New Access to and Reactions of P-Functional Acylphosphane Complexes

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Dedicated to Professor O. I. Kolodiazhnyi

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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

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 $\Pi^{[2]}$ 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 $\{[M] = ML_n, R = \text{organic substituent}, X = RC(O) \text{ or group 16 or 18 element}\}.$

Because of the known stabilizing ability of transitionmetal 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

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E-mail: r.streubel@uni-bonn.de phospha-enolate complex **5b**. The ambident reactivity of this compound was demonstrated in reactions with electrophiles such as PhC(O)Cl, MeI, and Me₃SiCl, which yielded *O*-substituted complexes **6a**,**b** and **8a**,**b** and *P*-substituted complex **7**.

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 ¹³C NMR spectra of complexes **4a–f** appeared at $\delta = 202.3-216.6$ 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 singlecrystal X-ray diffraction studies (Figure 1). The phosphorus



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).

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]

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 ($\mathbf{R} = \mathbf{Me}$, *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** [$\delta_{\rm P} = -19.0$ ppm, ${}^{1}J(P,W) = 179.2 \text{ Hz}$ 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 $\delta = -23.8$ ppm with a ¹J(P,W) coupling constant of 167.8 Hz (³¹P NMR spectrum, THF, 25 °C). The ¹³C{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 [$\delta_{\rm C}$ = 227.5 ppm, ¹J(C,P) = 18.1 Hz] than the starting material, complex 4a [$\delta_{\rm C}$ = 202.3 ppm, ${}^{1}J(C,P) = 1.3$ 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 ³¹P NMR spectrum at $\delta = 163.5$ 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 $(\eta^1$ -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 ³¹P NMR spectrum at $\delta = 7.03$ ppm [¹*J*(P,W) = 223.8 Hz, ²*J*(P,H) = 6.3 Hz, ²*J*(P,H) = 5.0 Hz]. In the ¹H NMR spectrum the *P*-methyl protons appeared as a doublet at $\delta = 2.15$ 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 ³¹P NMR resonances similar to those of **6a**,**b** [$\delta_{\rm P}$ = 106.9 ppm, ${}^{1}J(P,W) = 256.8 \text{ Hz}, {}^{2}J(P,H) = 17.8 \text{ Hz and } \delta_{P} = 101.9 \text{ ppm},$ ${}^{1}J(P,W) = 258.1 \text{ Hz}, {}^{2}J(P,H) = 8.9 \text{ Hz}$ and thus were assigned to the O-silylated alkylidenephosphane complexes **8a,b.** A minor product **9** (ca. 15%) with $\delta_{\rm P} = 120.7$ ppm $[{}^{1}J(P,W) = 251.7 \text{ Hz}, {}^{2}J(P,H) = 19.0 \text{ Hz}]$ 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 Me₃SiCl.

