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Investigations on the Reactivity of Li/Cl Phosphinidenoid Tungsten Complexes toward Various Iodine Compounds

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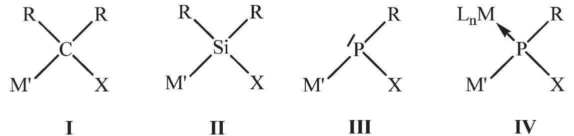
Reactivity studies of Li/Cl phosphinidenoid $W(CO)_5$ complexes **2a**,**b** toward various iodine compounds are reported. Transiently generated complexes **2a**,**b** yielded no selective reactions with 3-, 9-, and 9,12-diiodo *o*-carbaboranes **3a**−**c**, whereas clean transfer-iodination reaction occurred with *C*-iodo-substituted *o*-carbaboranes **3d**,**e**, thus giving chloro(iodo)phosphane complex **6a** in the case of **2a**. Complex **2a** was also reacted with iodo(phenyl)acetylene to yield complexes **6a**, **8**, and **9** in competing reactions. An independent pathway to chloro(iodo)phosphane complexes **6a**,**b** was reaction of complexes **2a**,**b** with elemental iodine at low temperature. All compounds were unambiguously characterized by elemental analysis, multinuclear NMR, IR, MS studies, and, in the case of **6a** and **9**, single-crystal X-ray diffraction.

Introduction

Carbenoids **I**[1] and silylenoids **II**[2] are versatile reactive intermediates in organic synthesis (Scheme 1). In contrast, phosphinidenoids **III** are still unknown, although some authors speculated[3] about their existence.

Recently, we reported the first examples of Li/X phosphinidenoid $W(CO)_5$ complexes (**IV**; X = F,[4] Cl[5]), stable in THF solution (X = F) up to 10 °C but unstable in the case of X = Cl above −40 °C, which decomposed upon warming to give mono- and dinuclear diphosphene complexes.[4,5] Reaction of the complex $[W(CO)_5(Li/ClPCH(SiMe_3)_2)]$ with methyl iodide yielded the corresponding *P*-Me-substituted phosphane complex and thus provided evidence for a nucleophilic, phosphanide complex-like reactivity. In addition, reactions of the same Li/Cl phosphinidenoid complex with π-systems such as dimethyl cyanamide, phenylacetylene, or benzaldehyde led to three-membered heterocycle complexes, which demonstrated a phosphinidene complex-like behavior. More recently, we obtained the first strong NMR spectroscopic evidence for complexes $[W(CO)_5(Li/FPCH(SiMe_3)_2)]$ and $[W(CO)_5(Li/ClPC_5Me_5)]$, although the bonding of lithium remained unclear. The latter complex also decomposed above −40 °C, giving a P,C-cage complex (cf. Scheme 2) comprising formally two phosphinidene complex units and revealing that one C_5Me_5 (= Cp*) ring was involved.[6] Here, results on new nucleophilic as well as iodination and exchange reactions of Li/Cl phosphinidenoid complexes are reported.

Scheme 1. Carbenoids, Silylenoids, Phosphinidenoids, and Complexes Thereof[a]



[a] R = ubiquitous organic substitutents; M′ = main group element metal; X = halogen; ML_n = transition metal complex.

Results and Discussion

In order to start examining the scope of nucleophilic reactions while focusing on iodine derivatives, we decided to start first on multifunctional iodocarbaboranes. These present C_c−H, B−H, B−I, and C−I functional groups and a

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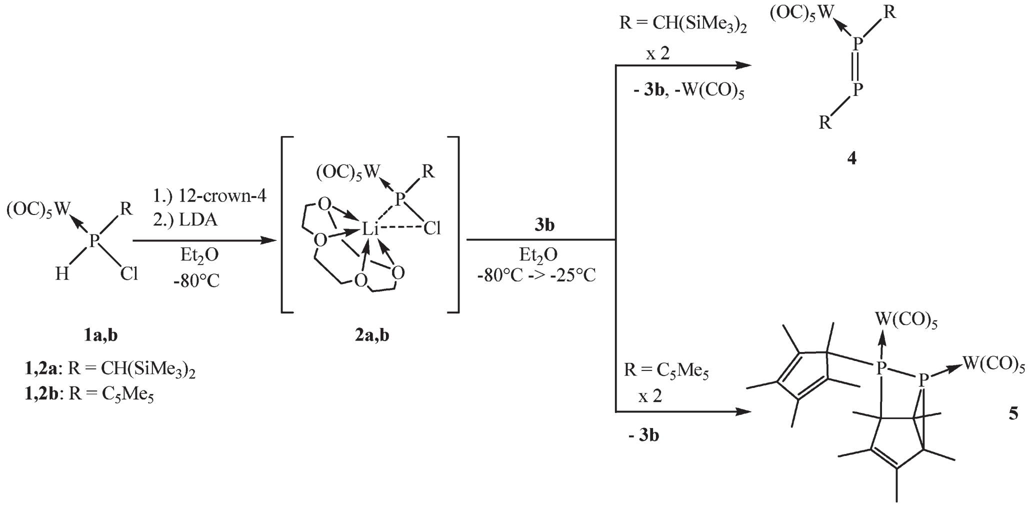
Scheme 2. Generation and Reaction of Li/Cl Phosphinidenoid Complexes 2a,b in the Presence of *B*-Iodo-Substituted *o*-Carbaborane 3b (shown as example)



