Organometallics **2007,** *26,* 4021−4024

Attempted Synthesis of 1-Aza-3λ^3-phospha-1-allenide Complexes: Structure and Reactions of an Unusual Phosphanide Complex

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Received March 13, 2007

Synthesis of the first *N*-lithiated cyanophosphanide complexes **5a**−**c** was achieved via reaction of complex **1** with ^{t}BuLi/12-crown-4, NaN(SiMe$_3$)$_2$/15-crown-5, or KO^{t}Bu/18-crown-6 at low temperature. Compounds **5a**−**c** were isolated and fully characterized by NMR and IR spectroscopy and elemental analysis. The structure of complex **5a**, as established by X-ray diffraction studies, revealed that the lithium is coordinated to nitrogen and the oxygen centers (of the crown ether unit). This geometry of **5a** is best described as a phosphanide complex isomeric to a phosphinidenoid complex. A phosphinidenoid-like behavior of **5a** was observed in the melt, evidenced by formation of cyclotriphosphane **4** via LiCN elimination and decomplexation. In solution **5a** reacted with methyl iodide (or methyl triflate) like a phosphanide, thus leading to *P*-methyl complex **8**.

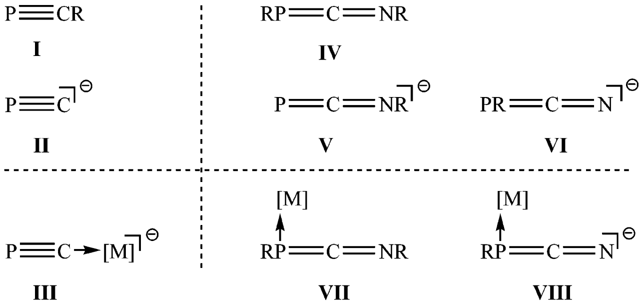
Introduction

The chemistry of *neutral* acyclic organophosphorus compounds having a monocoordinated phosphorus center such as phosphalkynes (**I**)[1] is now well established (Scheme 1).[2] In contrast, the related anionic system **II** is still unknown, but a first metal complex **III** of the true phosphorus analogue of cyanide (CP$^-$), termed cyaphide (**II**),[3] was discovered very recently. Similiarly, 1-aza-3-phosphaallenes[4] (**IV**) (monophosphacarbodiimides) have been known longer, but only **V** was established quite recently in the form of the potassium salt [K(18-crown-6)][1-Mes*-1-aza-3λ^3-phospha-3-allenide].[5] 1-Aza-3-phospha-1-allenides (**VI**) and/or complexes thereof (**VIII**) however are still unknown. Encouraged by the first preparation of η^1-1-aza-3-phosphaallene complexes (**VII**),[6] we report here our attempts to synthesize complexes **VIII**.

Experimental Results

As we recently gained facile access to the *P*-H functional cyanophosphane complex **1**,[7] we decided to study metalation reactions. The first reaction between **1** and ^{t}BuLi in THF at −80 °C was unsuccessful; we were not able to isolate the resulting product **2**, which has a ^{31}P{^{1}H} resonance at −149.7 ppm and a tungsten−phosphorus coupling constant magnitude of 106.8 Hz; no phosphorus−lithium coupling was observed (see DFT calculations). Repeating the reaction in THF by gradually warming to −10 °C resulted in the formation of **2** and an unknown byproduct, **3** (ratio 1:1), with a ^{31}P{^{1}H} resonance at −128.5 ppm (^1J(W,P) = 122.1 Hz). Upon warming to ambient temperature, complex **3** decomposed rapidly in solution to yield cyclotriphosphane **4**, previously described by Cowley et al.,[8] whereas complex **2** remained (Scheme 2).

Scheme 1. Neutral and Anionic Low-Coordinated Phosphorus Compounds and Complexes Thereof (R = ubiquitous organic substituents, [M] = transition-metal complex)



Finally, selective metalation of **1** and isolation of the products was achieved by addition of different bases (^{t}BuLi, NaN(SiMe$_3$)$_2$, or KO^{t}Bu) to solutions of complex **1** at −80 °C in the presence of stoichiometric amounts of the appropriate crown ether. After crystallization complexes **5a**−**c** were obtained in good yields (Scheme 3), which were stable in solution and in the solid state (under argon atmosphere).

