C*), 150.4 (d, $^2J_{P,C}$ = 7.8 Hz, PO*C*), 196.3 (d, $^2J_{P,C}$ = 6.5 Hz, *cis*-CO), 198.4 (d, $^2J_{P,C}$ = 27.2 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 99.0 (s$_{sat}$, $^1J_{W,P}$ = 274.7, $^1J_{P,H}$ = 335.7 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1915 [s, $\nu$(CO)], 1985 [s, $\nu$(CO)], 2072 [m, $\nu$(CO)], 2367 [w, $\nu$(PH)] cm$^{-1}$. MS: *m/z* (%) = 636.1 (41) [M]$^+$, 552.1 (55) [M – 3 CO]$^+$, 524.1 (28) [M – 4 CO]$^+$, 515.0 (60) [M – 2,6-Me$_2$C$_6$H$_3$O]$^+$, 487.0 (49) [M – 5 CO – 2,6-Me$_2$C$_6$H$_3$O]$^+$, 73.0 (100) [SiMe$_3$]$^+$. C$_{18}$H$_{25}$O$_6$PSi$_2$W (608.39): calcd. C 37.74, H 4.59; found C 37.76, H 4.65.

**Synthesis of 3e:** *n*-Butanol (90 μL, 1 mmol) was added to a solution of 2*H*-azaphosphirene complex **1** (1 mmol, 617 mg) in toluene (30 mL) and then stirred at 75 °C for 3 h. The solvents were then removed in vacuo (ca. 0.01 mbar), and the product was purified by column chromatography (SiO$_2$, –20 °C, eluent: petroleum ether) and obtained in the first fraction. Yellow single crystals were obtained from *n*-pentane solutions. Yield: 300 mg (0.51 mmol), 51%; m.p. 62 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 0.21 [s, 9 H, Si(CH$_3$)$_3$], 0.27 [s, 9 H, Si(CH$_3$)$_3$], 0.91 (d, $^3J_{H,H}$ = 1.3 Hz, 1 H, PC*H*), 0.94 (t, $^2J_{H,H}$ = 7.4 Hz, 3 H, OC$_3$H$_6$C*H$_3$*), 1.42 (m, $^2J_{H,H}$ = 7.4 Hz, 2 H, OC$_2$H$_4$C*H$_2$*CH$_3$), 1.66 (m, $^2J_{H,H}$ = 6.4 Hz, 2 H, OCH$_2$C*H$_2$*C$_2$H$_4$), 3.66 (m, $^2J_{H,H}$ = 6.5 Hz, 2 H, OC*H$_2$*C$_3$H$_6$), 7.83 (d, $^1J_{P,H}$ = 319.7 Hz, 1 H, P-H) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = –1.8 [d, $^3J_{P,C}$ = 1.9 Hz, Si(CH$_3$)$_3$], 0.0 [d, $^3J_{P,C}$ = 2.6 Hz, Si(CH$_3$)$_3$], 11.5 (s, OC$_3$H$_6$*C*H$_3$), 17.1 (s, OC$_2$H$_4$*C*H$_2$CH$_3$), 21.3 (d, $^3J_{P,C}$ = 13.6 Hz, OCH$_2$CH$_2$*C*$_2$H$_4$), 30.4 (d, $^1J_{P,C}$ = 8.4 Hz, PCH), 67.3 (d, $^2J_{P,C}$ = 4.5 Hz, O*C*H$_2$C$_3$H$_7$), 195.6 (d, $^2J_{P,C}$ = 7.8, $^1J_{W,C}$ = 125.4 Hz, *cis*-CO), 197.3 (d, $^2J_{P,C}$ = 24.6 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 102.5 (s$_{sat}$, $^1J_{W,P}$ = 267.0, $^1J_{P,H}$ = 320.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1921 [s, $\nu$(CO)], 1980 [s, $\nu$(CO)], 2070 [s, $\nu$(CO)], 2264 [w, $\nu$(PH)] cm$^{-1}$. MS: *m/z* (%) = 588.0 (75) [M]$^+$, 560.0 (34) [M – CO]$^+$, 448.0 (41) [M – 5 CO]$^+$, 73.0 (100) [SiMe$_3$]$^+$. C$_{16}$H$_{29}$O$_6$PSi$_2$W (588.40): calcd. C 32.66, H 4.97; found C 32.79, H 5.14.

**Synthesis of 4a:** A solution of **3a** (122 mg, 0.2 mmol) and 12-crown-4 (32 μL, 0.2 mmol) in diethyl ether (2 mL) was added dropwise to a solution of lithium diisopropylamide (LDA; 0.22 mmol), freshly prepared from *n*-butyllithium (1.6 M, 0.14 mL, 0.22 mmol) and diisopropylamine (30 μL, 0.2 mmol) in diethyl ether (2 mL), cooled to –78 °C, and the reaction mixture was stirred for 2 h. The solvent was then evaporated in vacuo and the residue washed with *n*-pentane at low temperature (ca. –50 °C). Yield: 400 mg (0.51 mmol), 50.6%; m.p. 75 °C. $^1$H NMR ([D$_8$]THF): $\delta$ = 0.08 [d, $^2J_{H,H}$ = 1.7 Hz, 9 H, Si(CH$_3$)$_3$], 0.17 [s, 9 H, Si(CH$_3$)$_3$], 2.28 (d, $^2J_{P,H}$ = 1.7 Hz, 1 H, PCH), 3.76 (s, 16 H, 12-crown-4), 7.01 (m, 5 H, Ph) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 1.7 [d, $^3J_{P,C}$ = 4.5 Hz, Si(CH$_3$)$_3$], 4.0 [d, $^3J_{P,C}$ = 1.3 Hz, Si(CH$_3$

