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Synthesis of Aminophosphane Complexes: Searching the Boundary between Phosphanide and Phosphinidenoid Complex Chemistry

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Dedicated to Professor U. Zenneck on the occasion of his 65th birthday

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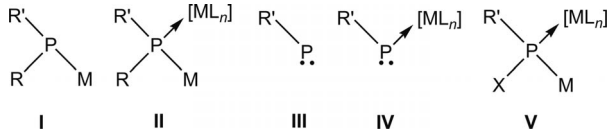
Aminophosphane complexes **3a–e** have been prepared by two different pathways: (1) the thermal reaction of 2*H*-azaphosphirene complex **1** with primary or secondary amine derivatives at 75 °C (**3a**,**b**,**d**,**e**) or (2) the reaction of chlorophosphane complex **2** with sodium diphenylamide (**3c**). In the latter case, complex **3c** was obtained together with the diphosphene complex **6**, thus providing evidence for the transient formation of Na/X phosphinidenoid complexes **4a**,**b** and/or the terminal phosphinidene complex **5**. Preliminary deprotonation studies, carried out on complex **3a** by using lithium diisopropylamide in TMEDA in the presence of 12-crown-4 at low temperature, yielded a mixture of the Li/NMe_2 phosphinidenoid complex **7** together with the nonligated phosphane derivative **8**, which could not be separated. Complexes **3a**,**b**,**d**,**e** and **6** were characterized by NMR and IR spectroscopy, MS, and elemental analysis. The structures of complexes **3c–e** and **6** were confirmed by single-crystal X-ray diffraction analysis.

Introduction

Phosphanides **I** and their complexes **II** (Scheme 1) are key reagents and ligands in both main-group and transition-metal chemistry; for example, lithium phosphanides[1] enable the formation of single and/or multiple bonds between phosphorus and carbon and/or metal atoms. Although much more reactive and short-lived, phosphanylidenes **III**[2] and their terminal complexes **IV**[2,3] have attracted the attention of experimental and theoretical chemists for more than four decades, and in particular the latter have become important building blocks in organophosphorus chemistry.



Scheme 1. Phosphanides **I** and their complexes **II**, phosphanylidenes **III** and their complexes **IV**, and M/X phosphinidenoid complexes **V** (R, R′ = organic substituent; M = alkali metal; ML_n = transition-metal fragment; X = Hal or alkoxy group).

Recently, Li/X phosphinidenoid complexes **V** were prepared by deprotonation of halogenophosphane complexes using lithium diisopropylamide (LDA) in the presence of 12-crown-4.[4,5] Because such complexes show low thermal stability, we became interested in examining the scope of this protocol and the properties of the complexes formed after deprotonation. Herein we report the synthesis of new 1,1′-bifunctional aminophosphane complexes and, in a preliminary study, the deprotonation of a (dimethylamino)-phospahne derivative.

Results and Discussion

Secondary phosphane derivatives RP(H)X, which contain P–H and P–X bonds (X = Cl, OR, NR_2, NHR), are relatively rare, because they are, in general, thermally unstable and can easily eliminate HX to form phosphanylidenes[6] or diphosphanes,[7] and/or undergo rearrangement reactions to form phosphane oxide compounds.[8] Thus, the classical complexation of a "free" phosphane derivative is not a viable method. Therefore, we used the protocols shown in Scheme 2 to prepare (amino)(organo)phosphane complexes: (1) 2*H*-azaphosphirene complex **1**[9] was heated in the presence of primary and secondary amines in toluene at 75 °C to yield **3a**,**b**,**d**,**e**, and (2) the chlorophosphane complex **2**[10] was treated with sodium diphenylamide in diethyl ether at –30 °C to give **3c**.

The aminophosphane complexes **3a–e** were obtained in good yields following column chromatography at low temperature or by washing with *n*-pentane (**3a**,**d**). Complexes **3a–e** were fully characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analysis. The structures of complexes **3c–e** were unambiguously confirmed by single-crystal X-ray diffraction.

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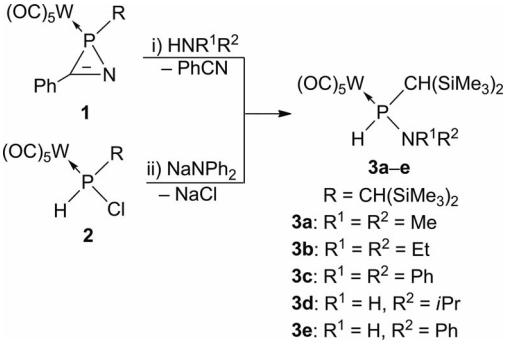


Scheme 2. Synthesis of aminophosphane complexes **3a**–**e**.

