Chemistry of 2*H*-Azaphosphirene Complexes, Part 21[+]

# Bond-Selective Nitrile Insertion into the 2*H*-Azaphosphirene Ring System as Induced by Tetracyanoethylene

**Rainer Streubel,* Hendrik Wilkens, and Peter G. Jones[a]**

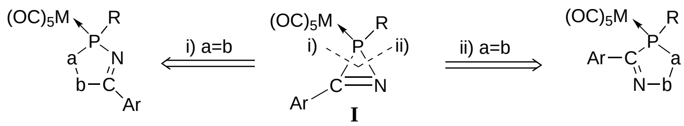
*Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday*

**Abstract:** Competitive reactions of 2*H*-azaphosphirene metal complexes **1a–c** (M = Cr, Mo, W) with 1-piperidinonitrile and tetracyanoethylene in toluene have been observed at elevated temperatures. For the case of complex **1c**, the $\Delta^5$-1,2-azaphospholene complex **2c** (as main product) and the 2*H*-1,4,2-diazaphosphole complex **3c** (as by-product) were separated from the product mixture. At ambient temperature and using 1-piperidinonitrile as solvent, bond and regioselective insertion of 1-piperidinonitrile into the P–N bond of 2*H*-azaphosphirene metal complexes **1a–c** (M = Cr, Mo, W) has been achieved in the presence of tetracyanoethylene (TCNE), yielding 2*H*-1,4,2-diazaphosphole metal complexes **3a–c**; analogous reactions in benzo- or acetonitrile afforded the 2*H*-1,4,2-diazaphosphole tungsten complexes **3d**, **e**. A preliminary study with the 2*H*-azaphosphirene tungsten complex **1c** and 1-piperidinonitrile as solvent has revealed that sub-stoichiometric amounts of TCNE (0.3 equiv) induce approximately 70% conversion of complex **1c**. NMR data of the complexes **2c** and **3a–e** and the X-ray structure of complex **3c** are discussed.

**Keywords:** 2*H*-azaphosphirene complexes · cyclizations · diazaphosphole complexes · phosphorus heterocycles · tungsten

## Introduction

Tetracyanoethylene (TCNE) has found a wide variety of applications in synthetic chemistry; for example, cycloaddition[2] and oxidation reactions of organic[3] and organometallic compounds,[2b, 4] give rise to various polynitrile derivatives. So far, examples for the use of TCNE as cycloaddition component and/or oxidising agent in organophosphorus chemistry are rare.[5–7] Recently, we reported on the synthesis of unsaturated five-membered *N*,*P*-heterocycle complexes by using [3+2] cycloaddition reactions of thermally[8] and photochemically generated[9] nitrilium phosphane ylide complexes to alkynes[8a,c, 9] and nitriles.[8b, 9, 10] Such reactions formally represent insertion reactions of a π system into the P–C bond i) of the three-membered ring of 2*H*-azaphosphirene complexes **I** (Scheme 1). We have now observed that nitriles can be inserted selectively into the P–N bond ii) of 2*H*-azaphosphirene complexes at ambient temperature if TCNE is present, thus representing a new access to 2*H*-1,4,2-diazaphosphole complexes. We also report a preliminary study on sub-stoichiometric reactions of TCNE with a 2*H*-azaphosphirene tungsten complex.




Scheme 1. Bond-selective insertion reactions of a=b into the 2*H*-azaphosphirene ring system (a=b denotes a π system).

## Results and Discussion

The outcome of the three-component reactions of the 2*H*-azaphosphirene complexes **1a**, **1b**,[11] and **1c**[12] with two equivalents of 1-piperidinonitrile and TCNE in toluene at 75 °C was surprising and depended significantly on the metal; complexes **1a**, **b** yielded no reaction products that could be identified or isolated. In the case of the tungsten complex **1c**, the $\Delta^5$-1,2-azaphospholene complex **2c**, a non-identified by-product ($\delta = 163.9$; $< 5\%$) and the 2*H*-1,4,2-diazaphosphole complex **3c** ($< 5\%$) were formed (Scheme 2); the reaction to

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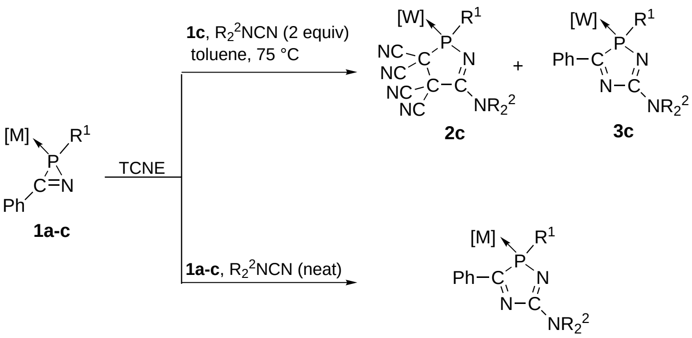
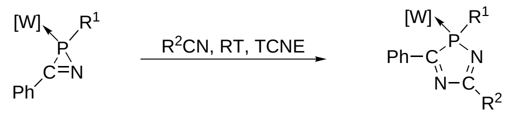