modulated reactivity depending on the occupied site in the cluster;[7] C_c corresponds to the cluster's carbon atoms. Another strong motivation was to get access to *B*-phosphanyl functional *o*-carbaboranes (hitherto unknown) by reacting phosphinidenoid complexes with various carbaborane species (Figure 1). With this aim in mind we generated Li/Cl phosphinidenoid complexes **2a**,**b** as previously described from complexes **1a**[8] and **1b**[9] in the presence of 3-iodo-, 9-iodo-, and 9,12-diiodo *o*-carbaboranes **3a**−**c**[7,10−12] (Scheme 2).

Unfortunately, ^{31}P and ^{11}B NMR studies of the reactions did not provide spectroscopic evidence of products possessing a B−P bond. Instead exclusively formation of **4**[5] and **5**[6] was observed. Nevertheless, in one of the reactions of complex **2a** with 9,12-diiodo *o*-carbaborane **3c** new products were observed by ^{31}P NMR spectroscopy that displayed resonances at 190.9 (^1J(W,P) = 268.3 Hz) and 170.6 (^1J(W,P) = 260.7 Hz, ^2J(P,H) = 15.3 Hz), which perhaps point to *o*-carbaboranyl-substituted chloro-(organo)-phosphane complexes, but due to rapid decomposition further investigations were prevented. Thus, after having observed the lack of reactivity of complexes **2a**,**b** toward B−I bonds, we addressed the question whether *C*-iodo *o*-carbaboranes might be better substrates for substitution reactions. To learn more about this possibility, 1-iodo-2-methyl- and 1-iodo-2-phenyl-substituted carbaboranes **3d**,**e** were synthesized on purpose by reaction of 1-methyl and 1-phenyl carbaborane, **7a**,**b**, respectively, with butyllithium and iodine at 0 °C. Li/Cl phosphinidenoid complexes **2a**,**b** were generated and reacted with 1-iodo-2-methyl- or 1-iodo-2-phenyl-substituted carbaboranes **3d**,**e**. Instead of a nucleophilic iodine substitution, we obtained an unprecedented intermolecular iodine-transfer reaction, thus resulting in the formation of *P*-iodo-substituted chlorophosphane complexes **6a**,**b** together with deiodinated carboranes **7a**,**b** (Scheme 3) as the major products. During these studies it did not became apparent if *C*-Li-carbaborane derivatives were transiently formed that eventually yielded **7a**,**b** (Scheme 3). The ^{31}P NMR spectra of complexes **6a**,**b** displayed data (**6a**: δ = 78.2, ^1J(W,P) = 311.5 Hz; **6b**: δ = 98.6, ^1J(W,P) = 309.0 Hz) with downfield-shifted resonances and increased tungsten−phosphorus coupling constant magnitudes, which both reflect the formal exchange of hydrogen by iodine in **1a**,**b**.

One straightforward way to deal with the relative acidity of the C_c−H bonds in carboranes is to consider that the C_c−H bond is the result of the overlap of an sp orbital on C with the hydrogen s orbital, and a similar picture can be drawn for the C−H bond in acetylene, and thus for the C−I bond in iodoacetylene derivatives. To check the consistency of the model, *in situ* generated iodo(phenyl)acetylene was mixed with the Li/Cl phosphinidenoid complex **2a** (instead of the carbaborane **3d**). Again, complex **6a** was formed but not as the major product, thus partly fulfilling our expectations. If the ratio of complex **2a** to iodo phenylacetylene was 1:1.6, a mixture of complexes **6a**, **8**, and **9** (ratio 6:1:11.7) was obtained (Scheme 4); if the ratio of the starting materials was 1:1, we obtained a different product ratio of 6:1:2. Formation of **6a** may be interpreted as substitution of Li$^+$ by I$^+$, partly meeting our expectations and thus backing the beforehand made assumption on the *C*-iodo carbaborane acting as a clean source of iodonium. In contrast, the formation of **8** and **9** is not understood.