The ^{31}P NMR resonances of complexes **3a**–**e** were observed in the range of $\delta \approx 5$–46 ppm with coupling constants $^{1}J_{(W,P)} = 250$–260 Hz and $^{1}J_{(P,H)} = 320$–357 Hz, which are consistent with those of the aminophosphane complexes published earlier by Mathey and co-workers.[3a,3b,11] In the ^{13}C NMR analysis, the carbon atoms directly bound to the phosphorus atom (abbrev. C^P) resonate at $\delta \approx 22$ ppm with a very small phosphorus–carbon coupling constant of ca. 4–8 Hz. The ^{1}H NMR spectra show the P–H proton signal at $\delta \approx 7$ ppm. The IR spectra of complexes **3a**–**e** (KBr pellets) display ν(P–H) stretching absorptions between 2220 and 2310 cm^{-1}, which are also in line with values reported previously.[11a,12,13] Selected NMR and IR data are given in Table 1.

Table 1. Selected NMR and IR data for complexes **3a**–**e**.

Complex	δ [ppm]/J [Hz]			$\tilde{\nu}$(P–H)[b] [cm^{-1}]
	$\delta(^{31}P)$/ $^{1}J_{(W,P)}$	$\delta(^{13}C^P)$/ $^{1}J_{(P,C)}$[a]	$\delta(^{1}H)$/ $^{1}J_{(P,H)}$	
3a	46.1/ 249.2	22.6/2.9	7.03/ 342.9	2270
3b	31.0/ 249.2	22.7/3.9	7.18/ 342.5	not observed
3c	23.7/ 263.2	–	–	–
3d	11.4/ 255.6	22.3/7.8	7.09/ 320.2	2226
3e	5.3/253.0	22.4/br	7.49/ 357.7	2310

[a] Carbon atoms directly bound to the phosphorus atom. [b] $\tilde{\nu}$ values of P–H stretching absorptions.

From Table 1 it is apparent that (diorganoamino)phosphane complexes **3a**–**c** have ^{31}P resonances that are shifted downfield relative to those of (organoamino)phosphane complexes **3d**,**e**. Note that the ν(P–H) stretching absorption was not observed for complex **3b**, although well-established by its P–H coupling constant in the NMR spectra. A similar observation was reported by Marinetti and Mathey[11a] for $[(CO)_5W(Ph)P(H)NEt_2]$; the reason for this phenomenon was and still is unclear.

The molecular structures of complexes **3c**–**e** were confirmed by single-crystal X-ray diffraction analysis (Figures 1, 2, and 3); all bond lengths and angles are within the normal range. One structural feature deserves mention: The

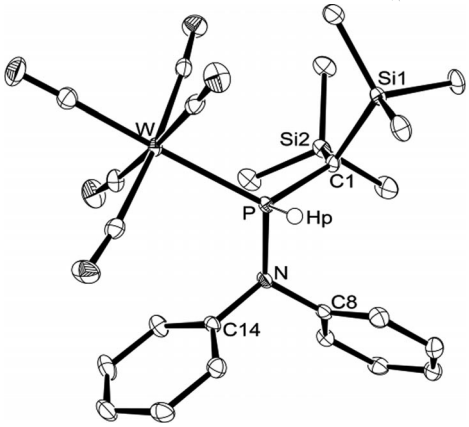


Figure 1. Molecular structure of complex **3c** in the crystal. All hydrogen atoms except Hp are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P–Hp 1.29(3), P–W 2.5305(7), P–N 1.717(2), P–C1 1.819(3), N–C8 1.488(3); N–P–W 118.13(8), N–P–C1 104.09(11), W–P–C1 121.58(9).

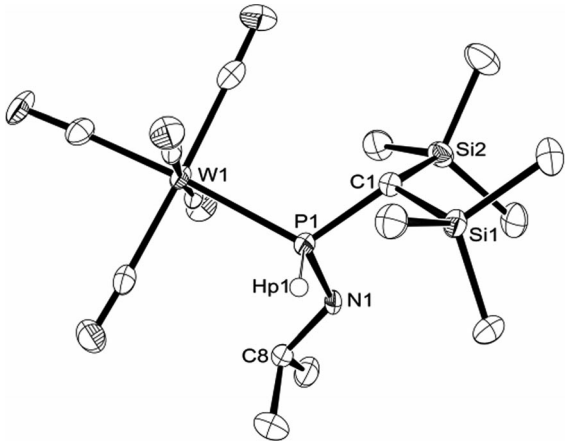


Figure 2. Molecular structure of complex **3d** in the crystal. All hydrogen atoms except Hp1 are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P1–Hp1 1.28(4), P1–N1 1.682(3), P1–C1 1.834(4), P1–W1 2.5049(10), N1–C8 1.476(4); N1–P1–W1 117.68(11), N1–P1–C1 104.32(16), W1–P1–C1 117.79(12).

