DOI: 10.1002/ejic.201001122

New Access to and Reactions of *P*-Functional Acylphosphane Complexes

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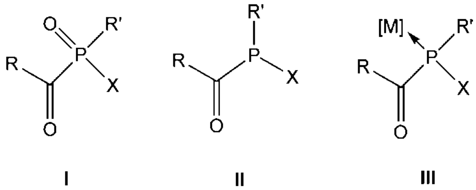
Dedicated to Professor O. I. Kolodiazhnyi

Keywords: Phosphanides / Phosphane ligands / Phosphaalkenes / Tungsten

P-Functional (acylphosphane)tungsten complexes **4a**–**f** have been prepared in good yields by the reaction of phosphinidenoid complexes **2a**–**d** with acyl chlorides **3a**,**b**. The reactions of acyl(chloro)phosphane complex **4a** at –80 °C with organolithium reagents selectively led to the formation of lithiated phospha-enolate complex **5b**. The ambident reactivity of this compound was demonstrated in reactions with electrophiles such as PhC(O)Cl, MeI, and Me_3SiCl, which yielded *O*-substituted complexes **6a**,**b** and **8a**,**b** and *P*-substituted complex **7**.

Introduction

Of the organophosphorus compounds containing a carbonyl group directly attached to a phosphorus atom the most important examples are mono- and bis(acyl)phosphane oxides **I** (Scheme 1), which have proved to be effective photoinitiators and have therefore raised great interest from industry and academia.[1] Although acylphosphane derivatives **II**[2] have been known for a long time, acylphosphanes coordinated to a transition-metal center (**III**) are less studied, and their synthetic potential is largely unexplored.[3]



Scheme 1. Functional acylphosphanes **I** and **II** and their complexes **III** {[M] = ML_n, R = organic substituent, X = RC(O) or group 16 or 18 element}.

Because of the known stabilizing ability of transition-metal complexes on otherwise highly reactive compounds, the increased stability of **III** could be safely assumed, and therefore they could mimic the chemical behavior of the corresponding carbon analogues, as expected from the diagonal relationship between carbon and phosphorus.[4] The main methods of preparation of mononuclear (acylphosphane)transition-metal complexes **III** include the reactions of phosphanes with metal complexes,[5] the migration of an acyl moiety from a transition-metal center to a phosphanido ligand,[3b,6] and the conversions of phosphanes ligated to transition-metal centers.[3a]

The first synthesis and reactions of (Li/X-phosphinidenoid)transition-metal complexes have recently been described;[7] it was shown that they can behave similarly to carbenoids[8] and silylenoids[9] as the corresponding phosphinidene complex behavior was observed.[7a,10] It was demonstrated that such species can react with electrophiles such as methyl iodide[7a] or iodoacetylene derivatives,[11] and thus they display nucleophilic behavior. As part of our ongoing research into M/X-phosphinidenoid complex chemistry we would like to report here on their reactions with acyl chlorides opening a general access to *P*-functional (acylphosphane)transition-metal complexes. Furthermore, we describe the reactivity of the latter towards organolithium compounds.

Results and Discussion

(Li/X-phosphinidenoid)metal complexes **2a**,**b** and Li/RO-phosphanide complexes **2c**,**d** were generated by lithiation of the corresponding *P*-H bifunctional phosphane complexes **1a**,[12] **1b**,[7b] and **1c**,**d**[13] with LDA in the presence of 12-crown-4 at –80 °C and allowed to react in situ with acyl chlorides **3a**,**b** to give selectively the (acylphosphane)tungsten complexes **4a**–**f** (Scheme 2). The reactivity of the complexes **2a**–**d** depended largely on the nature of the substituent X bonded to the phosphorus atom and, in general, complexes **2c**,**d** bearing alkoxy substituents at the phosphorus atom appeared to be less reactive than the halogen-substituted complexes **2a**,**b**.

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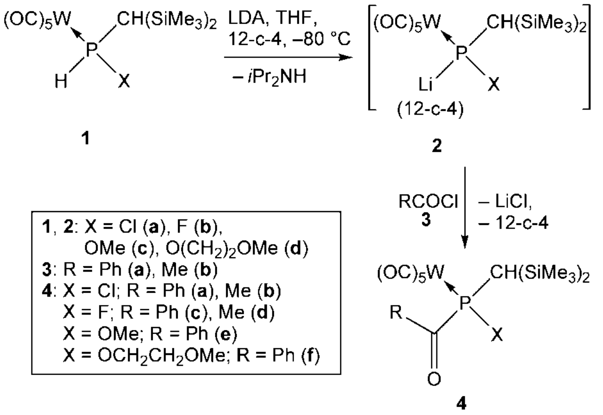


Scheme 2. Preparation of the *P*-functional (acylphosphane)tungsten complexes **4a**–**f**.

Complexes **4a**–**f** were obtained in good yields (70–85%) after silica gel column chromatography and/or after crystallization from *n*-pentane at low temperatures and were fully characterized; pure **4a**–**f** are stable under inert-gas conditions.

The signals of the carbonyl carbon atoms directly bonded to the phosphorus atom in the ^{13}C NMR spectra of complexes **4a**–**f** appeared at δ = 202.3–216.6 ppm. Interestingly, in the case of the *P*-chloro-substituted acylphosphane complexes **4a**,**b** these signals displayed surprisingly small P,C coupling constants (**4a**: J = 1.3 Hz; **4b**: J = 1.9 Hz) compared with the other complexes (**4c**–**f**: J = 7.1–19.6 Hz).

The IR spectra exhibit absorption bands of the carbonyl group of the acyl moieties in **4a**–**f** in the range 1648–1702 cm^{-1}. Maxima are observed in the UV spectra of the acylphosphane complexes **4a**–**f** in the range 229.5–235 nm.