Comparing the reactions of the alkyne or the carbaboranes with **2a**, the formation of **9** is of particular interest, as it clearly evidences the disparity in behavior of "1-R-1,2-$C_2B_{10}H_{10}$R" and "R-C≡C$^-$" units. The idea that complex **6a** was formed via some kind of iodine-atom transfer reaction (from **3c**,**d**) prompted us to investigate the reaction of *in situ* generated **2a**,**b** with elemental iodine at low temperature. Under these conditions complexes **6a**,**b** and lithium iodide were selectively formed; noteworthy is that oxidation of the Li/Cl phosphinidenoid complexes was not observed.

All final products were obtained in pure form by low-temperature column chromatography and were unambiguously

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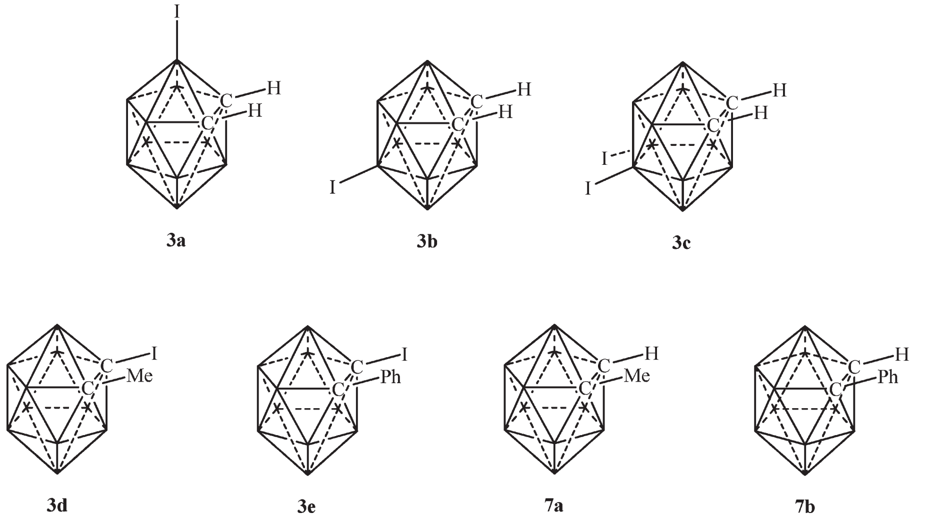
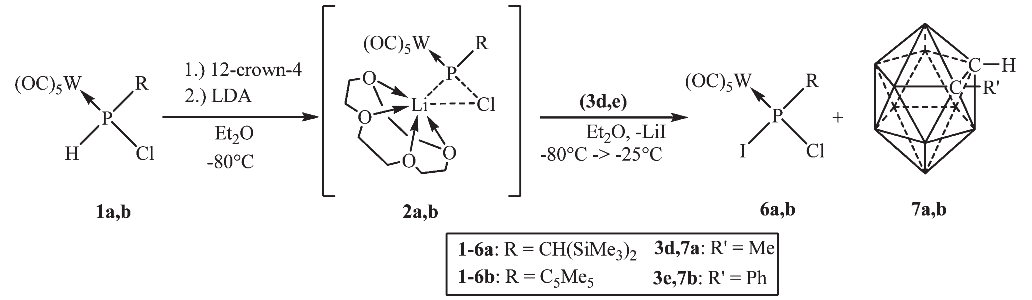
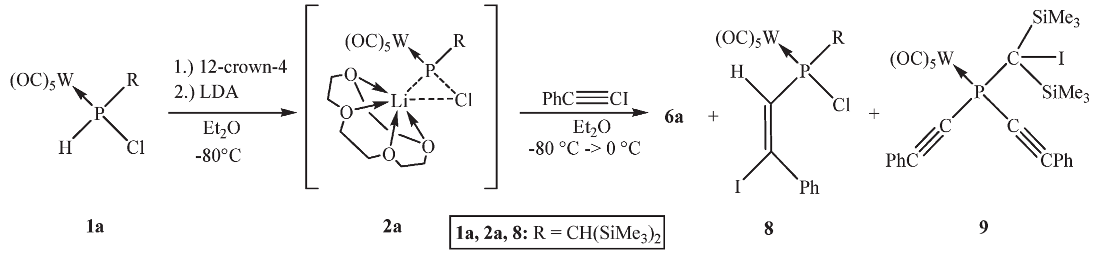


Figure 1. Carbaborane derivatives.

