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Synthesis and Reactions of the First Room Temperature Stable Li/Cl Phosphinidenoid Complex

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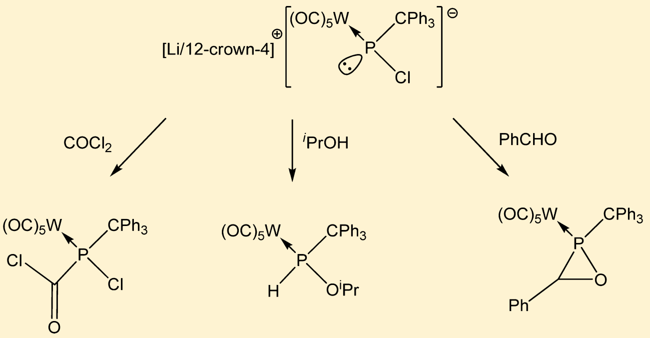
Supporting Information

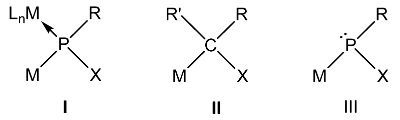


ABSTRACT: *P*-Trityl substituted Li/Cl phosphinidenoid tungsten(0) complex $(OC)_5W\{Ph_3CP(Li/12\text{-crown-}4)Cl\}$ (**3**) was prepared via chlorine/lithium exchange in complex $(OC)_5W\{Ph_3CPCl_2\}$ (**2**) using ^{t}BuLi in the presence of 12-crown-4 in tetrahydrofuran (THF) at low temperature; complex **3** possesses significantly increased thermal stability in contrast to previously reported analogue derivatives. Terminal phosphinidene-like reactivity of **3** was used in reactions with benzaldehyde and isopropyl alcohol as oxaphosphirane complex $(OC)_5W\{Ph_3CPC(Ph)O\}$ (**5**) and phosphinite complex $(OC)_5W\{Ph_3CP(H)O^iPr\}$ (**6**) were obtained selectively. Reaction of **3** with phosgene allowed to obtain the first kinetically stabilized chloroformylphosphane complex $(OC)_5W\{Ph_3CP(Cl)C(O)Cl\}$ (**4**). Density functional theory (DFT) calculations revealed remarkable differences in the degree of P−Li bond dissociation **3a**−**d**: using a continuum model **3** displays a covalent character of P−Li bond (COSMO (THF)) (**a**), which becomes elongated if 12-crown-4 is coordinated to lithium (**b**) and is cleaved if a dimethylether unit is additionally coordinated to lithium (**c**). A similar result was obtained for the case of $3(thf)_4$ in which also a solvent-separated ion pair structure is present (**d**). All products were unambiguously characterized by various spectroscopic means and, in the case of **2** and **4**−**6**, by single-crystal X-ray diffraction analysis. In all structures very long P−C bonds were determined being in the range from 1.896 to 1.955 Å.

■ INTRODUCTION

Phosphinidenoid complexes **I** represent a new unique class of transition-metal coordination compounds possessing unusual (formal) anionic *P*-ligands with dicoordinate phosphorus atoms having a bulky organic substituent and an electron-withdrawing group such as a halogen,[1] cyano,[2] alkoxide,[3] or amide.[4] During the past years a close relationship to the chemistry of carbenoids **II**[5] (Scheme 1) emerged as complexes **I** display terminal phosphinidene complex-like and nucleophilic reactivity.[6] In contrast to **I**, unligated phosphinidenoids **III** are still unknown, although some evidence for their transient formation has been reported.[7] So far, only two thermally labile Li/Cl phosphinidenoid tungsten(0) complex derivatives have been reported (R = $CH(SiMe_3)_2$[1a]and Cp*[1b]) that decompose around −45 to −30 °C, and which enabled access to various classes of compounds under very mild conditions.[6] Formal exchange of the substituent X at phosphorus, for example, halogen vs alkoxide,[3] led to a significant change in reactivity and stability, that is, a phosphanido complex reactivity came to the fore. Somehow similar is that exchange of lithium for bulky, "non-coordinating organic cations" in complexes **I** (X = F, Cl, OMe, OPh)[8] significantly increased their thermal stability, but the terminal phosphinidene complex-like reactivity[9] of the phosphinidenoid complexes was no longer observed. Therefore, the challenge to synthesize room temperature-stable derivatives **I** while keeping this specific and synthetically important reactivity remained.

Scheme 1. Phosphinidenoid Complexes I, Carbenoids II, and Phosphinidenoids III[a]



[a]ML_n = transition-metal complex; R, R′ = organic moieties, X = electronegative atom or group.

Kinetic stabilization of reactive molecular species through sterically demanding substituents bound to the reactive site (or a neighboring atom) is a well-documented strategy in reactive intermediate chemistry,[10] in general, and in organophosphorus chemistry in particular.[11] The bulkiness of the triphenylmethyl group ("trityl") combined with its intrinsic abilities to stabilize a negative and/or positive charge, or even a radical center makes

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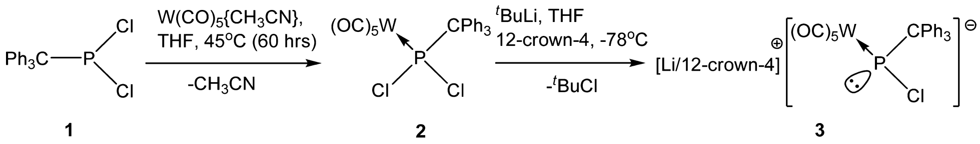
Scheme 2. Synthesis of Li/Cl Phosphinidenoid Complex 3 from Complex 2



the trityl group unique and has attracted interest from various angles since the early and fundamental work of Gomberg.[12] Schmutzler was first to demonstrate that the trityl group can be used in molecular phosphorus chemistry to great advantage[13] and to access a wide variety of very reactive and/or unstable compounds, for example, acyclic diphospha-urea derivatives,[14] 1,3-diphosphetane-2,4-dione, and acyl(chloro)-organophosphanes,[15] and more.[16] Grützmacher recognized the synthetic potential for low-coordinate phosphorus compounds and reported on the synthesis and reactivity of *C*-tritylphosphaalkyne.[17] It was again Schmutzler who found that trityl can serve as a leaving group,[18] but in this case only preliminary work was done; recent computational studies stressed the reactivity-determining key role of *P*-trityl groups in three-membered phosphorus heterocycles.[19] To date, only few coordination compounds of *P*-trityl substituted phosphane complexes have been reported.[20] Recently, we came into this field through the discovery that coupling between a trityl and sterically demanding *P*-functional phosphanyl complexes can occur to form a P−C bond either in the trityl periphery[21a] or, after a series of rearrangements, at the tertiary carbon of the trityl moiety, if the *para*-position was blocked by a methyl group.[21b]

Herein, we report the synthesis and reactions of the *P*-trityl substituted Li/Cl phosphinidenoid tungsten(0) complex, the first derivative to be stable in tetrahydrofuran (THF) solution at ambient temperature, while retaining the combined nucleophilic and terminal phosphinidene complex-like reactivity.