The molecular structure of **4a** was confirmed by single-crystal X-ray diffraction studies (Figure 1). The phosphorus atom in **4a** as ligand has a trigonal-pyramidal geometry [in the ligand the sum of the bond angles at P(1) is 301.8°] with a P–C(1) distance of 1.912(5) Å. The tendency towards P–C bond elongation in α-carbonyl derivatives of organophosphorus compounds (the sum of the covalent radii of P and C atoms is 1.83 Å) has been observed before for transition-metal-free acylphosphanes,[2,14] bis(acyl)phosphane oxides,[15] and nonfunctional (acylphosphane)transition-metal complexes.[3b,6a]

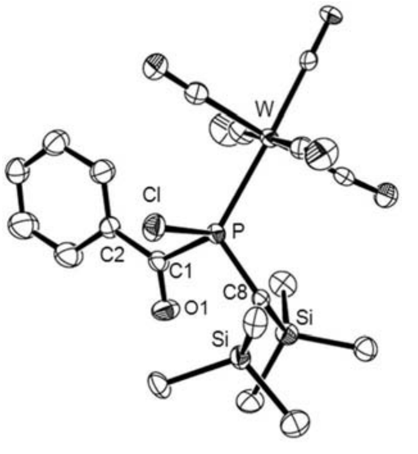
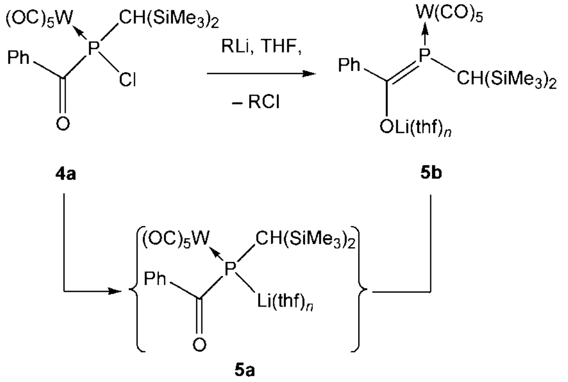


Figure 1. Crystal structure of complex **4a** (50% probability level, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.506(1), P–C(1) 1.912(5), P–C(8) 1.809(4), P–Cl 2.903(2), C(1)–O(1) 1.219(6), C(1)–C(2) 1.481(7); C(8)–P–C(1) 101.4(2), C(8)–P–Cl 107.30(15), C(1)–P–Cl(15) 93.13(16), C(2)–C(1)–P 123.4(4), O(1)–C(1)–P 114.7(3).

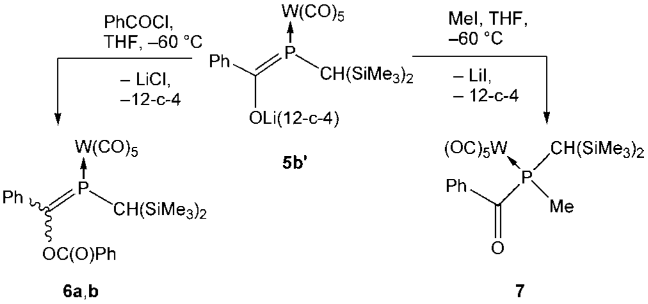
As a case in point, the reactions of complex **4a** with organolithium nucleophiles were studied to investigate the use of *P*-functional acylphosphane complexes in organophosphorus and coordination chemistry. It was found that the reactions of complex **4a** with RLi (R = Me, *n*Bu, or *t*Bu) in THF at –80 °C led to the selective formation of phospha-enolate complex **5b** without any evidence of nucleophilic attack on the *P*- and/or *W*-bonded carbonyl groups (Scheme 3).[3b]



Scheme 3. Reactions of complex **4a** with various organolithium compounds.

We propose that the first step is a chlorine/lithium exchange reaction that yields complex **5a** as a transient species, which rearranges to give complex **5b** [δ_P = –19.0 ppm, ^1J(P,W) = 179.2 Hz] as the thermodynamically more favored isomer. All the reactions were accompanied by a change in color from yellow to red. If the reactions were carried out in the presence of 12-crown-4, complex **5b′** was isolated in high yield with the lithium ion coordinated to 12-crown-4 (without THF). Complex **5b′** is characterized by a signal at δ = –23.8 ppm with a ^1J(P,W) coupling constant of 167.8 Hz (^{31}P NMR spectrum, THF, 25 °C). The ^{13}C{H} NMR spectrum displayed a signal for the α-carbon atom of **5b′** that was more downfield-shifted and had a larger C,P coupling constant [δ_C = 227.5 ppm, ^1J(C,P) = 18.1 Hz] than the starting material, complex **4a** [δ_C = 202.3 ppm, ^1J(C,P) = 1.3 Hz]. As no Li,P coupling was observed in the NMR spectra, we assume that the lithium cation is bonded to the oxygen atom in **5b′**. This is further supported by our reactivity studies (see below) and by results reported before for nonligated lithium acyl- and bis(acyl)phosphanides[16,17] in which the lithium ion is bound to the more electronegative oxygen atom and, additionally, to the solvent donor molecules.

The *O*-lithiated alkylidenephosphane complexes **5b** and **5b′** can be considered as phosphorus analogues of metal enolates derived from ketones.[18] To examine the reactivity of complex **5b′**, that is, the ratio of *O*- versus *P*-substitution, it was treated with various electrophiles (Schemes 4 and 5). The reaction of complex **5b′** with benzoyl chloride led to the selective formation of phosphaalkene complexes **6a**,**b**, which were obtained as a mixture of (*Z*)/(*E*) isomers (ratio ca. 2:1). Complexes **6a**,**b** displayed two resonances in the ^{31}P NMR spectrum at δ = 163.5 and 165.8 ppm, respectively, with a W,P coupling constant of 267.0 Hz (in both cases) but different P,H coupling constants for the CH proton of the *P*-substituent [^{2}J(P,H) = 8.9 Hz for **6a** (*Z*) and ^{2}J(P,H) = 17.8 Hz for **6b** (*E*)].



Scheme 4. Reactivity of **5b′** towards PhCOCl and MeI.

The molecular structure of the (*Z*)-phosphaalkene complex **6a**[19] was confirmed by single-crystal X-ray diffraction studies (Figure 2); suitable crystals were obtained from *n*-pentane solutions of the (*Z*)/(*E*) mixture at 24 °C.