$_3$], 25.4 (d, $^1J_{P,C}$ = 75.0 Hz, P$C$H), 68.6 (s, 12-crown-4), 118.1 (d, $^4J_{P,C}$ = 1.9 Hz, $m$-Ph), 119.4 (d, $^3J_{P,C}$ = 15.5 Hz, $o$-Ph), 128.8 (d, $^5J_{P,C}$ = 1.9 Hz, $p$-Ph), 162.2 (d, $^2J_{P,C}$ = 9.1 Hz, $i$-Ph), 206.4 (d, $^2J_{P,C}$ = 5.2 Hz, $cis$-CO), 210.3 (d, $^2J_{P,C}$ = 14.9 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 209.1 (s$_{sat}$, $^1J_{W,P}$ = 76.2 Hz) ppm. MS (ESI+): $m/z$ = 788.0 [M – 2 H]$^+$.

**Synthesis of 4b:** A solution of **3b** (109 mg, 0.2 mmol) and 12-crown-4 (32 μL, 0.2 mmol) in diethyl ether (2 mL) was added dropwise to a solution of lithium diisopropylamide (0.22 mmol), freshly prepared from $n$-butyllithium (1.6 M, 0.14 mL, 0.22 mmol) and diisopropyl-amine (30 μL, 0.2 mmol) in diethyl ether (2 mL), cooled to –78 °C, and the reaction mixture was stirred for 2 h. The resulting orange-red solution was characterized by NMR spectroscopy. $^1$H NMR ([D$_8$]THF): $\delta$ = 0.04 (s, 9 H, SiMe$_3$), 0.11 (d, $^4J_{P,H}$ = 1.5 Hz, 9 H, SiMe$_3$), 2.09 (s, 1 H, P$C$H), 3.13 (d, $^3J_{P,H}$ = 14.9 Hz, 3 H, POC$H_3$), 3.77 (s, 12 H, 12-crown-4) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 1.4 [d, $^3J_{P,C}$ = 12.3 Hz, Si($C$H$_3$)$_3$], 4.0 [s, Si($C$H$_3$)$_3$], 25.8 (d, $^1J_{P,C}$ = 66.6 Hz, P$C$H), 58.0 (d, $^2J_{P,C}$ = 29.1 Hz, PO$C$H$_3$), 69.1 (s, 12-crown-4), 208.1 (d, $^2J_{P,C}$ = 5.7 Hz, $cis$-CO), 212.1 (d, $^2J_{P,C}$ = 14.2 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 209.6 (s$_{sat}$, $^1J_{W,P}$ = 68.7 Hz) ppm.

**Synthesis of 4c:** A solution of **3c** (118 mg, 0.2 mmol) and 12-crown-4 (32 μL, 0.2 mmol) in diethyl ether (2 mL) was added dropwise to a solution of lithium diisopropylamide (0.22 mmol), freshly prepared from $n$-butyllithium (1.6 M, 0.14 mL, 0.22 mmol) and diisopropyl-amine (30 μL, 0.2 mmol) in diethyl ether (2 mL), cooled to –78 °C, and the reaction mixture was stirred for 2 h. Then the volatiles were removed in vacuo (ca. 10$^{-2}$ mbar), and the residue was characterized. $^1$H NMR (300.13 MHz, [D$_8$]THF): $\delta$ = 0.00 [d, $^4J_{P,H}$ = 1.5 Hz, 9 H, Si($C$H$_3$)$_3$], 0.10 [s, 9 H, Si($C$H$_3$)$_3$], 1.86 (br., 1 H, PCH), 3.18 (s, 3 H, POC$_2$H$_4$OC$H_3$), 3.45 (m, 2 H, POC$H_2$CH$_2$OCH$_3$), 3.50 (m, 2 H, POCH$_2$C$H_2$OCH$_3$), 3.69 (s, 16 H, 12-c-4) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, [D$_8$]THF): $\delta$ = –0.1 [d, $^3J_{P,C}$ = 4.5 Hz, Si($C$H$_3$)$_3$], 2.4 [s, Si($C$H$_3$)$_3$], 24.3 (d, $^1J_{P,C}$ = 68.5 Hz, PCH), 57.2 (s, PO$C_2$H$_4$O$C$H$_3$), 67.0 (s, 12-c-4), 68.1 (d, $^2J_{P,C}$ = 23.9 Hz, PO$C$H$_2$CH$_2$OCH$_3$), 72.3 (d, $^3J_{P,C}$ = 9.7 Hz, POCH$_2$$C$H$_2$OCH$_3$), 206.3 (d, $^2J_{P,C}$ = 5.2 Hz, $cis$-CO), 210.2 (d, $^2J_{P,C}$ = 14.2 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, [D$_8$]THF): $\delta$ = 208.8 (s$_{sat}$, $^1J_{W,P}$ = 69.0 Hz) ppm.