■ RESULTS AND DISCUSSION

The first hurdle to obtain the coordination compound as starting material could be overcome, and complex **2** was prepared via selective reaction of dichloro(triphenylmethyl)-phosphane **1**[13] with acetonitrile (pentacarbonyl)tungsten(0)[22] (Scheme 2). It should be noted that under these conditions only approximately 75% conversion of the starting phosphane **1** was achieved which could not be increased further by heating or addition of slight excess of the acetonitrile tungsten complex.[23] Complex **2** was obtained in 65% yield after column chromatography.

The composition of complex **2** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 1); for further information on crystallographic parameters of **2** as well as **4**−**6** see the Supporting Information. The molecular structure of **2** possesses a very long P−C bond of 1.955(2) Å (the sum of covalent radii of P and C atoms is 1.83 Å), which is significantly longer compared with that of the unligated phosphane **1** (1.9333(14) Å).[13,24]

Chlorine/lithium exchange in dichlorophosphane complex **2** was achieved with ^{t}BuLi in the presence of 12-crown-4 in THF at low temperature (−78 °C), which led to the quantitative formation of the corresponding Li/Cl phosphinidenoid complex **3** (Scheme 2). Formation of complex **3** is fast at −78 °C (completion in less than 20 min) and is accompanied by an immediate color change of the reaction mixture from colorless to dark-yellow. In the ^{31}P{^{1}H} NMR spectrum (THF-*d8*) complex **3** displays a signal at 252.1 ppm with a phosphorus−tungsten coupling constant of 77.6 Hz (cf. **2**: δ_P = 166.2 ppm, $^1J_{P,W}$ = 319.7 Hz); this signal displayed a shoulder on the high-field side (ratio of ca. 3:1) that corresponds to the ^{37}Cl isotopomer of **3**. Meanwhile, such ^{31}P NMR data are characteristic features for the class of phosphinidenoid complexes. The ^{7}Li NMR spectrum of **3** contains a sharp signal at −0.32 ppm, and no phosphorus−lithium coupling was observed between +25 and −60 °C. On the basis of DOSY NMR experiments on a related Li/F phosphinidenoid complex [(OC)$_5$W{(Me$_3$Si)$_2$CHP(Li/12-crown-4)F}],[25] it is established that the constitution of the species is that of solvent separated ion pairs and, therefore, the same is assumed for the present case of **3**. Remarkably, phosphinidenoid complex **3** is stable for many hours at 25 °C in THF solution (half-lifetime is about 12 h) and, notably, less than 30% of **3** decomposed after 2 h at 45 °C. In contrast to previously reported Li/Cl phosphinidenoid complexes, derivative **3** could be isolated as a yellow, highly moisture sensitive solid. Despite much effort, no single-crystals of **3** suitable for X-ray diffraction analysis were obtained, unfortunately.

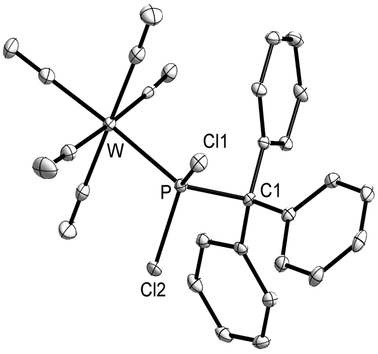


Figure 1. Molecular structure of complex **2** in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.4685(6), P−C(1) 1.955(2), P−Cl(1) 2.043(8), P−Cl(2) 2.063(8); C(1)−P−W 129.16(7), Cl(1)−P−Cl(2) 99.89(3), Cl(1)−P−C(1) 102.46(7), Cl(2)−P−C(1)101.80(7).

Surprisingly, the thermal decomposition of complex **3** in THF at 25 °C, monitored by ^{31}P NMR spectroscopy, led to a complicated, inseparable mixture of products, from which only the signal at −41.2 ppm (t$_{Sat}$, $^1J_{P,H}$= 329.3 Hz, $^1J_{P,W}$ = 225.1 Hz) could be assigned to the primary phosphane complex [(OC)$_5$W(Ph$_3$CPH$_2$)]. Surprisingly, no evidence for the formation of mono- or dinuclear *P*-trityl diphosphene complexes or the terminal phosphinidene complex was obtained, as it was expected in analogy to the case of *P*-*bis*(trimethylsilyl)methyl substituted Li/X phosphinidenoid complexes.[1a,c]

Because of the extraordinary thermal stability of **3**, it was tempting to probe if a phosphinidenoid complex could be

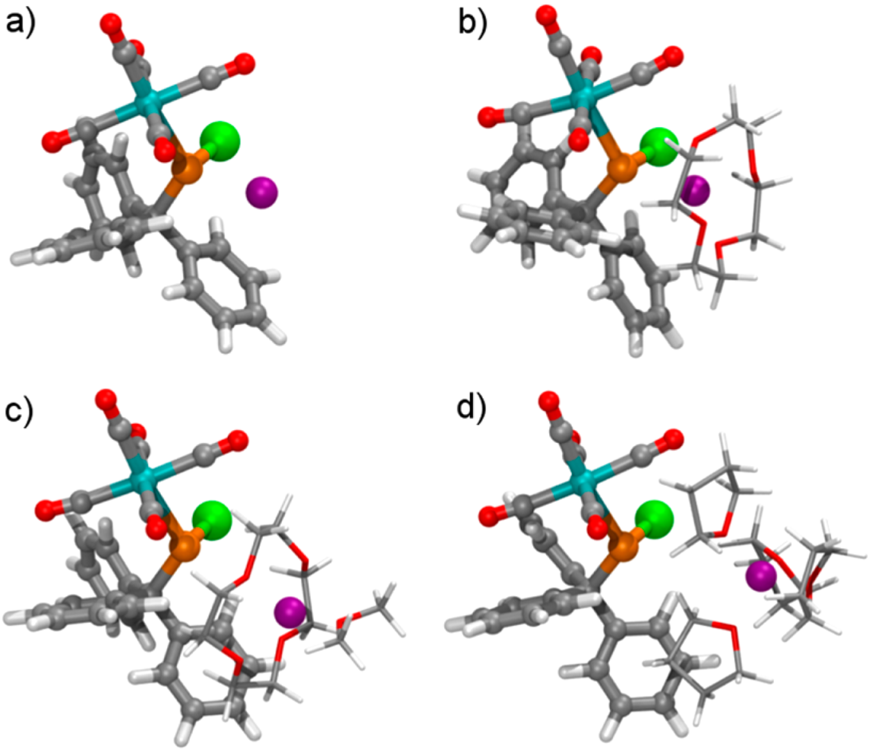


Figure 2. Calculated (COSMO$_{THF}$/B3LYP-D/def2-TZVP ecp) minimum energy structures for (a) complex **3** and its solvates with (b) 12-c-4, (c) 12-c-4 and Me_2O, and (d) four THF molecules. W, ice blue; P, orange; Cl, green; Li, purple.[26]

obtained without 12-crown-4, especially as it was not achieved before in the case of other Li/Cl phosphinidenoid derivatives (R = C_5Me_5 or $CH(SiMe_3)_2$). Therefore, complex **2** was treated with ^{t}BuLi *in the absence of 12-crown-4* in THF at low temperature (−78 °C) which yielded a product that displayed nearly the same ^{31}P NMR data as complex **3**, that is, 253.5 ppm ($^1J_{P,W}$ = 76.3 Hz), being also stable in solution and thus revealing that the presence of 12-crown-4 is not a *conditio sine qua non* for Li/Cl phosphinidenoid complexes.

