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Phosphinidenoid Complexes

Strong Evidence for a Transient Phosphinidenoid Complex**

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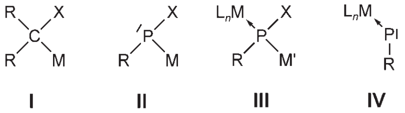
Dedicated to Professor Gottfried Huttner on the occasion of his 70th birthday

Carbenoids (**I**, Scheme 1) are versatile reactive intermediates in organic synthesis.[1] This situation does not hold for related phosphinidenoids (**II**) and mononuclear transition-metal complexes thereof (**III**). Their potential 1,1-elimination products however—terminal phosphinidene complexes (**IV**)—are important and well-established building blocks in organophosphorus chemistry, and these complexes are accessible from a variety of precursors.[2–4]

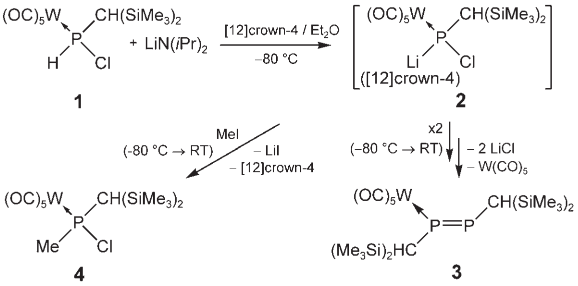


Scheme 1. Carbenoids (**I**), phosphinidenoids (**II**) and complexes thereof (**III**), and phosphinidene complexes (**IV**). R = ubiquitous organic substitutents; M′ = main-group metal; X = halogen; ML$_n$ = transition metal complex fragment.

First attempts to generate mononuclear phosphinidenoid complexes (**III**) as precursors of terminal phosphinidene complexes (**IV**) date back to 1975, when Huttner et al. attempted chlorine/lithium exchange on RPLi$_2$ (R = Ph) transition-metal complexes, which led to trigonal-planar dinuclear μ$_2$-phosphinidene complexes instead.[5] Although in subsequent studies chlorine/lithium exchange on RPCl$_2$ (R = alkyl) complexes could be controlled to yield diphosphene and diphosphane complexes,[6,7] strong evidence for transient formation of phosphinidenoid complexes [L$_n$M{RP(M′)X}] was not obtained. Formation of a phosphirane complex however (that could have formed from reaction of a transient phosphinidene complex with the solvent, THF) suggested the existence of [L$_n$M{RP(M′)X}] as an intermediate.[8]

For the Cu^I-catalyzed reaction of 7-phosphanorbornadiene complexes with alkenes, a reaction discovered by Mathey and Marinetti in 1984,[9], Lammertsma et al.[10] proposed that the phosphinidenoid [W(CO)$_5${PhP(Cu)Cl}] was the intermediate on the basis of calculations. In turn, Mathey and Compain generated the short-lived phosphanide complex [W(CO)$_5${PhP(F)}]$^-$ which acts as a strong anionic nucleophile; [Cs([18]crown-6)]$^+$ was most probably the counterion.[11] We gained access to [W(CO)$_5${RP(CNLi)([12]crown-4)}][12] (R = CH(SiMe$_3$)$_2$), the first structural isomer of a phosphinidenoid complex (**III**). Herein, we present a method to generate phosphinidenoid–transition-metal complexes under very mild conditions that can undergo selective substitution reactions and behave like a terminal phosphinidene complex.

Deprotonation of chloro(organo)phosphane complex **1**[13] with lithium diisopropylamide (LDA) in the presence of [12]crown-4 selectively generated complex **2** (Scheme 2).



Scheme 2. Generation and reactions of complex **2**.