**Synthesis of 4d:** A solution of **3d** (127 mg, 0.2 mmol) and 12-crown-4 (32 μL, 0.2 mmol) in diethyl ether (2 mL) was added dropwise to a solution of lithium diisopropylamide (0.22 mmol), freshly prepared from $n$-butyllithium (1.6 M, 0.14 mL, 0.22 mmol) and diisopropyl-amine (30 μL, 0.2 mmol) in diethyl ether (2 mL), cooled to –78 °C, and the reaction mixture was stirred for 2 h. Then the resulting orange-red solution was characterized by NMR spectroscopy (–40 °C). $^1$H NMR ([D$_8$]THF): $\delta$ = –0.08 (s, 9 H, Si$Me_3$), 0.10 (s, 9 H, Si$Me_3$), 0.95 (d, $^2J_{H,H}$ = 6.0 Hz, 12 H, HN$i$Pr$_2$-$H$), 2.08 (d, $^2J_{H,H}$ = 13.0 Hz, 3 H, PO-2,6-$Me_2$C$_6$H$_3$), 2.17 (s, 3 H, PO-2,6-$Me_2$C$_6$H$_3$), 2.32 (br. s, 1 H, PC$H$), 2.85 {oct, $^3J_{H,H}$ = 6.2 Hz, 2 H, NH[C$H$(CH$_3$)$_2$]$_2$}, 3.74 (s, 16 H, 12-c-4-$H$), 6.75 (m, $^3J_{H,H}$ = 7.3 Hz, 2 H, $m$-Ph-$H$), 6.93 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, $p$-Ph-$H$) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 1.3 [d, $^3J_{P,C}$ = 10.3 Hz, Si($C$H$_3$)$_3$], 2.9 [s, Si($C$H$_3$)$_3$], 20.8 (s, 2,6-$Me_2$C$_6$H$_3$), 22.7 (d, $^1J_{P,C}$ = 78.8 Hz, P$C$H), 68.7 (s, 12-c-4), 126.2 (d, $^5J_{P,C}$ = 1.9 Hz, $p$-Ph), 131.1 (d, $^4J_{P,C}$ = 1.9 Hz, $m$-Ph), 131.5 (d, $^3J_{P,C}$ = 3.9 Hz, $o$-Ph), 153.5 (d, $^2J_{P,C}$ = 8.4 Hz, P-O-$C$), 219.7 (d, $^2J_{P,C}$ = 12.9 Hz, $cis$-CO), 223.4 (d, $^2J_{P,C}$ = 21.3 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 215.3 (s$_{sat}$, $^1J_{W,P}$ = 69.9 Hz) ppm.

**Synthesis of 4e:** A solution of **3e** (118 mg, 0.2 mmol) and 12-crown-4 (32 μL, 0.2 mmol) in diethyl ether (2 mL) was slowly added to a solution of lithium diisopropylamide (0.22 mmol), freshly prepared from $n$-butyllithium (1.6 M, 0.14 mL, 0.22 mmol) and diisopropyl-amine (30 μL, 0.2 mmol) in diethyl ether (2 mL), cooled to –78 °C. Then the reaction mixture was stirred for 2 h, and the resulting yellow

solution was characterized by $^{31}$P NMR spectroscopy. $^{31}$P{$^1$H} NMR: $\delta$ = 201.1 (s$_{sat}$, $^1J_{W,P}$ = 68.7 Hz) ppm.

**Synthesis of 5a:** Methyl iodide (12 μL) was added through a syringe to a solution of freshly prepared complex **4a** that had been stirred for 0.5 h. Then the reaction mixture was stirred for another 2 h, the solution filtered, the solvent removed in vacuo (ca. 0.01 mbar), and the raw product purified by column chromatography (SiO$_2$, –20 °C; eluent: petroleum ether) after which yellow crystals were obtained. Yield: 470 mg (0.86 mmol), 43%; m.p. 127–130 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 0.27 [s, 9 H, Si($C$H$_3$)$_3$], 0.29 [s, 9 H, Si($C$H$_3$)$_3$], 1.79 (d, $^2J_{P,H}$ = 10.3 Hz, 1 H, P$C$H), 2.20 (d, $^2J_{P,H}$ = 4.7 Hz, 3 H, PC$H_3$), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, $o$-Ph), 7.16 ($^3J_{H,H}$ = 7.3 Hz, 1 H, $p$-Ph), 7.27 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, $m$-Ph) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 1.9 [d, $^3J_{P,C}$ = 3.2 Hz, Si($C$H$_3$)$_3$], 2.5 [d, $^3J_{P,C}$ = 2.0 Hz, Si($C$H$_3$)$_3$], 26.4 (d, $^1J_{P,C}$ = 18.1 Hz, P$C$H$_3$), 30.0 (d, $^1J_{P,C}$ = 11.1 Hz, P$C$H), 121.7 (d, $^3J_{P,C}$ = 3.6 Hz, Ph-$o$), 124.0 (d, $^5J_{P,C}$ = 1.9 Hz, Ph-$p$), 129.0 (d, $^4J_{P,C}$ = 1.0 Hz, Ph-$m$), 151.9 (d, $^2J_{P,C}$ = 6.6 Hz, PO$C$), 196.2 (d, $^2J_{P,C}$ = 7.5 Hz, $cis$-CO), 198.1 (d, $^2J_{P,C}$ = 25.7 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 142.4 (s$_{sat}$, $^1J_{W,P}$ = 279.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1920 [vs, $\nu$(CO)], 1984 [m, $\nu$(CO)], 2068 [s, $\nu$(CO)], 2961 [w, $\nu$(CH/CH$_3$)], 3440 [br, $\nu$(aromatic-H)] cm$^{-1}$. MS: $m/z$ = 622.0 [M]$^{+\cdot}$. C$_{19}$H$_{27}$O$_6$PSi$_2$W (622.41): calcd. C 36.67, H 4.37; found C 36.58, H 4.64.