To unravel the unprecedent dispensability of 12-crown-4 (12-c-4 for short) and to get further structural insight into the molecular structure of **3** in solution a quantum chemical calculation at the DFT (COSMO$_{THF}$/B3LYP-D/def2-TZVP, ECP for W) level was performed. Therefore, four differently solvated species were considered: the nonexplicitly solvated entity (without 12-crown-4 or any coordinating solvent molecule) (**a**), two derivatives including a 12-c-4 moiety without (**b**) and with a dimethyl ether unit (**c**) (the latter as a model for THF) and, last, one containing four explicit molecules of THF (**d**) (Figure 2).

Inspection of the resulting geometries revealed remarkable differences of the degree of P−Li bond dissociation. Structure **a** of **3** (without 12-c-4) shows a mainly covalent, short P−Li bond (Table 1), even if computed using a continuum model (COSMO$_{THF}$).[27] This results in a relatively low ionic character of the bond, as shown by the low negative electric charge at the $PW(CO)_5$ moiety. If a 12-c-4 unit is bound to Li (**b**) the P−Li bond is not significantly elongated unless a THF molecule (Me_2O as model) is coordinated (**c**). This in turn leads to P−Li bond elongation and the emergence of notable negative charge at phosphorus and the formation of a coordinated lithium cation! A very similar behavior is observed when four molecules of THF coordinate the lithium cation (**d**) which also produces a solvent-separated ion pair structure with a remarkably long P−Li bond distance and, therefore, significant ionic character; this supports the experimentally observed similarity of the NMR data for **3** in the absence or presence of 12-c-4.

Table 1. Selected Calculated Parameters Related to the Extent of P−Li Bond Dissociation in Solvates of 3

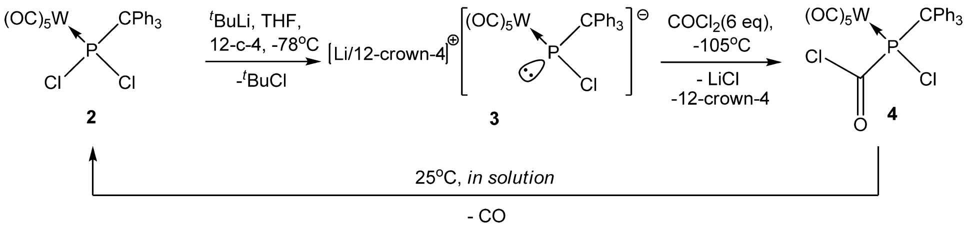
	$d_{P\cdots Li}$ [Å]	$q_{P/P[W]}$ [au][a]
3	2.462	0.33/−0.27
3·*(12-c-4)*	2.765	0.33/−0.31
3·*(12-c-4)(OMe$_2$)*	4.701	0.34/ −0.45
3·*(THF)$_4$*	5.260	0.27/−0.45

[a] Löwdin atomic charge at P and at the $PW(CO)_5$ moiety.

To investigate the reactivity of Li/Cl phosphinidenoid complex **3** a set of prototypical aspects were chosen. To obtain a chloroformylphosphane complex possessing increased thermal stability,[28] in situ prepared **3** was reacted with an excess of phosgene (30% solution in toluene) at −105 °C which was accompanied by immediate formation of a precipitate and led selectively to the (chloroformyl)tritylphosphane complex **4** (Scheme 3).

In contrast to known *P*-functional acyl(organo)phosphane complexes,[6f] chloroformyl derivative **4** *slowly* decomposed in solution at ambient temperature to give the dichlorophosphane complex **2** via extrusion of CO;[29] at 25 °C the half-lifetime of **4** is about 5 days (benzene).[30] Nevertheless, it was possible to isolate complex **4** in pure form at low temperature (−20 °C) in quite good yields (ca. 75%).[31] Complex **4** was obtained as a light-yellow solid, being stable under argon atmosphere at −20 °C. In the ^{31}P NMR spectrum the signal of complex **4** appeared at 148.6 ppm ($^1J_{P,W}$ = 278.5 Hz). The signal of the carbonyl carbon atom of the chloroformyl substituent was observed as a doublet ($^1J_{C,P}$ = 13.6 Hz) at 176.9 ppm. In the IR spectrum the absorption band of the carbonyl group of the chloroformyl

Scheme 3. Reaction Li/Cl Phosphinidenoid Complex 3 with Phosgene to Give 4



moiety appeared at 1747 cm^{-1} which is well distinguished from those of the W(CO)$_5$ unit (1942, 1959, 2078 cm^{-1}).

The molecular structure of the chloroformylphosphane complex **4** was confirmed by single-crystal X-ray diffraction studies, thus representing the first-ever structurally characterized molecular compound possessing a ClC(O)P unit (Figure 3). The two P−C bonds of complex **4** were found to be elongated: P−C(2) 1.945(5) and P−C(1) 1.899(5) Å. The elongation of P−C(1) in this case is expected, following the general tendency of P−C bond elongation in acylphosphane complexes.[cf.6f]

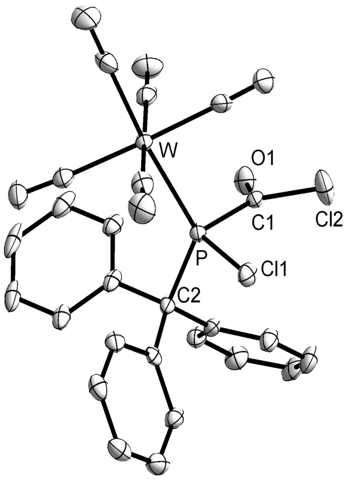
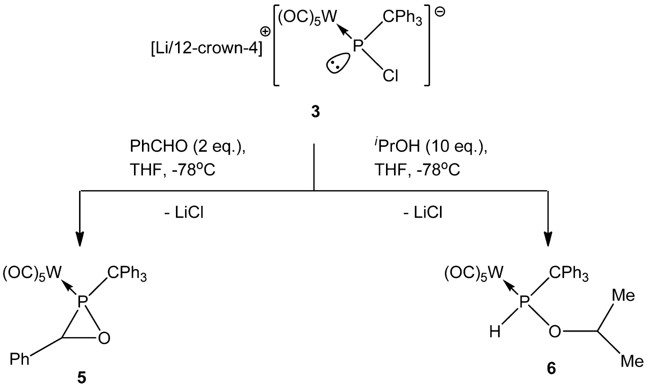


Figure 3. Molecular structure of complex **4** in the crystal (50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.472(2), P−C(1) 1.899(5), P−C(2) 1.945(5), P−Cl(1) 2.032(18), C(1)−Cl2 1.783(5), C(1)−P−Cl(1) 101.19 (17), C(2)−P−Cl(1) 103.36(17), C(1)−P−C(2) 103.0(2), Cl(2)−C(1)−P 116.0(3).