Warming up the reaction mixture to ambient temperature in the absence of any trapping reagents led to *E*-diphosphene complex **3**[14] and a product that is unstable at room temperature and which has a signal in the ^{31}P NMR spectrum at $\delta =$ 347.7 ppm (Et$_2$O, product ratio 4:1) with small phosphorus–tungsten coupling constants of 143.7 and 103.0 Hz. These NMR data are similar to those of the dinuclear *Z* diphosphene complex [L$_n$W(Mes)P=P(Mes)WL$_n$] (Mes = 2,4,6-trimethylphenyl, L$_n$ = (CO)$_5$; $\delta = 313.6$ ppm, CDCl$_3$, J(W,P) = 116 Hz).[14] Similar NMR spectroscopic data for a dinuclear *Z* diphosphene–tungsten complex were also reported by Yoshifuji et al. ($\delta = 332.0$ ppm; CDCl$_3$, J(W,P) = 145.0 and 116.0 Hz).[15] In contrast, the *E* diphosphene complex [L$_n$W(R)P=P(R)WL$_n$] (R = CH(SiMe$_3$)$_2$, L$_n$ = (CO)$_5$) has a

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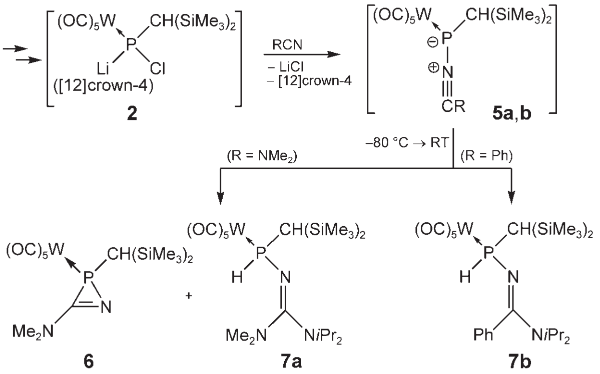
signal at $\delta = 342.2$ ppm with a coupling constant of $^{1}J(\mathrm{W,P}) = 268$ Hz ($CDCl_3$).[14]

To show that the phosphinidenoid complex **2** had formed, we examined its generation in the presence of methyl iodide and thus obtained *P*-methyl-substituted chlorophosphane complex **4** (Scheme 2) as the sole phosphorus-containing product, which showed without doubt the existence of intermediate complex **2**.

To investigate alternative routes to 2*H*-azaphosphirene complexes,[16] we reacted complex **2** with dimethylcyanamide, which gave 2*H*-azaphosphirene complex **6** selectively [17] if diluted solutions of **2** were used. At higher concentrations, a mixture of **6** and *N*-iminophosphane complex **7a** was obtained (ratio 1:1; Scheme 3). Complex **7a** is not a follow-up product of complex **6**, as reaction of isolated complex **6** with diisopropylamine at ambient temperature did not yield complex **7a**. Although complex **6** might stem from a formal [2+1] cycloaddition, the formation of complex **7a** hints at nitrilium phosphane-ylid **5a** as intermediate precursor for all final products. Complex **5a** can undergo valence isomerization to give **6** and/or regioselective 1,2-addition of diisopropylamine, formed during deprotonation of **1**, to yield **7a**. This was further supported by the reaction with benzonitrile, as in this case complex **7b** was obtained as the major product; the corresponding 2*H*-azaphosphirene complex was not observed.

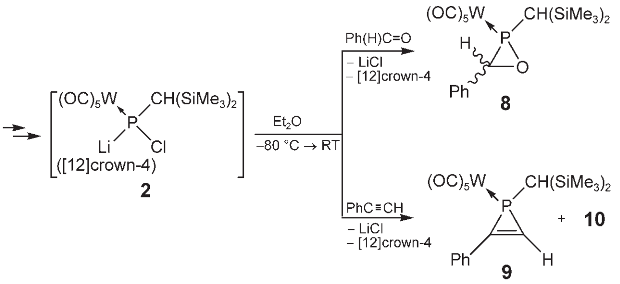


Scheme 3. Reaction of complex **2** with nitriles.