Scheme 3. Reaction of Li/Cl Phosphinidenoid Complexes 2a,b with *C*-Iodo-Substituted *o*-Carboranes 3d,e



Scheme 4. Reaction of Li/Cl Phosphinidenoid Complex 2a with Iodo(phenyl)acetylene



characterized by elemental analysis, NMR and IR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction studies in the cases of complexes **6a** and **9** (Figures 1 and 2).[13]

Structure Discussion

The unambiguously confirmed molecular structures of **6a** and **9** are displayed in Figures 2 and 3.[13] Complex **6a** shows a typical tetrahedral environment at the phosphorus center with a small C1−P−I (95.78(6)°) and a large W−P−C1 angle (120.05(16)°). In complex **6a** P−W, P−C1, and P−Cl bond lengths are slightly elongated compared to the corresponding dichlorophosphane tungsten complex reported before (P−W 2.4589(7), P−C 1.804(3), P−Cl 2.0598(9) Å), which probably is due to the larger iodine atom.[14]

A comparison of selected distances in complex **9** with corresponding bonds of $[\mathrm{Cr(CO)_5P(C{\equiv}CPh)_3}]$[15] (C≡C 1.176, P−C 174.8 and 175.3 Å) revealed more elongated C≡C and P−C bonds in the case of **9** (C8−C9 1.202(4), C16−C17 1.205(4), P−C8 1.762(3), and P−C16 1.762(3) Å). The P−C≡C bond angles of **9** are 167.5(3)° and 167.0(3)° and, thus, slightly bent toward the $\mathrm{W(CO)_5}$ group.

Conclusions

The reactivity of the transient Li/Cl phosphinidenoid complexes **2a**,**b** toward various iodine-containing compounds was examined in a series of experiments. With B−I containing *o*-carbaboranes **3a−c** no selective reactions were obtained with complexes **2a**,**b**, whereas with 1-iodo *o*-carbaboranes **3d**,**e** reacted with **2a**,**b** to yield the I/Cl mixed-substituted organophosphane complexes **6a**,**b** via iodine-transfer

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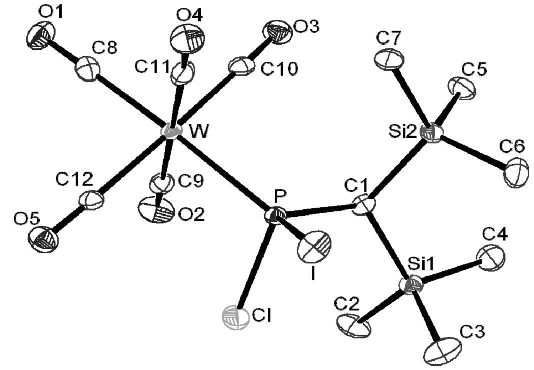

Figure 2. Structure of complex **6a** (50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.4742(12), P−C1 1.819(5), P−Cl 2.0988(17), P−I 2.4489(12), W−P−C1 120.05(16), Cl−P−I 95.78(6), C1−P−I 105.21(16), C1−P−Cl 106.89(17), W−P−Cl 107.64(6).

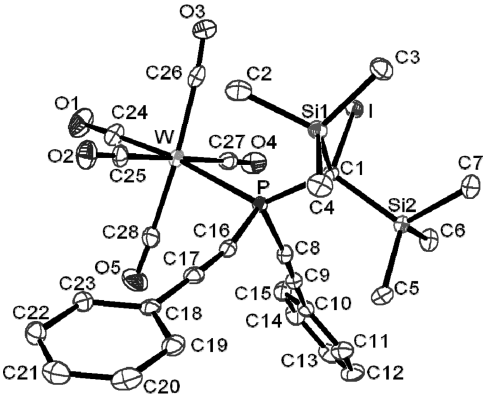

Figure 3. Structure of complex **9** (50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [deg]: W−P 2.5426(8), P−C1 1.859(3), P−C16 1.762(3), C16−C17 1.205(4), C17−C18 1.436(4), P−C8 1.762(3), C8−C9 1.202(4), C9−C10 1.440(4), I−C1 2.191(3); W−P−C1 130.35(10), C16−P−C8 102.12(14), C17−C16−P 178.5(3), C9−C8−P 167.0(3), P−C1−I 103.66, P−C1−Si1 112.43(15), P−C1−Si2 115.63(15).

reaction. Complexes **6a**,**b** could also be obtained with elemental iodine. Further studies using complex **2a** as a good case in point and iodo(phenyl)acetylene showed the formation of a mixture of complexes **6a**, **8**, and **9**, thus revealing multiple reaction pathways in this particular case; current studies are devoted to elucidate this problem. In total, these first results reveal that these novel reactive intermediates have a rich and surprisingly new chemistry.