To examine the reactivity further, the reaction of Li/Cl phosphinidenoid complex **3** with benzaldehyde or isopropyl alcohol was chosen (Scheme 4). Addition of 2 equiv of benzaldehyde to a solution of freshly prepared **3** (−78 °C) led to immediate precipitate formation and color change of the reaction mixture to light-yellow. The selective formation of the diastereomerically pure oxaphosphirane complex **5** was confirmed by ^{31}P NMR spectroscopy, and complex **5** was isolated in pure form as a stable white solid.

The ^{31}P NMR spectrum (C$_6$D$_6$) of **5** showed a signal at 16.0 ppm ($^1J_{P,W}$ = 311.5 Hz) which is significantly high-field shifted compared to those of analogous *P-bis*(trimethylsilyl)methyl and *P*-Cp* oxaphosphirane tungsten(0) complexes (40.4 ppm ($^1J_{P,W}$ = 308.2 Hz) in CDCl$_3$,[32] and 31.6 ppm ($^1J_{P,W}$ = 309.0 Hz)[33] in C$_6$D$_6$). In the ^{13}C NMR spectrum the signal of the oxaphosphirane ring carbon atom appeared at 60.4 ppm ($^1J_{C,P}$ = 23.6 Hz), which is close to the values reported before for similar derivatives.[32,33] The constitution of the product was unambiguously confirmed by X-ray diffraction studies (Figure 4).

Scheme 4. Reactions of Li/Cl Phosphinidenoid Complex 3 with Benzaldehyde and Isopropanol



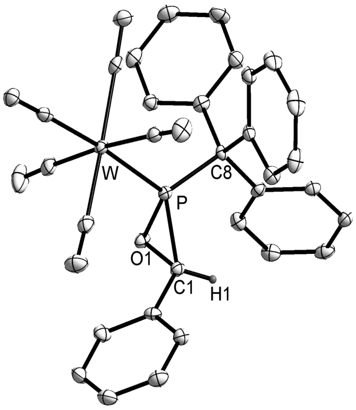


Figure 4. Molecular structure of oxaphosphirane complex **5** in the crystal (50% probability level, hydrogen atoms except H(1) are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.482(6), P−O(1) 1.669(16), O(1)−C(1) 1.468(3), C(1)−P 1.788(2), P−C(8) 1.896(2), O(1)−P−C(1) 50.12(9), C(1)−O(1)−P69.14(11), O(1)−C(1)−P 60.74(10).

The P−C(8) bond in *P*-trityl oxaphosphirane complex **5** (1.896(2) Å) keeps some elongation but is significantly shorter than in the *P*-trityl dichlorophosphane complex **2** although still longer than P−C bonds in related *P-bis*(trimethylsilyl)methyl and *P*-Cp* oxaphosphirane derivatives (1.794(6) and 1.855(3)).

Under similar conditions, Li/Cl phosphinidenoid complex **3** was then reacted with a 10-fold excess of isopropanol which led selectively to the isopropylphosphinite complex **6** (Scheme 4). The product was obtained in good yield (84%) as a white solid after column chromatography. The ^{31}P NMR signal of complex

3 was observed at 115.2 ppm ($^{1}J_{\mathrm{P,W}}$ = 278.5 Hz; $^{1}J_{\mathrm{P,H}}$ = 329.3 and $^{3}J_{\mathrm{P,H}}$ = 8.9 Hz). The single crystal X-ray crystallography study of **6** revealed also a long P−C bond of 1.913(1) Å (Figure 5), which is significantly elongated by comparison to complex **5** despite the fact that in this case a less electronegative and less bulky atom as hydrogen (not carbon) is bound to phosphorus.

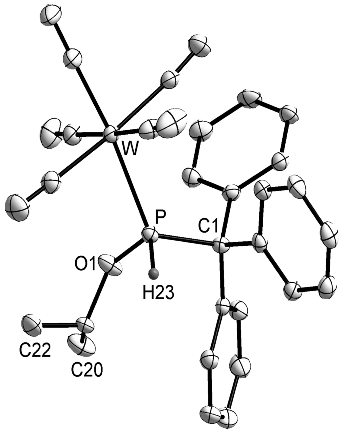


Figure 5. Molecular structure of isopropylphosphinite complex **6** in the crystal (50% probability level, hydrogen atoms except H(23) are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.524(7), P−C(1) 1.913(3), P−O(1) 1.608(2), O(1)−P−H(23) 104.2(11), O(1)−P−C(1) 104.77(11), C(1)−P−H(23) 98.1(11).

As complex **6** formally represents an insertion product of the terminal phosphinidene complex $[(CO)_5W(PCPh_3)]$ into the O−H bond of isopropanol, a ^{31}P NMR reaction monitoring was performed. Unfortunately, this only revealed a slow reaction of the alcohol with complex **3** at low temperature which became significantly faster above −10 °C. Notably, no evidence for any *P*-containing intermediate was obtained in this reaction of Li/Cl phosphinidenoid complex **3**. Therefore, one may conclude that reaction did not occur via the *P*-protonated intermediate, that is, complex **3** was directly converted into the final product, the isopropylphosphinite complex **6**, via an unknown pathway.

■ CONCLUSIONS

P-Trityl substituted complex **3** is the first-ever example of a Li/Cl phosphinidenoid tungsten(0) complex stable for hours in solution at ambient temperature. It also deserves mention that *P*-chloro phosphinidenoid derivatives may exist without 12-crown-4 if strongly coordinating solvent molecules such as THF can parallel the cation-interaction of the 12-crown-4 unit. In general and as shown by DFT calculations, a solvent-separated ion-pair structure of a *P*-chloro phosphanido-like complex having an enhanced *P*-anionic character is produced in solution. Perhaps the most notable aspect of this study is that the enhanced stability of **3** did not necessarily alter the reactivity as reactions with benzaldehyde or phosgene demonstrated, yielding complexes **4** and **5**, respectively. As complex **3** reacted with isopropanol to provide complex **6** via an unknown pathway, the (undetected) terminal phosphinidene complex $[(CO)_5W(PCPh_3)]$ might be involved. Noteworthy is that all molecular X-ray structures of *P*-trityl substituted complexes (**2**, **4**−**6**) display very long P−C bond distances in the range from 1.896 to 1.955 Å. This may hint to a masked functionality of the trityl group, for example, a tendency for P−C bond cleavage processes. Of particular interest is that a pure crystalline product of a chloroformylphosphane derivative was obtained in good yields (complex **4**), a class of compounds otherwise known to be highly unstable. Therefore, this *P*-Cl, *C*-Cl bifunctional building block may serve as new starting point and thus open new perspectives in synthetic organophosphorus chemistry.

