Reactivity of Sterically Unencumbered Transient Nitrilium Phosphanylide Complexes Towards 1-Piperidinocarbonitrile: A Case Study[‡]

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Dedicated to Professor Hans-Georg Schnöckel on the occasion of his 60th birthday

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The thermal decomposition of the 7-phosphanorbornadiene complexes **6a**,**b** in xylene at 120 °C in the presence of two equivalents of 1-piperidinocarbonitrile yielded the 2*H*-1,3,2-azaphosphole complexes **11a**,**b** and the 2*H*-1,4,2-azaphosphole complexes **12a**–**c** in ratios of 7:4 (**11a**:**12a**) and 1:5 (**11b**:**12b**). Remarkably, the two atropisomers **12b** and **12c** were obtained (ratio: 5:1) in the case of the *P*-phenyl-substituted 2*H*-1,4,2-azaphosphole complex. Interestingly, the product ratios of both reactions were approximately the same if neat 1-piperidinocarbonitrile was used as the solvent. The reaction of complexes **6a,b** with $Cu^{I}Cl$ and 1-piperidinocarbonitrile, with exclusion of light, also furnished the 2*H*-1,3,2-azaphosphole complexes **11a,b** as the main products. In the case of complex **6a**, a by-product was detected by ^{31}P NMR spectroscopy but could not be isolated. Complexes **11a,b**, **12a** and **13** were purified by column chromatography at low temperature and characterized by NMR and MS spectroscopic means and elemental analysis, whereas only a 1:1 mixture of **12b** and **12c** could be characterized.

Introduction

Nitrilium phosphanylide complexes with bulky substituents at the phosphorus have recently become established as new building blocks in N,P-heterophosphole synthesis and their reactivity towards different trapping reagents such as alkynes,[2] nitriles[3] or phosphaalkynes[4] has been explored. So far, their generation has relied on the use of the 2*H*-azaphosphirene complexes **1a,b** and can be achieved either thermally or photochemically;[5] the mild reaction conditions of the latter being synthetically very useful. The majority of these three-component reactions profit from transylidation reactions yielding the *P*-bis(trimethylsilyl)methyl- and *P*-pentamethylcyclopentadienyl-substituted nitrilium phosphanylide tungsten complexes **2a**,**b** as transient species.[3] Of special interest are those cases where dialkylamino-substituted nitriles such as 1-piperidinocarbonitrile were used as trapping reagent and solvent (**i**; Scheme 1), thus affording selectively the 2*H*-1,3,2-diazaphosphole complexes **3a**[3b] and **3b**;[3c] if toluene solutions were used (**ii** and **iii**; Scheme 1) then intramolecular reactions also took place. Depending on the substituent at the phosphorus center two different by-products were thus formed: the 2*H*-azaphosphirene complex **4**[3b] in the case of **2a** (route **ii**) or the C,N,P-cage compound **5**[3c] in the case of **2b** (route **iii**). So far, no dimerization of complexes **2a**,**b** has been observed in solution, although we obtained a dimer by melting the 2*H*-azaphosphirene complex **1a**.[6]

Very recently we demonstrated that transient nitrilium phosphanylide complexes with less bulky substituents at the phosphorus, such as **9a**,**b**, are accessible by thermal decomposition of the 7-phosphanorbornadiene complexes **6a**,**b** in the presence of 1-piperidinocarbonitrile; the reactive intermediates **9a**,**b** were trapped with dimethylacetylene dicarboxylate, thus yielding the 2*H*-1,2-azaphosphole complexes **10a**,**b** as the main products (Scheme 2).[1] Remarkably, in these reactions no Δ^3-oxazaphospholene complexes were formed from the [3+2] cycloaddition of **9a**,**b** with the C−O π-system of DMAD, as observed earlier for **2a**,**b**.[7,8] This finding provided the first evidence for the different reactivities of sterically unencumbered and encumbered nitrilium phosphanylide complexes.

Because of our interest in exploiting the chemistry of nitrilium phosphanylide complexes using this new and easy access, we decided to study the reactions of the 7-methyl- and 7-phenyl-phosphanorbornadiene complexes **6a**,**b** with 1-piperidinocarbonitrile, which should be a good model system. The quest for the generation of transient 2*H*-azaphosphirene complexes will also be discussed.