**Synthesis of 5b:** Methyl iodide (12 μL) was added through a syringe to a solution of freshly prepared complex **4b** that had been stirred for 0.5 h. Then the reaction mixture was stirred for another 2 h, the solution then filtered, and the solvent removed in vacuo (ca. 0.01 mbar). The raw product was further purified by column chromatography (SiO$_2$, –20 °C, eluent: petroleum ether). Yield: 34 mg (0.06 mmol), 30%; m.p. 125 °C. $^1$H NMR (CDCl$_3$): $\delta$ = 0.24 [s, 9 H, Si($C$H$_3$)$_3$], 0.28 [s, 9 H, Si($C$H$_3$)$_3$], 1.61 (d, $^2J_{P,H}$ = 10.8 Hz, 1 H, PC$H$), 1.94 (d, $^2J_{P,H}$ = 4.9 Hz, 3 H, PC$H_3$), 3.46 (d, $^3J_{P,H}$ = 13.0 Hz, 3 H, POC$H_3$) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = 2.8 [d, $^3J_{P,C}$ = 3.2 Hz, Si($C$H$_3$)$_3$], 3.4 [d, $^3J_{P,C}$ = 1.9 Hz, Si($C$H$_3$)$_3$], 24.2 (d, $^1J_{P,C}$ = 18.7 Hz, P$C$H$_3$), 29.8 (d, $^1J_{P,C}$ = 11.6 Hz, P$C$H), 52.9 (d, $^2J_{P,C}$ = 3.2 Hz, PO$C$H$_3$), 197.7 (d, $^2J_{P,C}$ = 7.1 Hz, $cis$-CO), 199.6 (d, $^2J_{P,C}$ = 23.9 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 130.4 (s$_{sat}$, $^1J_{W,P}$ = 269.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1933 [s, $\nu$(CO)], 2069 [m, $\nu$(CO)], 2963 [m, $\nu$(CH$_3$)] cm$^{-1}$. MS: $m/z$ (%) = 560.1 (22) [M]$^{+\cdot}$, 532.1 (20) [M – CO]$^{+\cdot}$, 504.1 (30) [M – 2 CO]$^{+\cdot}$, 476.0 (28) [M – 3 CO]$^{+\cdot}$, 420.1 (50) [M – 5 CO]$^{+\cdot}$, 374.0 (32) [M – 5 CO – (CH$_3$)$_2$O]$^{+\cdot}$, 223.1 (50) [M – W(CO)$_5$ – CH$_3$]$^{+\cdot}$, 73.0 (100) [SiMe$_3$]$^{+\cdot}$. C$_{14}$H$_{25}$O$_6$PSi$_2$W (560.34): calcd. C 30.01, H 4.50; found C 30.42, H 4.65.

**Synthesis of 5c:** Methyl iodide (12 μL) was added through a syringe to a solution of freshly prepared complex **4c** that had been stirred for 0.5 h. Then the reaction mixture was stirred for another 2 h, the solution filtered, and the solvent then removed in vacuo (ca. 0.01 mbar). The raw product was further purified by column chromatography (SiO$_2$, –20 °C, eluent: petroleum ether). Yield: 43 mg (0.07 mmol), 35%. $^1$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.26 [s, 9 H, Si($C$H$_3$)$_3$], 0.28 [s, 9 H, Si($C$H$_3$)$_3$], 1.61 (d, $^2J_{P,H}$ = 10.2 Hz, 1 H, PC$H$), 1.97 (d, $^2J_{P,H}$ = 4.9 Hz, 3 H, PCH$_3$), 3.32 (s, 3 H, POC$_2$H$_4$O$C$H$_3$), 3.56 (m, 2 H, POCH$_2$C$H_2$OCH$_3$), 3.78 (m, 2 H, POC$H_2$CH$_2$OCH$_3$) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ = 1.8 [d, $^3J_{P,C}$ = 3.1 Hz, Si($C$H$_3$)$_3$], 2.3 [d, $^3J_{P,C}$ = 2.1 Hz, Si($C$H$_3$)$_3$], 23.8 (d, $^1J_{P,C}$ = 18.9 Hz, PCH), 28.9 (d, $^1J_{P,C}$ = 12.4 Hz, PCH$_3$), 57.6 (s, POC$_2$H$_4$O$C$H$_3$), 64.8 (d, $^3J_{P,C}$ = 3.2 Hz, POCH$_2$$C$H$_2$OCH$_3$), 70.7 (d, $^2J_{P,C}$ = 8.1 Hz, PO$C$H$_2$CH$_2$OCH$_3$), 197.2 (d, $^2J_{P,C}$ = 8.0, $^1J_{W,C}$ = 125.5 Hz, $cis$-CO), 199.1 (d, $^2J_{P,C}$ = 23.2 Hz, $trans$-CO) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, CDCl$_3$): $\delta$ = 130.2 (s$_{sat}$, $^1J_{W,P}$ = 269.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2959 [w, $\nu$(CH/CH$_3$)], 2069 [s, $\nu$(CO)], 1921 [vs, $\nu$(CO)] cm$^{-1}$. MS (EI, 70 eV, $^{184}$W): $m/z$ (%) = 604.0 (16) [M]$^{+\cdot}$, 576.0 (16)