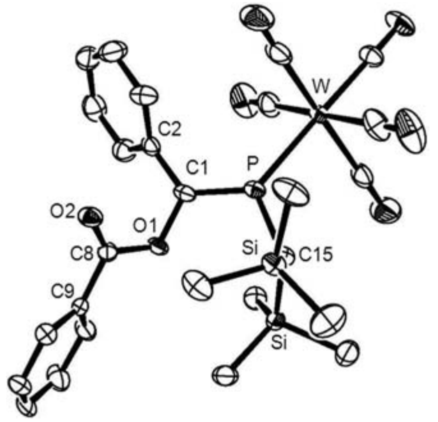
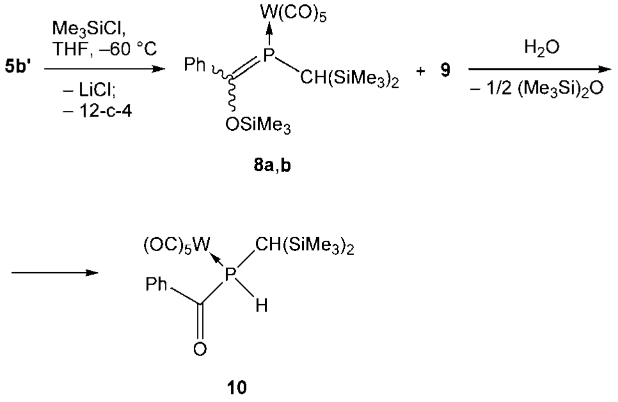


Figure 2. Crystal structure of complex **6a** (50% probability level, hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P(1) 2.473(8), P(1)–C(1) 1.676(4), P(1)–C(15) 1.811(3), C(1)–C(2) 1.474(5), C(1)–O(1) 1.410(4), C(8)–O(2) 1.203(4); C(1)–P(1)–W 127.25(12), C(1)–P(1)–C(15) 111.89(16), C(15)–P(1)–W 119.97(11).

The structure of complex **6a** contains all the features characteristic of (phosphaalkene)transition-metal complexes: The phosphorus and carbon centers of the P=C moiety have trigonal-planar environments [sum of the bond angles at P(1) and C(1) are 359.1 and 359.7°, respectively], the P(1)–C(1) bond length is 1.676(4) Å, which is in the typical range of P–C bond lengths in phosphaalkenes and (η^1-phosphaalkene)transition-metal complexes.[20]

When complex **5b′** was treated with methyl iodide, the *P*-methyl-substituted complex **7** was obtained selectively (Scheme 4); complex **7** showed a doublet of doublets in its ^{31}P NMR spectrum at δ = 7.03 ppm [^{1}J(P,W) = 223.8 Hz, ^{2}J(P,H) = 6.3 Hz, ^{2}J(P,H) = 5.0 Hz]. In the ^{1}H NMR spectrum the *P*-methyl protons appeared as a doublet at δ = 2.15 ppm [^{2}J(P,H) = 6.2 Hz].

The reactions of nonligated lithium acylphosphanides with trimethylsilyl chloride have previously been reported to give *O*-[16a] and *P*-substituted products.[16b] To examine the influence of the transition metal on the reactivity, complex **5b′** was treated with trimethylsilyl chloride at low temperatures (Scheme 5). In this case a mixture of three products was formed: two major products (ratio of 2:1) with ^{31}P NMR resonances similar to those of **6a**,**b** [δ_P = 106.9 ppm, ^{1}J(P,W) = 256.8 Hz, ^{2}J(P,H) = 17.8 Hz and δ_P = 101.9 ppm, ^{1}J(P,W) = 258.1 Hz, ^{2}J(P,H) = 8.9 Hz] and thus were assigned to the *O*-silylated alkylidenephosphane complexes **8a**,**b**. A minor product **9** (ca. 15%) with δ_P = 120.7 ppm [^{1}J(P,W) = 251.7 Hz, ^{2}J(P,H) = 19.0 Hz] could not be identified. If this solution of **8a**,**b** and **9** was treated with small amounts of water, the selective formation of complex **10** was observed; the final product **10** was isolated by column chromatography and fully characterized.



Scheme 5. Reaction of **5b′** with Me_3SiCl.

The existence of a P–H bond in **10** was revealed by its large coupling constant [δ_P = –39.8 ppm, ^{1}J(P,W) = 212.3 Hz, ^{1}J(P,H) = 319.5 Hz, ^{2}J(P,H) = 7.6 Hz].

Conclusions

It has been shown that the in situ reactions of phosphinidenoid complexes **2a**,**b** and phosphanide complexes **2c**,**d** with acyl chlorides represent a new method for the preparation of *P*-functional (acylphosphane)tungsten complexes. As illustrated for acyl(chloro)phosphane complex **4a**, reactions with various organolithium compounds do not lead to nucleophilic attack at the *P*- and *W*-bonded carbonyl groups but to the selective formation of *O*-lithiated derivatives **5b** and **5b′** as the final products. Complex **5b′** possesses ambident nucleophilic character, thus giving rise to

P- and *O*-substituted products depending on the nature of the electrophile employed. The chemistry of the transition-metal complexes of α-carbonyl-substituted phosphanes and their derivatives is currently under investigation.

Experimental Section

General Procedures: All the reactions were carried out under purified argon by using standard vacuum, Schlenk, and glove-box techniques. Solvents were dried and degassed by standard procedures. NMR spectroscopic data were recorded at 25 °C with a Bruker DMX 300 spectrometer (^{1}H: 300.13 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121.5 MHz) by using $CDCl_3$ or [D$_8$]THF (complex **5b′**) as solvent and internal secondary standard; chemical shifts are referenced to tetramethylsilane (^{1}H, ^{13}C: Ξ = 19.867187 MHz) and 85% H_3PO_4 (^{31}P: Ξ = 40.480742 MHz). Mass spectra were recorded with a MAT 95 XL Finnigan (EI, 70 eV, ^{184}W) spectrometer (selected data given). UV/Vis spectra were recorded with a Shimadzu UV-1650 PC spectrometer. Infrared spectra were recorded with a Thermo Nicolet 380 FT-IR spectrometer (selected data given). Elemental analyses were performed by using an Elementar VarioEL instrument. Melting points were determined with a Büchi apparatus, with samples sealed in capillaries under argon.

General Procedure for the Synthesis of Complexes 4a–f: A cooled solution (–50 °C) of the appropriate phosphane complex **1a** (440 mg, 0.8 mmol), **1b** (427 mg, 0.8 mmol), **1c** (437 mg, 0.8 mmol), or **1d** (472 mg, 0.8 mmol) and 12-crown-4 (0.13 mL, 0.84 mmol) in THF (4 mL) was added dropwise to a stirred solution of freshly prepared LDA (0.84 mmol) in THF (9 mL) at –80 °C. After 15 min at –80 °C, the acyl chloride **3a** (0.98 mL, 0.84 mmol) or **3b** (0.6 mL, 0.84 mmol) was added, and the reaction mixture was warmed up to 10 °C (ca. 2 h) in a cooling bath. The volatiles were evaporated in vacuo, *n*-pentane (15 mL) was added, and the precipitate was filtered off. The solvent was then removed and the residue subjected to column chromatography (–20 °C, petroleum ether, petroleum ether/diethyl ether = 10:0.5). Elution of the second band yielded complexes **4a**–**d**, which were crystallized from *n*-pentane at –80 °C.

