# Coordination of Phosphanide and Trialkylsilylphosphanide Ligands at Pentacarbonyltungsten Fragments: An NMR Spectroscopic and Structural Investigation

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ABSTRACT: *Trialkylsilylphosphanide ligands as pentacarbonyltungsten adducts such as the anions $[((CO)_5W)_2P(H)SiR_3]^-$ and $[(CO)_5W\text{-}PHSiR_3]^-$ with R = Me, iPr, and tBu are prepared by the reaction of $(thf)W(CO)_5$ with $MP(H)SiR_3$ or by the metathesis reaction of $((OC)_5W)_2PHLi_2$ with $ClSiR_3$ and characterized by NMR spectroscopy with a focus on $^{183}W$-NMR experiments. The solvent-separated ion pair $(tmeda)K^+ [((OC)_5W)_2P(H)SiiPr_3]^-$ crystallizes as a coordination polymer with a rather large P─Si bond length of 228.1 pm.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:420–425, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20128

## INTRODUCTION

Trialkylsilylphosphanides are widely used ligands in the organometallic synthesis in order to ensure solubility in common organic solvents or to prevent side and decomposition reactions. Sterically hindered trialkylsilyl groups such as $SiiPr_3$ and $SitBu_3$ have been used to stabilize various classes of compounds. Only very few but representative examples are the copper(I) tri(tert-butyl)silylphosphanediide from Wiberg and coworkers [1] and the central $Ca_4P_4$ heterocubane moiety in $(thf)_2Ca_6[PSitBu_3]_4\text{-}[P(H)SitBu_3]_4$ [2]. Furthermore, these demanding trialkylsilyl substituents are able to stabilize unique fragments as, for example, the extraordinary Ga–P–Ga heteroallyl system in dimeric tri(tert-butyl)-silylphosphanediyl gallium tri(tert-butyl)silylphosphanide [3]. The coordination of a pentacarbonyltungsten moiety at the lone pair of phosphorus atom lowers the oligomerization degree and allows the investigation of small but reactive molecules. Bis(tungstenpentacarbonyl) complexes of bis(pentafluorophenyl)phosphanides have been synthesized by Hoge et al. [4]. Furthermore, this $W(CO)_5$ fragments also offer another NMR probe which is directly bonded to the central phosphorus atom, and therefore $^{183}W$ NMR experiments are employed to investigate these complexes. Up to now, $^{183}W$ NMR spectroscopy is not a standard method due to the low receptivity ($1.04 \times 10^{-5}$) and therefore only very few data are available. In addition, most

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of these NMR experiments were performed on heteropolytungstates [5,6] and tungsten-coordinate polyphospazenes [7]. Herein, we describe the synthesis and spectroscopic characterization of trialkylsilylphosphanide ligands as pentacarbonyltungsten complexes such as $Li[((OC)_5W)_2P(H)SiR_3]$ with R = Me, $i$Pr.

## RESULTS AND DISCUSSION

### Synthesis

The synthesis of $(OC)_5W$-$PH_2Li$ starting from $(thf)W(CO)_5$ and $PH_4I$ has been published by Mathey and coworkers [8]. Another access to these compounds is guaranteed by the reaction of $(dme)LiPH_2$ with $(thf)W(CO)_5$ which offers an one-step synthesis for the mono(pentacarbonyltungsten) complex **1** and the bis(pentacarbonyltungsten) compound **2**, depending on the stoichiometry according to Eq. (1). **2** was recently described by Scheer et al. [9]. The reaction of $(dme)LiPH_2$ with $W(CO)_6$ cannot be recommended because it results in the formation of only trace amounts of **1** and **2** as a mixture and is accompanied by the formation of $PH_3$.