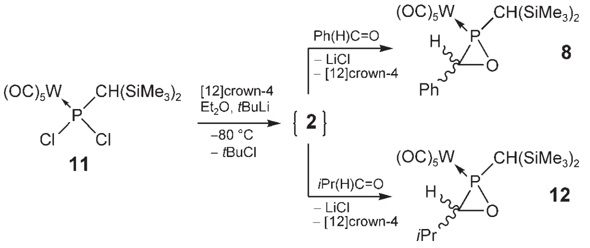
The formation of phosphinidenoid complex **2** in the presence of benzaldehyde and phenylacetylene lead to heterocyclic complexes **8**[18] and **9**,[18] respectively (Scheme 4). When phenylacetylene was used as reagent, another product **10** was observed which could not be isolated (products **9**/**10** in a ratio of 5:1) and had a signal in the ^{31}P NMR spectrum at $\delta = -78.3$ ppm and coupling constants of $^{1}J(\mathrm{W,P}) = 235.2$ Hz and $^{1}J(\mathrm{P,H}) = 354.8$ Hz.

Chlorine/lithium exchange of dichloro(organo)phosphane complex **11**[19] using *tert*-butyllithium at low temperature in the presence of [12]crown-4 along with benzaldehyde or butyraldehyde gave easier access to the phosphinidenoid complex **2**, yielding selectively oxaphosphirane complexes **8**[18] and **12**, respectively (Scheme 5).

All complexes were purified by column chromatography and fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. In addition, complexes **6** and **7a** were investigated by single-crystal diffraction studies, but the data shall not be discussed herein (see Supporting Information).



Scheme 4. Reaction of complex **2** with Ph(H)CO or PhC≡CH.



Scheme 5. Simpler access to complex **2**.

To gain some insight into the bonding of intermediate complex **2**, density-functional theory (DFT)[20] calculations were carried out on **2** and, for comparison, also on **2′**, for which the crown ether is absent. The gas-phase DFT structure of complex **2′** (Figure 1) has a lithium atom at phosphorus with a short Li···O contact (2.005 Å) to the oxygen atom of a carbonyl ligand, which is distorted by this interaction. The distance between the lithium and chlorine atoms is 3.774 Å, which is larger than the sum of covalent radii (2.33 Å) but below the sum of van der Waals radii taken from the solid state (4.00 Å).[21] The positive charge at lithium (and to a small extent at phosphorus) is counterbalanced by the negative charge at chlorine and the interacting oxygen of the carbonyl ligand. The structure of **2′** can be compared to the DFT-calculated structure of the fluoro-

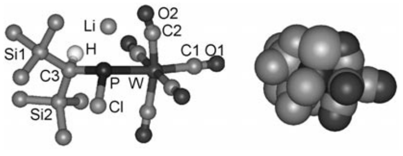


Figure 1. DFT gas-phase structure of **2′** (without [12]crown-4; B3LYP/6-311g(d,p), LanL2DZ at W); ball-and-stick model (left) and space-filling model (right). Selected bond lengths [Å] and angles [°]: W-P 2.631, P-Cl 2.160, P-Li 2.416, Cl-Li 3.774, P-C3 1.890, W-C1 2.024, W-C2 1.987, C1-O1 1.149, C2-O2 1.181; W-C2-O2 164.71, Cl-P-W 112.31, Cl-P-C3 103.65, W-P-C3 122.21, $\Sigma\sphericalangle$P 338.17°. Charges from a natural population analysis (Mulliken charges in brackets) of Hartree–Fock orbitals: P +0.201 (+0.203), W −0.933 (+0.773), Cl −0.401 (−0.358), C3 −1.502 (−1.198), C1 +0.688 (−0.028), O1 −0.578 (−0.288), C2 +0.680 (+0.064), O2 −0.743 (−0.429), Li +0.906 (+0.599).