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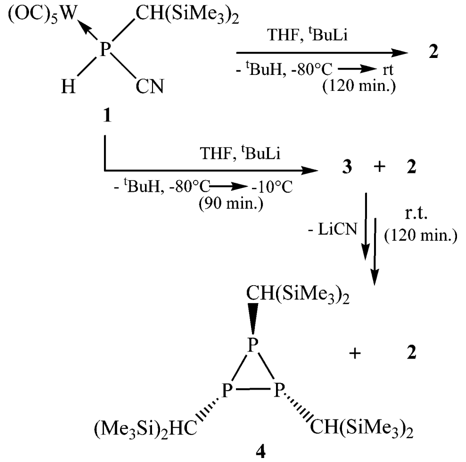
10.1021/om070240o CCC: $37.00

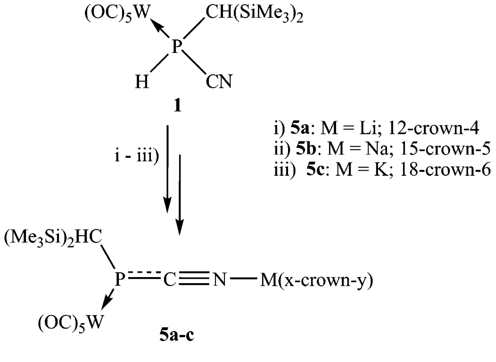
Scheme 2. Metalation of Complex 1



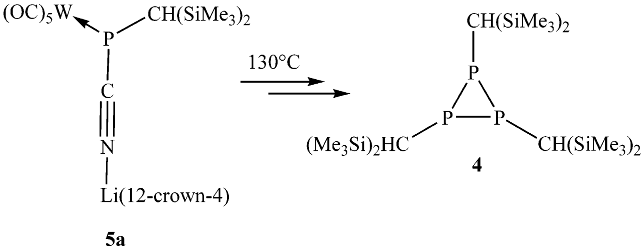
The $^{31}P\{^1H\}$ resonances of complexes **5a**−**c** were observed in a very narrow range of about −150 to −153 ppm, thus revealing comparatively more shielded phosphorus nuclei than in neutral 1-aza-3-phosphaallene complexes.[7] Furthermore, the small $^1J(W,P)$ coupling constant magnitudes of ca. 100 Hz provide (indirect) evidence for enhanced electron densities at the phosphorus centers in **5a**−**c**, leading to a decrease of the coupling constants. A similar observation was made earlier for phosphanide complexes.[9,10] No phosphorus−lithium coupling was observed in the ^7Li NMR of complex **5a** (THF-d_8, δ ^7Li = 0.1 ppm). The $^{13}C\{^1H\}$ resonances of the PCN units in **5a**−**c** are very similar to those of nitriles and very different from nonligated 1-aza-3-phosphaallenes[6] and/or complexes thereof[7] (both usually resonate at or above 200 ppm). CN stretch vibrations were observed in the range 2098 and 2121 cm^{-1}, which is characteristic for nitrile derivatives.[11] Therefore, we conclude that structure and bonding of **5a**−**c** in solution is quite similar to that found for the solid state (of **5a**).

Single-crystal X-ray analysis confirmed the molecular, monomeric structure of **5a** (Figure 1), which features a trigonal pyramidal geometry at the phosphorus atom (sum of bond angles at P1: 311.5°) and a nearly linear geometry of the unit C1−N1−Li1 (160.4(2)°) with a N1−Li1 distance of 1.977(3) Å. Therefore, we conclude that complex **5a** represents the first structural example of a phosphinidenoid-like[12] phosphanide complex rather than a 1-aza-3-phospha-3-allenide complex. This is also supported by the P1−C1 distance of 1.788(2) Å, which is significantly lengthened as compared to the 1-phosphaallene complex **6**[13] (1.631(2) Å) (Figure 2), which contains a trigonal planar coordinated phosphorus (bond angle sum at P: 359.7°),[14] thus suggesting a P−C single bond with only little double-bond contribution. The short C1−N1 distance of 1.153(2) Å reveals a slightly lengthened C−N triple bond, which still is significantly shorter than the C−N distance of the 1-aza-3-phosphaallene **7**[15] (1.210(4) Å) (Figure 2). In conclusion, the N−Li bond in **5a** has considerably more coordinative than covalent bond character.