Experimental Section

All operations were performed in an atmosphere of purified and dried argon. Solvents were distilled from sodium. NMR data were recorded on a Bruker Avance 300 spectrometer at 25 °C (if not mentioned otherwise) using C_6D_6 (**6a**,**b**) or $CDCl_3$ (**8**, **9**) as solvent and internal standard; shifts are given relative to tetramethylsilane (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz), external BF_3←OEt_2 (^{11}B and ^{11}B{^{1}H} 96.29 MHz), and 85% H_3PO_4 (^{31}P:, 121.5 MHz) in ppm. Mass spectra were recorded on a Kratos MS 50 spectrometer (EI, 70 eV); only *m*/*z* values are given. Elemental analyses were performed using an Elementa (Vario EL) analytical gas chromatograph. Infrared spectra were collected on a FT-IR Nicolet 380. Melting points were obtained on a Büchi 535 capillary apparatus. For compounds **3d**,**e**, elemental analyses were performed using a Carlo Erba EA1108 microanalyser, and IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. X-ray crystallographic analysis of **6a** and **9**: Data were collected on a Nonius KappaCCD diffractometer at 100 K using Mo Kα radiation (λ = 0.71073 Å). The structures were refined by full-matrix least-squares on F^2 (SHELXL-97[16]). All non-hydrogens were refined anisotropically. The hydrogen atoms were included in calculated positions using a riding model.

Synthesis of 1-Me,2-I-1,2-*closo*-$C_2B_{10}H_{10}$ (3d). To a stirring solution of 1-Me,1,2-*closo*-$C_2B_{10}H_{11}$ (500 mg, 3.16 mmol) in diethyl ether (20 mL) cooled to 0 °C in an ice−water bath was added, dropwise, a solution of *n*-butyllithium in hexane (2 mL, 1.6 M, 3.32 mmol) under nitrogen atmosphere. The suspension was stirred at room temperature for 0.5 h, then cooled again to 0 °C, at which point I_2 (842.0 mg, 3.32 mmol) was added in a single portion. The resulting solution was stirred at 0 °C for 30 min and at room temperature for a further 30 min, then extracted with 5% aqueous $Na_2S_2O_3$ (20 mL) and washed with water (2 × 5 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated *in vacuo* to give a pale yellow solid. The crude product was purified by silica gel flash chromatography at −10 °C under argon atmosphere, using diethyl ether as the eluting solvent to yield 1-Me,2-I-1,2-*closo*-$C_2B_{10}H_{10}$ (691 mg, 77%).

3d: ^{1}H NMR (CD_3COCD_3) [ppm] δ 2.25 (3 H, s); ^{1}H{^{11}B} NMR (CD_3COCD_3) [ppm] δ 2.83 (s, 3H), 2.66 (s, 3H), 2.31 (s, 2H), 2.25 (s, 3H), 2.13 (s, 2H), 1.91 (s, 1H); ^{13}C{^{1}H} NMR (CD_3COCD_3) [ppm] δ 75.68 (s), 27.81 (s), 16.93 (s); ^{11}B NMR (CD_3COCD_3) [ppm] δ −3.3 (d, ^{1}J(B,H) = 75 Hz, 2B), −5.4 (d, ^{1}J(B,H) = 90 Hz, 1B), −6.4 (d, ^{1}J(B,H) = 90 Hz, 2B), −6.9 (d, ^{1}J(B,H) = 87 Hz, 2B), −8.7 (d, ^{1}J(B,H) = 83 Hz, 2B), −9.5 (d, ^{1}J(B,H) = 80 Hz, 2B); FTIR (KBr) ν (cm^{-1}) 2937 (s, C_{alkyl}−H), 2590 (s, B−H). Anal. Calcd for $C_3B_{10}H_{13}I$: C 12.62, H 4.61. Found: C 13.04, H 4.74.

Synthesis of 1-Ph,2-I-1,2-*closo*-$C_2B_{10}H_{10}$ (3e). The synthetic procedure was the same as for **3d** using 1-Ph,1,2-*closo*-$C_2B_{10}H_{11}$ (250 mg, 1.14 mmol) in diethyl ether (25 mL) and a solution of *n*-butyllithium in hexane (0.75 mL, 1.6 M, 1.2 mmol) and I_2 (303.0 mg, 1.2 mmol). The workup was followed to obtain 1-Ph,2-I-1,2-*closo*-$C_2B_{10}H_{10}$ (278 mg, 71%).

