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Notes

Photochemical and Thermal Reactions of a 2*H*-Azaphosphirene Complex with Isonitriles

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*Summary: Photochemical ring opening of {2-[bis(trimethylsilyl)methyl]-3-phenyl-2H-azaphosphirene-κP}-pentacarbonyltungsten(0) (**1**) in diethyl ether in the presence of tert-butyl isocyanide (**2**) yields the η^1-1-aza-3-phosphaallene complex **4** at low temperature (−30 °C), the formation of which is explained via a 1,1-addition of **2** with the transiently formed terminal phosphinidene complex **3**. Complex **4** decomposed slowly at ambient temperature to furnish the [bis(trimethylsilyl)methyl]-cyanophosphane complex **5** and isobutene. The same result was obtained via thermal ring opening of complex **1** at high temperature. In contrast, thermolysis of **1** in the presence of cyclohexyl isocyanide (**7**) afforded the N-cyclohexyl-substituted η^1-1-aza-3-phosphaallene complex **8**. Complexes **4**, **5**, and **8** were unambiguously characterized by NMR and IR spectroscopy; the structure of complex **5** was established by X-ray crystal structure analysis. The structure of **5** and the energetics of its formation via decomposition of **4** were studied by DFT calculations, thus confirming the proposed reaction course.*

Introduction

Since the first synthesis of a stable 1-aza-3-phosphaallene by Kolodiazhnyi and co-workers,[1] the synthesis of allenes or cumulenes of the general formula E═C═E′, containing doubly bonded heavy elements such as E = P, As, Si, Ge, Sn and E′ = C, N, P, As, O, S, has become a new challenge in organoelement chemistry.[2] Access to stable 1-aza-3-phosphaallenes—and related compounds—relies on the use of sterically demanding substituents at the P and N atoms of the P═C═N moiety and is most often achieved via base-induced elimination reactions. Whereas the structures and reactivity of 1-aza-3-phosphaallenes have been intensively studied, very little is known about their complexes. Usually, η^2(*P*,*C*)-[3] (**I**) and η^2(*N*,*C*)-1-aza-3-phosphaallene complexes (**IIa**,**b**)[3,4] (Chart 1) are obtained using 1-aza-3-phosphaallenes and complexing agents. Very recently, the reaction of a nucleophilic terminal titanium phosphinidene complex with *tert*-butyl isocyanide was described, thus leading to a η^2-1-aza-3-phosphaallene complex (**IIb**) via formal insertion of the isonitrile moiety into the Ti−P bond.[4] To the best of our knowledge, η^1-1-aza-3-phosphaallene complexes are still unknown.

Chart 1. Examples of η^2-1-Aza-3-phosphaallene Complexes

I **IIa,b**

Mes* = 2,4,6-tris(*tert*butyl)-phenyl;
[M] = PtR_2, R = PPh_3, $P(c\text{-}C_6H_{11})_3$ (**I**);
[M] = $(C_5H_4SiMe_3)_2NbCl$, R = Ph (**IIa**);
[M] = Ti (nacnac)(^{t}BuNC)(^{t}BuCH$_2$C=N^{t}Bu), R = ^{t}Bu (**IIb**).

Recently, we have shown that 2*H*-azaphosphirene complexes[5] are effective precursors for highly reactive electrophilic terminal phosphinidene complexes bearing bulky substituents at phosphorus,[6] which can be used to access unusual three-membered phosphorus heterocycles. More fascinating was the observation that nitrilium phosphane−ylide complexes can be generated—via 1,1-addition of carbonitriles to the phosphorus center of the electrophilic phosphinidene complexes—and consequently used as new building blocks in phosphorus chemistry.[7] Therefore, we became interested in studies on the generation and synthetic potential of 1,1-adducts of electrophilic phosphinidene complexes with π systems possessing an element with an electron lone pair at the terminal position. Herein, we describe the first examples of 1,1-addition reactions of a transiently formed electrophilic terminal phosphinidene complex with isocyanides,