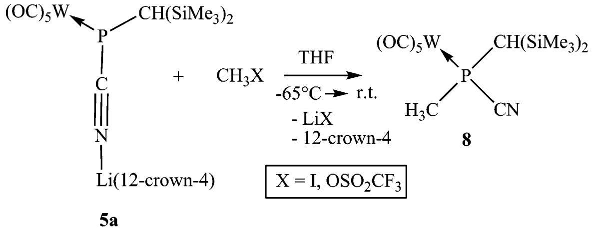
Scheme 3. Syntheses of Complexes 5a−c



Scheme 4. Phosphinidenoid-like Decomposition of Complex 5a in the Melt



Scheme 5. Phosphanide-like Reaction of Complex 5a



An investigation of the melt of complex **5a** revealed formation of cyclotriphosphane **4** as the main product together with other not yet identified products (Scheme 4). Thus, at least in the

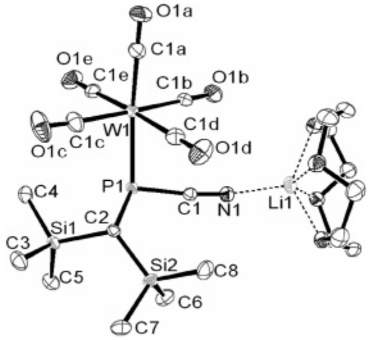


Figure 1. Molecular structure of **5a** (hydrogen atoms are omitted, ellipsoids represent 50% probability level): Selected bond lengths [Å] and angles [deg]: W1−P1 2.626(4), N1−C1 1.153(2), P1−C1 1.788(2), P1−C2 1.8739(16), Li1−N1 1.977(3); C1−N1−Li1 160.4(2), P1−C1−N1 171.6(2), C2−P1−W1 111.7(5), C1−P1−C2 103.4(7), C1−P1−W1 96.4(5).

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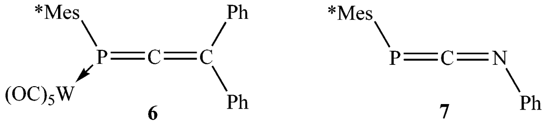
(12) The term *phosphinidenoid* is used here to describe a bonding situation at a formal phosphorus(III) center that has a very electropositive (group 1 metal) and an electronegative center (group 17 nonmetal) in a 1,1-position. In consequence, we use here *phosphinidenoid-like* to describe the N-coordination isomer.

(13) Yoshifuji, M.; Toyota, K.; Sato, T.; Inamoto, N.; Hirotsu, K. *Heteroat. Chem.* **1990**, *1*, 339.

(14) To the best of our knowledge no structures of η-(1)-1-aza-3-phosphaallene complexes have been described.

(15) Yoshifuji, M.; Niitsu, T.; Toyota, K.; Inamoto, N.; Hirotsu, K.; Odagaki, Y.; Higuchi, T.; Nagase, S. *Polyhedron* **1988**, *7*, 2213.

melt, **5a** displayed a “promising” phosphinidenoid-like reactivity. Disappointingly—and in contrast—thermal decomposition of **5a** in toluene did not furnish evidence for the formation of terminal phosphinidene complex [(CO)$_5$W{PCH(SiMe$_3$)$_2$}] if standard trapping experiments were performed.



6 **7**

Figure 2. 1-Phosphaallene complex **6**[13] and 1-aza-3-phosphaallene **7**.[15]

First studies on the reactivity of complex **5a** in solution toward electrophiles such as MeI and CF$_3$SO$_3$Me yielded the *P*-methyl-substituted phosphane complex **8** (Scheme 5); *N*-methylation of **5a**, even in case of the hard electrophile CF$_3$SO$_3$Me, was not observed. The ^{31}P{^{1}H} resonance of complex **8** at −21.4 ppm shows, as expected, a deshielding effect of the methyl group. The larger ^1J(W,P) coupling constant magnitudes of **8** (247.9 Hz) compared to that of complexes **5a**−**c** is interpretable in terms of a diminished electron density at the phosphorus center.

The structure of complex **8** was confirmed by X-ray diffraction studies (Figure 3), showing a longer P−C7 distance (1.8121(18) Å) together with a slightly shorter distance for N−C7 (1.144(2) Å) as was determined for **5a**. The PCN unit in **8** is approximately linear (171.35(17)°).