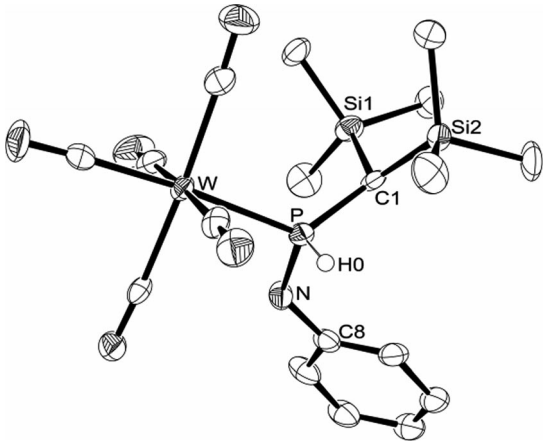
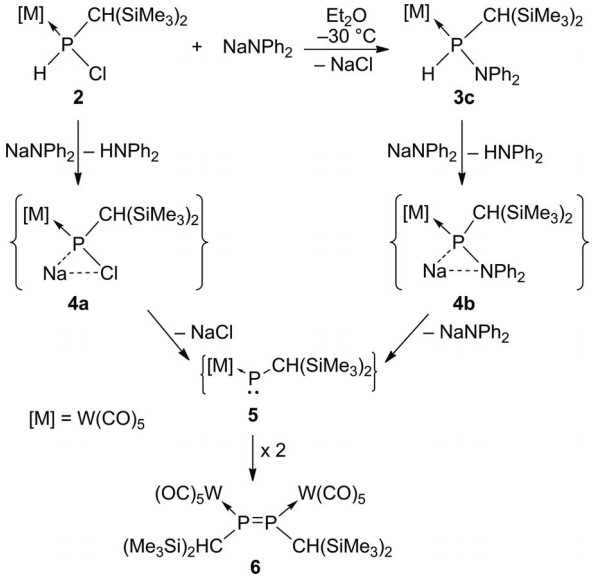


Figure 3. Molecular structure of complex **3e** in the crystal. All hydrogen atoms except Hp are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P–N 1.691(11), P–C1 1.835(13), P–W 2.516(3), N–C8 1.430(18); N–P–C1 107.8(6), C1–P–W 127.1(4), W–P–N 108.0(4).

orientation of the C–H bond of the $CH(SiMe_3)_2$ group relative to the P–W bond shows an s-*trans* conformation for complexes **3c**,**e**, whereas it is s-*cis* for complex **3d**.

Remarkably, in the synthesis of complex **3c**, the (*Z*)-diphosphene complex **6**[14] was also formed (ratio **6**/**3c** ≈ 1:1.5), which provides some evidence for the intermediate formation of the phosphinidene complex **5**. As the route to **6** is not apparent, we propose two different pathways (Scheme 3). As an alternative to chloro substitution to yield the aminophosphane complex **3c**, deprotonation of **2** may occur to give the Na/Cl phosphinidenoid complex **4a**. Alternatively, after the formation of complex **3c**, the Na/NPh_2 phosphinidenoid complex **4b** may be also formed by deprotonation. Both phosphinidenoid complexes **4a**,**b** may undergo elimination to give the diphosphene complex **6**, probably via the terminal phosphinidene complex **5**.



Scheme 3. Proposed pathways for the formation of complex **6**.

The ^{31}P resonance of complex **6** appears at δ = 324.4 ppm [$J_{(W,P)}$ = 146.5, 115.9 Hz], which is close to the values of related complexes (*Z*)-[$(OC)_5W$(Mes)P=P(Mes)-$W(CO)_5$] (Mes = 2,4,6-trimethylphenyl; δ = 313.6 ppm) and (*E*)-[$(OC)_5W\{(Me_3Si)_2HC\}P=P\{CH(SiMe_3)_2\}W(CO)_5$] ($\delta$ = 342.2 ppm).[15] However, the tungsten–phosphorus coupling constants are different for complexes with (*E*) and (*Z*) configurations. For example, the latter complex with (*E*) configuration has $J_{(W,P)}$ = 268 Hz, which is larger than that of the former (*Z*)-diphosphene complex [$J_{(W,P)}$ = 116 Hz]. The ^{31}P NMR spectroscopic data for complex **6** is much closer to that of the diphosphene complex described by Yoshifuji et al. [δ = 332 ppm; $J_{(W,P)}$ = 145, 116 Hz].[16]