3e: ^{1}H NMR (CD_3COCD_3) [ppm] δ 7.77 (d, ^{3}J(H,H) = 3 Hz, 2H), 7.55 (m, 3H); ^{1}H{^{11}B} NMR (CD_3COCD_3) [ppm] δ 7.77 (d, ^{3}J(H,H) = 3 Hz, 2H), 7.55 (m, 3H), 3.23 (br s, 2H), 2.88 (br s, 3H), 2.44 (br s, 2H), 2.26 (br s, 3H), 2.15 (br s, 1H); ^{13}C{^{1}H} NMR (CD_3COCD_3) [ppm] δ 132.87 (s), 131.34 (s), 128.98 (s), 84.67 (s), 20.89 (s); ^{11}B NMR (CD_3COCD_3) [ppm] δ −2.9 (d, ^{1}J(B,H) = 72 Hz, 2B), −6.9 (d, ^{1}J(B,H) = 81 Hz, 2B), −8.8 (m, ^{1}J(B,H) = 76 Hz, 6B); FTIR (KBr) ν (cm^{-1}) 3064, 2962 (w, C_{aryl}−H), 2632, 2599, 2574, 2572 (s, B−H), 1494 (s, C_{aryl}−C_{aryl}).

Reaction of Complexes 2a,b with 3d,e. To a solution of 0.11 mmol of lithium diisopropylamide (LDA, freshly prepared from 0.07 mL (0.11 mmol) of *n*-butyllithium and 16 μL (0.11 mmol) of diisopropylamine) in 0.5 mL of diethyl ether cooled to −80 °C was slowly added a solution of 55.1 mg (0.1 mmol) of **1a** (or 53.0 mg (0.1 mmol) of **1b**) and 17 μL (0.11 mmol) of 12-crown-4 in 0.5 mL of diethyl ether. Then a solution of 0.2 mmol of **3d** (57 mg) or **3e** (69 mg) in 0.5 mL of XXXX was added, and the reaction mixture was stirred for 2.5 h while gently warming to 0 °C. The solvent was removed under vacuum, and the residue was dissolved in C_6D_6 and analyzed by multinuclear NMR spectroscopy.

Synthesis of Complex 6a. To a solution of 0.44 mmol of lithium diisopropylamide (LDA, freshly prepared from

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0.28 mL (0.44 mmol) of *n*-butyllithium and 0.06 mL (0.44 mmol) of diisopropylamine) in 10 mL of diethyl ether cooled to −80 °C was slowly addded a solution of 221 mg (0.4 mmol) of **1a** and 65 μL (0.4 mmol) of 12-crown-4 in 5 mL of diethyl ether. Then a solution of 112 mg (0.44 mmol) of iodine in 5 mL of diethyl ether was dropped into the phosphinidenoid complex solution, and the reaction mixture was stirred for 3.5 h while gently warming to +10 °C. The solvent was removed under vacuum. The product was extracted five times with 3 mL of *n*-pentane. After evaporation, the yellow solid was dissolved with 2 mL of *n*-pentane and cooled to −80 °C. The precipitated crystals were separated from the solution by a syringe. The residue was dried under vacuum.

6a: yellow solid; yield 195 mg (0.29 mmol, 72%); mp 64−69 °C (dec); NMR spectroscopy (C_6D_6, 30 °C): ^{1}H NMR [ppm] δ 0.21 (s, 9H, $SiMe_3$), 0.27 (d, ^{4}J(P,H) = 0.57 Hz, 9H, $SiMe_3$), 2.55 (d, ^{2}J(P,H) = 5.19 Hz, 1H, PCH); ^{13}C{^{1}H} NMR [ppm] δ 0.0 (d, ^{3}J(P,C) = 4.5 Hz, $SiMe_3$), 1.0 (d, ^{3}J(P,C) = 3.2 Hz, $SiMe_3$) 39.5 (d, ^{1}J(P,C) = 31.7 Hz, PC), 195.8 (d_{Sat}, ^{1}J(W,C) = 128.0 Hz, ^{2}J(P,C) = 7.1 Hz, *cis*-CO), 196.8 (d_{Sat}, ^{2}J(P,C) = 44.3 Hz, *trans*-CO); ^{31}P{^{1}H} NMR [ppm] δ 78.2 (s_{Sat}, ^{1}J(W,P) = 311.5 Hz); MS *m*/*z* (%) 675.9 (4) [$(M)^+$]; FTIR (KBr) ν(CO) $\tilde{\nu}$ = 1951 (s), 1997 (m), 2079 (m) [cm^{-1}]. Anal. Calcd: C 21.30, H 2.83. Found: C 21.50, H 3.04. X-ray crystallographic analysis: Suitable pale yellow single crystals were obtained from concentrated *n*-pentane solutions. $C_{12}H_{19}ClIO_5PSi_2W$; crystal size 0.54 × 0.16 × 0.10 mm^3, monoclinic, $P21/n$, a = 14.7403(4) Å, b = 9.6381(2) Å, c = 15.3230(3) Å, $\alpha = 90°$, β = 101.3970(10)°, γ = 90°, V = 2133.99(8) $Å^3$, Z = 4, $2\theta_{max}$ = 55°, collected (independent) reflections = 20 403 (4838), R_{int} = 0.0856, μ = 7.188 mm^1, 218 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0394, wR_{21} (for all data) = 0.1042, max./min. residual electron density = 1.749/−4.643 e $Å^3$.