$$(1)$$
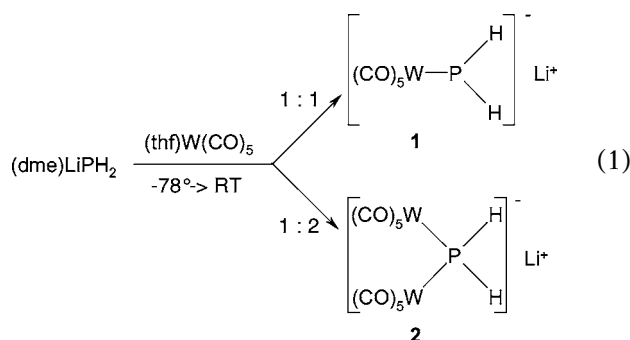
The preparation of the bis(tungstenpentacarbonyl) trialkylsilylphosphanides **3** and **4** can be achieved by the deprotonation reaction (metalation) of the phosphanide complex **2** with $n$BuLi at –78°C and a subsequent addition of $ClSiR_3$ with R = Me and $i$Pr, respectively, according to Eq. (2). The first reaction step results in the formation of a dilithium species which decomposes immediately at room temperature. Therefore, trapping of this intermediate at low temperature with an electrophile such as a chlorotrialkylsilane is mandatory. The lithiation of $(CO)_5W$-$PH_3$ with up to three equivalents of $n$BuLi was already investigated and published by Mathey et al.; the di and trilithium species of the type $(CO)_5WPHLi_2$ and $(CO)_5W$-$PLi_3$ were also not isolated and handled at room temperature and had to be

trapped by subsequent reactions with electrophiles. The sterically hindered trialkylsilylphosphanides **3** (R = Me) and **4** (R = $i$Pr) were characterized by NMR spectroscopy.



$$(2)$$
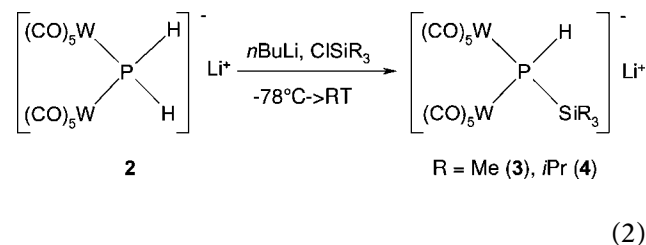
The synthesis of trialkylsilylphosphanides of the type $(CO)_5W$-$PH_{3-x}(SiMe_3)_x$ with $x = 0$ to 3 was also described by Mathey et al., reacting lithiated $(CO)_5$W-$PH_3$ with chlorotrialkylsilanes. As mentioned above, another access is offered by an one-step synthesis using potassium trialkylsilylphoshanides as starting materials. The reaction is very sensitive toward the stoichiometry because one or two $W(CO)_5$ fragments can bind to the phosphorus atom, thus leading to the mono(pentacarbonyltungsten) complexes **5** (with triisopropylsilyl) and **6** (with tritertbutylsilyl) and to the bis(pentacarbonyltungsten) complexes **7** (with triisopropylsilyl) and **8** (with tritertbutylsilyl), according to Eq. (3). The triisopropylsilylphosphanide **7** was characterized by X-ray crystallography.



$$(3)$$
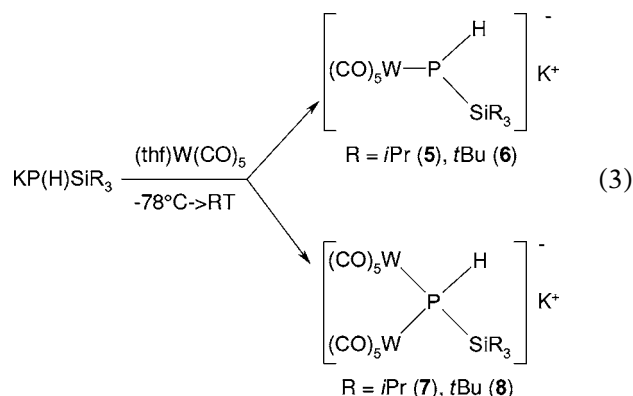
It was also possible to synthesize the bis(trialkylsilyl)phosphanide complex **9** by the reaction of $LiP(SiiPr_3)_2$ with $(thf)W(CO)_5$ according to Eq. (4), starting from $HP(SiiPr_3)_2$, which is lithiated at –78°C with $n$-BuLi.