The molecular structure of complex **6** was also confirmed by single-crystal X-ray diffraction (Figure 4). Although the first impression is that of a sterically crowded molecular compound, the P–P bond length in complex **6** [2.050(3) Å] is very similar to that of the (only other) (*Z*)-diphosphene complex [2.041(4) Å] reported by Yoshifuji et al.[16] The only hint of steric crowding can be derived from the two-fold s-*trans* conformation of the C–H and P–W bond [of $CH(SiMe_3)_2$] in **6**.

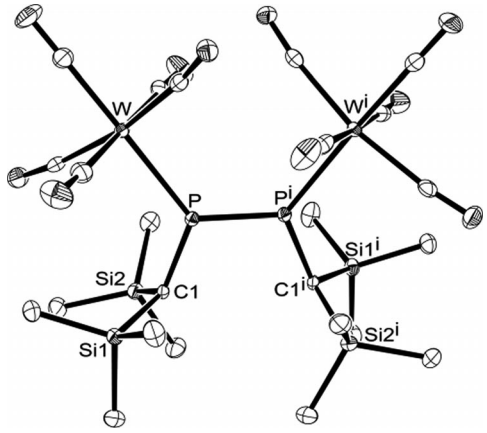


Figure 4. Molecular structure of complex **6** in the crystal. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P–P^i 2.050(3), P–W 2.5156(17), P–C1 1.819(6); W–P–P^i 125.99(4), W–P–C1 121.9(2), C1–P–P^i 111.7(2).

In a preliminary study we examined the deprotonation of complex **3a** with LDA in the presence of 12-crown-4 at –78 °C. The $^{31}P\{^1H\}$ NMR spectrum (Figure 5) displays a broadened quartet at δ = 101.8 ppm [$^1J_{(P,Li)}$ = 62.1 Hz] and a sharp singlet at δ = 39.1 ppm together with signals representing small amounts of other unidentified byproducts (<5%). Despite the absence of tungsten satellites, the quartet was tentatively assigned to the Li/NMe_2 phosphinidenoid complex **7** (Scheme 4) because of the downfield-shifted ^{31}P resonance and the phosphorus–lithium coupling.[17] As the singlet at δ = 39.1 ppm shows no tungsten–phosphorus coupling but a large phosphorus–proton coupling [$^1J_{(P,H)}$ = 195.9 Hz], we tentatively assigned this signal to the (free) ligand **8**. The ratio of these two major products changed over time; the signal intensity of complex **7** decreased after 50 h and that of compound **8** increased, the ratio of **7**/**8** changing from ca. 3:1 to ca. 1:1. Unfortunately,

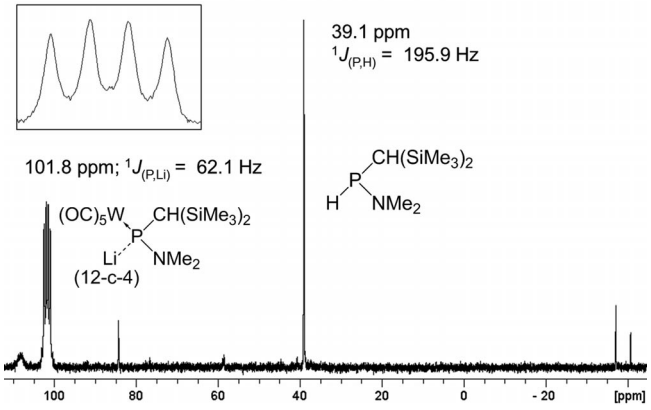
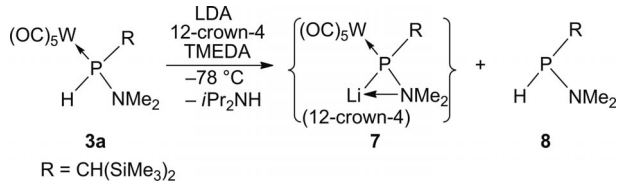


Figure 5. ^{31}P NMR spectrum of the reaction solution of complex **3a** and LDA showing tentative assignments.

the mechanism for the decomposition of complex **7** remains unclear as neither complex **7** nor compound **8** could be obtained by column chromatography or crystallization.