Results and Discussion

The thermal decomposition of the 7-phosphanorbornadiene complexes **6a**,**b**[9] in xylene in the presence of two

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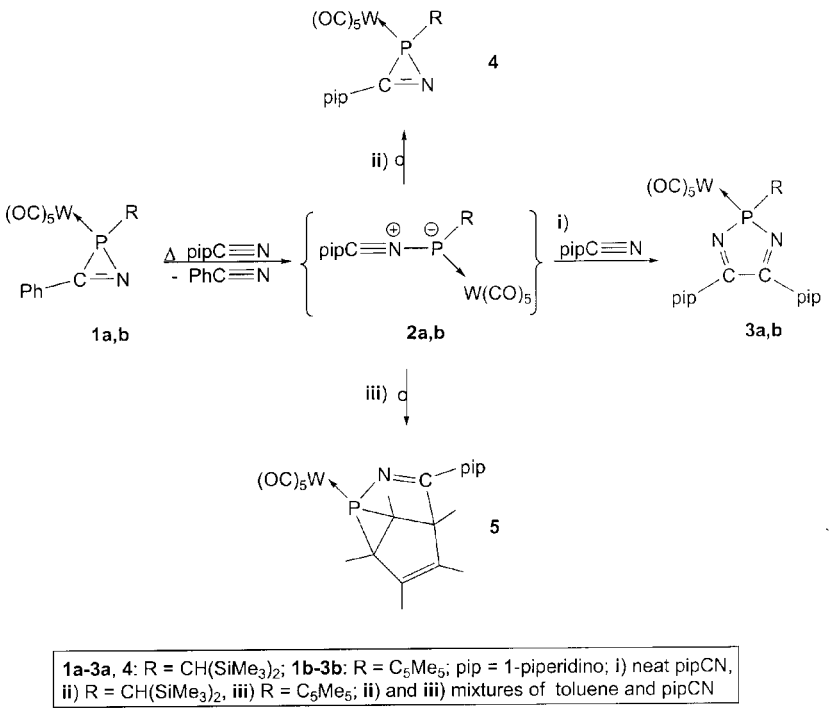
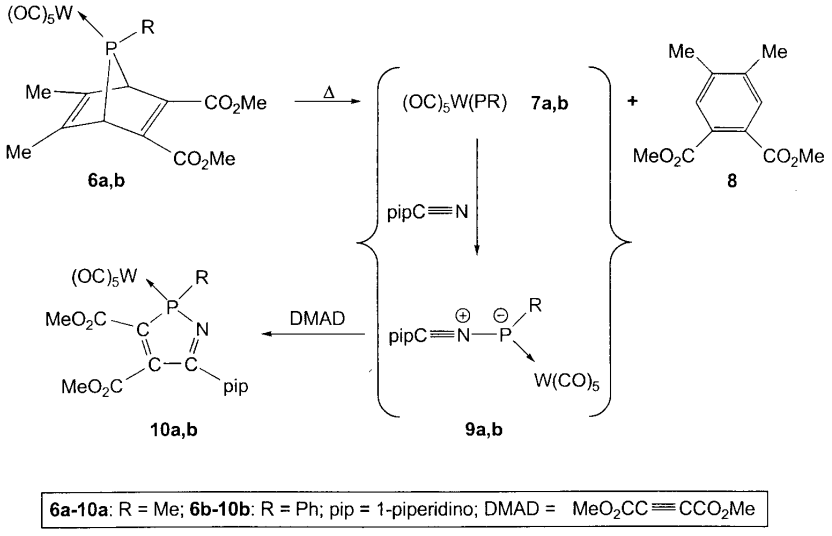