Complex 4a: Yellow solid; yield: 445 mg (0.68 mmol, 85%); m.p. 105 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 0.34 [s, 9 H, $Si(CH_3)_3$], 0.35 [d, ^4J(H,P) = 0.5 Hz, 9 H, $Si(CH_3)_3$], 1.98 [d, ^2J(H,P) = 4.1 Hz, 1 H, PCH], 7.53 (m, 2 H, Ph), 7.62 (m, 1 H, Ph), 8.17 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.4 [d, ^3J(C,P) = 2.5 Hz, $Si(CH_3)_3$], 3.62 [d, ^3J(C,P) = 3.2 Hz, $Si(CH_3)_3$], 30.5 [d, ^1J(C,P) = 14.2 Hz, PCH], 129.0 (s, Ph), 129.8 (s, Ph), 134.1 (s, Ph), 135.1 [d, ^2J(C,P) = 46.5 Hz, Ph], 196.6 [d$_{Sat}$, ^2J(C,P) = 6.4, ^1J(C,W) = 127.4 Hz, *cis*-CO], 198.2 [d, ^2J(C,P) = 31.6 Hz, *trans*-CO], 202.3 [d, ^1J(C,P) = 1.3 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 113.8 [s$_{Sat}$, ^1J(P,W) = 267.0 Hz] ppm. IR (KBr): ṽ = 574 (s), 593 (s), 772 (s), 859 (s), 1663 (s), 1909 (s), 2075 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 235.0 (1.54) nm. MS (EI, 70 eV): *m*/*z* (%) = 653.9 (1.5) [M]$^+$. $C_{19}H_{24}ClO_6PSi_2W$ (654.83): calcd. C 34.85, H 3.69; found C 34.89, H 3.87.

Complex 4b: Yellow-green solid; yield: 334 mg (0.56 mmol, 70%); m.p. 59 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 0.29 [s, 9 H, $Si(CH_3)_3$], 0.34 [d, ^4J(H,P) = 0.5 Hz, 9 H, $Si(CH_3)_3$], 1.89 [d, ^2J(H,P) = 9.2 Hz, 1 H, PCH], 2.75 [d, ^3J(H,P) = 5.1 Hz, 3 H, CH_3] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.14 [d, ^3J(C,P) = 3.2 Hz, $Si(CH_3)_3$], 3.34 [d, ^3J(C,P) = 3.2 Hz, $Si(CH_3)_3$], 26.71 [d, ^1J(C,P) = 49.7 Hz, PCH], 28.38 [d, ^2J(C,P) = 18.7 Hz, CH_3], 196.46 [d$_{Sat}$, ^2J(C,P) = 6.4, ^1J(C,W) = 126.8 Hz, *cis*-CO], 197.9 [d, ^2J(C,P) = 30.4 Hz, *trans*-CO], 209.9 [d, ^1J(C,P) = 1.9 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 115.4 [s$_{Sat}$, ^1J(P,W) = 260.6 Hz] ppm. MS (EI, 70 eV): *m*/*z* (%) = 592.0 (8) [M]$^+$. IR (KBr): ṽ = 543 (s), 567 (s), 597 (s), 682 (m), 859 (s), 1003 (m), 1119 (m), 1254 (s) 1347 (s), 1702 (s), 1949 (s), 2075 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 230.0 (1.5), 305.0 (0.153), 346.5 (0.100) nm. $C_{14}H_{22}ClO_6PSi_2W$ (592.76): calcd. C 28.37, H 3.74; found C 28.58, H 3.90.

Complex 4c: Yellow solid; yield: 378 mg (0.59 mmol, 74%); m.p. 58 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 0.21 [d, ^4J(P,H) = 1.9 Hz, 9 H, $Si(CH_3)_3$], 0.38 [s, 9 H, $Si(CH_3)_3$], 1.90 [d, ^2J(H,P) = 10.3 Hz, 1 H, PCH], 7.53 (m, 2 H, Ph), 7.65 (m, 1 H, Ph), 8.08 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 2.56 [dd, ^3J(C,P) = 2.9, ^3J(C,F) = 1.8 Hz, $Si(CH_3)_3$], 3.44 [d, ^3J(C,P) = 2.3 Hz, $Si(CH_3)_3$], 32.6 [dd, ^1J(C,P) = 11.3, ^2J(C,F) = 4.1 Hz, PCH], 128.98 [d, ^4J(C,P) = 1.1 Hz, Ph], 129.36 [d, ^3J(C,P) = 6.5 Hz, Ph], 134.3 (s, Ph), 135.8 [dd, ^2J(C,P) = 40.5, ^3J(C,F) = 2.3 Hz, Ph], 196.31 [dd$_{Sat}$, ^2J(C,P) = 7.1, ^3J(C,F) = 2.9, ^1J(C,W) = 128.5 Hz, *cis*-CO], 198.0 [d, ^2J(C,P) = 29.2 Hz, *trans*-CO], 207.3 [d, ^1J(C,P) = 13.1 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 193.27 [d$_{Sat}$, ^1J(P,W) = 281.0, ^1J(P,F) = 858.3 Hz] ppm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ = –113.4 [d$_{Sat}$, ^2J(F,W) = 11.2, ^1J(F,P) = 858.3 Hz] ppm. IR (KBr): ṽ = 568 (s), 596 (s), 778 (s), 847 (s), 1115 (s), 1209 (s), 1256 (s), 1648 (s), 1950 (s), 2075 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs) = 232.5 (1.553), 393.5 (0.042) nm. MS (EI, 70 eV): *m*/*z* (%) = 638.0 (10) [M]$^+$. $C_{19}H_{24}FO_6PSi_2W$ (638.37): calcd. C 35.75, H 3.79; found C 36.00, H 3.62.