Scheme 4. Synthesis of complexes **7** and **8** by reaction of complex **3a** with LDA.

Although the phosphorus–lithium coupling constant[17,18] strongly suggests complex **7**, the data of derivative **8** are similar to those of one of the very few 1,1′-bifunctional P–H phosphane derivatives, $[(Me_3Si)_2HCP(H)N(SiMe_3)_2]$ [δ = 5.9 ppm; $^1J_{(P,H)}$ = 210.0 Hz], to have been reported previously.[19] Note that deprotonation of H/NR_2 phosphane complexes with LDA seems not to be the predominant process and/or the products formed do not possess sufficiently high thermal stability, which is in stark contrast to Li/OR phosphinidenoid complexes with alkyl or aryl groups R,[20] which can be used as reagents at ambient temperature.

Conclusions

New 1,1′-bifunctional aminophosphane complexes **3a**–**e** have been synthesized by two routes. In the case of **3c**, an especially interesting observation was that the targeted complex **3c** was formed together with the (*Z*)-diphosphene complex **6**, which provides the first hint of transient Na/X phosphinidenoid complexes **4a**,**b** and/or the terminal phosphinidene complex **5**. The results of a preliminary study on the deprotonation of complex **3a** showed the formation of a main product, tentatively assigned to the Li/NMe_2 phosphinidenoid complex **7** featuring a P–Li bond. Interestingly, complex **7** decomposes to yield the P–H phosphane derivative **8** by an unknown pathway. Future work will address the latter as well as try to unveil a slowly emerging structure–reactivity relationship of M/X phosphinidenoid complexes.

Experimental Section

General: All operations were performed in typical flame-dried Schlenk glassware under argon that had been purified and dried. Solvents were used after distillation from sodium wire/benzophenone. NMR spectra were recorded with a Bruker Avance 300 spectrometer at 25 °C in $CDCl_3$ solutions. Chemical shifts are given in ppm relative to tetramethylsilane (^{1}H: 300.1 MHz; ^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded with a Kratos MS 50 spectrometer (EI, 70 eV); only *m*/*z* values are given. IR spectra were recorded with an FT-IR Nicolet 380 spectrometer. Melting points were measured with a Büchi 535 capillary apparatus. Elemental analyses were performed by using an Elementa (vario EL) analytical gas chromatograph.

X-ray Crystallographic Analysis of 3c–e and 6: Data were collected with a Nonius–KappaCCD diffractometer at 123 K by using Mo-K_α radiation (λ = 0.71073 Å). The structures were refined by full-matrix least squares on F^2 (SHELXL-97[21]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions by using a riding model. CCDC-855282 (**3c**), -855283 (**3d**), -855284 (**3e**), and -855285 (**6**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Complex 3a: Dimethylamine (0.5 mL, 1.0 mmol) was added to a stirred solution of 2*H*-azaphosphirene complex **1** (617 mg, 1.0 mmol) in toluene (30 mL) and heated at 75 °C for 3 h. After removal of all volatiles in vacuo (ca. 10^{-2} mbar), the final product **3a** was purified by washing with *n*-pentane at low temperature (–60 °C). Yellow solid; yield: 173 mg (0.31 mmol, 31%); m.p. 35 °C. ^{1}H NMR: δ = 0.25 [s, 9 H, $Si(CH_3)_3$], 0.26 [d, $^4J_{(P,H)}$ = 0.6 Hz, 9 H, $Si(CH_3)_3$], 1.16 [dd, $^2J_{(P,H)}$ = 6.0, $^4J_{(H,H)}$ = 2.5 Hz, 1 H, PCH], 2.76 [d, $^3J_{(P,H)}$ = 10.9 Hz, 6 H, $N(CH_3)_2$], 7.03 [d, $^1J_{(P,H)}$ = 342.9 Hz, 1 H, PH] ppm. ^{13}C{^{1}H} NMR: δ = 0.0 [d, $^3J_{(P,C)}$ = 2.6 Hz, $Si(CH_3)_3$], 0.5 [d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$], 22.6 [d, $^1J_{(P,C)}$ = 3.9 Hz, PCH], 42.8 [d, $^2J_{(P,C)}$ = 5.2 Hz, $N(CH_3)_2$], 195.1 [d, $^2J_{(P,C)}$ = 7.1, $^1J_{(W,C)}$ = 126.0 Hz, *cis*-CO], 201.8 [d, $^2J_{(P,C)}$ = 22.6 Hz, *trans*-CO] ppm. ^{31}P{^{1}H} NMR: δ = 46.1 [d_{sat}, $^1J_{(W,P)}$ = 249.2, $^1J_{(P,H)}$ = 342.1 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 1917 [vs, ν(CO)], 2069 [s, ν(CO)], 2270 [w, ν(PH)], 2958 [w, ν(CH/CH_3)] cm^{-1}. MS (EI): *m*/*z* (%) = 559.1 (38) $[M]^{+\cdot}$, 531.1 (30) $[M - CO]^{+\cdot}$, 503.1 (34) $[M - 2\ CO]^{+\cdot}$, 475.0 (100) $[M - 3\ CO]^{+\cdot}$, 417.0 (80) $[M - 5\ CO]^{+\cdot}$, 234.1 (52) $[M - W(CO)_5]^{+\cdot}$, 73.0 (70) $[SiMe_3]^{+\cdot}$. $C_{14}H_{26}NO_5PSi_2W$ (559.36): calcd. C 30.06, H 4.69, N 2.50; found C 30.88, H 4.39, N 2.56.