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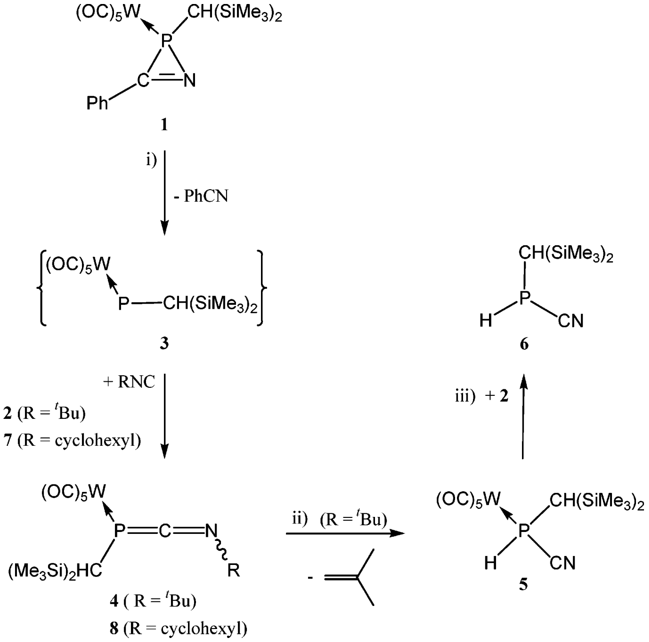
10.1021/om049014u CCC: $30.25

Scheme 1. Photochemical and Thermal Reactions of Complex 1 with Isonitriles 2 and 7[a]



[a] Legend: (i) diethyl ether, −30 °C, 120 min (R = ^{t}Bu) or toluene, 75 °C, 45 min (R = cyclohexyl); (ii) *n*-pentane, room temperature, slow; (iii) toluene, 110 °C, 90 min.

thus giving the first η^1-1-aza-3-phosphaallene complexes; one of them (the *N-tert*-butyl-substituted complex) exhibits an unprecedented reactivity pattern: i.e., ω-H transfer to the low-coordinated phosphorus center with expulsion of isobutene.

Results and Discussion

Photochemical ring opening of the 2*H*-azaphosphirene complex **1** in diethyl ether in the presence of *tert*-butyl isocyanide (**2**) yielded selectively the η^1-1-aza-3-phosphaallene complex **4** at low temperature. On the basis of our earlier findings on the photochemistry of 2*H*-azaphosphirene complex **1**,[8] we assume that complex **4** is formed via a 1,1-addition of the isonitrile **2** with the transiently formed terminal phosphinidene complex **3** (Scheme 1). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR reaction monitoring revealed that complex **4** (δ −136.6, $^1J_{\mathrm{P,W}} = 194.5$ Hz) is formed in $\mathrm{Et_2O}$ at −30 °C, but after 48 h at ambient temperature the amount of **4** had decreased in favor of the [bis(trimethylsilyl)methyl]cyanophosphane complex **5** and isobutene. The latter was identified by ^{1}H NMR spectroscopy. Complex **5** was also obtained on subjecting the 2*H*-azaphosphirene complex **1** to thermal ring opening, but under these conditions **5** was formed together with two minor products (<5%), **6** ($\delta(^{31}\mathrm{P})$ −104.7, $^1J_{\mathrm{P,H}} = 223.8$ Hz) and **7** ($\delta(^{31}\mathrm{P})$ −41.7, $^1J_{\mathrm{P,W}} = 216.6$, $^1J_{\mathrm{P,H}} = 326.8$ Hz). The product **6** could be obtained as the main product, if the thermal reaction with **5** was carried out at 70 °C in the presence of 1 equiv of **2**. It should be noted that bis(*tert*-butyl)-1-aza-3-phosphaallene is stable with regard to a ω-H transfer reaction from the *N-t*-Bu group to phosphorus (*it can be purified through distillation*).[1]

For comparison, we carried out the thermolysis of **1** in the presence of cyclohexyl isocyanide (**7**) and obtained the η^1-1-aza-3-phosphaallene complex **8** in a more clean reaction. Interestingly, complex **8** was stable in solution at room temperature, thus showing the necessity of a (more) pendant group to promote H transfer and decomposition (Scheme 1). However, also surprisingly, the diphosphene complex **9**[9]—usually not obtained in thermal reactions of complex **1**!—was also formed in this reaction (Scheme 2). The reaction pathway to **9** is unclear at the moment.