DFT Calculations

To assess the influence of Li-crown and free Li coordination to the PCN unit of phosphinidenoid [(OC)$_5$WP(CH(SiMe$_3$)$_2$)(CN)Li], we performed DFT calculations including ^{31}P NMR chemical shifts (Table 1). Three local minima of crown-free coordinated Li could be located (**5′**−**5‴**, Figure 4), the most stable of which is **5″**, where Li coordinates η^2 to nitrogen and a carbonyl ligand. In the next stable isomer, **5‴**, Li coordinates η^3 to a distorted PCN unit (∠PCN 157°). At least in the gas phase ordinary η^1-Li−P-coordinated isomer **5′** is less stable than **5‴** by 59 kJ/mol. The most likely candidate for crown-free **5a** is compound **5″**, which is an *N*-coordination isomer of phosphinidenoid complex **5′**.

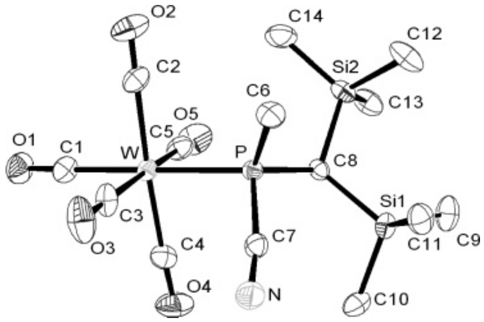
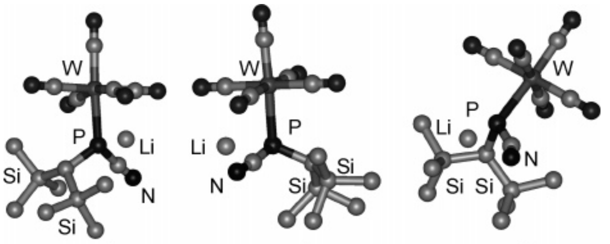


Figure 3. Molecular structure of **8** (hydrogen atoms are omitted for clarity; ellipsoids represent 30% probability level): Selected bond lengths [Å] and angles [deg]: W−P 2.492(4), P−C6 1.821(17), P−C7 1.812(18), P−C8 1.818(15), C7−N 1.142(2); C7−P−C6 96.97(9), C8−P−C7 106.54(8), C7−P−W 103.75(6), C8−P−W 120.80(5), N−C7−P 171.35(17).



5′ η^1-Li **5″** η^2-Li **5‴** η^3-Li

Figure 4. Three different modes of Li coordination in [(OC)$_5$WP(CH(SiMe$_3$)$_2$)(CN)Li].[16]

Table 1. Relative Gibbs Free Energies, ^{31}P NMR Chemical Shifts,[17] and Selected Bond Lengths and Angles of 5′−5‴

	rel Δ*G* [kJ/mol]	δ ^{31}P [ppm]	W−P [Å]	P−CN [Å]	(P)C−N [Å]	Li−P [Å]	Li−N [Å]	∠PCN [deg]
5′	59	−149	2.661	1.778	1.161	2.432	4.387	174.33
5″	0	−132	2.707	1.768	1.172	4.175	1.885	172.17
5‴	46	−71	2.611	1.782	1.175	2.549	2.076	157.04
5a		−139	2.704	1.781	1.166	4.799	1.935	171.56

According to the DFT-calculated ^{31}P NMR chemical shifts, direct coordination of lithium to phosphorus in **5′** results in the most shielded phosphorus, while η^3-coordinated Li effects a significant downfield shift. The difference in ^{31}P NMR chemical shifts between **5″** and **5a** reflects the effect of “crowning”: removal of 12-crown-4 from **5a** to yield **5″** results in a downfield shift of 7 ppm in the ^{31}P NMR. Thus a good guess for complex **2** (Scheme 1) is crown-free complex **5″**.