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

Conclusions

It has been shown that the in situ reactions of phosphinidenoid complexes 2a,b and phosphanide complexes 2c,dwith 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 transitionmetal 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 (¹H: 300.13 MHz; ¹³C: 75.5 MHz; ³¹P: 121.5 MHz) by using CDCl₃ or [D₈]THF (complex 5b') as solvent and internal secondary standard; chemical shifts are referenced to tetramethylsilane (¹H, ¹³C: Ξ = 19.867187 MHz) and 85% H₃PO₄ $(^{31}P: \Xi = 40.480742 \text{ MHz})$. Mass spectra were recorded with a MAT 95 XL Finnigan (EI, 70 eV, ¹⁸⁴W) 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 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.). ¹H NMR (CDCl₃): $\delta = 0.34$ [s, 9 H, Si(CH₃)₃], 0.35 [d, ⁴*J*(H,P) = 0.5 Hz, 9 H, Si(CH₃)₃], 1.98 [d, ²*J*(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. ¹³C{¹H} NMR (CDCl₃): $\delta = 3.4$ [d, ³*J*(C,P) = 2.5 Hz, Si(CH₃)₃], 3.62 [d, ³*J*(C,P) = 3.2 Hz, Si(CH₃)₃], 30.5 [d, ¹*J*(C,P) = 14.2 Hz, PCH], 129.0 (s, Ph), 129.8 (s, Ph), 134.1 (s, Ph), 135.1 [d, ²*J*(C,P) = 46.5 Hz, Ph], 196.6 [d_{Sat}, ²*J*(C,P) = 6.4, ¹*J*(C,W) = 127.4 Hz, cis-CO], 198.2 [d, ²*J*(C,P) = 31.6 Hz, trans-CO], 202.3 [d, ¹*J*(C,P) = 1.3 Hz, C(O)P] ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 113.8$ [s_{Sat}, ¹*J*(P,W) = 267.0 Hz] ppm. IR (KBr): $\tilde{v} = 574$ (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]⁺. C₁₉H₂₄CIO₆PSi₂W (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.). ¹H NMR (CDCl₃): $\delta = 0.29$ [s, 9 H, Si(CH₃)₃], 0.34 [d, ⁴*J*(H,P) = 0.5 Hz, 9 H, Si(CH₃)₃], 1.89 [d, ²*J*(H,P) = 9.2 Hz, 1 H, PCH], 2.75 [d, ³*J*(H,P) = 5.1 Hz, 3 H, CH₃] ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 3.14$ [d, ³*J*(C,P) = 3.2 Hz, Si(CH₃)₃], 3.34 [d, ³*J*(C,P) = 3.2 Hz, Si(CH₃)₃], 26.71 [d, ¹*J*(C,P) = 49.7 Hz, PCH], 28.38 [d, ²*J*(C,P) = 18.7 Hz, CH₃], 196.46 [d_{Sat}, ²*J*(C,P) = 6.4, ¹*J*(C,W) = 126.8 Hz, *cis*-CO], 197.9 [d, ²*J*(C,P) = 30.4 Hz, *trans*-CO], 209.9 [d, ¹*J*(C,P) = 1.9 Hz, C(O)P] ppm. ³¹P{¹H} NMR $\begin{array}{l} ({\rm CDCl}_3): \delta = 115.4 \; [{\rm s}_{{\rm Sat}}, {}^1J({\rm P},{\rm W}) = 260.6 \; {\rm Hz}] \; {\rm ppm. \; MS \; (EI, \; 70 \; eV):} \\ m/z \; (\%) = \; 592.0 \; (8) \; [{\rm M}]^+. \; {\rm IR \; (KBr): \; } \tilde{\nu} = \; 543 \; ({\rm s}), \; 567 \; ({\rm s}), \; 597 \; ({\rm s}), \\ 682 \; ({\rm m}), \; 859 \; ({\rm s}), \; 1003 \; ({\rm m}), \; 1119 \; ({\rm m}), \; 1254 \; ({\rm s}) \; 1347 \; ({\rm s}), \; 1702 \; ({\rm s}), \\ 1949 \; ({\rm s}), \; 2075 \; ({\rm s}) \; {\rm cm^{-1}}. \; {\rm UV/Vis \; (n-pentane): λ (abs.) = \; 230.0 \; (1.5), \\ 305.0 \; (0.153), \; 346.5 \; (0.100) \; {\rm nm. \; C}_{14}{\rm H}_{22}{\rm ClO}_6{\rm PSi}_2{\rm W} \; (592.76): \; {\rm calcd.} \\ {\rm C \; 28.37, \; H \; 3.74; \; found \; {\rm C \; 28.58, \; H \; 3.90.} \end{array}$