Scheme 2. Insertion reactions into the P–C and P–N bond of complexe **1a–c** under various conditions. [M] = M(CO)$_5$; M = Cr, Mo, W; R$^1$ = CH(SiMe$_3$)$_2$; NR$_2^2$ = 1-piperidino.

form **2c** represents the first example of a 1,3-dipolar cycloaddition of a nitrilium phosphane ylide complex to an alkene derivative. Owing to this partial success and the surprising formation of the 2*H*-1,4,2-diazaphosphole complex **3c**, which was the "wrong" regioisomer, ref. [8b] we performed the same reactions again at ambient temperature. In this case, the 2*H*-1,4,2-diazaphosphole complexes **3a–c** were the main products; remarkably, $\Delta^5$-1,2-azaphospholene complexes **2a–c** were not formed under these conditions. Despite the mild reaction conditions, we also observed by-product formation in the case of complexes **1a**, **b**, most probably deriving from rapid subsequent transformations of the primarily formed complexes **3a, b**. In order to obtain the pure complexes **3a**, **b**, we had to perform the reactions of **1a**, **b** in 1-piperidinonitrile at ambient temperature (**3a**), and to stop the reaction after 1.5 h, or at 75 °C (1 h) by using 0.2 equivalents of TCNE; the reaction of complex **1b** at ambient temperature with two equivalents of TCNE was not so selective. It should be stressed that complexes **3a–c** were not formed at ambient temperature if TCNE was *absent*. Unfortunately, the fate of TCNE could not be elucidated in any case and, therefore, the mechanism of these insertion reactions is still unkown (Scheme 2).

A preliminary study on the effect of the 1-piperidinonitrile concentration on the reaction with the 2*H*-azaphosphirene tungsten complex **1c** and two equivalents of TCNE at 75 °C showed that increasing the amount of of 1-piperidinonitrile led preferably to complex **3c** and shorter reaction times; for example, with four equivalents the reaction was complete in 50 minutes and gave ≅10–15% **3c** or with 150 equivalents (neat 1-piperidinonitrile) the reaction was complete in 5 minutes. and gave ≅90–95% **3c** (crude product yields). It is remarkable that at 75 °C in neat 1-piperidinonitrile, the formation of complex **2c** was completely suppressed and yields of more than 90% of **3c** were obtained, even if the TCNE concentration was lowered from 2 to 0.3 equivalents. It is also notable that at ambient temperature and with two equivalents of TCNE, the reaction in neat 1-piperidinonitrile was complete after 1.5 h, whereas with 0.3 equivalents of TCNE it stopped at 70% turnover of complex **1c**, but could be completed by warming to 75 °C for 2–3 minutes. In neither case did the exclusion of light show an influence on the reaction courses or reaction times.

Another preliminary study showed that 2*H*-azaphosphirene tungsten complex **1c** also reacted with two equivalents of TCNE in benzo- or acetonitrile at ambient temperature to yield regioselectively the 2*H*-1,4,2-diazaphosphole complexes **3d**[8b] and **3e** after three days (**3d**) or 30 h (**3e**) (Scheme 3).




Scheme 3. TCNE-induced insertion reactions of benzo- and acetonitrile into the P–N bond of complex **1c**. [W] = W(CO)$_5$; R$^1$ = CH(SiMe$_3$)$_2$; **3d**: R$^2$ = Ph; **3e**: R$^2$ = Me.

Attempts to use ethylcyanoformate failed; we obtained only an inseparable product mixture in this case. For the case of benzonitrile, we repeated the reaction of complex **1c** with 0.3 equivalents of TCNE and observed a decreased turnover of **1c**; after 25 h **3d** had formed in approximately 55% yield and no further transformation of **1c** was observed at ambient temperature (monitored by $^{31}$P NMR spectroscopy).

The complexes **2c** and **3a–e** were isolated by low-temperature column chromatography and crystallisation. The constitutions of the complexes are unambiguously established by their NMR spectroscopic data and were confirmed by single-crystal X-ray diffraction in the case of complex **3c**. All complexes show the structurally important resonances for the imino-carbon atoms, which lie between $\delta$ = 162 and 173 for the PN*C* carbon atoms with coupling constant magnitudes $|J(^{31}P,^{13}C)|$ of about 5–7 Hz and between $\delta$ = 190 and 200 for the P*C*N carbon atoms with $|J(^{31}P,^{13}C)|$ of about 20–22 Hz. This assignment is consistent with previous NMR measurements of heterocycles having the P–N=C–E structural unit;[8b] it is noteworthy that heterocycle complexes with the P–C=N–E unit tend to have $^{13}$C resonances at lower field.