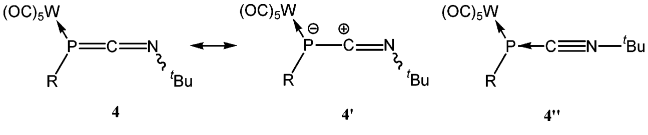
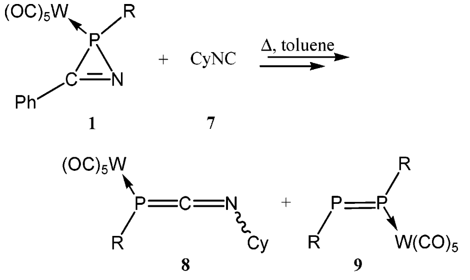


Figure 1. The 1-aza-3-phosphaallene complex **4**, its resonance structure **4′** with a phosphanide-type phosphorus center, and an adduct, the isocyanide phosphinidene complex **4″** (R = $\mathrm{CH(SiMe_3)_2}$).

Scheme 2. Thermolysis of Complex 1 in the Presence of Cyclohexyl Isocyanide (R = $\mathrm{CH(SiMe_3)_2}$)



Complexes **4**, **5**, and **8** were unambiguously characterized by NMR and IR spectroscopy, and additionally, **5** was characterized by X-ray diffraction studies. Complex **4** displayed a $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance at −136.6 ppm and a $^{13}\mathrm{C}\{^1\mathrm{H}\}$ resonance for the carbon atom of the 1-aza-3-phosphaallene moiety at 195.5 ppm ($^1J_{\mathrm{P,C}} = 3.9$ Hz). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ resonance of **4** at high field and the very small P,C coupling constant magnitude point to a structural motive, which is characterized by an enhanced negative charge at phosphorus (Figure 1), thus explaining at the same time the chemical shielding and the small tungsten−phosphorus coupling constant of $^1J_{\mathrm{W,P}} = 194.5$ Hz.

It has been recognized previously by Mathey et al.[10] that negatively charged phosphorus centers of complexes have a significant effect on various NMR parameters; very nice examples are the complex [$\mathrm{(OC)_5WPH_3}$] ($\delta(^{31}\mathrm{P})$ −183, $^1J_{\mathrm{W,P}} = 216$ Hz) and its dilithium phosphanide complex [$\mathrm{(OC)_5WP(Li)H_2}$] ($\delta(^{31}\mathrm{P})$ −273, $^1J_{\mathrm{W,P}} = 68$ Hz).[10] It should be also taken into account that it is known from a series of η^1 and η^2 platinum phosphaalkene complexes that the $^1J_{\mathrm{Pt,P}}$ coupling constant magnitude can be seen as a proof for the coordination mode, because the value of the η^1 mode is significantly larger—by roughly 1 order of magnitude.[11] Although some η^1 and η^2 tungsten phosphaalkene

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complexes have been described, there is not much NMR data available.[12]

In the IR spectra of uncomplexed 1-aza-3-phosphaallenes a strong band between 1830 and 1915 cm^{-1} due to the asymmetric stretch of the P=C=N unit has been found to be characteristic for this class of compounds.[2a] In the IR spectra of η^2(P,C)- and η^2(CN)-coordinated 1-aza-3-phosphaallene complexes a strong band in the region 1800−2000 cm^{-1} is absent. Instead, a band at 1577 cm^{-1} (ν(C=N)) was found for [η^2(*P*,*C*)-Mes*P=C=NPh]Pt($Ph_2P(CH_2)_2PPh_2$)[3a] and at 1505 cm^{-1} (ν(P=C)) for [η^2(*C*,*N*)-Mes*P=C=NPh]Nb(Cl)($(C_5H_4SiMe_3)_2$).[3b] The IR spectrum of **4** shows a very strong and broad band at 1942 cm^{-1} and a strong band at 849 cm^{-1}. A band in the region 1500−1600 cm^{-1} was not observed. According to the DFT frequency calculation[13] (unscaled calculated frequencies in brackets) the band at 1942 cm^{-1} (2020 cm^{-1}) contains the asymmetric stretching vibration of the C=N moiety; the band at 849 cm^{-1} (895 cm^{-1}) can be assigned to the P=C stretching. These findings are further strong evidence for the η^1 coordination of the 1-aza-3-phosphaallene ligand in **4**, in agreement with its NMR data.