(methyl)phosphanide complex [$(OC)_5Cr\{PF(Me)\}]^-$, for which Mathey and Compain also found a significant bending of the equatorial CO ligands towards phosphorus; the HOMO was ascribed to the pronounced phosphorus lone pair.[11]

Coordination of the [12]crown-4 moiety to lithium in **2′** significantly increases the distance between phosphorus and lithium atoms from 2.416 (in **2′**) to 2.652 Å (in **2**) and the P−Cl bond from 2.160 (**2′**) to 2.217 Å (**2**), whereas the distortion of the equatorial carbonyl ligand vanishes (Figure 2). The combination of a decreased W-P-C angle (122.21° vs. 112.03° in **2**) and a decreased sum of bond angles at P (from 338.17 (**2′**) to 323.91°) can be interpreted as the formation of a pronounced, stereochemically active electron lone pair at phosphorus. The natural population analysis showed that the positive charge at phosphorus is somewhat larger in **2** than in **2′**. As the Cl−P bond length increases, the Cl–Li distance decreases accordingly (from 3.774 (**2′**) to 3.465 Å), which can be understood as the beginnings of the generation and expulsion of lithium chloride.

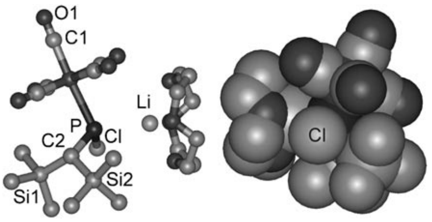


Figure 2. Gas-phase DFT structure of complex **2**; ball-and-stick model (left) and space-filling model (right). Selected bond lengths [Å] and angles [°]: W-P 2.652, P-Cl 2.217, P-Li 2.652, P-C2 1.905, Cl-Li 3.465, W-C1 2.011, C1-O1 1.154; Cl-P-W 110.43, Cl-P-C2 101.45, W-P-C2 112.03, $\Sigma\measuredangle$P 323.91°. Charges from a natural population analysis (Mulliken charges in brackets) of Hartree–Fock orbitals: P +0.248 (+0.162), W −0.963 (+0.733), Cl −0.462 (−0.460), C2 −1.515 (−1.227), C1 +0.678 (−0.039), O1 −0.606 (−0.314), Li +0.853 (+0.816).

We have shown that a transient phosphinidenoid complex can be formed selectively by deprotonation or chlorine/lithium exchange reactions under very mild conditions, and reactivity was illustrated by the synthesis of heterocyclic three-membered rings. DFT calculations showed that additional binding of the phosphinidenoid complex to [12]crown-4 leads to a more positively charged and more pyramidal phosphorus, which has a weaker contact to lithium and chlorine than without the crown ether.

Experimental Section

All the reactions were carried out under an atmosphere of purified and dried argon using standard Schlenk techniques. Solvents were dried over sodium wire and distilled under argon. NMR data were recorded on a Bruker DMX 300 spectrometer at 30 °C using $CDCl_3$ as solvent and internal standard; shifts are given relative to tetramethylsilane (^{13}C: 75.5 MHz, ^{29}Si: 59.6 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded on a Kratos MS 50 spectrometer (EI, 70 eV). Melting points were determined using a Büchi apparatus, with samples sealed in capillaries under argon. Selected NMR and MS data are given below.