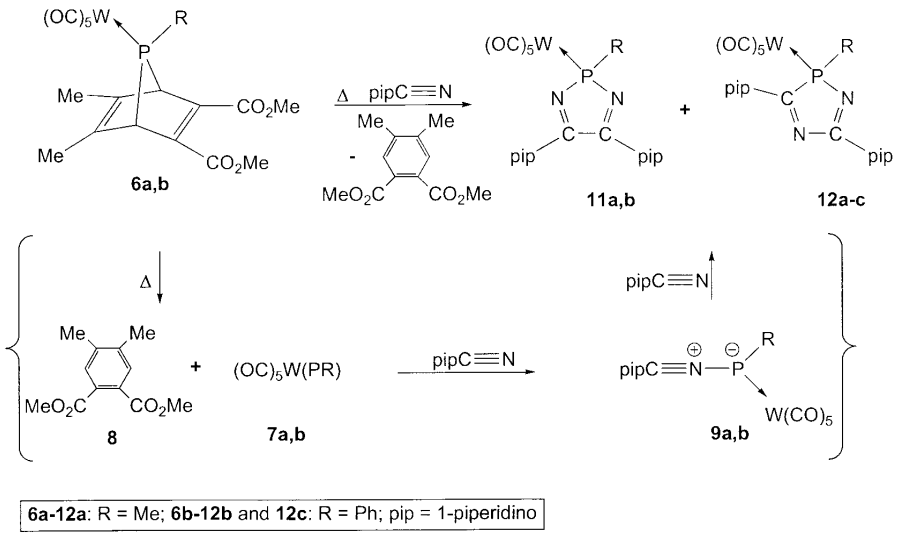
Scheme 1. Generation and reactions of bulky substituted nitrilium phosphanylide complexes



Scheme 2. Trapping reaction of nitrilium phosphanylide complexes **9a**,**b** with DMAD

equivalents of 1-piperidinocarbonitrile at 120 °C yielded the 2*H*-1,3,2-azaphosphole complexes **11a**,**b** and, surprisingly, the 2*H*-1,4,2-azaphosphole complexes **12a**,**b** *and* **12c** (Scheme 3). The ratios of the two regioisomers **11** and **12** were 7:4 (**11a**:**12a**) and 1:5 (**11b**:**12b**), as determined by ^{31}P NMR spectroscopy. Remarkably, the *P*-phenyl-substituted 2*H*-1,4,2-azaphosphole complex was obtained as a mixture of two atropisomers **12b**,**c** (5:1 ratio), in contrast to the methyl derivative **12a**. The complexes **11a,b** and **12a** were separated by double low-temperature column chromatography, whereas only a 1:1 mixture of **12b**,**c** could be isolated. According to the spectroscopic data of complexes **12b**,**c** we propose that the atropisomerism originates from differently orientated C(2)-bonded pyramidal piperidino nitrogen centers, which can be *cisoid* or *transoid* with respect to the pentacarbonyltungsten group and which have a hindered rotation around the C(2)−N bond (Figure 1). According to monitoring of the reaction by ^{31}P NMR spectroscopy, 2*H*-azaphosphirene complexes were not formed under these conditions.

Astonishingly, the deviation from the formerly observed product ratios was less than 5% if neat 1-piperidinocarbonitrile was used as solvent. The appropriate *P*-phenyl-substituted 2*H*-azaphosphirene complex was eventually de-



Scheme 3. Thermal decomposition of 7-phosphanorbornadiene complexes **6a**,**b** in neat 1-piperidinocarbonitrile or 1-piperidinocarbonitrile toluene solutions