[M − CO]$^{+•}$, 548.0 (40) [M − 2 CO]$^{+•}$, 520.0 (65) [M − 3 CO]$^{+•}$, 464.1 (25) [M − 5 CO]$^{+•}$, 73.1 (100) [SiMe$_3$]$^{+•}$. C$_{16}$H$_{29}$O$_7$PSi$_2$W (604.40): calcd. C 31.80, H 4.84; found C 32.51, H 5.05.

**Synthesis of 5d:** Methyl iodide (12 µL) was added through a syringe to a solution of freshly prepared complex **4d** that had been stirred for 0.5 h. Then the reaction mixture was stirred for another 1 h. The solution was then filtered and the solvent removed in vacuo (ca. 0.01 mbar). The raw product was then purified further by column chromatography (SiO$_2$, −20 °C). Yield: 196 mg (0.3 mmol), 15%. $^1$H NMR (CDCl$_3$): $\delta$ = 0.27 (d, $^2J_{H,H}$ = 8.4 Hz, 18 H, Si*Me*$_3$), 1.28 (d, $^2J_{P,H}$ = 10.4 Hz, PC*H*), 2.21 (d, $^2J_{P,H}$ = 6.0 Hz, 3 H, PC*H*$_3$), 2.26 (s, 6 H, 2,6-*Me*$_2$C$_6$H$_3$), 6.80 (d, $^2J_{H,H}$ = 7.5 Hz, 1 H, *p*-Ph), 6.93 (d, $^2J_{H,H}$ = 7.5 Hz, 2 H, *m*-Ph) ppm. $^{13}$C{$^1$H} NMR: $\delta$ = −0.1 (s, SiMe$_3$), 1.9 (d, $^3J_{P,C}$ = 2.5 Hz, SiMe$_3$), 17.1 [s, PO-2,6-(CH$_3$)$_2$-C$_6$H$_3$], 28.6 (d, $^1J_{P,C}$ = 16.8 Hz, PCH$_3$), 30.2 (d, $^1J_{P,C}$ = 25.4 Hz, PCH), 120.3 (s, *p*-Ph), 127.4 (s, *m*-Ph), 128.5 (d, $^3J_{P,C}$ = 2.3 Hz, *o*-Ph), 151.5 (d, $^2J_{P,C}$ = 9.3 Hz, POC), 195.3 (d, $^2J_{P,C}$ = 6.8 Hz, *cis*-CO), 198.1 (d, $^2J_{P,C}$ = 25.0 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR: $\delta$ = 134.0 (s$_{sat}$, $^1J_{W,P}$ = 273.4 Hz) ppm.