$$(4)$$
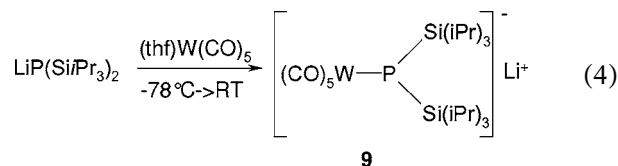
Deprotonation of the above-described phosphanide anions $[((OC)_5W)_2P(H)SiR_3]^-$ can lead to synthetic useful phosphanediides due to the combination of a kinetic protection by demanding trialkylsilyl groups and a blocking of the lone pair at the phosphorus atom by $W(CO)_5$ fragments. The synthetic application of the above-described phosphanides is currently under investigation.

## Molecular Structure of 7

In addition to the solution structures derived from NMR spectroscopic experiments, the molecular structure of **7** was also determined by X-ray crystallography. The molecular structure of **7** and the numbering scheme are represented in Fig. 1. This complex consists of a solvent-separated ion pair with a potassium cation coordinated by a bis-
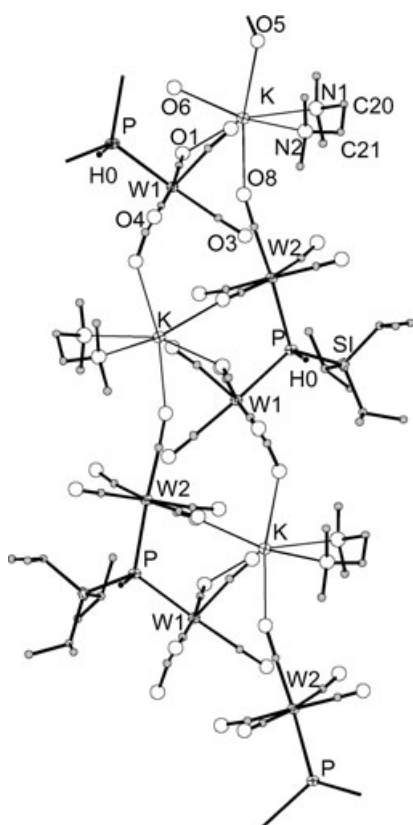


FIGURE 1 View on the coordination polymer and numbering scheme of **7**. The ellipsoids show a probability of 30%. Only the P-bonded hydrogen atoms are drawn with an arbitrary radius, the toluene molecule is not shown for clarity reasons. Selected bond lengths (pm): P1—W1 263.1(3), P1—W2 263.6(3), P1—Si1 228.0(4), P1—H1 155(4); coordination of K1: K1-O1 280.6(10), K1—N1 283.9(10), K1—N2 283.9(10), K1—O2′ 290.4(9), K1—O6′ 282.5(10), K1—O5″ 279.1(9), K1—O8‴ 273.8(8).

(dimethylamino)ethane (TMEDA) molecule and a $[((OC)_5W)_2P(H)SiiPr_3]^-$ anion.

The P1—Si1 bond length of 228 pm is very similar to the values found for the phosphanes $P(SiMe_3)_3$ [10], $HP(SiiPr_3)_2$ (P—Si: 226 pm [11]), and the planar $P(SiiPr_3)_3$ [12] or the complexes $(CO)_5WP(SiMe_3)(C(OEt)(o\text{-}Tol))$ (P—Si: 227 pm; P—W: 251 pm; W—P—Si: 126.8° [13]) and $(OC)_5Cr\text{-}P(SiMe_3)_3$ [14]. The average W—P1 distance of 263 pm is slightly larger compared with the $[((CO)_5W)_2PH_2]^-$ anion [9] (W—P: 258 pm; P—W—P: 126.8°). This fact can be explained by the steric demand of the P-bonded trialkylsilyl group which is also responsible for the smaller W1—P1—W2 bond angle of 117.8°.