The DFT-calculated HOMO of **5a** contains the lone pair at phosphorus (Figure 5) and shows, furthermore, CN antibonding and metal−ligand participation. From the shape of the HOMO some nucleophilic character of the phosphanide caused by the exposed P-lone pair can be concluded; likewise electrophilic attack at phosphorus could be the preferred reaction type.[16]

Conclusions

We have presented a high-yield synthesis of structurally unprecedented phosphanide complexes **5a**−**c**. The spectroscopic and structural characteristics are best described as that of a phosphanide complex with an unusual structural motif in the solid state: the metal$^{\mathrm{I}}$ cation is coordinated to nitrogen, not to phosphorus. Thus **5a** is the first example of an (*N*-coordination) isomer of a phosphinidenoid complex. First studies on the

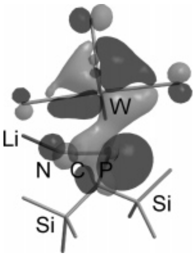


Figure 5. HOMO of **5a** (12-crown-4 omitted for clarity) at B3LYP/6-311g(d,p), ECP at W.[18]

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(16) All DFT calculations were performed using GAUSSIAN03, Rev. B.02 at B3LYP/6-311**; tungsten was described by LanL2DZ, the ECP by P. J. Hay and W. R. Wadt: *J. Chem. Phys.* **1985**, *82*, 270.

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(18) The HOMO of **5a** was plottted at an isosurface value of 0.035; dark color: positive sign. Selected bond lengths [Å] and angles [deg] using the numbering of Figure 1: W−P 2.704; N−C1 1.166; P−C1 1.781; Li−N 1.935; C1−N−Li 1.602; P−C1−N 171.6; C2−P−W 111.9; C1−P−C2 103.9; C1−P1−W1 98.0. The following charges are observed from a natural population analysis: P +0.354, C(N) +0.060, N −0.609, Li +0.835; it should be noted that the W(CO)$_5$ group participates significantly in electron delocalization.

reactivity of the complex revealed an ambiguous behavior: that of a phosphinidenoid-like complex in the melt and that of a phosphanide complex in solution. The latter was demonstrated by reactions with MeI and CF_3SO_3Me. DFT calculations lend further support to a high electron density at phosphorus as inferred from the high shielding observed in the ^{31}P NMR of **5a**−**c**.

Experimental Section

General Procedures. All reactions were carried out in 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 THF-d_8 (**5a**−**c**) and C_6D_6 (**8**) 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). IR spectra were recorded on a Nicolet 380 FT-IR spectrometer (Thermo). The mass spectrum of **8** was recorded on a Kratos MS 50 spectrometer. Elemental analyses were performed using a Elementar (Vario EL) analytical gas chromatograph. Melting points were determined using a Büchi apparatus, with samples sealed in capillaries under argon.

General Procedure for the Synthesis of Complexes 5a−**c.** A 0.133 mL (0.2 mmol) sample of a 1.5 M ^{t}BuLi solution in *n*-hexane (i), or a cooled solution (−80 °C) of 36.7 mg (0.2 mmol) of sodium bis(trimethylsilyl)amide in 2 mL of THF (ii), or a cooled solution (−80 °C) of 22.4 mg (0.2 mmol) of potassium *tert*-butoxide in 2 mL of THF (iii) was added dropwise to a stirred solution of 108.0 mg (0.2 mmol) of **1** in 4 mL of Et_2O and 1 equiv of 12-crown-4 (i), of **1** in 3 mL of THF and 1 equiv of 15-crown-5 (ii), or of **1** in 3 mL of THF and 1 equiv of 18-crown-6 (iii) under argon atmosphere. The reaction mixture was allowed to warm slowly to room temperature within 3.5 h. The solvent was removed under vacuum (ca. 0.01 bar), and the yellow residues were washed twice with 1 mL of diethyl ether and twice with 1 mL of *n*-pentane and dried under reduced pressure. Pale yellow solids were thus obtained.

Complex 5a. Yield: 142 mg (0.196 mmol, 98.3%). Mp: 115−120 °C (dec). ^{1}H NMR: δ 3.66 (s, 16H, 12-crown-4), 0.34 (d, 1H, ^{2}J(P,H) = 1.89 Hz, $CHSiMe_3$), 0.20 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR: δ 204.8 (d, ^{2}J(P,C) = 13.9 Hz; CO_{trans}), 202.2 (d_{sat}, ^{2}J(W,C) = 4.5 Hz; CO_{cis}), 141.0 (d; ^{1}J(P,C) = 116.4 Hz; PCN), 70.6 (s, 12-crown-4), 7.0 (d, ^{1}J(P,C) = 49.8 Hz, $CH(SiMe_3)_2$), 1.6 (s, $SiMe_3$), 1.5 (s, $SiMe_3$). ^{31}P{^{1}H} NMR: δ −152.9 (s_{sat}, ^{1}J(W,P) = 100.4 Hz). ^{29}Si{^{1}H} NMR: δ 0.9 (s, $SiMe_3$), 0.8 (s, $SiMe_3$). Selected IR data of **5a** (KBr): $\tilde{\nu}$ 600 (ν(P−C)), 1873, 1882, 1900 (s, ν(CO)), 1958 (m, ν(CO)), 2050 (w, ν(CO)), 2121 (w, ν(C≡N)) cm^{-1}. Anal. Calcd for $C_{21}H_{35}LiNO_9PSi_2W$: C, 34.87; H, 4.88; N, 1.94. Found: C, 34.48; H, 4.99; N, 1.81.