4: Compound **1** (300 mg, 0.545 mmol), [12]crown-4 (0.089 mL, 0.545 mmol), and MeI (0.034 mL, 0.55 mmol) were dissolved in Et_2O (11 mL) in a cooled (−35 °C) dropping funnel. This solution was then added dropwise to a cooled (−80 °C) suspension of freshly prepared LDA (58.9 mg, 0.55 mmol) in Et_2O (5.5 mL) and the reaction mixture was stirred for 20 h. The suspension was allowed to stand, LiI was removed by filtration, and the solvent removed under reduced pressure (ca. 0.01 bar). The residue was dissolved in petroleum ether/diethyl ether 1:1 (2 mL) and subjected to column chromatography (neutral SiO_2, −20 °C, petroleum ether). Complex **4** was obtained as a colorless solid upon evaporation of the fourth fraction. Yield: 24 mg (78%); m.p. 80 °C (decomp); ^{1}H NMR: $\delta = 2.47$ (d, 3H, ^{2}J(P,H) = 3.78 Hz, CH_3), 1.77 (d, 1H, ^{2}J(P,H) = 8,97 Hz, PCH($SiMe_3$)$_2$), 0.38 ppm (s, 18H, SiMe_3); ^{13}C{^{1}H} NMR: $\delta = 198.4$ (^{2}J(P,C) = 30.1 Hz, CO_{trans}), 196.2 (^{2}J(P,C) = 7.4 Hz, CO_{cis}), 31.1 (^{1}J(P,C) = 13.6 Hz, PCH) 30.8 (^{1}J(P,C) = 18.4 Hz, CH$_3$), 2.5 (^{3}J(P,C) = 2.9 Hz, SiMe_3), 2.0 ppm (^{3}J(P,C) = 3.6 Hz, SiMe_3); ^{31}P{^{1}H} NMR: $\delta =$ 105.4 ppm (s_{sat}, ^{1}J(P,W) = 273.4 Hz); MS: m/z (%): 564.0 (28) [M^+].

6 and **7a**: Compound **1** (550 mg, 1 mmol), [12]crown-4 (0.179 mL, 1.1 mmol), and dimethylcyanamide (0.407 mL, 5 mmol) were dissolved in Et_2O (3 mL) and added to a cooled (−30 °C) dropping funnel. This solution was then added dropwise to a cooled (−80 °C) solution of freshly prepared LDA (117.8 mg, 1.1 mmol) in Et_2O (7 mL) and the reaction mixture was stirred for 3 h until the reaction bath had warmed to 0 °C. The orange solution was filtered to remove LiCl and the solvent was removed under reduced pressure (ca. 0.01 bar). The residue was dissolved in 2×2 mL diethyl ether and subjected to column chromatography (neutral Al_2O_3, −20 °C, petroleum ether). Complex **7a** was obtained as the first fraction using 80 mL of eluent (petroleum ether/diethyl ether 95:5). Complex **6** was obtained as the second fraction using 40 mL of eluent (petroleum ether/diethyl ether 95:5) and the third fraction using 50 mL of eluent (petroleum ether/diethyl ether 50:50). The second and third fraction were combined. Compounds **6** and **7a** were obtained as off-white and colourless solids, respectively, after evaporation of solvent. **6**: Yield: 169 mg (29%); m.p. 78 °C (decomp); ^{1}H NMR: $\delta = 3.31$ (br s, 3H, NCH_3), 3.15 (br s, 3H, NCH_3), 0.73 (d, 1H, ^{2}J(P,H) = 2.90 Hz, PCH), 0.32 (s, 9H, SiMe_3), 0.20 ppm (s, 9H, SiMe_3); ^{13}C{^{1}H} NMR: $\delta = 197.6$ (d, ^{2}J(P,C) = 34.3 Hz; CO_{trans}), 195.4 (d, ^{2}J(P,C) = 9.1; CO_{cis}), 176.1 (d, ^{2}J(P,C) = 12.3 Hz; PNC), 39.9 (s, NCH$_3$), 35.8 (s, NCH$_3$), 29.6 (d, ^{1}J(P,C) = 26.5 Hz, PCH), 1.08 (d, ^{3}J(P,C) = 3.6 Hz, SiMe_3), 0.10 ppm (d, ^{3}J(P,C) = 2.9 Hz, SiMe_3); ^{31}P{^{1}H} NMR: $\delta = -65.7$ ppm (s_{sat}, ^{1}J(P,W) = 293.7 Hz). MS: m/z (%): 584 (10) [M^+]. **7a**: Yield: 180 mg (26%); m.p. 83 °C (decomp); ^{1}H NMR: $\delta = 7.60$ (dd, 1H, ^{1}J(P,H) = 306.7 Hz, ^{3}J(H,H) = 2.55 Hz, PH), 3.88 (m_c, 2H, N(C(H)Me$_2$)$_2$)), 2.88 (s, 6H, CN(CH_3)$_2$), 1.29 (d, 6H, ^{3}J(H,H) = 6.99 Hz, N(C(H)(CH_3)$_2$)), 1.26 (d, 6H, ^{3}J(H,H) = 6.89 Hz, N(C(H)-(CH_3)$_2$), 0.80 (dd, 1H, ^{2}J(P,H) = 4.34 Hz, ^{3}J(H,H) = 2.55 Hz, PCH), 0.30 (s, 9H, SiMe_3), 0.21 ppm (s, 9H, SiMe_3); ^{13}C{^{1}H} NMR: $\delta = 199.7$ (d, ^{2}J(P,C) = 20.7 Hz; CO_{trans}), 197.5 (d, ^{2}J(P,C) = 7.4 Hz; CO_{cis}), 160.1 (d, ^{2}J(P,C) = 8.7 Hz; PNC), 48.7 (s, N(CHMe$_2$)$_2$), 40.0 (d, ^{2}J(P,C) = 1.9 Hz; N(CH$_3$)$_2$), 22.6 (s, N(C(H)(CH$_3$)$_2$)), 20.9 (s, N(C(H)(CH$_3$)$_2$)), 20.1 (d, ^{1}J(P,C) = 23.0 Hz, CH(SiMe$_3$)$_2$), 1.7 (d, ^{3}J(P,C) = 2.6 Hz, SiMe_3), 0.0 ppm (d, ^{3}J(P,C) = 2.6 Hz, SiMe_3); ^{31}P{^{1}H} NMR: $\delta = -3.4$ ppm (s_{sat}, ^{1}J(W,P) = 246.7 Hz). MS: m/z (%): 685 (5) [M^+].