■ EXPERIMENTAL PART

General Procedures. All manipulations involving air- and moisture sensitive compounds were carried out under an atmosphere of purified argon by using standard Schlenk-line techniques or in a glovebox. Solvents were dried with appropriate drying agents such as sodium-wire/acetophenone and degassed before use. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data were recorded on a Bruker DMX 300 spectrometer. MAS NMR: Varian 400 Infinity+, 4 mm MAS NMR triple-resonance probe (25 °C). Infrared spectra were recorded on a Thermo Nicolet 380 FT-IR spectrometer (selected data given). Mass spectra were recorded on a MAT 90 Finnigan spectrometer (selected data given). Melting points were determined using a Buchi Type S apparatus with samples sealed in capillaries under argon, and are uncorrected. Elemental analyses were performed using an ElementarVarioEL instrument.

Synthesis of $[(OC)_5W\{Ph_3CPCl_2\}]$(2). Dichloro(triphenylmethyl)-phosphane **1**[13] (3.55 g, 10.3 mmol) dissolved in 25 mL of freshly distilled THF was added to a stirred solution of $[W(CO)_5(CH_3CN)]$[22] (3.76 g, 10.3 mmol) in 25 mL of THF. The reaction mixture was heated at 45 °C for about 64 h while stirring. After removing of all volatiles in vacuum, the residue was adsorbed on a small amount of Al_2O_3, and column chromatography was performed (Al_2O_3, −15 °C, eluent: petrol ether/dichloromethane from 10/1 to 10/4). Evaporation of the solvents gave complex **2** as a white crystalline solid.

Yield: 4.5 g (65%); mp 176 °C (dec.). ^{1}H NMR ($CDCl_3$): 7.38−7.49 (15 H, m, CPh_3).^{13}C{^{1}H} NMR ($CDCl_3$): 75.5 (d, $^{1}J_{\mathrm{C,P}}$ = 10.7 Hz, CP), 127.9 (d, $^{5}J_{\mathrm{C,P}}$ = 1.8 Hz, *para*-Ph), 128.5 (d, $^{5}J_{\mathrm{C,P}}$ = 2.1 Hz, *para*-Ph), 128.9 (d,$^{4}J_{\mathrm{C,P}}$ = 1.9 Hz, *meta*-Ph), 128.9 (d, $^{4}J_{\mathrm{C,P}}$ = 3.9 Hz, *meta*-Ph), 130.9 (d, $^{3}J_{\mathrm{C,P}}$ = 3.8 Hz, *ortho*-Ph), 131.1 (d, $^{3}J_{\mathrm{C,P}}$ = 8.7 Hz, *ortho*-Ph), 140.3 (d, $^{2}J_{\mathrm{C,P}}$ = 6.4 Hz, *ipso*-Ph), 140.8 (d, $^{2}J_{\mathrm{C,P}}$ = 10.8 Hz, *ipso*-Ph), 195.9 (d_{Sat}, $^{2}J_{\mathrm{C,P}}$ = 7.1 Hz, $^{1}J_{\mathrm{C,W}}$ = 128.7 Hz, *cis*-CO), 198.9 (d, $^{2}J_{\mathrm{C,P}}$ = 48.0 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): 166.2 (s_{Sat}, $^{1}J_{\mathrm{P,W}}$ = 319.7 Hz). IR (KBr; υ_{max}/cm^{-1}): 1942 (vs, CO), 1955 (vs, CO), 2082 (s, CO). Anal. Calcd. for $C_{24}H_{15}Cl_2O_5PW$: C, 43.08; H, 2.26. Found: C, 43.13; H, 2.53.

Synthesis of $[Li(12\text{-}crown\text{-}4)(THF)_n][(OC)_5W\{Ph_3CPCl\}]$ (3) for the Spectroscopic Characterization. To a stirred solution of phosphane complex **2** (67 mg, 0.1 mmol) and 12-crown-4 (17.5 μL, 0.11 mmol) in 0.8 mL of THF-*d8* was added dropwise solution of ^{t}BuLi in *n*-hexane (1.6 M, 0.07 mL) at −78 °C to give a dark-yellow solution. After 20 min stirring at −78 °C solution was quickly transferred via double-needle to a cooled (−90 °C) NMR tube.

3:[34] ^{1}H NMR ($CDCl_3$, −40 °C): 3.69 (s, 16 H, 12-crown-4), 7.0−7.65 (15 H, m, CPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$, −40 °C): 67.5 (s, 12-crown-4), 68.1(d, $^{1}J_{\mathrm{C,P}}$ = 13.3 Hz, CP), 125.0 (s, *para*-Ph), 125.2 (s, *para*-Ph), 126.1 (d, $^{5}J_{\mathrm{C,P}}$ = 1.5 Hz, *para*-Ph), 126.9 (s, *meta*-Ph), 127.5 (s, *meta*-Ph), 128.4 (s, *meta*-Ph), 129.9 (d, $^{3}J_{\mathrm{C,P}}$ = 18.3 Hz, *ortho*-Ph), 131.9 (s, *ortho*-Ph), 132.2 (d, $^{3}J_{\mathrm{C,P}}$ = 10.1 Hz, *ortho*-Ph), 148.7 (d, $^{2}J_{\mathrm{C,P}}$ = 22.2 Hz, *ipso*-Ph), 149.9 (s, *ipso*-Ph), 150.6 (d, $^{2}J_{\mathrm{C,P}}$ = 9.6 Hz, *ipso*-Ph), 202.4 (d_{Sat}, $^{2}J_{\mathrm{C,P}}$ = 7.8 Hz, $^{1}J_{\mathrm{C,W}}$ = 127.5 Hz, *cis*-CO), 206.8 (d, $^{2}J_{\mathrm{C,P}}$ =15.0 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$, −40 °C): 252.1 (s_{Sat}, $^{1}J_{\mathrm{P,W}}$ = 77.6 Hz) − major, 252.01 (s_{Sat}, $^{1}J_{\mathrm{P,W}}$ = 77.6 Hz) − minor.