Complex 4c: Yellow solid; yield: 378 mg (0.59 mmol, 74%); m.p. 58 °C (dec.). ¹H NMR (CDCl₃): $\delta = 0.21$ [d, ⁴J(P,H) = 1.9 Hz, 9 H, Si(CH₃)₃], 0.38 [s, 9 H, Si(CH₃)₃], 1.90 [d, ${}^{2}J$ (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. ¹³C{¹H} NMR (CDCl₃): $\delta = 2.56$ [dd, ³J(C,P) = 2.9, ³J(C,F) = 1.8 Hz, Si(CH₃)₃], 3.44 [d, ${}^{3}J(C,P)$ = 2.3 Hz, Si(CH₃)₃], 32.6 [dd, ${}^{1}J(C,P) = 11.3$, ${}^{2}J(C,F) = 4.1$ Hz, PCH], 128.98 [d, ${}^{4}J(C,P) =$ 1.1 Hz, Ph], 129.36 [d, ${}^{3}J(C,P) = 6.5$ Hz, Ph], 134.3 (s, Ph), 135.8 $[dd, {}^{2}J(C,P) = 40.5, {}^{3}J(C,F) = 2.3 Hz, Ph], 196.31 [dd_{Sat}, {}^{2}J(C,P) =$ 7.1, ${}^{3}J(C,F) = 2.9$, ${}^{1}J(C,W) = 128.5$ Hz, *cis*-CO], 198.0 [d, ${}^{2}J(C,P)$ = 29.2 Hz, trans-CO], 207.3 [d, ${}^{1}J(C,P)$ = 13.1 Hz, C(O)P] ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 193.27 [d_{Sat}, {}^{1}J(P,W) = 281.0, {}^{1}J(P,F)$ = 858.3 Hz] ppm. ¹⁹F{¹H} NMR (CDCl₃): δ = -113.4 [d_{Sat}, ${}^{2}J(F,W) = 11.2$, ${}^{1}J(F,P) = 858.3$ Hz] ppm. IR (KBr): $\tilde{v} = 568$ (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]⁺. C₁₉H₂₄FO₆PSi₂W (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.). ¹H NMR (CDCl₃): $\delta = 0.21$ [d, ⁴J(H,P) = 1.7 Hz, 9 H, Si(CH₃)₃], 0.31 [s, 9 H, Si(CH₃)₃], 1.92 [d, ${}^{2}J$ (H,P) = 12.1 Hz, 1 H, PCH], 2.61 [dd, ${}^{3}J(H,P) = 3.6$, ${}^{4}J(H,F) = 2.6$ Hz, 3 H, CH₃] ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 2.35$ [dd, ³*J*(C,P) = 2.6, ⁴*J*(C,F) = 2.6 Hz, Si(CH₃)₃], 2.97 [d, ${}^{3}J(C,P)$ = 1.9 Hz, Si(CH₃)₃], 28.03 [dd, ${}^{1}J(C,P) = 42.0, {}^{2}J(C,F) = 1.9 \text{ Hz}, \text{ PCH}, 31.56 \text{ [dd, } {}^{1}J(C,P) = 11.6,$ ${}^{2}J(C,F) = 7.7$ Hz, CH₃], 195.47 [dd_{Sat}, ${}^{2}J(C,P) = 7.1$, ${}^{3}J(C,F) = 3.2$, ${}^{1}J(C,W) = 128.5 \text{ Hz}, \text{ cis-CO}, 197.8 \text{ [d, } {}^{2}J(C,P) = 27.8 \text{ Hz}, \text{ trans-}$ CO], 216.6 [dd, ${}^{1}J(C,P) = 19.6$, ${}^{2}J(C,F) = 13.5$ Hz, C(O)P] ppm. ³¹P{¹H} NMR (CDCl₃): δ = 189.4 [d_{Sat}, ¹J(P,W) = 275.9, ¹J(P,F) = 841.8 Hz] ppm. ¹⁹F{¹H} NMR (CDCl₃): δ = -121.8 [d_{Sat}, ${}^{1}J(F,W) = 11.2, {}^{1}J(P,F) = 841.8 \text{ Hz} \text{ ppm. IR (KBr): } \tilde{v} = 567 \text{ (m)},$ 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]⁺. C14H22FO6PSi2W (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%). ¹H NMR (CDCl₃): δ = 0.21 [s, 9 H, Si(CH₃)₃], 0.32 [s, 9 H, Si(CH₃)₃], 2.06 [d, ${}^{2}J$ (H,P) = 11.7 Hz, 1 H, PCH], 3.60 [d, ${}^{3}J$ (H,P) = 13.0 Hz, 3 H, POCH₃], 7.51 [t, ${}^{3}J(H,H)$ = 7.7 Hz, 2 H, Ph], 7.62 $[t, {}^{3}J(H,H) = 7.7 Hz, 1 H, Ph], 8.05 [d, {}^{3}J(H,H) = 7.4 Hz, 2 H, Ph]$ ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 2.9$ [d, ³J(C,P) = 3.1 Hz, Si(CH₃)₃], 3.4 [d, ${}^{3}J(C,P) = 2.8$ Hz, Si(CH₃)₃], 27.3 [d, ${}^{1}J(C,P) =$ 3.6 Hz, PCH], 56.3 [d, ${}^{2}J(C,P) = 3.3$ Hz, POCH₃], 128.9 (s, Ph), 129.0 (s, Ph), 133.6 (s, Ph), 135.3 [d, ${}^{2}J(C,P) = 36.5$ Hz, Ph], 196.9 $[d_{Sat}, {}^{2}J(C,P) = 7.1, {}^{1}J(C,W) = 118.2 \text{ Hz}, cis-CO], 198.0 \text{ [d}, {}^{2}J(C,P)$ = 26.8 Hz, trans-CO], 208.8 [d, ${}^{1}J(C,P)$ = 12.1 Hz, C(O)P] ppm. ³¹P{¹H} NMR (CDCl₃): δ = 154.1 [s_{Sat}, ¹J(P,W) = 273.4 Hz] ppm. IR (KBr): $\tilde{v} = 505$ (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]⁺. C₂₀H₂₇O₇PSi₂W (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%). ¹H NMR (CDCl₃): $\delta = 0.17$ [s, 9 H, Si(CH₃)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, OCH₃), 3.59 (m, 2 H, CH₂OCH₃), 3.91 (m, 2 H, POCH₂), 7.52 [t, ${}^{3}J(H,H) = 7.9$ Hz, 2 H, Ph], 7.61 [t, ${}^{3}J(H,H) = 7.7$ Hz, 1 H, Ph], 8.17 [d, ${}^{3}J(H,H) = 8.1$ Hz, 2 H, Ph] ppm. ${}^{13}C{}^{1}H$ NMR (CDCl₃): $\delta = 2.8 \text{ [d, } {}^{3}J(\text{C},\text{P}) = 3.1 \text{ Hz}, \text{ Si}(\text{CH}_{3})_{3}\text{]}, 3.4 \text{ [d, } {}^{3}J(\text{C},\text{P}) = 2.8 \text{ Hz},$ Si(CH₃)₃], 27.5 [d, ${}^{1}J(C,P) = 5.2$ Hz, PCH], 58.3 (s, POCH₃), 68.1 $[d, {}^{3}J(C,P) = 3.2 \text{ Hz}, CH_{2}OCH_{3}], 71.3 [d, {}^{2}J(C,P) = 8.4 \text{ Hz},$ POCH₂], 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, ${}^{2}J(C,P)$ = 7.1 Hz, *cis*-CO], 198.0 [d, ${}^{2}J(C,P) = 27.2 \text{ Hz}, \text{ trans-CO}, 208.4 \text{ [d, }{}^{1}J(C,P) = 7.1 \text{ Hz}, C(O)P$ ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = 153.5 [s_{Sat}, {}^{1}J(P,W) = 278.5 Hz]$ ppm. IR (KBr): $\tilde{v} = 575$ (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]⁺. C₂₂H₃₁O₈PSi₂W (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 μ L, 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 npentane at room temperature to give 5b' as a yellow-orange solid. Yield: 216 mg (0.269 mmol, 90%); m.p. 186 °C (dec.). ¹H NMR $([D_8]THF): \delta = 0.21 [s, 18 H, 2 Si(CH_3)_3], 0.33 [d, {}^2J(H,P) = 3.6 Hz,$ 1 H, PCH], 3.61 (s, 16 H, 12-crown-4), 7.16 (m, 3 H, Ph), 7.49 (m, 2 H, Ph) ppm. ¹³C{¹H} NMR ([D₈]THF): $\delta = 2.03$ [s, Si(CH₃)₃], 2.07 [s, Si(CH₃)₃], 17.13 [d, ${}^{1}J(C,P) = 24.5$ Hz, PCH], 69.08 (s, 12crown-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, ${}^{2}J(C,P) =$ 48.5 Hz, Ph], 200.1 [d_{Sat}, ${}^{2}J(C,P) = 3.2$, ${}^{1}J(C,W) = 125.4$ Hz, *cis*-CO], 204.3 [d, ${}^{2}J(C,P) = 19.4$ Hz, trans-CO], 227.5 [d, ${}^{1}J(C,P) =$ 18.1 Hz, PhCP] ppm. ³¹P{¹H} NMR ([D₈]THF): $\delta = -23.3$ [s_{Sat}, ${}^{1}J(P,W) = 167.8 \text{ Hz}$ ppm. ${}^{7}\text{Li}\{{}^{1}\text{H}\}$ NMR ([D₈]THF): $\delta = -0.24$ (s) ppm. IR (Nujol): $\tilde{v} = 581$ (s), 766 (s), 843 (m), 1022 (s), 1087 (s), 1136 (s), 1243 (s), 1918 (s), 2056 (s) cm^{-1} . $C_{27}H_{40Li}O_{10}PSi_2W$ (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 μ L, 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): $\tilde{v} = 573$ (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]⁺. C₂₆H₂₉O₇PSi₂W (724.49): calcd. C 43.10, H 4.03; found C 43.12, H 4.29. 6a: ¹H NMR (CDCl₃): $\delta = 0.28$ [s, 18 H, 2 Si(CH₃)₃], 1.41 $[d, {}^{2}J(H,P) = 8.9 \text{ Hz}, 1 \text{ H}, \text{ PCH}], 7.31 (m, 3 \text{ H}, \text{Ph}'), 7.5 (m, 2 \text{ H}, 1 \text{ H})$ Ph), 7.54 (m, 1 H, Ph), 7.60 (m, 2 H, Ph), 8.0 (m, 2 H, Ph') ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 1.76$ [s, Si(CH₃)₃], 1.80 [s, Si(CH₃)₃], $32.5 \text{ [d, } {}^{1}J(\text{C},\text{P}) = 13.6 \text{ Hz}, \text{ PCH]}, 128.6 \text{ (s, Ph)}, 128.8 \text{ (s, Ph)}, 129.0 \text{ ($ $[d, {}^{4}J(C,P) = 1.3 \text{ Hz}, \text{ Ph}], 129.6 [d, {}^{3}J(C,P) = 2.6 \text{ Hz}, \text{ Ph}], 130.4 (s, c)$ Ph'), 130.0 (s, Ph), 134.2 (s, Ph'), 137.6 [d, ²*J*(C,P) = 16.1 Hz, Ph], 164.2 [d, ${}^{3}J(C,P) = 9.0$ Hz, PhC(O)O], 182.1 [d, ${}^{1}J(C,P) = 23.9$ Hz, (Ph)(O)C=P], 195.4 [d_{Sat}, ${}^{2}J(C,P) = 5.2$, ${}^{1}J(C,W) = 126.1$ Hz, *cis*-CO], 198.4 [d, ²*J*(C,P) = 31.0 Hz, *trans*-CO] ppm. ³¹P NMR