The cyanophosphane complex **5**—the first of its kind—shows a ^{31}P resonance at −69.9 ppm ($^1J_{W,P}$ = 242.9, $^1J_{P,H}$ = 358.3 Hz) and a ^{1}H resonance for the hydrogen atom directly bonded to the phosphorus at δ 6.2, which is low-field shifted versus uncomplexed derivatives of the type RP(H)CN (R = Me, $\delta(^1H)$ 4.15; R = ^{t}Bu, $\delta(^1H)$ 3.98).[14] Nevertheless, some steric (and electronic) effects can be taken into account if compared with 1,3,5-$^tBu_3C_6H_2$-P(H)CN ($\delta(^1H)$ 5.95).[14] The phosphane **6**—which could be converted into complex **5** by reaction with [W(CO)$_5$(thf)]—shows a ^{31}P resonance at −104.8 ppm ($^1J_{P,H}$ = 224.8 Hz) and a ^{13}C resonance of the cyano group at 121.0 ppm ($^1J_{P,C}$ = 77.6 Hz). These NMR parameters are in good agreement with the data of 1,3,5-$^tBu_3C_6H_2$-P(H)CN ($\delta(^{31}P)$ −101.6, $^1J_{P,H}$ = 249.7 Hz, $\delta(^{13}C^{CN})$ 121.2, $^1J_{P,C}$ = 74.4 Hz).[14]

The structure of **5** was confirmed by single-crystal X-ray crystallography (Figure 2).

The NMR data of **8** are very similar to those of **4**; **8** displays a $^{31}P\{^1H\}$ resonance at −141.4 ppm ($^1J_{P,W}$ = 192.0 Hz) and a $^{13}C\{^1H\}$ resonance of the central carbon atom of the 1-aza-3-phosphaallene unit at 195.4 ppm with a low ^1J(P,C) coupling constant magnitude of 8.7 Hz.

Because silylene derivatives and terminal electrophilic phosphinidene complexes often show interesting similarities in structure, bonding, and reactivity, it seems interesting to compare our results with those obtained from reactions of stable and/or transient diorganosilylenes with isonitriles. For example, Tokitoh et al. reported on a reaction of a silylene bearing sterically demanding arene substituents with ^{t}BuNC, from which a hydrocyanosilane derivative and isobutene were obtained as final products.[15a] The same authors also presented spectroscopic and theoretical evidence (using DFT calculations) that the primary product has the structure of a Lewis acid/base adduct rather than a 1-aza-3-silaallene.[15a,b]

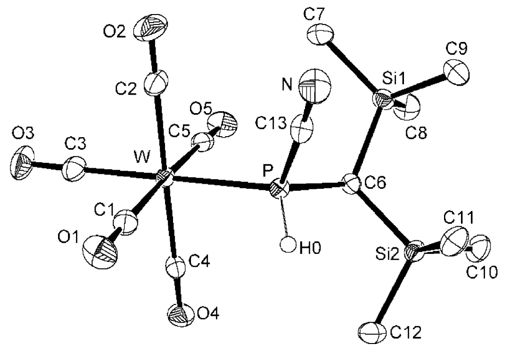

Figure 2. Molecular structure of **5** in the crystal state (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): W−P, 2.4753(5); P−C(13), 1.816(2); P−C(6), 1.8129(18); N−C(13), 1.127(3); N−C(13)−P, 176.91(19); C(13)−P−W, 114.40(6); C(6)−P−W, 123.84(6); C(6)−P−C(13), 102.82(8). For a comparison of experimental and calculated structures see Figure 3.