Complex 4d: White solid; yield: 364 mg (0.63 mmol, 79%); m.p. 49 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 0.21 [d, ^4J(H,P) = 1.7 Hz, 9 H, $Si(CH_3)_3$], 0.31 [s, 9 H, $Si(CH_3)_3$], 1.92 [d, ^2J(H,P) = 12.1 Hz, 1 H, PCH], 2.61 [dd, ^3J(H,P) = 3.6, ^4J(H,F) = 2.6 Hz, 3 H, CH_3] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 2.35 [dd, ^3J(C,P) = 2.6, ^4J(C,F) = 2.6 Hz, $Si(CH_3)_3$], 2.97 [d, ^3J(C,P) = 1.9 Hz, $Si(CH_3)_3$], 28.03 [dd, ^1J(C,P) = 42.0, ^2J(C,F) = 1.9 Hz, PCH], 31.56 [dd, ^1J(C,P) = 11.6, ^2J(C,F) = 7.7 Hz, CH_3], 195.47 [dd$_{Sat}$, ^2J(C,P) = 7.1, ^3J(C,F) = 3.2, ^1J(C,W) = 128.5 Hz, *cis*-CO], 197.8 [d, ^2J(C,P) = 27.8 Hz, *trans*-CO], 216.6 [dd, ^1J(C,P) = 19.6, ^2J(C,F) = 13.5 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 189.4 [d$_{Sat}$, ^1J(P,W) = 275.9, ^1J(P,F) = 841.8 Hz] ppm. ^{19}F{^{1}H} NMR ($CDCl_3$): δ = –121.8 [d$_{Sat}$, ^1J(F,W) = 11.2, ^1J(P,F) = 841.8 Hz] ppm. IR (KBr): ṽ = 567 (m), 596 (s), 846 (s), 1012 (s), 1121 (s), 1252 (s), 1698 (s), 1942 (s), 2078 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 229.5 (1.430), 298.0 (0.144), 340.0 (0.070) nm. MS (EI, 70 eV): *m*/*z* (%) = 575.9 (17) [M]$^+$. $C_{14}H_{22}FO_6PSi_2W$ (576.3): calcd. C 29.18, H 3.85; found C 29.51, H 3.97.

Complex 4e: Yellow viscous liquid; yield: 338 mg (0.52 mmol, 65%). ^{1}H NMR ($CDCl_3$): δ = 0.21 [s, 9 H, $Si(CH_3)_3$], 0.32 [s, 9 H, $Si(CH_3)_3$], 2.06 [d, ^2J(H,P) = 11.7 Hz, 1 H, PCH], 3.60 [d, ^3J(H,P) = 13.0 Hz, 3 H, $POCH_3$], 7.51 [t, ^3J(H,H) = 7.7 Hz, 2 H, Ph], 7.62 [t, ^3J(H,H) = 7.7 Hz, 1 H, Ph], 8.05 [d, ^3J(H,H) = 7.4 Hz, 2 H, Ph] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 2.9 [d, ^3J(C,P) = 3.1 Hz, $Si(CH_3)_3$], 3.4 [d, ^3J(C,P) = 2.8 Hz, $Si(CH_3)_3$], 27.3 [d, ^1J(C,P) = 3.6 Hz, PCH], 56.3 [d, ^2J(C,P) = 3.3 Hz, $POCH_3$], 128.9 (s, Ph), 129.0 (s, Ph), 133.6 (s, Ph), 135.3 [d, ^2J(C,P) = 36.5 Hz, Ph], 196.9 [d$_{Sat}$, ^2J(C,P) = 7.1, ^1J(C,W) = 118.2 Hz, *cis*-CO], 198.0 [d, ^2J(C,P) = 26.8 Hz, *trans*-CO], 208.8 [d, ^1J(C,P) = 12.1 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 154.1 [s$_{Sat}$, ^1J(P,W) = 273.4 Hz] ppm. IR (KBr): ṽ = 505 (w), 574 (s), 599 (s), 694 (w), 844 (w), 1100 (w), 1256 (s), 1670 (s), 1929 (s), 2072 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs) = 231.5 (1.703) nm. MS (EI, 70 eV): *m*/*z* (%) = 650.1 (16) [M]$^+$. $C_{20}H_{27}O_7PSi_2W$ (650.41): calcd. C 36.93, H 4.18; found C 37.93, H 5.05.

Complex 4f: Yellow viscous liquid; yield: 344 mg (0.50 mmol, 62%). ^{1}H NMR ($CDCl_3$): δ = 0.17 [s, 9 H, $Si(CH_3)_3$], 0.30 [s, 9 H, Si-

(CH$_3$)$_3$], 2.16 [d, ^2J(H,P) = 12.7 Hz, 1 H, PCH], 3.26 (s, 3 H, OCH$_3$), 3.59 (m, 2 H, C*H*$_2$OCH$_3$), 3.91 (m, 2 H, POC*H*$_2$), 7.52 [t, ^3J(H,H) = 7.9 Hz, 2 H, Ph], 7.61 [t, ^3J(H,H) = 7.7 Hz, 1 H, Ph], 8.17 [d, ^3J(H,H) = 8.1 Hz, 2 H, Ph] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 2.8 [d, ^3J(C,P) = 3.1 Hz, Si(CH$_3$)$_3$], 3.4 [d, ^3J(C,P) = 2.8 Hz, Si(CH$_3$)$_3$], 27.5 [d, ^1J(C,P) = 5.2 Hz, PCH], 58.3 (s, POCH$_3$), 68.1 [d, ^3J(C,P) = 3.2 Hz, *C*H$_2$OCH$_3$], 71.3 [d, ^2J(C,P) = 8.4 Hz, PO*C*H$_2$], 128.8 (s, Ph), 129.4 (s, Ph), 133.6 (s, Ph), 135.8 [d, ^2J(C,P) = 35.5 Hz, Ph], 197.1 [d, ^2J(C,P) = 7.1 Hz, *cis*-CO], 198.0 [d, ^2J(C,P) = 27.2 Hz, *trans*-CO], 208.4 [d, ^1J(C,P) = 7.1 Hz, C(O)P] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 153.5 [s$_{\mathrm{Sat}}$, ^1J(P,W) = 278.5 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 575 (s), 599 (s), 695 (s), 801 (m), 843 (m), 1096 (m), 1260 (s), 1447 (s), 1647 (s), 1931 (s), 2072 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 232.0 (1.314) nm. MS (EI, 70 eV): *m/z* (%) = 694.1 (16) [M]$^+$. C$_{22}$H$_{31}$O$_8$PSi$_2$W (694.46): calcd. C 38.05, H 4.50; found C 38.17, H 5.28.