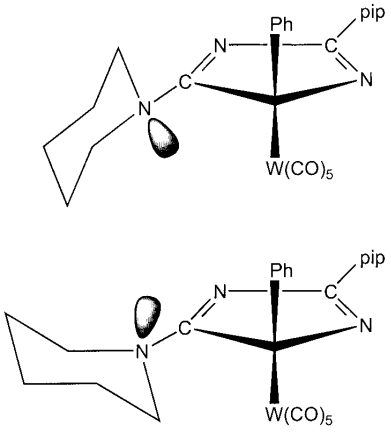


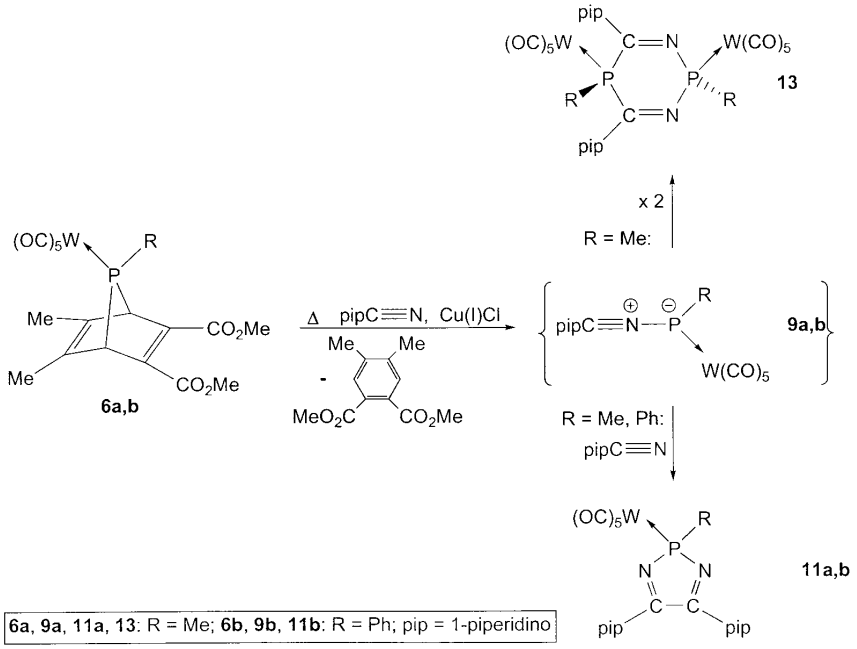
Figure 1. Proposed structures for the atropisomeric 2*H*-1,2,4-diazaphosphole complexes **12b**,**c**

tected in very small amounts (< 3% according to the ^{31}P NMR spectrum; δ = −47.9) only in the case of complex **1b**; the related *P*-bis(trimethylsilyl)methyl-substituted 2*H*-azaphosphirene complex was observed at δ = −70.3.[3b]

Because of the known thermal instability of 2*H*-azaphosphirene complexes, we decided to carry out a preliminary study on the use of Cu^{I}Cl as catalyst for the decomposition,[10] and were thus able to lower the temperature substantially to 65−70 °C. Although we performed the reaction of the complexes **6a**,**b** with 1-piperidinocarbonitrile — with and without exclusion of light[11] — the ^{31}P NMR spectra showed no further evidence for 2*H*-azaphosphirene complexes. Remarkably, the reaction of complex **6b** with 1-piperidinocarbonitrile and catalytic amounts of Cu^{I}Cl in toluene at 70 °C and with exclusion of light furnished the 2*H*-1,3,2-azaphosphole complex **11b** selectively. In the case of complex **6a** the 2*H*-1,3,2-azaphosphole complex **11a** and a complex **13** were formed in a 6:4 ratio (Scheme 4). Unfortunately, the latter complex could not be isolated by column chromatography due to decomposition. Nevertheless, a comparison of the ^{31}P NMR spectroscopic data of complex **13** [δ = 73.2, $J(^{31}P,^{31}P)$ = 25.6, $^{1}J(^{183}W,^{31}P)$ = 217.9 Hz; δ = 68.7, $J(^{31}P,^{31}P)$ = 25.6, $^{1}J(^{183}W,^{31}P)$ = 259.7 Hz] with {2,5-bis[bis(trimethylsilyl)methyl]-4,6-diphenyl-2,5-dihydro-1,3-diaza-2,5-diphosphinine-κP^2]}pentacarbonyltungsten(0)[6] [δ = 79.9, $J(^{31}P,^{31}P)$ = 15.3, $^{1}J(^{183}W,^{31}P)$ = 266.1 Hz; δ = −0.6, $J(^{31}P,^{31}P)$ = 15.3 Hz] provides some evidence for the constitution of complex **13** as the head-to-tail dimer of complex **9a**.