The calculated structure of complex **4** (Figure 3) exhibits a slightly pyramidalized phosphorus (sum of bond angles at P 347°) and an almost linear PCN unit (P−C−N = 172°) with a P−C(N) distance 6% shorter than in the cyanophosphane complex **5**. In comparison with complex **4** the calculated C−N stretching frequency of **5** is shifted by 290 cm^{-1} toward greater wavenumbers. With respect to the question of whether the structure is that of a Lewis acid/base adduct, with a pseudopyramidal phosphorus geometry, or that of a 1-aza-3-phosphaallene complex, our results support the bonding description of **4** (more) in terms of a 1-aza-3-phosphaallene, as deduced from the NMR data. To attain a better understanding of the proposed decomposition reaction of complex **4**, we calculated the enthalpy and free energy of this process (Figure 3). According to our calculations the release of isobutene from **4** is exothermal by 15 kJ/mol and exergonic by 60 kJ/mol.[13]

Conclusions

The 1,1-additions of a transiently formed electrophilic terminal phosphinidene complex to isonitriles yielded the first η^1-1-aza-3-phosphaallene complexes. Unexpectedly, it was also demonstrated that an unprecedented reactivity pattern can emerge: i.e., ω-H transfer to a low-coordinated phosphorus center. Interestingly, the latter finding again demonstrates the close vicinity of coordinatively unsaturated transition-metal and main-group-element centers, which we soon hope to exploit further in the field of activation of small molecules.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of deoxygenated dry argon, using standard Schlenk techniques with conventional glassware, and solvents were dried according with standard procedures under an argon atmosphere. NMR spectra were recorded on a Bruker AX 300 spectrometer (121.5 MHz for ^{31}P, 75.0 MHz for ^{13}C, and 300.1 MHz for ^{1}H) using C_6D_6 and $CDCl_3$ as solvent and internal standard; shifts are given relative to external tet-

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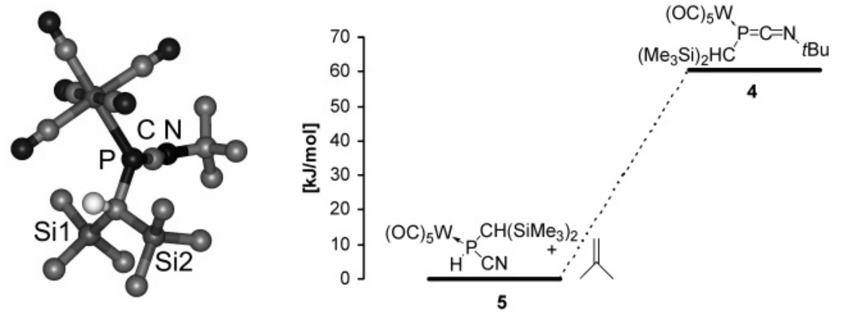

Figure 3. Calculated molecular structures (gas phase) of **4** and **5**; ΔG for the decomposition of **4** to yield **5** and isobutene. Selected bond lengths (Å) and angles (deg) are as follows. **4**: W−P, 2.611; P−C(N), 1.690; P−C(H), 1.878; C(N)−N, 1.197; N−C(P), 1.197; N−C−P, 171.88; C(N)−N−C, 137.59; C(N)−P−W, 114.48; C(H)−P−W, 125.08; C(H)−P−C(N), 107.48. **5** (deviations from the X-ray structure in percent are given in parentheses): W−P, 2.548 (+2.9); P−C(13), 1.802 (−0.8); P−C(6), 1.852 (+2.1); N−C(13), 1.156 (+2.5); N−C(13)−P, 177.51 (+0.3); C(13)−P−W, 116.17 (+1.5); C(6)−P−W, 123.13 (−0.6); C(6)−P−C(13), 103.99 (+1.1).[13]

ramethylsilane (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P); only coupling constant magnitudes are given. Electron impact (EI, 70 eV) mass spectra were recorded on a Kratos MS 50 mass spectrometer. The IR spectrum of **4** (KBr pellet) was recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed with an Elementar Vario EL analytical gas chromatograph.