Reaction of Complex 4a with Alkyllithium Reagents. Representative Protocol for the Synthesis of 5b′ by Using *n*BuLi: A solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.2 mL, 0.32 mmol) was added dropwise to a stirred solution of complex **4a** (196 mg, 0.3 mmol) and 12-crown-4 (51 µL, 0.32 mmol) in THF (6 mL) at –78 °C to give a red solution. The mixture was warmed to 0 °C in a cooling bath. After removing the solvent, the residue was washed with *n*-pentane at room temperature to give **5b′** as a yellow-orange solid. Yield: 216 mg (0.269 mmol, 90%); m.p. 186 °C (dec.). ^{1}H NMR ([D$_8$]THF): δ = 0.21 [s, 18 H, 2 Si(CH$_3$)$_3$], 0.33 [d, ^2J(H,P) = 3.6 Hz, 1 H, PCH], 3.61 (s, 16 H,12-crown-4), 7.16 (m, 3 H, Ph), 7.49 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 2.03 [s, Si(CH$_3$)$_3$], 2.07 [s, Si(CH$_3$)$_3$], 17.13 [d, ^1J(C,P) = 24.5 Hz, PCH], 69.08 (s, 12-crown-4), 127.76 [d, J(C,P) = 1.2 Hz, Ph], 127.9 [d, J(C,P) = 12.2 Hz, Ph], 128.3 [d, J(C,P) = 1.9 Hz, Ph], 146.8 [d, ^2J(C,P) = 48.5 Hz, Ph], 200.1 [d$_{\mathrm{Sat}}$, ^2J(C,P) = 3.2, ^1J(C,W) = 125.4 Hz, *cis*-CO], 204.3 [d, ^2J(C,P) = 19.4 Hz, *trans*-CO], 227.5 [d, ^1J(C,P) = 18.1 Hz, Ph*C*P] ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = –23.3 [s$_{\mathrm{Sat}}$, ^1J(P,W) = 167.8 Hz] ppm. ^{7}Li{^{1}H} NMR ([D$_8$]THF): δ = –0.24 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 581 (s), 766 (s), 843 (m), 1022 (s), 1087 (s), 1136 (s), 1243 (s), 1918 (s), 2056 (s) cm^{-1}. C$_{27}$H$_{40\mathrm{Li}}$O$_{10}$PSi$_2$W (802.53): calcd. C 40.41, H 5.02; found C 40.52, H 5.02.

Complexes 6a,b: A solution of *n*-butyllithium in hexane (1.6 M, 0.2 mL, 0.32 mmol) was added dropwise to a stirred solution of complex **4a** (196 mg, 0.3 mmol) and 12-crown-4 (51 µL, 0.32 mmol) in THF at –78 °C. After warming the reaction mixture to –60 °C (20 min) in a cooling bath, benzoyl chloride (37.2 µL, 0.32 mmol) was added dropwise. The mixture was left to warm up in a cooling bath for 1.5 h. The solvent was evaporated, *n*-pentane (5 mL) was added, and the precipitate was filtered off. After evaporation of the solvent, the residue was crystallized from *n*-pentane at low temperatures to give a mixture of **6a**,**b** (**6a**/**6b** = 2:1) as a yellow solid. Yield: 130 mg (0.18 mmol, 60%). IR (KBr): $\tilde{\nu}$ = 573 (s), 593 (s), 705 (m), 854 (m), 1017 (s), 1042 (s), 1162 (s), 1254 (s), 1746 (s), 1942 (s), 2073 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 235.0 (1.355), 380.50 (0.223) nm. MS (EI, 70 eV): *m/z* (%) = 724.0 (4) [M]$^+$. C$_{26}$H$_{29}$O$_7$PSi$_2$W (724.49): calcd. C 43.10, H 4.03; found C 43.12, H 4.29. **6a**: ^{1}H NMR (CDCl$_3$): δ = 0.28 [s, 18 H, 2 Si(CH$_3$)$_3$], 1.41 [d, ^2J(H,P) = 8.9 Hz, 1 H, PCH], 7.31 (m, 3 H, Ph′), 7.5 (m, 2 H, Ph), 7.54 (m, 1 H, Ph), 7.60 (m, 2 H, Ph), 8.0 (m, 2 H, Ph′) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 1.76 [s, Si(CH$_3$)$_3$], 1.80 [s, Si(CH$_3$)$_3$], 32.5 [d, ^1J(C,P) = 13.6 Hz, PCH], 128.6 (s, Ph), 128.8 (s, Ph), 129.0 [d, ^4J(C,P) = 1.3 Hz, Ph], 129.6 [d, ^3J(C,P) = 2.6 Hz, Ph], 130.4 (s, Ph′), 130.0 (s, Ph), 134.2 (s, Ph′), 137.6 [d, ^2J(C,P) = 16.1 Hz, Ph], 164.2 [d, ^3J(C,P) = 9.0 Hz, Ph*C*(O)O], 182.1 [d, ^1J(C,P) = 23.9 Hz, (Ph)(O)*C*=P], 195.4 [d$_{\mathrm{Sat}}$, ^2J(C,P) = 5.2, ^1J(C,W) = 126.1 Hz, *cis*-CO], 198.4 [d, ^2J(C,P) = 31.0 Hz, *trans*-CO] ppm. ^{31}P NMR (CDCl$_3$): δ = 163.5 [d$_{\mathrm{Sat}}$, ^2J(P,H) = 8.9, ^1J(P,W) = 267.0 Hz] ppm. **6b**: ^{1}H NMR (CDCl$_3$): δ = 0.28 [s, 18 H, 2 Si(CH$_3$)$_3$], 2.64 [d, ^2J(H,P) = 18.3 Hz, 1 H, PCH], 7.35 (m, 3 H, Ph′), 7.47 (m, 2 H, Ph), 7.56 (m, 1 H, Ph), 7.61 (m, 2 H, Ph), 8.08 (m, 2 H, Ph′) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 1.67 [d, Si(CH$_3$)$_3$], 1.71 [s, Si(CH$_3$)$_3$], 22.4 [d, ^1J(C,P) = 31.0 Hz, PCH], 128.6 [d, ^4J(C,P) = 1.9 Hz, Ph], 129.1 (s, Ph′), 129.5 (s, Ph′), 129.9 [d, ^3J(C,P) = 2.6 Hz, Ph], 130.3 (s, Ph), 130.5 (s, Ph′), 134.1 (s, Ph′), 137.4 [d, ^2J(C,P) = 14.2 Hz, Ph], 163.5 [d, ^3J(C,P) = 11.6 Hz, Ph*C*(O)O], 181.4 [d, ^1J(C,P) = 21.9 Hz, (Ph)(O)*C*=P], 195.5 [d$_{\mathrm{Sat}}$, ^2J(C,P) = 5.2, ^1J(C,W) = 126.1 Hz, *cis*-CO], 197.3 [d, ^2J(C,P) = 31.6 Hz, *trans*-CO] ppm. ^{31}P NMR (CDCl$_3$): δ = 165.8 [d$_{\mathrm{Sat}}$, ^2J(P,H) = 17.8, ^1J(P,W) = 267.0 Hz] ppm.