7b: Yellow solid; yield: 532 mg (74%); m.p. 89 °C (decomp); ^{1}H NMR: $\delta = 7.46$ (m, 3H, Ph), 7.28 (m, 1H, Ph), 7.11 (m, 1H, Ph), 6.33 (dd, 1H, ^{1}J(P,H) = 315.3 Hz, ^{3}J(H,H) = 5.00 Hz, PH), 4.45 (br s, 1H, N(C(H)Me$_2$)$_2$), 3.69 (m_c, 1H, N(C(H)Me$_2$)$_2$), 1.52 (d, 3H, ^{3}J(H,H) = 6.70 Hz, N(C(H)(CH_3)$_2$)), 1.43 (d, 3H, ^{3}J(H,H) = 6.80 Hz, N(C(H)(CH_3)$_2$)), 1.07 (d, 6H, ^{3}J(H,H) = 6.70 Hz, N(C(H)(CH_3)$_2$)), 0.97 (dd, 1H, ^{2}J(P,H) = 8.12 Hz, ^{3}J(H,H) = 5.00 Hz, PCH), 0.28 (s, 9H, SiMe$_3$), 0.05 ppm (s, 9H, SiMe$_3$); ^{13}C{^{1}H} NMR: $\delta = 200.3$ (d, ^{2}J(P,C) = 13.6 Hz; CO_{trans}), 197.6 (d, ^{2}J(P,C) = 7.8 Hz; CO_{cis}), 160.5 (d, ^{2}J(P,C) = 9.1 Hz; PNC), 134.1 (d, ^{3}J(P,C) = 12.9 Hz; *i*-Ph-C), 128.2