(CDCl₃): $\delta = 163.5 [d_{Sat}, {}^{2}J(P,H) = 8.9, {}^{1}J(P,W) = 267.0 Hz] ppm.$ **6b** $: {}^{1}H NMR (CDCl₃): <math>\delta = 0.28 [s, 18 H, 2 Si(CH_3)_3], 2.64 [d, {}^{2}J(H,P) = 18.3 Hz, 1 H, PCH], 7.35 (m, 3 H, Ph'), 7.47 (m, 2 H, Ph), 7.56 (m, 1 H, Ph), 7.61 (m, 2 H, Ph), 8.08 (m, 2 H, Ph') ppm. {}^{13}C{}^{1}H} NMR (CDCl_3): <math>\delta = 1.67 [d, Si(CH_3)_3], 1.71 [s, Si(CH_3)_3], 22.4 [d, {}^{1}J(C,P) = 31.0 Hz, PCH], 128.6 [d, {}^{4}J(C,P) = 1.9 Hz, Ph], 129.1 (s, Ph'), 129.5 (s, Ph'), 129.9 [d, {}^{3}J(C,P) = 2.6 Hz, Ph], 130.3 (s, Ph), 130.5 (s, Ph'), 134.1 (s, Ph'), 137.4 [d, {}^{2}J(C,P) = 14.2 Hz, Ph], 163.5 [d, {}^{3}J(C,P) = 11.6 Hz, PhC(O)O], 181.4 [d, {}^{1}J(C,P) = 21.9 Hz, (Ph)(O)C=P], 195.5 [d_{Sat}, {}^{2}J(C,P) = 5.2, {}^{1}J(C,W) = 126.1 Hz, cis-CO], 197.3 [d, {}^{2}J(C,P) = 31.6 Hz, trans-CO] ppm. {}^{31}P NMR (CDCl_3): <math>\delta = 165.8 [d_{Sat}, {}^{2}J(P,H) = 17.8, {}^{1}J(P,W) = 267.0 Hz] ppm.$