Synthesis of Complex 6b. To a solution of 0.5 mmol of lithium diisopropylamide (LDA, freshly prepared from 0.32 mL (0.5 mmol) of *n*-butyllithium and 0.07 mL (0.5 mmol) of diisopropylamine) in 5 mL of diethyl ether cooled to −80 °C was slowly added a solution of 221 mg (0.42 mmol) of **1b** and 68 μL (0.42 mmol) of 12-crown-4 in 5 mL of diethyl ether. Then a solution of 107 mg (0.42 mmol) of iodine in 1 mL of diethyl ether was dropped into the phosphinidenoid complex solution, and the reaction mixture was stirred for 3.5 h while gently warming to 0 °C. The liquid was filtered from the solid and dried under vacuum. The raw product was purified further by column chromatography (Al_2O_3, −20 °C) using *n*-pentane.

6b: orange solid; yield 161 mg (0.25 mmol, 59%); mp 104 °C (dec); NMR spectroscopy (C_6D_6, 30 °C): ^{1}H NMR [ppm] δ 1.37 (d, J(P,H) = 16.4 Hz, 3H, Cp*(C1)-CH_3), 1.56 (ddq, J(P,H) = 7.4 Hz, J(H,H) = 3.2 Hz, J(H,H) = 1.1 Hz, 6H, Cp*-CH_3), 1.75 (br s, 3H, Cp*-CH_3), 1.79 (br s, 3H, Cp*-CH_3); ^{13}C{^{1}H} NMR [ppm] δ 10.4 (d, J(P,C) = 2.6 Hz, Cp*-CH_3) 10.5 (d, J(P,C) = 2.6 Hz, Cp*-CH_3) 11.8 (d, J(P,C) = 0.6 Hz, Cp*-CH_3) 12.1 (s, Cp*-CH_3) 16.5 (d, ^{2}J(P,C) = 6.8 Hz, Cp*(C1)-CH_3) 65.5 (d, ^{1}J(P, C) = 19.4 Hz, Cp*(C1)), 133.5 (d, J(P,C) = 3.2 Hz, Cp*), 133.6 (d, J(P,C) = 1.3 Hz, Cp*), 145.0 (d, J(P,C) = 10.0 Hz, Cp*), 145.1 (d, J(P,C) = 9.7 Hz, Cp*), 195.6 (d_{Sat}, ^{2}J(P,C) = 7.1 Hz, *cis*-CO), 196.7 (d_{Sat}, ^{2}J(P,C) = 44.9 Hz, *trans*-CO); ^{31}P{^{1}H} NMR δ 98.6 (s_{Sat}, ^{1}J(W,P) = 309.0 Hz); MS *m*/*z* (%) 652 (1) [$(M)^+$]; FTIR (KBr; ν(CO)) $\tilde{\nu}$ = 1939 (s), 1995 (m), 2078 (m) [cm^{-1}]. Anal. Calcd: C 27.61, H 2.32. Found: C 28.26, H 2.50.

Synthesis of Complexes 8 and 9. To a solution of 1.1 mmol of lithium diisopropylamide (LDA, freshly prepared from 0.69 mL (1.0 mmol) of *n*-butyllithium and 0.14 mL (1.0 mmol) of diisopropylamine) in 10 mL of diethyl ether cooled to −90 °C was slowly added a solution of 550 mg (1 mmol) of **1a** and 180 μL (1.1 mmol) of 12-crown-4 in 10 mL of diethyl ether. After 5 min an *in situ* prepared solution of iodo phenylacetylene was added. The reaction mixture was stirred for 2 h while slowly warming to 0 °C. Then the solvents were evaporated, and the residue was suspended with 10 mL of diethyl ether. The products were adsorbed on Al_2O_3 purified by column chromatography (Al_2O_3, −20 °C) using (1) petroleum ether and (2) a mixture of petroleum ether and diethyl ether (19:1 and 18:2). The second fraction contained **8**, which after removal of the solvents was obtained as a pale yellow solid and was subsequently washed with 2 mL of *n*-pentane. **9** was obtained from the third and fourth fraction as a sunflower yellow powder, which was subsequently washed three times with 2 mL of *n*-pentane to yield the pure product as a pale yellow powder.