Each potassium atom interconnects three $[((OC)_5W)_2P(H)SiiPr_3]^-$ anions and displays a coordination number of seven. The position of the carbonyl ligands *trans* to the phosphanide substituent as well as the coordination of potassium cations at the oxygen atom lead to a lengthening of the C—O bonds; however, a detailed discussion is not appropriate due to rather large standard deviations.

The $(tmeda)K^+$ cations and $[((OC)_5W)_2P(H)\text{-}SiiPr_3]^-$ anions form a one-dimentional coordination polymer in the solid state shielded by the potassium-bound TMEDA ligands and the phosphorus-bound triisopropylsilyl substituents. The chain-like coordination polymer is represented in Fig. 1; however, these chains form a layer structure due to additional contacts between potassium cations and carbonyl oxygen atoms. Between these layers toluene molecules are intercalated and show no short contacts to the coordinatively saturated potassium atoms.

## NMR Spectroscopy

The identity of the pentacarbonyltungsten phosphanides **2–9** results unequivocally from their NMR data which are summarized in Table 1. The $^{31}$P NMR signals of the anions appear at high field ($\delta = -266.7$ to $-409.2$) and are accompanied by $^{183}$W-satellites due to isotopomers having $^{183}$W atoms (I = 1/2, natural abundance 14.28%) in the molecule. The relative intensity of the satellites with respect to the main signal reveals the number of tungsten atoms and thus the number of $W(CO)_5$ units attached to phosphorus (14.28% for one and 24.48% for two tungsten atoms, respectively). The *P*-bonded proton and silyl group, the presence of which is indicated by characteristic coupling patterns and constants $^1J_{PH}$ and $^1J_{PSi}$, complete the coordination sphere of the phosphorus atoms.

**TABLE 1** NMR Data of Compounds **1–9**

|  | $[(OC)_5$ $WPH_2Li$ **1** | $[(OC)_5W]_2$ $PH_2Li$ **2** | $[(OC)_5W]_2$ $PHSiMe_3Li$ **3**[a] | $[(OC)_5W]_2$ $PHSiiPr_3Li$ **4/7** | $(OC)_5$ $WPHSiiPr_3K$ **5** | $(OC)_5$ $WPHSitBu_3K$ **6** | $[(OC)_5W]_2$ $PHSitBu_3K$ **8** | $(OC)_5$ $WP(SiiPr_3)_2Li$ **9** |
|---|---|---|---|---|---|---|---|---|
| $\delta^{31}P$ | −276.3 | −266.7 | −292.1 | −327.3 | −335.1 | −322.8 | −339.6 | −409.2 |
| $^1J_{WP}$ | 73.0 | 146.5 | 138.3 | 140.9 | 77.0 | 85.7 | 141.9 | 136.1 |
| $^1J_{PH}$ | 164.3 | 265.2 | 244.9 | 240.2 | 170.2 | 180.2 | 234.5 |  |
| $\delta^{183}W$ |  | −3349.5 | −3308.8 | −3231.7 |  |  |  |  |
| $\delta^1H\,(PH)$ |  | 1.92 | 0.78 | 1.16 | −1.94 | −1.78 |  |  |
| $\delta^{13}C$ trans-CO |  | 202.7 | 202.2 | 202.4 | 204.8 | 205.2 | 205.9 | 202.4 |
| $^1J_{WC}$ |  | 154.9 | 153.4 | 150.3 |  |  |  | 157.8 |
| $^2J_{PC}$ |  | 12.7 | 11.3 | 11.5 | 10.0 | 10.5 | 13.0 | 11.8 |
| cis-CO |  | 200.4 | 201.4 | 202.6 | 202.9 | 203.4 | 203.7 | 202.6 |
| $^1J_{WC}$ |  | 124.9 | 125.2 | 125.5 |  | 125.0 | 128.6 | 125.3 |
| $^2J_{PC}$ |  | 4.8 | 4.2 | 3.9 | 3.5 | 3.9 | 3.5 | 2.3 |
| $\delta^{29}Si$ |  |  | 12.5 | 17.2 | 23.5 | 25.9 | 22.1 |  |
| $^1J_{PSi}$ |  |  | 17.1 | 5.0 | 58.4 | 70.3 | 8.3 |  |

[a]SiMe$_3$: $\delta^1H = 0.31$, $^3J_{PH} = 5.1$ Hz; $\delta^{13}C = 2.3$, $^2J_{C,P} = 8.3$ Hz, $^3J_{WC} = 48.4$ Hz.