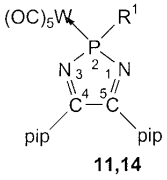
As expected, the ^{13}C NMR spectra of the 2*H*-1,3,2-azaphosphole complexes **11a,b** showed one resonance for the PN*C* imino carbon atoms of the ring between δ = 160.7 and 161.6 with coupling constant magnitudes $|J(^{31}P,^{13}C)|$ of ca. 2.5−6.4 Hz; the data of the complexes **14a**[3b] and **14b**[3c] are also listed in Table 1 for comparison. Three resonances were observed for the methylene carbon atoms of the 1-piperidino substituent, as expected for such 2*H*-1,3,2-azaphosphole complexes.[3b,3c] More surprising were the ^{13}C NMR spectra of the 2*H*-1,4,2-azaphosphole complexes **12a**−**c** (Table 2). Here the resonances for both types of imino carbon atoms were observed in a comparably narrow range between δ = 160 and 185 and the coupling constant magnitudes $|J(^{31}P,^{13}C)|$ were also considerably smaller (ca. 2−15 Hz) than those observed for the derivatives **15a**,[3b] **15b**[5] and **15c**[12] [values between δ = 195 and 200 (P*C*N) and δ = 163 and 170 (PN*C*); $|J(^{31}P,^{13}C)|$ ca. 1−30 Hz]. Therefore, we could only make tentative assignments in the present study. As expected, each 1-piperidino substituent of **12a**−**c** shows more than three resonances for the methylene carbon atoms, although in some cases only collapsed signals were observed.

Within each class of compounds the bulky substituted derivatives **14** and **15** tend to have ^{31}P resonances at significantly lower field; for example, the resonances of **15a**,[3b] and **15b**[5] are observed in the range δ = 110−123 with characteristic coupling constants $|J(^{183}W,^{31}P)|$ of 228−234 Hz, whereas **12a**−**c** were observed in the range δ = 70−80 with



Scheme 4

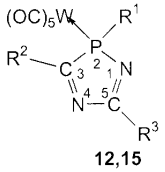
Table 1. Selected ^{31}P and ^{13}C NMR spectroscopic data of the 2*H*-1,3,2-diazaphosphole tungsten complexes **11a**,**b** and **14a**[3b] and **14b**[3c] ($CDCl_3$, δ in [ppm]; *J* in [Hz]; pip = 1-piperidino)



11,14

Comp.	R^1	δ ^{31}P	^1J(W,P)	δ $^{13}C^{4/5}$	$^{(2+3)}J$(P,C)
11a	Me	125.2	262.4	161.3	5.9
11b	Ph	125.6	270.1	160.7	5.8
14a	$CH(SiMe_3)_2$	133.2	264.3	160.7	6.4
14b	C_5Me_5	137.7	278.1	161.6	2.5

Table 2. Selected ^{31}P and ^{13}C NMR spectroscopic data of the 2*H*-1,4,2-diazaphosphole tungsten complexes **12a**−**c** and **15a**,[3b] **15b**[5] and **15c**[12] ($CDCl_3$, δ in [ppm]; *J* in [Hz], #: not resolved, bis = $CH(SiMe_3)_2$, *Z* = CO_2Et, pip = 1-piperidino)



12,15

Comp.	R^1	R^2	R^3	δ ^{31}P	^1J(W,P)	δ $^{13}C^3$	*J*(P,C)	δ $^{13}C^5$	*J*(P,C)
12a	Me	pip	pip	70.6	248.5	185.6	2.6	167.3	3.9
12b	Ph	pip	pip	80.3	257.2	160.4	11.0	159.9	5.2
12c	Ph	pip	pip	78.8	254.0	165.6	15.2	169.2	4.2
15a	bis	Ph	Ph	110.6	227.9	198.5	22.3	169.5	5.1
15b	bis	Z	Ph	122.4	233.6	195.6	29.8	167.2	7.0
15c	bis	Ph	pip	110.6	227.9	199.9	22.1	163.4	#

coupling constants $|J(^{183}W,^{31}P)|$ of 248−258 Hz. These differences in the chemical shifts and the tungsten-phosphorus couplings seem to be mainly caused by different steric interactions of the organic substituents at the phosphorus center and the pentacarbonyltungsten group.

EI mass spectrometric experiments revealed that these 2*H*-1,3,2-azaphosphole and 2*H*-1,4,2-diazaphosphole complexes preferentially lose carbon monoxide and show cleavage of the C−N bonds between the different heterocyclic ring systems subsequent to the ionisation process; this behavior has also been observed for the bulky substituted derivatives **14**[3b,3c] and **15**.[3,5,12]

In conclusion, we have shown that the chemistry of nitrilium phosphanylide complexes can be further exploited using 7-methyl- and 7-phenyl-phosphanorbornadiene complexes and 1-piperidinocarbonitrile, thus providing a new access to 2*H*-1,3,2-azaphosphole and 2*H*-1,4,2-diazaphosphole complexes. Furthermore, we obtained new insights into the reactivity of nitrilium phosphanylide complexes that are sterically unencumbered at phosphorus, and we provide first evidence for the transient formation of a *P*-phenyl-substituted 2*H*-azaphosphirene complex.