**Synthesis of 6:** A solution of phosphane complex **3a** (61 mg, 0.1 mmol) and 12-crown-4 (20 µL, 0.1 mmol) in diethyl ether (0.5 mL) was added dropwise to a solution of freshly prepared lithium diisopropylamide at −78 °C. The reaction solution was stirred for 0.5 h. Evaporation of the solvent in vacuo (ca. 0.01 mbar) led to a yellow compound, which upon dissolving in CDCl$_3$ immediately changed color to dark red. Evaporation of all volatiles, washing of the residue with *n*-pentane at low temperature (ca. −60 °C), and drying gave complex **6** as an orange powder, which crystallized from Et$_2$O at ambient temperature as light-orange crystals. Yield: 58 mg (0.09 mmol), 90%; m.p. 100 °C. $^1$H NMR (300.13 MHz, CDCl$_3$): $\delta$ = 0.30 [s, 9 H, Si(CH$_3$)$_3$], 0.34 [s, 9 H, Si(CH$_3$)$_3$], 1.72 [s, 18 H, NC(CH$_3$)$_3$], 1.98 (d, $^2J_{P,H}$ = 7.0 Hz, 1 H, PCH), 7.27 (m, 5 H, Ph), 7.68 (s, 2 H, NC*H*) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ = 1.7 [d, $^3J_{P,C}$ = 3.6 Hz, Si(CH$_3$)$_3$], 2.0 [d, $^3J_{P,C}$ = 2.4 Hz, Si(CH$_3$)$_3$], 29.3 [s, NC(*C*H$_3$)$_3$], 59.7 [s, N*C*(CH$_3$)$_3$], 118.9 (s, N*C*CN), 121.1 (d, $^3J_{P,C}$ = 5.3 Hz, *o*-Ph), 125.1 (d, $^4J_{P,C}$ = 2.2 Hz, *m*-Ph), 129.1 (d, $^5J_{P,C}$ = 1.0 Hz, *p*-Ph), 151.5 (d, $^2J_{P,C}$ = 7.2 Hz, POC), 195.0 (d, $^2J_{P,C}$ = 7.9, $^1J_{W,C}$ = 126.9 Hz, *cis*-CO), 197.2 (d, $^2J_{P,C}$ = 39.8 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, CDCl$_3$): $\delta$ = 186.7 (s$_{sat}$, $^1J_{W,P}$ = 335.7, $^2J_{P,H}$ = 6.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2970 [w, $\nu$(CH/CH$_3$)], 2078 [m, $\nu$(CO)], 1999 [m, $\nu$(CO)], 1942 [vs, $\nu$(CO)], 1915 [s, $\nu$(CO)] cm$^{-1}$. MS (EI, 70 eV, $^{184}$W): *m/z* (%) = 641.9 (30) [M]$^{+•}$, 544.8 (50) [M − OPh]$^{+•}$, 501.9 (17) [M − 5 CO]$^{+•}$, 283.1 (100) [M − 5 CO − Cl]$^{+•}$, 73.0 (60) [SiMe$_3$]$^{+•}$. C$_{18}$H$_{24}$ClO$_6$PSi$_2$W (642.83): calcd. C 33.63, H 3.76; found C 33.97, H 3.79.

**Synthesis of 8:** A solution of phenylacetylene (0.1 mL, 1.0 mmol) was added to freshly prepared complex **4a** in THF (5 mL) at −78 °C; the color immediately changed to red. After 0.5 h of stirring, phenylacetylene (0.1 mL) was added and the mixture heated at reflux for 2 h, which was accompanied of a color change to dark red. After cooling to ambient temperature, MeOTf was added to quench the reaction. After evaporation of all volatiles in vacuo (ca. 0.01 mbar), the raw product was purified by column chromatography (SiO$_2$, −20 °C, 2 × 11 cm, eluent: petroleum ether/Et$_2$O, 10:1). Complex **8** was obtained from the second fraction as a brownish yellow solid after evaporation. Yield: 449 mg (0.62 mmol), 62%. $^1$H NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta$ = 0.36 [s, 9 H, Si(CH$_3$)$_3$], 0.43 [s, 9 H, Si(CH$_3$)$_3$], 1.23 (s, 1 H, PCH), 1.31 (br., 3 H, Me), 7.22 (m, 5 H, Ph), 7.41 (t, $^3J_{H,H}$ = 3.9 Hz, 5 H, Ph), 7.64 (d, $^2J_{P,H}$ = 4.6 Hz, 1 H, PC*H*=C) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, CD$_2$Cl$_2$): $\delta$ = 2.8 [d, $^3J_{P,C}$ = 3.9 Hz, Si(CH$_3$)$_3$], 3.6 [d, $^3J_{P,C}$ = 1.9 Hz, Si(CH$_3$)$_3$], 22.7 (s,

C=CCH$_3$), 25.8 (d, $^1J_{P,C}$ = 11.0 Hz, PCH), 123.1 (d, $^4J_{P,C}$ = 3.9 Hz, Ph), 125.3 (d, $^5J_{P,C}$ = 1.9 Hz, Ph), 127.3 (d, $^3J_{P,C}$ = 18.8 Hz, Ph), 129.3 (s, Ph), 130.2 (d, $^5J_{P,C}$ = 1.9 Hz, Ph), 135.9 (d, $^3J_{P,C}$ = 16.2 Hz, Ph), 150.9 (d, $^2J_{P,C}$ = 18.7 Hz, *i*-Ph), 154.0 (d, $^2J_{P,C}$ = 5.8 Hz, *i*-Ph), 175.7 (d, $^1J_{P,C}$ = 26.5 Hz, P*C*=C), 205.2 (d, $^2J_{P,C}$ = 5.2 Hz, *cis*-CO), 208.8 (d, $^2J_{P,C}$ = 30.1 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta$ = 154.1 (s$_{sat}$, $^1J_{W,P}$ = 269.6 Hz) ppm. $^{29}$Si{$^1$H} NMR (59.6 MHz, CD$_2$Cl$_2$): $\delta$ = 0.1 [d, $^2J_{P,Si}$ = 10.1 Hz, PCHSi(CH$_3$)$_3$], 0.3 [d, $^2J_{(P,Si)}$ = 3.4 Hz, PCHSi(CH$_3$)$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 2960 [s, $\nu$(CH/CH$_3$)], 2070 [s, $\nu$(CO)], 2019 [vs, $\nu$(CO)], 1932 [vs, $\nu$(CO)], 1592 [w, $\nu$(*trans* C=C)] cm$^{-1}$. MS (EI, 70 eV, $^{184}$W): *m/z* (%) = 724.1 (10) [M]$^{+•}$, 696.1 (19) [M − CO]$^{+•}$, 640.1 (50) [M − 3 CO]$^{+•}$, 612.1 (23) [M − 4 CO]$^{+•}$, 597.1 (24) [M − 4 CO − Me]$^{+•}$, 367.1 (39) [M − W(CO)$_5$ − P]$^{+•}$, 73.0 (100) [SiMe$_3$]$^{+•}$.