The identity of the anions is further supported by $^{183}W$ NMR spectra of **2–4**, which show a doublet at high field ($\delta = -3231$ to $-3350$) in a range characteristic for phosphanyl-substituted pentacarbonyltungsten complexes [15,16]. The coupling constants $^1J_{WP}$, $^1J_{PH}$, and $^1J_{PSi}$ show the expected dependency on the coordination number of the phosphorus atom [17]. Thus $^1J_{WP}$ value of the three-coordinate phosphorus atom in **1,5,6**, and **9** (73–136 Hz) is smaller than of the four-coordinated phosphorus in **2–4,7,8** (138–146 Hz). The $^1J_{PH}$ couplings show a similar behavior (Table 1). In the case of **5** and **6** the values observed for $^1J_{PSi}$ (70.3 and 58.4 Hz, respectively) are in a range characteristic for silylphosphanes, while much smaller values (5–17 Hz) are found for the P,Si-coupling to the tetra-coordinate phosphorus atom in **3,4/7**, and **8** [17]. In the W(CO)$_5$ unit, the carbon atom of the CO ligand *trans* to the coordinated phosphorus atom shows larger values for $^1J_{WC}$ (150–158 Hz) and $^2J_{PC}$ (10–13 Hz) compared to those of the CO ligands in *cis*-position (124–129 Hz and 2–5 Hz, respectively). $^{13}C$ chemical shifts as well as $^1J_{WP}$ and $^2J_{PC}$ coupling constants compare well to those observed for phosphanyl-substituted pentacarbonyltungsten complexes [15].

## EXPERIMENTAL

### General Remarks

All reactions were performed in an argon atmosphere using standard Schlenk techniques. All solvents were dried with Na/benzophenone and distilled prior to use. NMR spectra were recorded on a Jeol Eclipse-400 spectrometer operating at 400.18 MHz for $^1H$, at 100.63 MHz for $^{13}C$, at 141.99 MHz for $^{31}P$, at 79.50 MHz for $^{29}Si$, and at 16.67 MHz for $^{183}W$. Chemical shifts are given with respect to SiMe$_4$ ($^1H$, $^{13}C$, $^{29}Si$), 85% H$_3$PO$_4$ ($^{31}P$), and 1 M solution of Na$_2$WO$_4$ in D$_2$O ($^{183}W$) as external standards. The $^{183}W$ NMR spectra were recorded using 0.1 m solutions in THF and a low frequency probe. Typically 25,000 scans were applied with pulse width of 30°, acquisition time of 1.3 s, and pulse delay of 1 s, resulting in 16 h total accumulation time. The NMR data are listed in Table 1. Starting materials were prepared by known literature procedures: (dme)LiPH$_2$ [18], KP(H)SiiPr$_3$ [19], KPHSi(tBu)$_3$ [19], HP(SiiPr$_3$)$_2$ [11]; (thf)W(CO)$_5$ was prepared by UV-irradiation of W(CO)$_6$ in THF solution [8].

*Li[(OC)$_5$W-PH$_2$] (1).* A solution of (thf)W(CO)$_5$ (3.3 mmol) in 30 mL of THF was added dropwise at –78°C to a suspension of (dme)LiPH$_2$ (390 mg, 3.0 mmol) in 20 mL of THF. The cooling was removed, and the reaction mixture was allowed to warm slowly up to r.t. The $^{31}P$-NMR spectrum of the solution shows no formation of by products. This solution was used for subsequent reaction steps.