Experimental Section

General Procedures: All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^1H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) with [D]chloroform and

[D_6]benzene as both solvent and internal standard; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Finnigan Mat 8430 (70 eV); apart from the *m*/*z* values of the molecule ions, only *m*/*z* values with intensities of more than 20% are given. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed by using a Carlo Erba analytical gas chromatograph. The κ*P* notation differentiates between *P*- and *N*-coordination of the appropriate heterocycle to the metal.

Procedure for the Synthesis of the Diazaphosphole Complexes 11a,b and 12a−c: Compound **1a** (0.45 g, 0.85 mmol) or **1b** (0.56 g, 0.85 mmol) and 1-piperidinocarbonitrile (0.2 mL, 1.7 mmol), dissolved in 5 mL of xylene, were heated for 3.5−4 h at 120 °C with slow stirring. When the reaction was complete (as monitored by ^{31}P NMR spectroscopy), the solution was evaporated to dryness in vacuo (ca. 0.01 mbar), and the residue subjected to low-temperature column chromatography on silica (−32 °C, *n*-hexane/diethyl ether, 10:1). The eluates were evaporated to dryness in vacuo (ca. 0.01 mbar), and the residues recrystallised from *n*-pentane at −20 °C.

Pentacarbonyl[2-methyl-2*H*-1,3,2-diazaphosphole-4,5-di(1-piperidino)-κ*P*]tungsten(0) (11a): Yield: 210 mg (42%), m.p. 108 °C. (decomp.); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22,8 (s, $NCH_2CH_2\mathit{C}H_2$), 24.4 (s, $NCH_2\mathit{C}H_2CH_2$), 25.5 [d, ^1J(P,C) = 27.5 Hz, PCH_3), 50.0 (s, $N\mathit{C}H_2CH_2CH_2$), 161.3 [d, $^{(2+3)}J$(P,C) = 5.9 Hz, PN=*C*], 196.3 [d, ^2J(P,C) = 8.0, ^1J(W,C) = 125.6 Hz, *cis*-CO], 200.4 [d, ^2J(P,C) = 22.9 Hz, *trans*-CO]; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 125.2 [s, ^1J(W,P) = 264.4 Hz); ^{31}P NMR ($CDCl_3$): δ = 125.2 [q, ^2J(P,H) = 6.8, ^1J(W,P) = 264.4 Hz]; MS (EI, ^{184}W): *m*/*z* (%) = 590 (51) [M^+], 562 (19) [$(M - CO)^+$], 534 (46) [$(M - 2CO)^+$], 506 (62) [$(M - 3CO)^+$], 478 (66) [$(M - 4CO)^+$], 450 (100) [$(M - 5CO)^+$], 84 (30) [$C_5H_{10}N^+$]; $C_{18}H_{23}N_4O_5PW$ (590.2): calcd. C 36.63, H 3.93, N 9.49; found C 36.42, H 3.78, N 9.39.

Pentacarbonyl[2-methyl-2*H*-1,4,2-diazaphosphole-3,5-di(1-piperidino)-κ*P*]tungsten(0) (12a): Yield: 130 mg (26%), m.p. 94 °C. (decomp.); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.8 [d, ^1J(P,C) = 20.3 Hz, PCH_3], 22.8 (br. s, $NCH_2CH_2\mathit{C}H_2$), 24.1 (s, $NCH_2\mathit{C}H_2\mathit{C}H_2$), 24.4 (s, $NCH_2\mathit{C}H_2CH_2$), 25.0 (s, $NCH_2CH_2\mathit{C}H_2$), 25.8 (s, $NCH_2\mathit{C}H_2CH_2$), 43.8 (s, $N\mathit{C}H_2CH_2CH_2$), 47.6 (s, $N\mathit{C}H_2CH_2CH_2$), 49.8 (s, $N\mathit{C}H_2CH_2CH_2$), 50.6 [d, ^3J(P,C) = 5.5 Hz, $N\mathit{C}H_2CH_2CH_2$], 167.3 [d, $^{(2+3)}J$(P,C) = 3.9 Hz, PN=*C*], 185.6 [d, $^{(1+4)}J$(P,C) = 2.6 Hz, P=*C*N], 196.5 [d, ^2J(P,C) = 7.1 Hz, *cis*-CO], 200.0 [d, ^2J(P,C) = 22.1 Hz, *trans*-CO]; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 70.6 [s, ^1J(W,P) = 248.5 Hz]; ^{31}P NMR ($CDCl_3$): δ = 70.6 [q, ^2J(P,H) = 6.3, ^1J(W,P) = 248.5 Hz]; MS (*neg.*-CI, NH_3, ^{184}W): *m*/*z* (%) = 589 (100) [$(M - H)^-$], 324 (42) [$W(CO)_5$]; (*pos.*-CI, NH_3, ^{184}W): *m*/*z* (%) = 591 (85) [$(M + H)^+$]; $C_{18}H_{23}N_4O_5PW$ (590.2): calcd. C 36.63, H 3.93, N 9.49; found C 36.48, H 3.81, N 9.43.