**Synthesis of 9:** MeLi (0.25 mL, 1.6 M in hexane, 0.4 mmol) was added dropwise to a solution of *P*-methoxyphosphane complex **3b** (221 mg, 0.4 mmol) and 12-crown-4 (67 µL, 0.42 mmol) in thf (3 mL), cooled to −78 °C. After stirring of the reaction mixture for 0.5 h, a solution of benzaldehyde (40 µL, 0.4 mmol) in THF (3 mL) was added (by syringe) to freshly prepared complex **4b** at −78 °C without any color change. After stirring for another 0.5 h, MeOTf (44 µL, or 24 µL of MeI) was added to quench the reaction. All the volatiles were then removed in vacuo (ca. 0.01 mbar), and the raw product was purified by column chromatography (SiO$_2$, −20 °C, 2 × 5 cm, eluent: petroleum ether). The second fraction contained products **9** and another byproduct in a 3:1 ratio. Column-chromatographic separation was performed on the second fraction, but the ratio did not change. $^{31}$P NMR (121.5 MHz, THF): $\delta$ = 161.8 (s$_{sat}$, $^1J_{W,P}$ = 275.9, $^3J_{P,H}$ = 15.3 Hz) ppm. MS (EI, 70 eV, $^{184}$W): *m/z* (%) = 666.1 (10) [M]$^{+•}$, 582.1 (39) [M − 3 CO]$^{+•}$, 526.1 (21) [M − 5 CO]$^{+•}$, 179.0 (100) [M − W(CO)$_5$ − CH(SiMe$_3$)$_2$]$^{+•}$, 73.0 (48) [SiMe$_3$]$^{+•}$.

**Synthesis of 13:** A solution of phosphane complex **3a** (61 mg, 0.1 mmol) and 12-crown-4 (20 µL, 0.1 mmol) in diethyl ether (0.5 mL) was added dropwise to a solution of freshly prepared lithium diisopropylamide at −78 °C, and the mixture was stirred for 0.5 h. Tetra-*n*-butylammonium fluoride (0.5 mL, 1 M in thf) was then added. The solution changed color immediately from orange to pale yellow. After stirring for another 1 h, the solvent was removed in vacuo (ca. 0.01 mbar), and the residue was washed with *n*-pentane at low temperature (ca. −50 °C). Yield: 43 mg (0.068 mmol), 68%. $^1$H NMR (300.13 MHz, [D$_8$]THF): $\delta$ = 0.92 (t, $^2J_{H,H}$ = 7.4 Hz, 24 H, C*H*$_3$(CH$_2$)$_3$N), 1.33 [m, $^2J_{H,H}$ = 7.4 Hz, 16 H, CH$_3$C*H*$_2$(CH$_2$)$_2$N$^+$], 1.57 (m, $^2J_{H,H}$ = 7.4 Hz, 16 H, C$_2$H$_5$C*H*$_2$CH$_2$N$^+$), 1.73 (dd, $^2J_{P,H}$ = 5.3 Hz, 3 H, PC*H*$_3$), 3.31 (m, $^2J_{H,H}$ = 7.2 Hz, 16 H, C$_3$H$_5$C*H*$_2$N$^+$), 6.33 (t, $^2J_{H,H}$ = 7.4 Hz, 1 H, Ph), 6.67 (d, $^2J_{H,H}$ = 7.4 Hz, 2 H, *m*-Ph), 6.87 (d, $^2J_{H,H}$ = 7.6 Hz, 2 H, Ph), 8.11 (qd, $^1J_{P,H}$ = 300.6, $^2J_{P,H}$ = 5.3 Hz, PH) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, [D$_8$]THF): $\delta$ = 14.2 (s, NC$_3$H$_7$*C*H$_3$), 20.8 (s, NC$_2$H$_5$*C*H$_2$CH$_3$), 24.9 (s, NCH$_2$*C*H$_2$C$_2$H$_5$), 28.1 (d, $^1J_{P,C}$ = 22.6 Hz, PCH$_3$), 59.4 (s, N*C*H$_2$C$_3$H$_7$), 200.0 (d, $^2J_{P,C}$ = 9.7 Hz, *cis*-CO), 204.0 (d, $^2J_{P,C}$ = 10.5 Hz, *trans*-CO) ppm. $^{31}$P{$^1$H} NMR (121.5 MHz, [D$_8$]THF): $\delta$ = 33.2 (s$_{sat}$, $^1J_{W,P}$ = 227.6, $^1J_{P,H}$ = 300.1 Hz) ppm.