Synthesis of 4. A 91 mg portion (1.1 mmol) of ^{t}BuNC and 617 mg (1 mmol) of **1** were dissolved in 400 mL of diethyl ether and irradiated for 2 h at −30 °C (low-pressure Hg lamp; λ 254 nm). Subsequent evaporation of the solvent (ca. 0.01 mbar) and column chromatography (silanized silica gel, −50 °C, *n*-pentane) yielded **4** as a red oil (first eluted fraction) as a 4:1 mixture with **5**. Selected NMR data of **4**: ^{13}C{^{1}H} NMR δ −0.8 (d, $^3J_{P,C}$ = 4.2 Hz, SiMe$_3$), −0.5 (d, $^3J_{P,C}$ = 2.9 Hz, SiMe$_3$), 27.8 (d, $^1J_{P,C}$ = 24.9 Hz, *C*H(SiMe$_3$)$_2$), 61.2 (d, $^3J_{P,C}$ = 12.9 Hz, PCN*C*), 28.1 (s, C(*C*H$_3$)$_3$), 195.3 (d, $^2J_{P,C}$ = 3.2 Hz, *cis*-CO), 195.5 (d, $^1J_{P,C}$ = 3.9 Hz, P*C*N), 200.0 (d, $^2J_{P,C}$ = 24.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR δ −136.6 (s, $^1J_{P,W}$ = 194.5 Hz). Selected IR data of **4** (KBr): $\tilde{\nu}$ 848.5 (ν(P=C)), 1880.0−1942.0 (broad, ν(CO) and ν(C=N)), 2069.6 (ν(CO)) cm^{-1}.

Synthesis of 5. A 91 mg portion (1.1 mmol) of ^{t}BuNC and 617 mg (1 mmol) of **1** were dissolved in 2 mL of toluene and heated at 75 °C for 45 min. The solvent was evaporated (ca. 0.01 mbar), and the remaining solid was washed twice with 2 mL of *n*-pentane and twice with 2 mL of diethyl ether and dried under vacuum (ca. 0.01 mbar); air-stable colorless solid, yield 450 mg (83.2%), mp 153 °C dec. Anal. Calcd for **5**: C, 28.85; H, 3.72; N, 2.59. Found: C, 28.32; H, 3.72; N, 2.54. Selected NMR data of **5**: ^{1}H NMR δ 0.28 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$), 0.63 (d, 1H, $^2J_{P,H}$ = 2.8 Hz, C*H*(SiMe$_3$)$_2$), 6.20 (d, 1H, $^1J_{P,H}$ = 358.3 Hz, P*H*); ^{13}C{^{1}H} NMR δ −0.21 (d, $^3J_{P,C}$ = 3.3 Hz, SiMe$_3$), 1.04 (d, $^3J_{P,C}$ = 4.1 Hz, SiMe$_3$), 12.23 (d, $^1J_{P,C}$ = 7.3 Hz, *C*H(SiMe$_3$)$_2$), 116.8 (d, $^1J_{P,C}$ = 1.9 Hz, P*C*N), 193.8 (d, $^2J_{P,C}$ = 5.8 Hz, $^1J_{W,C}$ = 126.1 Hz, *cis*-CO), 195.9 (d, $^2J_{P,C}$ = 27.2 Hz, *trans*-CO); ^{31}P{^{1}H} NMR δ −69.9 (s, $^1J_{P,W}$ = 242.9 Hz). Selected MS data for **5** (EI, 70 eV): *m/z* 541 [M$^+$, 68]. Selected IR data of **5** (KBr): $\tilde{\nu}$ 1900.0−1950.0 (broad, ν(CO)), 1991.6 (ν(CO)), 2080.6 (ν(CO)) cm^{-1}.