Complex 5b. Yield: 157 mg (0.2 mmol, 100%). Mp: 131 °C (dec). ^{1}H NMR: δ 3.72 (s, 20H, 15-crown-5), 0.38 (d, 1H, ^{2}J(P,H) = 1.50 Hz, $CHSiMe_3$), 0.22 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR: δ 203.9 (d, ^{2}J(P,C) = 13.9 Hz; CO_{trans}), 201.0 (d, ^{2}J(P,C) = 4.5 Hz; CO_{cis}), 135.9 (d, ^{1}J(P,C) = 113.8 Hz; PCN), 68.0 ppm (s, 15-crown-5), 5.9 (d, ^{1}J(P,C) = 50.1 Hz, $CH(SiMe_3)_2$), 0.1 (s, $SiMe_3$), 0,0 (s, $SiMe_3$). ^{31}P{^{1}H} NMR: δ −150.5 (s_{sat}, ^{1}J(W,P) = 99.2 Hz). ^{29}Si {^{1}H} NMR: δ 0.8 (s, $SiMe_3$), 0.7 (s, $SiMe_3$). Selected IR data of **5b** (KBr): $\tilde{\nu}$ 598 (ν(P−C)), 1864, 1897, 1926 (s, ν(CO)), 2051 (w, ν(CO)), 2105.4 (w, ν(C≡N)) cm^{-1}. Anal. Calcd for $C_{23}H_{39}NNaO_{10}PSi_2W$: C, 35.26; H, 5.02; N, 1.79. Found: C, 35.32; H, 5.11; N, 1.73.

Complex 5c. Yield: 167 mg (0.2 mmol, 100%). Mp: 125−130 °C (dec). ^{1}H NMR: δ 3.66 (s, 24H, 18-crown-6), 0.38 (d, 1H, ^{2}J(P,H) = 1.1 Hz, $CHSiMe_3$), 0.22 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR: δ 204.0 (d, ^{2}J(P,C) = 13.9 Hz; CO_{trans}), 201.1 (d, ^{2}J(P,C) = 4.5 Hz; CO_{cis}), 134.8 (d, ^{1}J(P,C) = 111.5 Hz; PCN), 69.4 (s, 18-crown-6), 5.9 (d, ^{1}J(P,C) = 50.1 Hz, $CH(SiMe_3)_2$), 0.1 (s, $SiMe_3$), −0.1 (s, $SiMe_3$). ^{31}P{^{1}H} NMR: δ −149.9 (s_{sat}, ^{1}J(W,P) = 99.2 Hz). ^{29}Si{^{1}H} NMR: δ 0.7 (s, $SiMe_3$), 0.5 (s, $SiMe_3$). Selected IR data of **5c** (KBr): $\tilde{\nu}$ 597 (ν_{as}(P−C)), 1859, 1896, 1924 (s, ν(CO)), 1955 (sh, ν(CO)), 2049 (w, ν(CO)), 2098 (w, ν(C≡N)) cm^{-1}. Anal. Calcd for $C_{25}H_{43}KNO_{11}PSi_2W$: C, 35.59; H, 5.14; N, 1.66. Found: C, 35.18; H, 5.17; N, 1.55.

Complex 8. To a cooled and stirred solution of 144.0 mg (0.199 mmol) of **5a** in 3 mL of THF was added 56.5 mg (0.398 mmol) of methyl iodide under stirring at −65 °C. After warming to room temperature (2.5 h) under continuous stirring, solvent and excess methyl iodide were removed under reduced pressure. The residue was submitted to low-temperature column chromatography with 10 mL of petroleum ether/diethyl ether (1:1) and 20 mL of petroleum ether (SiO_2; −20 °C, petrol ether); four fractions were thus collected. Evaporation of the first and second fraction yielded **8** as a colorless solid.