(s, Ph-C), 128.0 (s, Ph-C), 127.7 (s, Ph-C), 125.5 (d, $J(\mathrm{P,C}) = 25.9$ Hz; Ph-C), 21.4 (br d, *i*Pr-$\mathrm{C}H_3$), 20.3 (d, $^1J(\mathrm{P,C}) = 12.9$ Hz, $C\mathrm{H(SiMe_3)_2}$), 20.2 (s, *i*Pr-$C\mathrm{H_3}$), 20.0 (s, *i*Pr-$C\mathrm{H_3}$) 1.9 (d, $^3J(\mathrm{P,C}) = 1.9$ Hz, $\mathrm{Si}Me_3$), 0.0 ppm (d, $^3J(\mathrm{P,C}) = 2.9$ Hz, $\mathrm{Si}Me_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: $\delta = 8.9$ ppm ($\mathrm{s_{sat}}$, $^1J(\mathrm{W,P}) = 256.9$ Hz). MS: m/z (%): 718 (24) $[M^+]$.

8 and **12**: A solution of *tert*-butyllithium (0.3 mL, 1.5 M, 0.46 mmol) was added dropwise to a solution of **11** (200 mg, 0.31 mmol) in diethyl ether (10 mL), [12]crown-4 (0.051 mL, 0.31 mmol) and benzaldehyde (0.032 mL, 0.31 mmol) or butyraldehyde (0.027 mL, 0.31 mmol) at −80 °C with stirring. The solution was stirred for 90 minutes while gently warming to 0 °C. The solvents were then removed in vacuo (ca. 10^{-2} bar) and the residues extracted with *n*-pentane (20 mL). The product was purified by column chromatography ($\mathrm{Al_2O_3}$, −30 °C, petroleum ether). After evaporation, the raw product was washed with a small amount of *n*-pentane at −20 °C. **8**: Yield: 102 mg (0.18 mmol, 44 %); for further data see Ref. [18]. **12**: Yield: 106 mg (53 %); m.p. 86 °C (decomp); ^{1}H NMR: $\delta = 2.75$ (d, 1 H, $^2J(\mathrm{P,H}) = 9.8$ Hz, $\mathrm{POC}H$), 1.60 (m, 1 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 1.21 (d, 3 H, $^2J(\mathrm{H,H}) = 6.7$ Hz, $\mathrm{C}H_3\mathrm{O}$), 1.17 (d, 3H ,$^2J(\mathrm{H,H}) = 6.5$ Hz, $\mathrm{C}H_3$), 1.05 (m, 1 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$), 0.30 (s, 9 H, $\mathrm{SiMe_3}$), 0.25 ppm (s, 9 H, $\mathrm{SiMe_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR: $\delta = 195$ (d, $^2J(\mathrm{P,C}) = 33.6$ Hz, $C\mathrm{O_{trans}}$), 193.4 (d, $^2J(\mathrm{P,C}) = 8.4$, $C\mathrm{O_{cis}}$), 62.9 (d, $J(\mathrm{P,C}) = 28.7$ Hz, $\mathrm{P}C\mathrm{O}$), 28.7 (d, $C\mathrm{H(SiMe_3)_2}$, $J(\mathrm{P,C}) = 17.1$ Hz), 29.0 (d, $C\mathrm{HCH_3}$, $J(\mathrm{P,C}) = 3.3$ Hz), 17.4 (d, $J(\mathrm{P,C}) = 11.6$ Hz, $\mathrm{CH}C\mathrm{H_3}$), 17.2 (s, $\mathrm{CH}C\mathrm{H_3}$), 0.0 (d, $J(\mathrm{P,C}) = 2.6$ Hz, $\mathrm{Si}Me_3$), −0.4 ppm (d, $J(\mathrm{P,C}) = 4.5$ Hz, $\mathrm{Si}Me_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: $\delta = 31.9$ ppm ($\mathrm{s_{sat}}$, $^1J(\mathrm{W,P}) = 298.8$ Hz); MS: m/z (%): 586 (10) $[M^+]$.

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