Synthesis of 3 (without 12-crown-4):[34] Prepared analogously, without using 12-crown-4. ^{1}H NMR ($CDCl_3$, −40 °C): 7.13−7.73 (15 H, m, CPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$, −40 °C): 68.1 (d,$^{1}J_{\mathrm{C,P}}$ = 12.4 Hz, CP), 124.8 (s, *para*-Ph), 125.1 (s, *para*-Ph), 125.9 (d, $^{5}J_{\mathrm{C,P}}$ = 1.5 Hz, *para*-Ph), 126.8 (s, *meta*-Ph), 127.4 (s, *meta*-Ph), 128.3 (s, *meta*-Ph), 129.9 (d, $^{3}J_{\mathrm{C,P}}$ = 19.2 Hz, *ortho*-Ph), 131.9 (s, *ortho*-Ph), 132.3 (d, $^{3}J_{\mathrm{C,P}}$ = 11.2 Hz, *ortho*-Ph), 149.0 (d, $^{2}J_{\mathrm{C,P}}$ = 21.4 Hz, *ipso*-Ph), 149.6 (s, *ipso*-Ph), 150.8 (d, $^{2}J_{C,P}$ = 10.5 Hz, *ipso*-Ph), 202.4 (d$_{Sat}$, $^{2}J_{C,P}$ = 7.9 Hz, $^{1}J_{C,W}$ = 126.8 Hz, *cis*-CO), 207.0 (d, $^{2}J_{C,P}$ =14.8 Hz, *trans*-CO). ^{31}P{^{1}H} NMR (CDCl$_3$, −40 °C): 253.5 (s$_{Sat}$, $^{1}J_{P,W}$ = 76.3 Hz) − major, 252.4 (s$_{Sat}$, $^{1}J_{P,W}$ = 76.3 Hz) − minor. ^{7}Li NMR (CDCl$_3$, −40 °C): −0.31 (s).

Isolation of [Li(12-crown-4)][(OC)$_5$W{Ph$_3$CPCl}] (3). To a stirred solution of phosphane complex **2** (267.6 mg, 0.4 mmol) and 12-crown-4 (70 μL, 0.44 mmol) in 15 mL of diethyl ether was added dropwise a solution of ^{t}BuLi in *n*-hexane (1.6 M, 0.28 mL) at −78 °C to give a yellow solution with light-yellow precipitate. It was allowed to warm up to −15 °C (ca. 2 h), and the liquid was removed via a double-ended needle. The residue was washed with diethyl ether (3 × 2 mL, −20 °C) and dried at 0 °C for 2 h at 10^{-2} mbar.

Yield: yellow solid, 253 mg (77%).^{31}P MAS NMR: 255.9 ppm.

Synthesis of [(OC)$_5$W{Ph$_3$CP(Cl)C(O)Cl}] (4). To a stirred solution of phosphane complex **2** (468 mg, 0.7 mmol) and 12-crown-4 (0.122 mL, 0.77 mmol) in 10 mL of THF at −78 °C was added dropwise a solution of ^{t}BuLi in *n*-hexane (1.6 M, 0.49 mL). The obtained yellow solution (~20 min) was cooled to −90 °C and quickly transferred via a cooled double-ended needle to a precooled (−105 °C) intensively stirred solution of phosgene (ca. 20% in toluene, d 0.94, 2.21 mL). The mixture was warmed to −20 °C in a cooling bath, and the volatiles were evaporated in vacuum. The residue was cooled to −20 °C and extracted with cooled diethyl ether (40 mL). After removing of the solvent in vacuum, the solid residue was washed with diethyl ether (3 × 3 mL) to give **4** as a light-yellow powder.

Yield: 360 mg (74%); mp 174 °C (dec.). ^{1}H NMR (C$_6$D$_6$): 6.91−7.47 (m, 15 H, 3 Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 74.6 (d, $^{1}J_{C,P}$ = 3.6 Hz, P$\underline{C}$Ph$_3$), 128.6−128.9 (m, Ph), 129.6 (d, $J_{C,P}$ = 3.2 Hz, Ph), 130.8 (d, $J_{C,P}$ = 6.9 Hz, Ph), 133.3 (d, $J_{C,P}$ = 7.9 Hz, Ph), 141.2 (s, *ipso*-Ph), 141.4 (d, $^{2}J_{C,P}$ = 6.1 Hz, *ipso*-Ph), 141.9 (d, $^{2}J_{C,P}$ = 5.7 Hz, *ipso*-Ph), 176.9 (d, $^{1}J_{C,P}$ = 13.6 Hz, PCO), 195.1 (d$_{Sat}$, $^{2}J_{C,P}$ = 5.9 Hz, $^{1}J_{C,W}$ = 127.4 Hz, *cis*-CO), 197.1 (d, $^{2}J_{C,P}$ = 37.4 Hz, *trans*-CO). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 148.6 (s$_{Sat}$, $^{1}J_{P,W}$ = 278.5 Hz). IR (KBr; υ_{max}/cm^{-1}): 1747 (m, CO), 1942 (vs, CO), 1959 (vs, CO), 2078 (s, CO). Anal. Calcd. for C$_{25}$H$_{15}$Cl$_2$O$_6$PW: C, 43.07; H, 2.17. Found: C, 43.67; H, 2.58.

Synthesis of [(OC)$_5$W{Ph$_3$CPOC(H)Ph}] (5). To a freshly synthesized Li/Clphosphinidenoid complex **3** (from phosphane complex **2** (334 mg, 0.5 mmol), 12-crown-4 (87.5 μL, 0.55 mmol), ^{t}BuLi (1.6 M in *n*-hexane, 0.35 mL) in 9 mL of THF) was added benzaldehyde (0.1 mL, 1 mmol) at −78 °C leading to formation of a white precipitate. The reaction mixture was warmed up to −15 °C in a cooling bath (ca. 2 h), and volatiles were evaporated in vacuum. The product was extracted with diethyl ether (40 mL), filtered through Celite, and, after evaporation of the solvent in vacuum, washed with diethyl ether (3 × 1 mL) at −50 °C, dried, and thus obtained as a white solid.

Yield: 274.1 mg (78%); mp 128 °C. ^{1}H NMR (C$_6$D$_6$): 4.14 (2 H, d, $^{2}J_{H,P}$ = 2.1 Hz, CHP), 6.97−7.24 (15 H, m, 3Ph), 7.64 (5 H, m, Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 60.4 (d, $^{1}J_{C,P}$ = 23.6 Hz, PCO), 67.7 (d, $^{1}J_{C,P}$ = 8.1 Hz, P$\underline{C}$Ph$_3$), 126.9 (d, $J_{C,P}$ = 3.9 Hz, Ph), 128.7 (d, $J_{C,P}$ = 2.1 Hz, Ph), 129.0 (d, $J_{C,P}$ = 1.7 Hz, Ph), 129.1 (s, Ph), 131.1 (d, $J_{C,P}$ = 6.9 Hz, Ph), 140.4 (d, $^{2}J_{C,P}$ = 2.3 Hz, *ipso*-Ph), 194.6 (d$_{Sat}$, $^{2}J_{C,P}$ = 8.2 Hz, $^{1}J_{C,W}$ = 126.3 Hz, *cis*-CO), 196.3 (d, $^{2}J_{C,P}$ = 40.9 Hz, *trans*-CO). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 16.01 (s$_{Sat}$, $^{1}J_{P,W}$ = 311.5 Hz). IR (KBr; υ_{max}/cm^{-1}): 1905 (vs, CO), 1945 (vs, CO), 2077 (s, CO). MS (EI, 70 eV): *m*/*z* (%): 704.1 (0.2) [M]$^+$ .Anal. Calcd. for C$_{31}$H$_{21}$O$_6$PW: C, 52.86; H, 3.01. Found: C, 52.89; H, 3.21.