*(thf)$_n$Li[((OC)$_5$W)$_2$PH$_2$] (2).* A solution of (thf)W(CO)$_5$ (22 mmol) in 30 mL THF was slowly added to a suspension of (dme)LiPH$_2$ (1,30 g, 10 mmol) in 50 mL of THF at –78°C. After complete addition the cooling was removed and the the reaction mixture was slowly warmed to r.t. The color of the solutions turned red. The volume of the reaction mixture was reduced to approximately 30 mL. After

cooling to –30°C all solid materials were separated by filtration. The solvent was removed under reduced pressure, and red oil of $[((OC)_5W)_2PH_2]Li$ in THF remains. No side products were detected by ^{31}P-NMR spectroscopy.

*[(W(CO)₅)₂PHSiMe₃]Li (3).* A hexane solution of *n*-BuLi (4.8 mL of a 2.5 M hexane solution) was added dropwise to a solution of $[((OC)_5W)_2PH_2]Li$ (10 mmol) in 50 mL of THF at –78°C. Then $ClSiMe_3$ (1.5 mL, 12 mmol) was added slowly to this refrigerated reaction solution. The mixture was allowed to warm up to room temperature. The volume was reduced to approximately 30 mL. After one day at –30°C all solid materials were removed by filtration. After distillation of the solvent red oil remains as ^{31}P-NMR spectroscopic pure $Li[(W(CO)_5)_2PHSiMe_3]$ with THF.

*(Li/K)[((CO)₅W)₂P(H)SiiPr₃] (4/7) Method a (4):.* A solution of *n*BuLi in hexane (4.8 mL of a 2.5 M solution) and thereafter 2.6 mL of $ClSiiPr_3$ (12 mmol) were added dropwise to a solution of $Li[((CO)_5W)_2PH_2]$ (10 mmol) in 50 mL of THF at –78°C. The reaction mixture was allowed to slowly warm up to r.t., and then its volume was reduced to approximately 30 mL. After storage for one day at –30°C the solid materials were separated by filtration. The ^{31}P-NMR spectrum of the solution showed sideproduct-free $Li[((CO)_5W)_2P(H)SiiPr_3]$ in THF. This solution was used for further synthetic procedures without isolation of the compound.

*Method b (7):* A solution of $(thf)W(CO)_5$ (2.8 mmol) in 10 mL of THF was added slowly to a suspension of $KP(H)SiiPr_3$ (290 mg, 1.27 mmol) in 20 mL of THF at –78°C. This mixture was allowed to warm up to r.t. The color of the solution turned light red. The volume of the reaction mixture was reduced to 10 mL. After storage for one day at –30°C the solid materials were separated by filtration. After removal of the solvent by distillation the residue consists of red oil, which is pure $K[((CO)_5W)_2P(H)SiiPr_3]$ in THF. The addition of tmeda (10 mmol) led to the formation of red crystals at –30°C, which melt at 127°C.

*K[(OC)₅W-P(H)SiiPr₃] (5).* A solution of $(thf)W(CO)_5$ (0.35 mmol) in 5 mL of THF was slowly added to a suspension of $KPHSi(iPr)_3$ (153 mg, 0.67 mmol) in 10 mL of THF at –78°C. The mixture was allowed to warm up to room temperature slowly. The color of the solutions turns light red. The ^{31}P-NMR spectrum of the solution shows 40% product. The solution was directly used for synthesis.

*K[(OC)₅W-P(H)SitBu₃] (6).* A solution of $W(CO)_5THF$ (1.5 mmol) in 5 mL of THF was slowly

added to a suspension of $KP(H)SitBu_3$ (427 mg, 1.58 mmol) in 10 mL of THF at –78°C. The mixture was allowed to warm up to r.t. The color of the solution turned light red. The ^{31}P-NMR spectrum of the solution showed a turnover of 83%. This solution was used without further work-up procedures.