Synthesis of Complex 3b: Diethylamine (0.1 mL, 1.0 mmol) was added to a solution of 2*H*-azaphosphirene complex **1** (617 mg, 1.0 mmol) in toluene (30 mL) at 75 °C. The reaction mixture was heated whilst stirring for 3 h. After removal of all volatiles in vacuo (ca. 10^{-2} mbar), the final product **3b** was purified by column chromatography at low temperature on silica gel (–20 °C, 2 × 11 cm, petroleum ether/Et_2O = 9:1). Yellow viscous liquid; yield: 123 mg (0.21 mmol, 21%). ^{1}H NMR: δ = 0.25 [s, 9 H, $Si(CH_3)_3$], 0.26 [s, 9 H, $Si(CH_3)_3$], 1.08 [d, $^2J_{(P,H)}$ = 1.7 Hz, 1 H, PCH], 1.13 [t, $^3J_{(H,H)}$ = 14.2 Hz, 6 H, NCH_2CH_3], 3.10 (m, 4 H, NCH_2CH_3), 7.18 [d, $^1J_{(P,H)}$ = 342.5 Hz, 1 H, PH] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ = 0.0 [d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$], 0.2 [d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$], 11.2 [d, $^3J_{(P,C)}$ = 4.5 Hz, NCH_2CH_3], 22.7 [d, $^1J_{(P,C)}$ = 3.9 Hz, PCH], 43.4 [d, $^2J_{(P,C)}$ = 5.2 Hz, NCH_2CH_3], 196.0 [d, $^2J_{(P,C)}$ = 6.5, $^1J_{(W,C)}$ = 125.4 Hz, *cis*-CO], 197.0 [d, $^2J_{(P,C)}$ = 23.3 Hz, *trans*-CO] ppm. ^{31}P{^{1}H} NMR: δ = 31.0 [d_{sat}, $^1J_{(W,P)}$ = 249.2, $^1J_{(P,H)}$ = 342.0 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 1932 [vs, ν(CO)], 2069 [s, ν(CO)] cm^{-1}. MS (EI): *m*/*z* (%) = 587.1 (40) $[M]^{+\cdot}$, 559.1 (8) $[M - CO]^{+\cdot}$, 531.1 (18) $[M - 2\ CO]^{+\cdot}$, 503.1 (95) $[M - 3\ CO]^{+\cdot}$, 445.1 (38) $[M - 5\ CO]^{+\cdot}$, 262.1 (90) $[M - W(CO)_5]^{+\cdot}$, 73.0 (58) $[SiMe_3]^{+\cdot}$. $C_{16}H_{30}NO_5PSi_2W$ (587.41): calcd. C 32.72, H 5.15, N 2.38; found C 33.25, H 5.23, N 2.29.

Synthesis of Complexes 3c and 6: A solution of chlorophosphane complex **2** (550 mg, 1.0 mmol) in diethyl ether (10 mL) was added to a stirred solution of sodium diphenylamide (210 mg, 1.1 mmol) in diethyl ether (10 mL) at –30 °C. The reaction solution was stirred for 3 h and warmed up to room temperature. After removal of all volatiles in vacuo (ca. 10^{-2} mbar), the final products were purified by column chromatography on silica gel [–20 °C, 2 × 11 cm, petroleum ether/Et_2O = 100:0 (for 1st fraction), 90:10 (for 2nd fraction)].

3c: Yellow solid, crystallized from Et_2O at –30 °C; yield: 68 mg (0.1 mmol, 10%); m.p. 39 °C. ^{31}P{^{1}H} NMR: δ = 23.7 [d_{sat}, $^1J_{(W,P)}$ = 263.2 Hz, $^1J_{(P,H)}$ = 330.6 Hz] ppm.