Complex 7: Methyl iodide (26 µL, 0.42 mmol) was added dropwise to a stirred solution of complex **5b′** (0.3 mmol) in THF (prepared as described above) at –60 °C. The mixture was left to warm up with stirring in a cooling bath for 1.5 h. The solvent was evaporated in vacuo, and the residue was subjected to column chromatography (–20 °C, petroleum ether/diethyl ether = 10:0.5). The product obtained was crystallized from *n*-pentane at –50 °C to give **7** as a yellow solid. Yield: 99 mg (0.156 mmol, 52%); m.p. 94 °C. ^{1}H NMR (CDCl$_3$): δ = 0.15 [s, 9 H, Si(CH$_3$)$_3$], 0.38 [s, 9 H, Si(CH$_3$)$_3$], 1.14 [d, ^2J(H,P) = 10.2 Hz, 1 H, PCH], 2.15 [d, ^2J(H,P) = 6.2 Hz, 3 H, PCH$_3$], 7.52 (m, 2 H, Ar), 7.61 (m, 1 H, Ph), 8.03 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 3.58 [d, ^3J(C,P) = 2.6 Hz, Si(CH$_3$)$_3$], 3.65 [d, ^3J(C,P) = 2.6 Hz, Si(CH$_3$)$_3$], 16.70 [d, ^1J(C,P) = 1.3 Hz, PCH], 20.5 [d, ^1J(C,P) = 26.5 Hz, PCH$_3$], 129.3 (s, Ph), 129.38 [d, ^3J(C,P) = 1.3 Hz, Ph], 133.86 (s, Ph), 136.1 [d, ^2J(C,P) = 41.4 Hz, Ph], 197.8 [d$_{\mathrm{Sat}}$, ^2J(C,P) = 5.8, ^1J(C,W) = 126.7 Hz, *cis*-CO], 198.6 [d, ^2J(C,P) = 21.3 Hz, *trans*-CO], 208.6 [d, ^1J(C,P) = 7.1 Hz, Ph*C*(O)P] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 7.03 [s$_{\mathrm{Sat}}$, ^1J(P,W) = 223.8 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 576. (s), 598 (s), 772 (m), 835 (s), 862 (s), 1253 (s), 1652 (s), 1936 (s), 2069 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 231.5 (1.461), 249.0 (1.294), 350.5 (0.059) nm. MS (EI, 70 eV): *m/z* (%) = 634.0 (4) [M]$^+$. C$_{20}$H$_{27}$O$_6$PSi$_2$W (634.41): calcd. C 37.86, H 4.29; found C 37.78, H 4.60.

Complex 10: Trimethylsilyl chloride (77 µL, 0.6 mmol) was added dropwise to a stirred solution of complex **5b′** (0.3 mmol) in THF (prepared as described above) at –60 °C. The mixture was left to warm up with stirring in a cooling bath for 1.5 h, and then water (11 µL, 0.6 mmol) was added. The solvent was evaporated in vacuo, and the residue was subjected to column chromatography (–20 °C, petroleum ether, petroleum ether/diethyl ether = 10:0.5) to give **10** as yellow oil, which formed a crystalline material at 4 °C in 2 weeks. Yield: 121 mg (0.195 mmol, 65%); m.p. 41 °C; R_f = 0.37 (petroleum ether). ^{1}H NMR (CDCl$_3$): δ = 0.20 [s, 9 H, Si(CH$_3$)$_3$], 0.39 [s, 9 H, Si(CH$_3$)$_3$], 0.60 [d, ^2J(H,P) = 7.0 Hz, 1 H, PCH], 6.77 [d, ^1J(H,P) = 319.5 Hz, 1 H, PH], 7.53 (m, 2 H, Ph), 7.64 (m, 1 H, Ph), 7.89 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 0.36 [d, ^3J(C,P) = 2.6 Hz, Si(CH$_3$)$_3$], 2.93 [d, ^3J(C,P) = 3.2 Hz, Si(CH$_3$)$_3$], 12.2 [d, ^1J(C,P) = 7.1 Hz, PCH], 127.9 (s, Ph), 129.3 (s, Ph), 134.6 (s, Ph), 137.0 [d, ^2J(C,P) = 40.0 Hz, Ph], 196.5 [d$_{\mathrm{Sat}}$, ^2J(C,P) = 5.8, ^1J(C,W) = 126.1 Hz, *cis*-CO], 198.5 [d, ^2J(C,P) = 21.9 Hz, *trans*-CO], 208.0 [d, ^1J(C,P) = 12.9 Hz, Ph*C*(O)P] ppm. ^{31}P NMR (CDCl$_3$): δ = –39.8 [dd$_{\mathrm{Sat}}$, ^1J(P,H) = 319.5, ^1J(P,W) = 212.3, ^2J(P,H) = 7.6 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 573 (s), 627 (s), 854 (m), 1255 (s), 1652 (s), 1936 (s), 2071 (s) cm^{-1}. UV/Vis (*n*-pentane): λ (abs.) = 234.0 (1.448), 347.0 (0.053) nm. MS (EI, 70 eV): *m/z* (%) = 619.9 (17) [M]$^+$. C$_{19}$H$_{25}$O$_6$PSi$_2$W (620.38): calcd. C 36.78, H 4.06; found C 37.22, H 4.28.