Attempted Synthesis of 6. A 20.8 mg portion (0.25 mmol) of ^{t}BuNC and 135.3 mg (0.25 mmol) of **5** were dissolved in 2 mL of toluene and heated at 110 °C for 90 min. The solvent was evaporated (ca. 0.01 mbar) and the residue subjected to column chromatography (silica gel, −50 °C, *n*-pentane)—but this proved unsuccessful (!), as **6** decomposed during the column chromatography. ^{31}P NMR spectroscopic analysis of the crude residue showed a 20:1 mixture of **6** and **5** (by integration) and contained, most probably, small amounts of some carbonyl complexes. Selected NMR data of **6**: ^{1}H NMR δ −0.02 (d, 9H, $^4J_{P,H}$ = 1.1 Hz, SiMe$_3$), 0.66 (s, 9H, SiMe$_3$), 1.06 (d, 1H, $^2J_{P,H}$ = 7.1 Hz, C*H*(SiMe$_3$)$_2$), 3.70 (d, 1H, $^1J_{P,H}$ = 224.8 Hz, P*H*); ^{13}C{^{1}H} NMR δ 121.0 (d, $^1J_{P,C}$ = 77.6 Hz, P*C*N); ^{31}P NMR −104.5 ($^1J_{P,H}$ = 224.8 Hz).

Synthesis of 8. An 84 mg portion (0.77 mmol) of cyclohexyl isocyanide (**7**) and 475 mg (0.77 mmol) of **1** were dissolved in 1.2 mL of toluene and heated for 45 min at 75 °C. Subsequent evaporation of the solvent (ca. 0.01 mbar) and column chromatography (silanized silica gel, −50 °C, *n*-pentane) yielded **8** in the second fraction as a red oil. Yield: 285 mg (59.6%). The first eluted fraction yielded **9** (NMR data are in accord with the literature data).[9] Anal. Calcd for **8**: C, 36.60; H, 4.85; N, 2.25. Found: C, 36.42; H, 4.78; N, 2.22. Selected NMR data for **8**: ^{13}C{^{1}H} NMR δ 0.0 (d, ^1J(P,C) = 2.9 Hz, SiMe$_3$), 1.1 (d, ^1J(P,C) = 3.2 Hz, SiMe$_3$), 22.9 (s, 2 × Cy *C*H$_2$), 24.0 (s, Cy *C*H$_2$), 26.5 (d, ^1J(P,C) = 24.2 Hz, *C*H(SiMe$_3$)$_2$), 32.0 (s, 2 × Cy *C*H$_2$), 60.3 (d, ^3J(P,C) = 12.8 Hz, N*C*H), 195.4 (d, ^1J(P,C) = 8.7 Hz, P*C*N), 196.5 (d, ^2J(P,C) = 3.2 Hz, *cis*-CO), 200.1 (d, ^2J(P,C) = 24.9 Hz, *trans*-CO); ^{31}P{^{1}H} NMR δ −141.4 (s, ^1J(P,W) = 192.0 Hz). Selected MS data for **8** (EI, 70 eV): *m/z* 623.1 [M$^+$, 34].

Crystal Structure Determination of 5, $C_{13}H_{20}NO_5PSi_2W$. Crystal data: triclinic, space group $P\bar{1}$, a = 6.9618(4) Å, b = 9.6073(8) Å, c = 16.1541(9) Å, α = 73.219(3)°, β = 89.975(3)°, γ = 81.823(3) °, U = 1022.98(12) Å^3, Z = 2, T = −140 °C. Data collection: a crystal with dimensions ca. 0.16 × 0.15 × 0.08 mm was used to register 19 997 intensities (Mo Kα radiation, $2\theta_{max}$ = 60°) on a Bruker SMART 1000 CCD diffractometer. An absorption correction was performed with SADABS. Structure refinement: full-matrix least squares on F^2 (program SHELXL-97)[16] to wR2 = 0.0346 and R1 = 0.0159 for 218 parameters, 21 restraints (to displacement parameters to the light atoms), and 5954 independent reflections. The phosphane hydrogen H0 was refined freely; other H atoms were included using a riding model or rigid methyl groups. See http://www.rsc.org/suppdata for crystallographic data in CIF or other electronic format (the structure was deposited with the number 246853).

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Supporting Information Available: Crystallographic data (CIF file) for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.