Synthesis of [(OC)$_5$W{Ph$_3$CPOC(H)O^{i}Pr}] (5). To freshly synthesized Li/Cl phosphinidenoid complex **3** (from phosphane complex **2** (669 mg, 1 mmol), 12-crown-4 (0.17 mL, 1.1 mmol), ^{t}BuLi (1.6 M in *n*-hexane, 0.7 mL) in 10 mL of THF) was added isopropyl alcohol (1 mL, 13 mmol) at −78 °C. The reaction mixture was warmed up to 0 °C in a cooling bath (ca. 2h). After further stirring at 25 °C for 1.5 h volatiles were evaporated in vacuum. The product was purified by column chromatography (Al$_2$O$_3$, −15 °C, petrol ether/dichloromethane = 10/2) to give **5** as a solid.

Yield: 530 mg (80.5%); mp 107 °C (dec.). ^{1}H NMR (C$_6$D$_6$): 0.69 (3 H, d, $^{3}J_{H,H}$ = 6.1 Hz, CH$_3$), 0.80 (3 H, d, $^{3}J_{H,H}$ = 6.1 Hz, CH$_3$), 3.72−3.92 (1 H, m, OCH), 6.86−7.45 (15 H, m, 3Ph), 7.68 (1 H, d, $^{3}J_{H,P}$ = 329.3 Hz, PH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 22.4 (d, $^{3}J_{C,P}$ = 3.1 Hz, CH$_3$), 23.3 (d, $^{3}J_{C,P}$ = 5.0 Hz, CH$_3$), 64.0 (d, $^{1}J_{C,P}$ = 20.4 Hz, PC), 75.5 (d, $^{2}J_{C,P}$ = 9.0 Hz, OCH), 127.6 (d, $^{5}J_{C,P}$ = 2.1 Hz, *para*-Ph), 128.5 (s, *meta*-Ph), 131.0 (d, $^{3}J_{C,P}$ = 6.5 Hz, *ortho*-Ph), 142.9 (s, *ipso*-Ph), 196.8 (d$_{Sat}$, $^{2}J_{C,P}$ = 7.4 Hz, $^{1}J_{C,W}$ = 126.1 Hz, *cis*-CO), 198.8 (d, $^{2}J_{C,P}$ = 29.5 Hz, *trans*-CO). ^{31}P{^{1}H} NMR (C$_6$D$_6$): 115.21 (s$_{Sat}$, $^{1}J_{P,W}$ = 278.5 Hz). IR (KBr; υ_{max}/cm^{-1}): 1922 (vs, CO), 1943 (vs, CO), 2073 (s, CO). MS (EI, 70 eV): *m*/*z* (%): 658.1 (1.8) [(M)$^+$]. Anal. Calcd. for C$_{27}$H$_{23}$O$_6$PW: C, 49.26; H, 3.52. Found: C, 49.23; H, 3.62.

X-ray Data Collection, Structure Solution, and Refinement. Single crystals of complexes **2**, **4**, and **5** were obtained in diethyl ether at −20 °C; crystals of **6** from THF/pentane mixture (slow diffusion) at 25 °C. The data for crystals **2** and **5** were collected on a Bruker X8-KappaApexII diffractometer at 123(2) K, and for **4** and **6** on a Nonius KappaCCD device at 100(2) K by using graphite monochromated Mo Kα radiation, λ = 0.71073 Å (Supporting Information, Table 1). The structures were solved by Patterson methods (SHELXS-97) and refined by full-matrix least-squares on F^2 (SHELXL-97).

Crystallographic data of **2**, **4**−**6** have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC 884453 (**2**), 884452 (**4**), 884454 (**5**), and 884455 (**6**). This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. This material and further informations are available free of charge in the Internet at http://pubs.acs.org.

■ COMPUTATIONAL DETAILS

All calculations have been carried out with the ORCA electronic structure program package[35] with all structures being optimized in redundant internal coordinates at the density functional theory (DFT) level using the B3LYP[36] functional together with the new efficient RIJCOSX algorithm[37] and the def2-TZVP basis set.[38] For W the [SD(60,MWB)] effective core potential was employed.[39] A damped semiempirical correction accounting for the major part of the contribution of dispersion forces to the energy was included[40] and denoted with suffix -D after the name of the functional (B3LYP-D). Solvent effects (THF) were taken into account via the COSMO solvation model.[27] Atomic charges were computed from the Löwdin population analysis.[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of crystallographic parameters for **2**, **4**−**6** and Cartesian coordinates (Å) and energies (au) for all computed species. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Rheinhard Schmutzler on the occasion of his 77th birthday.

■ REFERENCES

(1) (a) Özbolat, A.; von Frantzius, G.; Pérez, J. M.; Nieger, M.; Streubel, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 9327. (b) Bode, M.; Daniels, J.; Streubel, R. *Organometallics* **2009**, *28*, 4636. (c) Özbolat, A.; von Frantzius, G.; Hoffbauer, W.; Streubel, R. *J. Chem. Soc., Dalton Trans.* **2008**, 2674.

(2) Özbolat, A.; von Frantzius, G.; Ionescu, E.; Schneider, S.; Nieger, M.; Jones, P. G.; Streubel, R. *Organometallics* **2007**, *26*, 4021.

(3) Duan, L.; Schnakenburg, G.; Streubel, R. *Eur. J. Inorg. Chem.* **2012**, 3490.

(4) Duan, L.; Schnakenburg, G.; Streubel, R. *Organometallics* **2011**, *30*, 3246.

(5) Braun, M. In *The Chemistry of Organolithium Compounds*, Part 2; Rappoport, Z., Marek, I., Eds.; John Wiley & Sons Ltd: New York, 2004; pp 829−900.