6: Pink solid, crystallized from Et_2O at –30 °C; yield: 220 mg (0.21 mmol, 21%); m.p. 143–145 °C. ^1H NMR: δ = 0.17 [s, 36 H, $Si(CH_3)_3$], 3.40 [d, $^2J_{(P,H)}$ = 2.2 Hz, 2 H, PCH] ppm. $^{13}C\{^1H\}$ NMR: δ = 1.8 [s, $Si(CH_3)_3$], 33.2 [d, $^1J_{(P,C)}$ = 36.7 Hz, PCH], 196.4 [d, $^2J_{(P,C)}$ = 4.0 Hz, *cis*-CO], 201.8 [d, $^2J_{(P,C)}$ = 14.4 Hz, *trans*-CO] ppm. $^{31}P\{^1H\}$ NMR: δ = 324.2 [s_{sat}, $^1J_{(W,P)}$ = 146.5, $^1J_{(P,H)}$ = 115.9 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 1254 [w, ν(P=P)], 1927 [s, ν(CO)], 1987 [m, ν(CO)], 2062 [m, ν(CO)], 2077 [s, ν(CO)] cm^{-1}. MS (EI): *m*/*z* (%) = 1028.0 (25) $[M]^{+\cdot}$. $C_{24}H_{38}O_{10}P_2Si_4W_2$ (1028.55): calcd. C 28.03, H 3.72; found C 28.47, H 4.26.

Synthesis of Complex 3d: Isopropylamine (0.14 mL, 1.0 mmol) was added to a stirred solution of 2*H*-azaphosphirene complex **1** (617 mg, 1.0 mmol) in toluene (30 mL) at 75 °C, and the reaction mixture was stirred for 3 h. After removal of all volatiles in vacuo (ca. 10^{-2} mbar), the final product **3d** was purified by washing with *n*-pentane at low temperature (–60 °C). Yellow solid, crystallized from *n*-pentane at –30 °C; yield: 200 mg (0.33 mmol, 33%); m.p. 73 °C. ^1H NMR: δ = 0.25 [d, $^4J_{(P,H)}$ = 0.6 Hz, 9 H, $Si(CH_3)_3$], 0.29 [d, $^4J_{(P,H)}$ = 0.4 Hz, 9 H, $Si(CH_3)_3$], 0.96 [d, $^2J_{(P,H)}$ = 6.2 Hz, 1 H, PCH], 1.18 [d, $^2J_{(H,H)}$ = 6.4 Hz, 6 H, $NCH(CH_3)_2$], 3.26 (br., 1 H, NH), 3.40 [q, $^3J_{(P,H)}$ = 7.0 Hz, 1 H, $NCH(CH_3)_2$], 7.09 [d, $^1J_{(P,H)}$ = 320.2 Hz, 1 H, PH] ppm. $^{13}C\{^1H\}$ NMR: δ = –1.3 [d, $^3J_{(P,C)}$ = 2.3 Hz, $Si(CH_3)_3$], 0.0 [d, $^3J_{(P,C)}$ = 3.2 Hz, $Si(CH_3)_3$], 22.3 [d, $^1J_{(P,C)}$ = 7.8 Hz, PCH], 22.7 [d, $^3J_{(P,C)}$ = 4.5 Hz, $NCH(CH_3)_2$], 46.2 [d, $^2J_{(P,C)}$ = 3.2 Hz, $NCH(CH_3)_2$], 195.1 [d, $^2J_{(P,C)}$ = 7.1 Hz, *cis*-CO], 197.4 [d, $^2J_{(P,C)}$ = 22.0 Hz, *trans*-CO] ppm. $^{31}P\{^1H\}$ NMR: δ = 11.4 [d_{sat}, $^1J_{(W,P)}$ = 255.6 Hz, $^1J_{(P,H)}$ = 320.4 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 1920 [vs, ν(CO)], 2068 [s, ν(CO)], 2226 [w, ν(PH)], 2956 [w, ν(CH/CH_3)] cm^{-1}. MS (EI): *m*/*z* (%) = 573.0 (49) $[M]^{+\cdot}$, 545.0 (41) $[M – CO]^{+\cdot}$, 517.0 (39) $[M – 2\ CO]^{+\cdot}$, 489.0 (85) $[M – 3\ CO]^{+\cdot}$, 461.0 (20) $[M – 4\ CO]^{+\cdot}$, 433.0 (71) $[M – 5\ CO]^{+\cdot}$, 73.0 (82) $[SiMe_3]^{+\cdot}$. $C_{15}H_{28}NO_5PSi_2W$ (573.39): calcd. C 31.42, H 4.92, N 2.44; found C 31.80, H 4.98, N 2.21.