**X-ray Crystallographic Analysis of 3a,d,e, 5a, and 6:** Data were collected with a Nonius–KappaCCD diffractometer at 123 K by using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The structures were refined by full-matrix least squares on $F^2$ (SHELXL-97[27]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions by using a riding model. CCDC-867925 (for **3a**), -867926 (for **3d**), -867927 (for **3e**), -867928 (for **5a**), and -867929 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge

from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal Data for Complex 3a:** Yellow single crystals of **3a** were grown from *n*-pentane solution at –30 °C. $C_{18}H_{25}O_6PSi_2W$, crystal size $0.24 \times 0.23 \times 0.08$ mm, triclinic, $P\bar{1}$, $a = 12.8195(2)$, $b = 13.38630(10)$, $c = 14.26660(10)$ Å, $\alpha = 103.8230(2)$, $\beta = 92.7380(10)$, $\gamma = 90.3910(10)°$, $V = 2374.19(4)$ Å$^3$, $Z = 4$, $2\theta_{max} = 55°$, collected (independent) reflections 78053 (10860), $R_{int} = 0.0464$, $\mu = 5.062$ mm$^{-1}$, 525 refined parameters, 0 restraints, $R1$ [for $I > 2\sigma(I)$] = 0.0226, $wR2$ (for all data) = 0.0535, max./min. residue electron density = 2.549/–1.650 $e$ Å$^{-3}$.

**Crystal Data for Complex 3d:** Pale-yellow single crystals of **3d** were grown from *n*-pentane solution at –30 °C. $C_{20}H_{29}O_6PSi_2W$, crystal size $0.60 \times 0.59 \times 0.40$ mm, triclinic, $P\bar{1}$, $a = 9.4714(2)$, $b = 9.9051(3)$, $c = 15.0145(3)$ Å, $\alpha = 96.4330(10)$, $\beta = 103.0160(10)$, $\gamma = 111.9870(10)°$, $V = 1242.16(5)$ Å$^3$, $Z = 2$, $2\theta_{max} = 56°$, collected (independent) reflections 16042 (5921), $R_{int} = 0.0513$, $\mu = 4.842$ mm$^{-1}$, 284 refined parameters, 0 restraints, $R1$ [for $I > 2\sigma(I)$] = 0.0245, $wR2$ (for all data) = 0.0640, max./min. residue electron density = 2.244/–1.767 $e$ Å$^{-3}$.

**Crystal Data for Complex 3e:** Yellow single crystals of **3e** were grown from *n*-pentane solution at –30 °C. $C_{16}H_{29}O_6PSi_2W$, crystal size $0.33 \times 0.24 \times 0.22$ mm, orthorhombic, $P2_12_12_1$, $a = 11.1201(3)$, $b = 11.9397(3)$, $c = 17.9401(4)$ Å, $V = 2381.92(10)$ Å$^3$, $Z = 4$, $2\theta_{max} = 55°$, collected (independent) reflections 17207 (5328), $R_{int} = 0.0359$, $\mu = 5.043$ mm$^{-1}$, 351 refined parameters, 0 restraints, $R1$ [for $I > 2\sigma(I)$] = 0.0214, $wR2$ (for all data) = 0.0385, max./min. residue electron density = 1.217/–0.962 $e$ Å$^{-3}$.

**Crystal Data for Complex 5a:** Yellow single crystals of **5a** were grown from concentrated diethyl ether solution at –30 °C. $C_{19}H_{27}O_6PSi_2W$, crystal size $0.60 \times 0.40 \times 0.12$ mm, monoclinic, $P2_1$, $a = 9.7329(6)$, $b = 12.5170(7)$, $c = 11.2360(7)$ Å, $\beta = 115.163(2)°$, $V = 1238.94(13)$ Å$^3$, $Z = 2$, $2\theta_{max} = 56°$, collected (independent) reflections 11600 (5293), $R_{int} = 0.0337$, $\mu = 4.853$ mm$^{-1}$, 270 refined parameters, 1 restraint, $R1$ [for $I > 2\sigma(I)$] = 0.0162, $wR2$ (for all data) = 0.0414, max./min. residue electron density = 0.965/–1.511 $e$ Å$^{-3}$.

**Crystal Data for Complex 6:** Colorless single crystals of **6** were grown from concentrated diethyl ether solution at room temperature. $C_{18}H_{24}ClO_6PSi_2W$, crystal size $0.56 \times 0.40 \times 0.32$ mm, monoclinic, $P2_1/c$, $a = 14.9583(2)$, $b = 14.2798(4)$, $c = 11.6683(3)$ Å, $\beta = 97.233(2)°$, $V = 2472.53(10)$ Å$^3$, $Z = 4$, $2\theta_{max} = 56°$, collected (independent) reflections 34586 (5961), $R_{int} = 0.0587$, $\mu = 4.971$ mm$^{-1}$, 269 refined parameters, 1 restraint, $R1$ [for $I > 2\sigma(I)$] = 0.0221, $wR2$ (for all data) = 0.0486, max./min. residue electron density = 1.593/–0.995 $e$ Å$^{-3}$.

## Acknowledgments

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