*K[((OC)₅W)₂P(H)SitBu₃] (8).* A solution of $(thf)W(CO)_5$ (1.40 mmol) in 10 mL of THF was slowly added to a suspension of $KP(H)SitBu_3$ (173 mg, 0.64 mmol) in 10 mL of THF at –78°C. The mixture was slowly warmed to r.t. The color of the solution turned to light red. The volume of the reaction mixture was reduced to 10 mL. After storage for one day at –30°C the solid materials were separated by filtration. After removal of the solvent, $K[((OC)_5W)_2P(H)SitBu_3]$ remains as a red and ^{31}P-NMR spectroscopic pure oil.

*Li[(OC)₅W-P(SiiPr₃)₂] (9).* A 2.5 M hexane solution of *n*BuLi (3.5 mL) was added dropwise to a solution of $HP(SiiPr_3)_2$ (2,77 g, 8.0 mmol) in 30 mL of THF at –78°C. After 30 min the mixture was warmed to r.t. The reaction mixture was cooled again to –78°C and slowly treated with a solution of $(thf)W(CO)_5$ (10 mmol) in 30 mL of THF. The continuation of the reaction was observed by ^{31}P-NMR spectroscopy. After a quantitative turnover the solution was used directly for further reaction procedures.

## X-Ray Structure Determination of 7

Data was collected on a STOE IPDS diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) using oil-coated rapidly cooled single crystals. Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 2.

The structure was solved by direct methods with the program SIR97 [20] and refined with the software packages SHELXL-93 and SHELXL-97 [21]. Neutral scattering factors were taken from Cromer and Mann [22] and for the hydrogen atoms from Stewart et al. [23]. All non-hydrogen atoms were refined anisotropically. The carbon atoms of the intercalated toluene molecule were considered isotropically with one common U value, whereas the H atoms of this molecule were not included in the refinement procedures. The P-bound hydrogen atom was considered with a P—H bond length of 155 pm and a 1.2 fold U value of the neighboring P atom. All other hydrogen atoms were considered with a riding model under restriction of ideal tetrahedral symmetry at the corresponding carbon atoms.

**TABLE 2**  Crystallographic Data of **7** as well as Details of the Structure Solution and Refinement Procedures

| Compound | $(tmeda)K\ [((OC)_5W)_2$ $P(H)SiiPr_3]\cdot 1/2\ toluene$ |
|---|---|
| Formula | $C_{28.5}H_{42}KN_2O_{10}PSiW_2$ |
| fw (g mol$^{-1}$) | 1038.48 |
| $T$ (K) | 200 |
| Space group [26] | $P2_1/n$ (no. 14) |
| $a$ (pm) | 832.03(1) |
| $b$ (pm) | 3124.38(5) |
| $c$ (pm) | 1544.44(3) |
| $\beta(°)$ | 100.0336(7) |
| $V$ (nm$^3$) | 3.9535(1) |
| $Z$ | 4 |
| $d_{calcd}$ (g cm$^3$) | 1.738 |
| $\mu$ (mm$^{-1}$) | 6.039 |
| $F(000)$ | 1996 |
| Scan range (°) | $6.4<2\theta<42.0$ |
| Measured data | 25774 |
| Unique data ($R_{int}$) | 4241 (0.104) |
| Absorption. corr. | Numerical |
| Max./min. transmission | 0.865/0.707 |
| Parameters | 392 |
| Restraints | 3 |
| $wR_2^a$ (all data, on $F^2$) | 0.0866 |
| $R_1^a$ (all data) | 0.0699 |
| Data with $I>2\sigma(I)$ | 3166 |
| $R_1[I>2\sigma(I)]$ | 0.0416 |
| GOOF s$^b$ on $F^2$ | 1.03 |
| Residual dens. (e nm$^{-3}$) | 908/−767 |
| CCDC number | CCDC-257202 |

$^a$Definition of the $R$ values: $R_1 = (\Sigma\|F_o|-|F_c\|)/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2)+(0.0385P)^2$, where $P = (F_o^2+2F_c^2)/3$.
$^b s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

## ACKNOWLEDGMENTS

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