Synthesis of Complex 3e: Aniline (92 μL, 1.0 mmol) was added to a stirred solution of 2*H*-azaphosphirene complex **1** (617 mg, 1.0 mmol) in toluene (30 mL) at 75 °C, and then the reaction mixture was stirred for 3 h. After removal of all volatiles in vacuo (ca. 10^{-2} mbar), the final product **3e** was purified by column chromatography on silica gel (–20 °C, 2 × 9.5 cm, petroleum ether/Et_2O = 9:1). Yellow solid, crystallized from *n*-pentane at –30 °C; yield: 297 mg (0.49 mmol, 49%); m.p. 90 °C. ^1H NMR: δ = 0.20 [d, $^4J_{(P,H)}$ = 0.4 Hz, 9 H, $Si(CH_3)_3$], 0.28 [d, $^4J_{(P,H)}$ = 0.8 Hz, 9 H, $Si(CH_3)_3$], 1.83 [dd, $^2J_{(P,H)}$ = 13.6 Hz, $^3J_{(H,H)}$ = 7.6 Hz, 1 H, PCH], 3.97 (br., 1 H, NH), 6.85 [d, $^3J_{(H,H)}$ = 7.5 Hz, 2 H, *o*-Ph], 7.00 [t, $^3J_{(H,H)}$ = 7.6 Hz, 1 H, *p*-Ph], 7.33 [t, $^3J_{(H,H)}$ = 7.4 Hz, 2 H, *m*-Ph], 7.49 [d, $^1J_{(P,H)}$ = 357.7 Hz, 1 H, PH] ppm. $^{13}C\{^1H\}$ NMR: δ = 0.0 [d, $^3J_{(P,C)}$ = 1.3 Hz, $Si(CH_3)_3$], 15.1 [d, $^1J_{(P,C)}$ = 7.8 Hz, PCH], 115.9 [d, $^3J_{(P,C)}$ = 4.5 Hz, *o*-Ph], 120.0 (s, *p*-Ph), 128.1 (s, *m*-Ph), 141.2 [d, $^2J_{(P,C)}$ = 9.7 Hz, *ipso*-Ph-C], 195.1 [d, $^2J_{(P,C)}$ = 6.5 Hz, *cis*-CO], 196.6 [d, $^2J_{(P,C)}$ = 23.2 Hz, *trans*-CO] ppm. $^{31}P\{^1H\}$ NMR: δ = 5.3 [d_{sat}, $^1J_{(W,P)}$ = 253.0 Hz, $^1J_{(P,H)}$ = 357.3 Hz] ppm. IR (KBr): $\tilde{\nu}$ = 1904 [s, ν(CO)], 1918 [s, ν(CO)], 1946 [vs, ν(CO)], 1986 [m, ν(CO)], 2071 [s, ν(CO)], 2310 [w, ν(PH)], 2960 [w, ν(CH/CH_3)], 3419 [br., ν(NH)] cm^{-1}. MS (EI): *m*/*z* (%) = 607.1 (40) $[M]^{+\cdot}$, 579.1 (9) $[M – CO]^{+\cdot}$, 551.1 (8) $[M – 2\ CO]^{+\cdot}$, 523.1 (100) $[M – 3\ CO]^{+\cdot}$, 73.0 (42) $[SiMe_3]^{+\cdot}$. $C_{18}H_{26}NO_5PSi_2W$ (607.40): calcd. C 35.59, H 4.31, N 2.31; found C 35.73, H 4.61, N 2.06.

Generation of Complexes 7 and 8: A solution of **3a** (56 mg, 0.1 mmol) and 12-crown-4 (16 μL) in tetramethylethylenediamine (TMEDA; 1 mL) was added dropwise to a solution of LDA [0.11 mmol; freshly prepared from *n*-butyllithium (75 μL, 1.6 M, 0.11 mmol) and diisopropylamine (20 μL, 0.1 mmol) in diethyl ether (1 mL)] in TMEDA (1 mL) and cooled to –78 °C. The reaction mixture was stirred for 1 h, and then a $^{31}P\{^1H\}$ NMR spectrum was recorded. **7:** δ = 101.8 [q, $^1J_{(P,Li)}$ = 62.1 Hz] ppm. **8:** δ = 39.1 [s, $^1J_{(P,H)}$ = 195.9 Hz] ppm.

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