Crystallographic Data: Crystal structure data for complex **4a** (C$_{19}$H$_{24}$ClO$_6$PSi$_2$W): *M* = 654.83, orthorhombic, $P2_12_12_1$, *a* =

9.5057(2), b = 10.8944(2), c = 24.2214(5) Å, V = 2508.34(9) Å^3, Z = 4, $d_{\text{calcd.}}$ = 1.734 Mg/m^3, μ = 4.901 mm^{-1}, T = 123(2) K. A total of 21607 reflections were measured with a Nonius–KappaCCD diffractometer by using monochromated Mo-K_α radiation (λ = 0.71073 Å), 5981 of which were unique (R_{int} = 0.0598). A semi-empirical absorption correction from equivalents was applied (min./max. transmission 0.1615/0.3087). The structure was solved by Patterson methods and refined by full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: R_1 = 0.0293, wR_2 = 0.0584. R values (all data): R_1 = 0.0369, wR_2 = 0.0607, min./max. electron difference –1.360/1.090 e/Å^3. Crystal-structure data for complex **6a** ($C_{26}H_{29}O_7PSi_2W$): M = 724.49, monoclinic, $P2_1/n$, a = 10.4754(2), b = 20.3304(4), c = 28.9785(5) Å, V = 6083.8(2) Å^3, Z = 8, $d_{\text{calcd.}}$ = 1.582 Mg/m^3, μ = 3.968 mm^{-1}, T = 123(2) K. A total of 56829 reflections were measured with a Nonius–KappaCCD diffractometer by using monochromated Mo-K_α radiation (λ = 0.71073 Å), of which 14413 were unique (R_{int} = 0.0671). A semi-empirical absorption correction from equivalents was applied (min./max. transmission 0.1993/0.2998). The structure was solved by Patterson methods and refined with full-matrix least-squares fitting against F^2 for all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: R_1 = 0.0311, wR_2 = 0.0675. R values (all data): R_1 = 0.0431, wR_2 = 0.0700, min./max. electron difference –1.454/1.190 e/Å^3. CCDC-785125 (**4a**) and -785126 (**6a**) 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.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (STR 411/26-1) and the COST action cm0802 "PhoSciNet" is gratefully acknowledged.

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[1] a) S. Jockusch, N. J. Turro, *J. Am. Chem. Soc.* **1998**, *120*, 11773–11777; b) W. Sluggett, P. F. McGarry, I. V. Koptyug, N. J. Turro, *J. Am. Chem. Soc.* **1996**, *118*, 7367–7372; c) U. Kolczak, G. Rist, K. Dietliker, J. Wirz, *J. Am. Chem. Soc.* **1996**, *118*, 6477–6489.

[2] G. Becker, W. Becker, O. Mundt, *Phosphorus Sulfur Silicon Relat. Elem.* **1983**, *14*, 267–283.

[3] a) A. Marinetti, F. Mathey, *Phosphorus Sulfur Silicon Relat. Elem.* **1984**, *19*, 311–317; b) J.-J. Brunet, R. Chauvin, B. Donnadieu, E. Thepaut, *J. Organomet. Chem.* **1998**, *579*, 198–205.

[4] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy. From Organophosphorus to Phospha-organic Chemistry*, Wiley, Chichester, **1998**, pp. 1–14.

[5] a) E. Lindner, A. Thasitis, *Z. Anorg. Allg. Chem.* **1974**, *409*, 35–44; b) E. Lindner, R. D. Merkle, W. Hiller, R. Fawzi, *Chem. Ber.* **1986**, *119*, 659–668.

[6] a) J.-J. Brunet, A. Caperucci, R. Chauvin, B. Donnadieu, *J. Organomet. Chem.* **1997**, *533*, 79–81; b) H. Adams, N. A. Bailey, P. Blenkiron, M. J. Morris, *J. Chem. Soc., Dalton Trans.* **1997**, 3589–3598.

[7] a) A. Özbolat, G. von Frantzius, J. M. Pérez, M. Nieger, R. Streubel, *Angew. Chem.* **2007**, *119*, 9488–9491; *Angew. Chem. Int. Ed.* **2007**, *46*, 9327–9330; b) A. Özbolat, G. von Frantzius, W. Hoffbauer, R. Streubel, *Dalton Trans.* **2008**, 2674–2676.

[8] M. Braun in *The Chemistry of Organolithium Compounds*, part 2 (Eds: Z. Rappoport, I. Marek), Wiley, **2004**, pp. 829–900.

[9] a) K. Tamao, A. Kawachi, M. Asahara, A. Toshimitsu, *Pure Appl. Chem.* **1999**, *71*, 393–400; b) G. Molev, D. Bravo-Zhivotovskii, M. Karni, B. Tumanskii, M. Botoshansky, Y. Apeloig, *J. Am. Chem. Soc.* **2006**, *128*, 2784–2785.

[10] a) R. Streubel, M. Bode, J. M. Pérez, G. Schnakenburg, J. Daniels, M. Nieger, P. G. Jones, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1163–1171; b) S. Fankel, H. Helten, G. von Frantzius, G. Schnakenburg, J. Daniels, V. Chu, C. Muller, R. Streubel, *Dalton Trans.* **2010**, *39*, 3472–3481.

[11] R. Streubel, A. Öbolat-Schön, M. Bode, J. Daniels, G. Schnakenburg, F. Teixidor, C. Vinas, A. Vaca, A. Pepiol, P. Farras, *Organometallics* **2009**, *28*, 6031–6035.

[12] R. Streubel, S. Priemer, F. Ruthe, P. G. Jones, *Eur. J. Inorg. Chem.* **2000**, 1253–1259.

[13] L. Duan, G. Schnakenburg, R. Streubel, unpublished results.

[14] E. Lindner, M. Steinwand, S. Hoehne, *Chem. Ber.* **1982**, *115*, 2478–2486.

[15] H. Grützmacher, J. Geier, D. Stein, T. Ott, H. Schönberg, R. H. Sommerlade, S. Boulmaaz, J.-P. Wolf, P. Murer, T. Ulrich, *Chimia* **2008**, *62*, 18–22.

[16] a) G. Becker, M. Rössler, W. Uhl, *Z. Anorg. Allg. Chem.* **1981**, *473*, 7–19; b) G. Becker, M. Rössler, E. Schneider, *Z. Anorg. Allg. Chem.* **1978**, *439*, 121–133; c) G. Becker, W. Schwarz, N. Seidler, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, *612*, 72–82.

[17] G. Becker, M. Birkhahn, W. Massa, W. Uhl, *Angew. Chem.* **1980**, *92*, 756–757; G. Becker, M. Birkhahn, W. Massa, W. Uhl, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 741–742.

[18] Similar proposals have been made previously for the nonligated lithium monoacylphosphanides (ref.[16]) and for the lithiated derivatives of transition-metal-substituted acylphosphanes, see: L. Weber, K. Reizig, M. Frebel, *Chem. Ber.* **1986**, *119*, 1857–1867.

[19] The configuration is given for the free phosphaalkene ligand.

[20] a) F. Mathey, *Angew. Chem.* **2003**, *115*, 1616–1643; F. Mathey, *Angew. Chem. Int. Ed.* **2003**, *42*, 1578–1604; b) T. C. Klebach, R. Lourens, F. Bickelhaupt, *J. Organomet. Chem.* **1981**, *210*, 211–221.

Received: October 20, 2010