(6) Some recent examples from different areas; for oxaphosphirane complexes see: (a) Streubel, R.; Bode, M.; Pérez, J. M.; Schnakenburg, G.; Daniels, J.; Nieger, M.; Jones, P. G. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1163. (b) Pérez, J. M.; Klein, M.; Kyri, A. W.; Schnakenburg, G.; Streubel, R. *Organometallics* **2012**, *30*, 5636. For azaphosphiridine complexes: (c) Fankel, S.; Helten, H.; von Frantzius, G.; Schnakenburg, G.; Daniels, J.; Chu, V.; Müller, C.; Streubel, R. *Dalton Trans.* **2010**, *39*, 3427. (d) Streubel, R.; Villalba Franco, J. M.; Schnakenburg, G.; Espinosa Ferao, A. *Chem. Commun.* **2012**, *48*, 5986. For a cyclic phosphane complexes: (e) Streubel, R.; Özbolat-Schön, A.; Bode, M.; Daniels, J.; Schnakenburg, G.; Teixidor, F.; Vinas, C.; Vaca, A.; Pepiol, A.; Farras, P. *Organometallics* **2009**, *28*, 6031. (f) Nesterov, V.; Duan, L.; Schnakenburg, G.; Streubel, R. *Eur. J. Inorg. Chem.* **2011**, 567.

(7) (a) Lang, H.; Mohr, G.; Shiedsteger, O.; Huttner, G. *Chem. Ber.* **1985**, *118*, 574. (b) Yoshifuji, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3343.

(8) Duan, L.; Nesterov, V.; Runyon, J.; Arduengo, A. J., III; Streubel, R. *Aust. J. Chem.* **2011**, *64*, 1583.

(9) Reviews: (a) Mathey, F. *Dalton Trans.* **2007**, 1861. (b) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95. (c) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127. (d) Mathey, F.; Huy, N. H. T.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938.

(10) *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley-Interscience: Hoboken, NJ, 2004.

(11) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990.

(12) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.

(13) Plack, V.; Goerlich, J. R.; Fischer, A.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1080.

(14) Plack, V.; Goerlich, J. R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 919.

(15) Plack, V.; Goerlich, J. R.; Fischer, A.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1979.

(16) (a) Plack, V.; Schmutzler, R. *Phosphorus, Sulfur and Silicon* **1999**, *144−146*, 273 , and references cited therein. (b) Plack, V.; Goerlich, J. R.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1278. (c) Baskar, V.; Shanmugam, M.; Sanudo, E. C.; Shanmugam, M.; Collison, D.; McInnes, E. J. L.; Wei, Q.; Winpenny, R. E. *Chem. Commun.* **2007**, *37*, 39. (d) Chandrasekhar, V.; Sasikumar, P. *Dalton Trans.* **2008**, 6475. (e) Lux, K.; Schön, O.; Karaghiosoff, K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2465.

(17) Cordaro, J. G.; Stein, D.; Grützmacher, H. *J. Am. Chem. Soc.* **2006**, *128*, 14962.

(18) (a) Plack, V.; Goerlich, J. R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1940. (b) See also ref 15.

(19) Espinosa, A.; Streubel, R. *Chem.—Eur. J.* **2012**, *18*, 13405 ; here the SET-induced homolytic P-C bond cleavage of *P*-trityl substituted oxaphosphirane complexes is described.

(20) (a) See ref 13. (b) Plack, V.; Goerlich, J. R.; Fischer, A.; Thönnessen, H.; Jones, P. G.; Schmutzler, R. *J. Fluor. Chem.* **2000**, *101*, 125.

(21) (a) Özbolat-Schön, A.; Bode, M.; Schnakenburg, G.; Anoop, A.; van Gastel, M.; Neese, F.; Streubel, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6894. (b) Nesterov, V.; Özbolat-Schön, A.; Schnakenburg, G.; Shi, L.; Cangönül, A.; van Gastel, M.; Neese, F.; Streubel, R. *Chem.—Asian. J.* **2012**, *7*, 1708.

(22) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793.

(23) Previously reported attempts to obtain $L_2Mo(CO)_4$ complexes via reaction of Ph_3CPCl_2(**1**) with $(NOR)Mo(CO)_4$ failed, in contrast to analogous reactions of *P*-trityl phosphanes with different substitution pattern at phosphorus $[Ph_3CP(X)Y$, (X = Cl, Y = H; X = Y = F; X = Y = H)], see: refs 13, and 20b.

(24) A number of structurally characterized unligated trityl-P(III) and -P(V) compounds with different substitution at phosphorus have been reported recently, see: Gushwa, A. F.; Belabassi, Y.; Montchamp, J.-L.; Richards, A. F. *J. Chem. Crystallogr.* **2009**, *39*, 337.

(25) Özbolat-Schön, A.; von Frantzius, G.; Schnakenburg, G.; Gudat, D.; Streubel, R. submitted for publication.

(26) Molecular structures were generated with VMD − Visual Molecular Dynamics. Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graphics*, **1996**, *14*, 33−38. Home page: http://www.ks.uiuc.edu/Research/vmd/.

(27) COSMO solvation model: (a) Klamt, A.; Schüürmann, G. *J. Chem. Soc. Perkin Trans. 2* **1993**, *220*, 799. (b) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2224.

(28) Nesterov, V.; Heurich, T.; Streubel, R. *Pure Appl. Chem.*, accepted for publication.

(29) Unligated P (III) chloroformylphosphanes are known to be unstable: they decompose either similarly to give *P*-chloro derivatives via extrusion of CO or, in case of *P*-trimethylsilyl substituted derivatives, to give phosphaketenes or dimers, ref 14 and references cited therein, (b) Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O.J., Eds.; Thieme: Stuttgart, Germany, 1990; pp 188−191.

(30) Stability of chloroformylphosphane complex **4** in solution significantly increases upon decrease of the solvent polarity, for example, from THF to benzene.

(31) Previously were reported only impure Ph_3C-substituted P(III) chloroformylphosphanes, and no structural data are available, see ref 15.

(32) Streubel, R.; Kusenberg, A.; Jeske, J.; Jones, P. G. *Angew. Chem., Int. Ed.* **1994**, *33*, 2427.

(33) Bode, M.; Schnakenburg, G.; Jones, P. G.; Streubel, R. *Organometallics* **2008**, *27*, 2664.

(34) Solvent signals are omitted for clarity.

(35) Neese, F.; *ORCA—An ab initio, DFT and semiempirical SCF-MO package*, Version 2.9.0; Max Planck Institute for Bioinorganic Chemistry: Mülheim an der Ruhr, Germany, 2012; Web page: http://www.mpibac.mpg.de/bac/logins/neese/description.php.

(36) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(37) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. *Chem. Phys.* **2009**, *356*, 98.

(38) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(39) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor.Chim.Acta*, **1990**, *77*, 123−141. ECP parameters for W [SD(60,MWB)] have been obtained from the pseudopotential library of the Stuttgart/Cologne group, at http://www.theochem.uni-stuttgart.de/pseudo-potentials/.

(40) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(41) (a) Löwdin, P.-O. *J. Chem. Phys.* **1950**, *18*, 365. (b) Löwdin, P.-O. *Adv. Quantum Chem.* **1970**, *5*, 185. (c) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry. Introduction to advanced electronic structure theory*; Dover Publications: Mineola, NY, 1989.