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. ¹H NMR (CDCl₃): $\delta = 0.15$ [s, 9 H, Si(CH₃)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, PCH₃], 7.52 (m, 2 H, Ar), 7.61 (m, 1 H, Ph), 8.03 (m, 2 H, Ph) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 3.58 [d, ³J(C,P) = 2.6 Hz, Si(CH₃)₃], 3.65 [d, ${}^{3}J(C,P) = 2.6$ Hz, Si(CH₃)₃], 16.70 [d, ${}^{1}J(C,P) = 1.3 \text{ Hz}, \text{ PCH}], 20.5 \text{ [d, } {}^{1}J(C,P) = 26.5 \text{ Hz}, \text{ PCH}_{3}], 129.3$ (s, Ph), 129.38 [d, ${}^{3}J(C,P) = 1.3$ Hz, Ph], 133.86 (s, Ph), 136.1 [d, ${}^{2}J(C,P) = 41.4 \text{ Hz}, \text{ Ph}], 197.8 [d_{Sat}, {}^{2}J(C,P) = 5.8, {}^{1}J(C,W) =$ 126.7 Hz, *cis*-CO], 198.6 [d, ${}^{2}J(C,P) = 21.3$ Hz, *trans*-CO], 208.6 [d, ${}^{1}J(C,P) = 7.1 \text{ Hz}, PhC(O)P] \text{ ppm. } {}^{31}P{}^{1}H} \text{ NMR (CDCl_3): } \delta = 7.03$ $[s_{Sat}, {}^{1}J(P,W) = 223.8 \text{ Hz}] \text{ ppm. IR (KBr): } \tilde{v} = 576. \text{ (s), } 598 \text{ (s), } 772$ (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]⁺. C₂₀H₂₇O₆PSi₂W (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). ¹H NMR (CDCl₃): $\delta = 0.20$ [s, 9 H, Si(CH₃)₃], 0.39 [s, 9 H, Si(CH₃)₃], 0.60 [d, ${}^{2}J$ (H,P) = 7.0 Hz, 1 H, PCH], 6.77 [d, ${}^{1}J$ (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. ¹³C{¹H} NMR (CDCl₃): $\delta = 0.36$ [d, ³J(C,P) = 2.6 Hz, Si(CH₃)₃], 2.93 [d, ${}^{3}J(C,P) = 3.2$ Hz, Si(CH₃)₃], 12.2 [d, ${}^{1}J(C,P) = 7.1$ Hz, PCH], 127.9 (s, Ph), 129.3 (s, Ph), 134.6 (s, Ph), 137.0 [d, ${}^{2}J(C,P) = 40.0$ Hz, Ph], 196.5 [d_{Sat}, ${}^{2}J(C,P) = 5.8$, ${}^{1}J(C,W)$ = 126.1 Hz, *cis*-CO], 198.5 [d, ${}^{2}J(C,P)$ = 21.9 Hz, *trans*-CO], 208.0 $[d, {}^{1}J(C,P) = 12.9 \text{ Hz}, PhC(O)P] \text{ ppm. } {}^{31}P \text{ NMR (CDCl_3): } \delta =$ $-39.8 \, [dd_{Sat}, {}^{1}J(P,H) = 319.5, {}^{1}J(P,W) = 212.3, {}^{2}J(P,H) = 7.6 \, Hz]$ ppm. IR (KBr): $\tilde{v} = 573$ (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]⁺. C₁₉H₂₅O₆PSi₂W (620.38): calcd. C 36.78, H 4.06; found C 37.22, H 4.28.

Crystallographic Data: Crystal structure data for complex **4a** $(C_{19}H_{24}ClO_6PSi_2W)$: M = 654.83, orthorhombic, $P2_12_12_1$, a =

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9.5057(2), b = 10.8944(2), c = 24.2214(5) Å, V = 2508.34(9) Å³, Z = 4, $d_{\text{calcd.}}$ = 1.734 Mg/m³, 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 semiempirical 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/Å³. Crystal-structure data for complex **6a** ($C_{26}H_{29}O_7P$ -Si₂W): M = 724.49, monoclinic, $P2_1/n$, a = 10.4754(2), b =20.3304(4), c = 28.9785(5) Å, V = 6083.8(2) Å³, Z = 8, $d_{calcd.} =$ 1.582 Mg/m^3 , $\mu = 3.968 \text{ mm}^{-1}$, T = 123(2) K. A total of 56829 reflections were measured with a Nonius-KappaCCD diffractometer by using monochromated Mo- K_a radiation ($\lambda = 0.71073$ 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/ Å³. 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.

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