Yield: 71 mg (0.128 mmol, 64%). Mp: 82 °C (dec). ^{1}H NMR: δ 1.56 (d, ^{2}J(P,H) = 5.8 Hz, CH_3), 0.86 (d, ^{1}H, ^{2}J(P,H) = 3.5 Hz, $CH(SiMe_3)_2$), 0.13 (s, 9H, $SiMe_3$), 0.01 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR: δ 196.7 (d, ^{2}J(P,C) = 25.2 Hz; CO_{trans}), 195.3 (d, ^{2}J(P,C) = 6.5 Hz; CO_{cis}), 120.9 (d; ^{1}J(P,C) = 8.4 Hz; PCN), 19.1 (d, ^{1}J(P,C) = 32,3 Hz, PCH_3), 17.6 (d, ^{1}J(P,C) = 2.3 Hz, $CH(SiMe_3)_2$), 1.0 (d, ^{3}J(P,C) = 4.2 Hz, $SiMe_3$), −0,5 (d, ^{3}J(P,C) = 2.9 Hz, $SiMe_3$). ^{31}P{^{1}H} NMR: δ −21.4 (s_{sat}, ^{1}J(P,W) = 247.9 Hz). ^{29}Si{^{1}H} NMR: δ 3.2 (d, ^{2}J(P,Si) = $SiMe_3$), 0.7 (s, $SiMe_3$). Selected MS data for **8** (EI, 70 eV): *m/z* (%) 555.1 (39) [M^{+}]. HR-MS: calcd 553.0257, found 553.0255. Anal. Calcd for $C_{13}H_{22}ClO_5PSi_2W$: C, 27.65; H, 3.93. Found: C, 27.86; H, 4.01.

Crystallographic Data. Crystal structure data of complex **5a** ($C_{21}H_{35}LiNO_9PSi_2W$): monoclinic, $P2_1/n$ (no. 14); $a = 11.0667(1)$ Å, $b = 14.1932(1)$ Å, $c = 19.6561(1)$ Å, $\beta = 97.798(1)°$, $V = 3058.87(4)$ Å;^{3} $Z = 4$; $\rho = 1.571$ Mg/m^{3}, μ(Mo Kα) = 3.950 mm^{-1}. A total of 47 663 reflections were measured on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 123(2) K, 6985 reflections were unique ($R_{int} = 0.0473$). A semiempirical absorption correction from equivalents was applied (min./max. transmission = 0.31929/0.52237). The structure was solved with Patterson methods and refined with full-matrix least-squares against F^2 of all reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined as rigid groups. R values [$I > 2\sigma(I)$]: $R_1 = 0.0159$, $wR_2 = 0.0407$. R values [all data]: $R_1 = 0.0183$, $wR_2 = 0.0414$, Min./max. difference electron density: −1.150/0.576 e Å^{-3}.

Crystal structure data of complex **8** ($C_{14}H_{22}NO_5PSi_2W$): $M = 555.33$, $C2/c$, $a = 3442.9(3)$ pm, $b = 994.18(8)$ pm, $c = 1359.88(12)$ pm, $\beta = 112.682(2)°$, $V = 4.2947$ nm^{3}, $Z = 8$, $d_{calc} = 1.718$ Mg/m^{3}, $\mu = 5.6$ mm^{-1}, $T = 133$ K. A colorless tablet (0.4 × 0.35 × 0.18 mm) was used to record 42 980 intensities ($2\theta_{max}$ 61°) using monochromated Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiscans) 6565 unique reflections ($R_{int} = 0.024$) were used for all calculations (program SHELXL-97). Hydrogen atoms were refined as rigid methyl groups. The final $wR(F^2)$ was 0.039, with conventional $R(F) = 0.015$, for 224 parameters; highest peak 1534, hole −466 e/nm^{3}.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-615101 (**5a**) and CCDC-615127 (**8**). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223-336-033) or via e-mail (deposit@ccdc.cam.ac.uk) or from the url (www.ccdc.cam.ac.uk/data_request/cif).

Acknowledgment. Financial support was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie; furthermore we thank the John von Neumann Institute for Computing (Jülich) for computing time (HBN12).

OM070240O