8: pale yellow solid; yield 74 mg (0.095 mmol, 10%); mp 132−135 °C (dec); ^{1}H NMR [ppm] δ 0.30 (s, 18H, $(SiMe_3)_2$), 1.69 (d, 1H, ^{2}J(P,H) = 4.96 Hz, PC*H*), 7.40 (d, 1H, ^{2}J(P,H) = 16.8 Hz, PC*H*), 7.45 (m, 2H, Ph), 7.28 (m, 3H, Ph); ^{13}C{^{1}H} NMR [ppm] δ 1.6 (d, ^{1}J(P,C) = 4.1 Hz, $SiMe_3$), 2.2 (d, ^{1}J(P,C) = 2.7 Hz, $SiMe_3$), 33.1 (d, ^{1}(P,C) = 9.1 Hz, P-*C*H), 112.6 (d, ^{3}J(P, C) = 3.3 Hz, i-Ph), 127.6 (s, o-Ph), 127.7 (s, m-Ph), 128.8 (s, p-Ph), 139.8 (d, ^{2}J(P,C) = 4.4 Hz, PCH*C*IPh), 140.7 (d, ^{1}J(P,C) = 11.0 Hz, P*C*HCIPh), 195.7 (d, ^{1}J(W,C) = 127.6 Hz, ^{2}J(P,C) = 7.1 Hz, *cis*-CO), 197.8 (d, ^{2}J(P,C) = 33.0 Hz, *trans*-CO) ppm; ^{31}P{^{1}H} NMR [ppm] δ 89.7 (d_{Sat}, ^{1}J(W,P) = 283.6 Hz); MS *m*/*z* (%) 777.9 (1) [$(M)^+$]; FTIR (KBr) ν(CO) $\tilde{\nu}$ = 2074 (m), 1984 (m), 1923 (s); ν(C=C): 1598 (w), 1967 (w), 1581 (w) [cm^{-1}]. Anal. Calcd C 30.85, H 3.24. Found: C 30.53, H 3.32.

9: pale yellow solid; yield 159 mg (0.19 mmol, 19%); mp 116−120 °C (dec); ^{1}H NMR [ppm]: δ 0.5 (s, 18H, $(SiMe_3)_2$), 7.4 (m, 10H, CCPh 2×); ^{13}C{^{1}H} NMR [ppm] δ 3.5 (s, $(SiMe_3)_2$), 85.5 (d, ^{1}J(P,C) = 73.9 Hz, P-*C*C-Ph), 109.1 (d, ^{2}J(P,C) = 13.7 Hz, P-C*C*-Ph), 120.7 (s, ipso-Ph−C), 128.3 (s, ortho-Ph-CH), 129.9 (s, para-Ph-CH), 131.7 (s, meta-Ph-CH), 198.0 (d, ^{2}J(P,C) = 6.6 Hz, *cis*-CO), 200.1 (d, ^{2}J(P,C) = 28.6 Hz, *trans*-CO); ^{31}P{^{1}H} NMR [ppm] δ 19.2 (d_{Sat}, ^{1}J(W,P) = 265.8 Hz); MS *m*/*z* (%): 715.1 (0.5) [$(M)^+ - I$]; FTIR (KBr) ν(CO) $\tilde{\nu}$ = 2070 (m), 1981 (m), 1924 (s); ν(C≡C) 2163 (m) [cm^{-1}]. Anal. Calcd: C 39.92, H 3.35. Found: C 39.77, H 3.42.

X-ray Crystallographic Analysis. Suitable pale yellow single crystals were obtained from concentrated diethyl ether solutions. $C_{28}H_{28}IO_5PSi_2W$; crystal size 0.44 × 0.40 × 0.39 mm^3, monoclinic, $P21/n$, a = 12.4156(3) Å, b = 14.4943(5) Å, c = 17.6597(5) Å, $\alpha = 90°$, β = 91.404(2)°, γ = 90°, V = 3177.00(16) $Å^3$, Z = 4, $2\theta_{max}$ = 55°, collected (independent) reflections = 31 420 (7154), R_{int} = 0.0535, μ = 4.767 mm^1, 349 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0263, wR_{21} (for all data) = 0.0685, max./min. residual electron density = 1.726/−1.684 e $Å^3$.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **6a** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of **6a** and **9** have also been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-729255 (**6a**) and CCDC-729255 (**9**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data _request/cif.