{Pentacarbonyl[2-phenyl-2*H*-1,3,2-diazaphosphole-4,5-di(1-piperidino)-κ*P*]tungsten(0)} (11b): Yield: 338 mg (61%), m.p. 127 °C. (decomp.); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.2 (s, $NCH_2CH_2\mathit{C}H_2$), 24.2 (s, $NCH_2\mathit{C}H_2CH_2$), 48.8 (s, $N\mathit{C}H_2CH_2CH_2$), 127.3 [d, ^2J(P,C) = 9.7 Hz, *o*-Ph], 128.6 [d, ^3J(P,C) = 12.4 Hz, *m*-Ph], 129.4 [d, ^4J(P,C) = 1.9 Hz, *p*-Ph], 136.9 [d, ^1J(P,C) = 43.5 Hz, *i*-Ph], 160.7 [d, ($^{(2+3)}J$(P,C) = 5.8 Hz, PN=*C*], 195.5 [d, ^2J(P,C) = 8.1 Hz, *cis*-CO], 199.6 [d, ^2J(P,C) = 23.7 Hz, *trans*-CO]; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 126.3 [s, ^1J(W,P) = 272.0 Hz]; ^{31}P NMR ($CDCl_3$): δ = 126.3 [t, ^3J(P,H) = 9.6, ^1J(W,P) = 272.0 Hz]; MS (EI, ^{184}W): *m*/*z* (%) = 652 (42) [M^+], 624 (6) [$(M - CO)^+$], 596 (4) [$(M - 2CO)^+$], 568 (33) [$(M - 3CO)^+$], 540 (35) [$(M - 4CO)^+$], 512 (100) [$(M - 5CO)^+$], 84 (25) [$C_5H_{10}N^+$]; $C_{23}H_{25}N_4O_5PW$ (652.3): calcd. C 42.35, H 3.86, N 8.59, found C 41.85, H 3.82, N 8.49.

A 1:1 mixture of complexes **12b**,**c** was obtained, which was slightly contaminated with **12a** (ca. 10%); the mixture was analyzed by spectroscopic means and elemental analysis.

{Pentacarbonyl[2-phenyl-2*H*-1,4,2-diazaphosphole-3,5-bis(1-piperidino)-κ*P*]tungsten(0)} (12b,c): ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.7 (br. s, $NCH_2CH_2\mathit{C}H_2$), 24.0 (br. s, $NCH_2CH_2\mathit{C}H_2$), 24.4 (br. s, $NCH_2\mathit{C}H_2CH_2$), 24.6 (br. s, $NCH_2\mathit{C}H_2CH_2$), 25.2 (br. s, $NCH_2\mathit{C}H_2CH_2$), 25.8 (br. s, $NCH_2\mathit{C}H_2CH_2$), 46.9 (s, $N\mathit{C}H_2CH_2CH_2$), 47.8 (br. s, $N\mathit{C}H_2CH_2CH_2$), 48.8 (br. s, $N\mathit{C}H_2CH_2CH_2$), 49.7 (s, $N\mathit{C}H_2CH_2CH_2$), 49.9 (s, $N\mathit{C}H_2CH_2CH_2$), 50.9 [d, ^3J(P,C) = 5.7 Hz, $N\mathit{C}H_2CH_2CH_2$], 127.7 [d, ^2J(P,C) = 10.6 Hz, *o*-Ph], 128.9 [d, ^2J(P,C) = 9.9 Hz, *o*-Ph], 131.2 [d, ^4J(P,C) = 2.1 Hz, *p*-Ph], 129.9 [d, ^3J(P,C) = 13.5 Hz, Ph], 130.2 (s, *p*-Ph), 131.2 [d, ^1J(P,C) = 41.5 Hz, *i*-Ph], 131.5 [d, ^3J(P,C) = 8.8 Hz, *m*-Ph], 133.3 [d, ^1J(P,C) = 31.6 Hz, *i*-Ph], 159.9 [d, *J*(P,C) = 5.1 Hz, N=*C*], 160.4 [d, *J*(P,C) = 11.0 Hz, N=*C*], 165.6 [d, *J*(P,C) = 15.1 Hz, N=*C*], 169.2 [d, *J*(P,C) = 4.0 Hz, N=*C*], 195.5 [d, ^2J(P,C) = 7.3 Hz, *cis*-CO], 196.4 [d, ^2J(P,C) = 7.4 Hz, *cis*-CO], 198.5 [d, ^2J(P,C) = 25.9 Hz, *trans*-CO], 200.0 [d, ^2J(P,C) = 23.4 Hz, *trans*-CO]; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 80.3 [s, ^1J(W,P) = 257.2 Hz]; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 78.8 [s, ^1J(W,P) = 254.0 Hz]; $C_{23}H_{25}N_4O_5PW$ (652.3): calcd. C 42.35, H 3.86, N 8.59, found C 42.05, H 3.83, N 8.51.

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[1] R. Streubel, U. Schiemann, P. G. Jones, N. H. Tran Huy, F. Mathey, *Angew. Chem.* **2000**, *112*, 3845−3847; *Angew. Chem. Int. Ed.* **2000**, *39*, 3686−3688.
[2] [2a] R. Streubel, H. Wilkens, A. Ostrowski, C. Neumann, F. Ruthe, P. G. Jones, *Angew. Chem.* **1997**, *109*, 1549−1550; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1492−1493; [2b] U. Rohde, F. Ruthe, P. G. Jones, R. Streubel, *Angew. Chem.* **1999**, *111*, 158−160; *Angew. Chem. Int. Ed.* **1999**, *38*, 215−217; [2c] H. Wilkens, A. Ostrowski, J. Jeske, F. Ruthe, P. G. Jones, R. Streubel, *Organometallics* **1999**, *18*, 5627−5642.
[3] [3a] H. Wilkens, J. Jeske, P. G. Jones, R. Streubel, *Chem. Commun.* **1997**, 2317−2318; [3b] H. Wilkens, F. Ruthe, P. G. Jones, R. Streubel, *Chem. Eur. J.* **1998**, *4*, 1542−1553; [3c] R. Streubel, U. Schiemann, N. Hoffmann, Y. Schiemann, P. G. Jones, D. Gudat, *Organometallics* **2000**, *19*, 475−481.
[4] F. G. N. Cloke, P. B. Hitchcock, U. Schiemann, R. Streubel, J. F. Nixon, D. J. Wilson, *Chem. Commun.* **2000**, 1659−1660.
[5] R. Streubel, H. Wilkens, F. Ruthe, P. G. Jones, *Chem. Commun.* **1999**, 2127−2128.
[6] R. Streubel, H. Wilkens, F. Ruthe, P. G. Jones, *Chem. Commun.* **2000**, 2453−2454.
[7] H. Wilkens, F. Ruthe, P. G. Jones, R. Streubel, *Chem. Commun.* **1998**, 1529−1530.
[8] U. Schiemann, PhD Thesis, Technische Universität Braunschweig, Braunschweig 2001.
[9] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc., Chem. Commun.* **1982**, 667−668.
[10] A. Marinetti, F. Mathey, *Organometallics* **1984**, *3*, 456−461.
[11] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *Nouv. J. Chim.* **1984**, *8*, 453−457.
[12] R. Streubel, H. Wilkens, P. G. Jones, *Chem. Eur. J.* **2000**, *7*, 3997−4000.

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