**Abstract in German:** *Die 2H-Azaphosphiren-Komplexe **1a–c** (M = Cr, Mo, W) zeigen Konkurrenzreaktionen mit 1-Piperidinonitril und Tetracyanoethylen (TCNE) in Toluol bei 75 °C; im Fall von Komplex **1c** konnte der $\Delta^5$–1,2-Azaphospholen-Komplex **2c** (Hauptprodukt) und der 2H-1,4,2-Diazaphosphol-Komplex **3c** (Nebenprodukt) isoliert werden. Verwendet man 1-Piperidinonitril als Lösungsmittel und führt die Umsetzungen bei Raumtemperatur und in Gegenwart von TCNE durch, so erreicht man eine bindungs- und regioselektive Insertion von 1-Piperidinonitril in die P-N Bindung der 2H-Azaphosphiren-Komplexe **1a–c** (M = Cr, Mo, W) und erhält so die 2H-1,4,2-Diazaphosphol-Komplexe **3a–c**; analoge Reaktionen mit/in Benzo- oder Acetonitril geben die 2H-1,4,2-Diazaphosphol-Komplexe **3d, e**. Wie eine Vorstudie an dem 2H-Azaphosphiren-Komplex **1c**, gelöst in 1-Piperidinonitril, zeigt, reichen bereits substöchiometrische Mengen an TCNE aus (z. B. 0.3 Äquivalente), um eine ca. 70% Transformation von Komplex **1c** zu bewirken. Die NMR-Daten der Komplexe **2c** und **3a–e** werden diskutiert und das Ergebnis der Röntgenstrukturanalyse von Komplex **3c** vorgestellt.*

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The $^{31}P$ resonances are observed in the range of $\delta = 100-110$ with characteristic coupling constants $|J(^{183}W,^{31}P)|$ of about 228–240 Hz, whereby a weak electronic interaction of the *C*-substituents with the $\pi$ system of the five-membered ring can be concluded from the NMR parameters. EI mass spectrometric experiments revealed that 2*H*-1,4,2-diazaphosphole and $\Delta^5$-1,2-azaphospholene complexes lose carbon monoxide and show fragmentation of exocyclic bonds of the heterocycles *and* heterocycle fragmentations after the ionisation process. This behavior is in accord with observations made for 2*H*-1,4-diazoles.[13]

The molecular structure of complex **3c**[14] (Figure 1) confirms the constitution of the heterocyclic ring system and shows C–N atom double bond lengths (N1–C7 1.298(4) and N2–C6 1.291(4) Å) similar to those in **3d**[8b] and only slightly different endocyclic P–N and P–C distances.

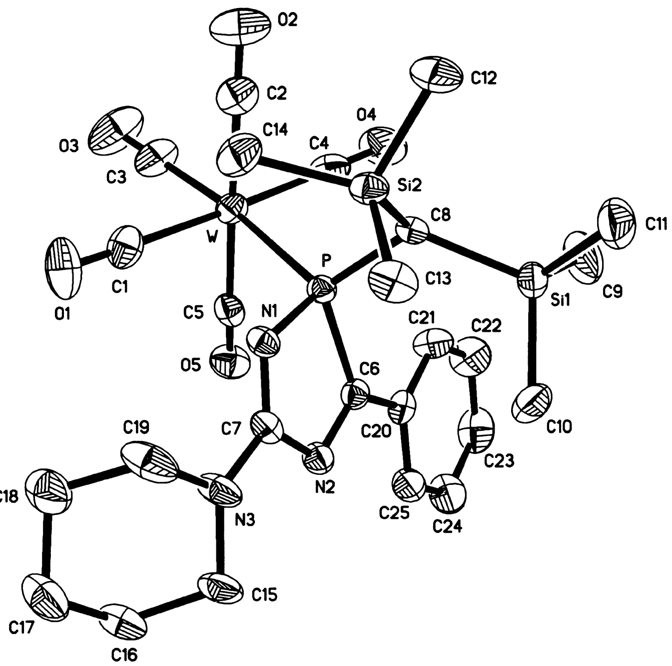


Figure 1. Molecular structure of complex **3c** (ellipsoids represent 40% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–C1 2.053(4), W–P 2.5278(12), P–N1 1.678(3), P–C6 1.880(3), P–C8 1.829(3), N1–C7 1.298(4), N2–C7 1.423(4), N2–C6 1.291(4), C7–N3 1.343(4); N1-P-W 114.61(9), C8-P-W 118.43(9), N1-P-C6 89.90(13), P-N1-C7 109.8(2), N1-C7-N2 120.8(3), C7-N2-C6 109.4(2), N2-C6-P 110.0(2).

In conclusion, a novel and highly efficient access to 2*H*-1,4,2-diazaphosphole complexes is reported. The reactions proceed under very mild conditions and give products with high regioselectivities. Experiments aimed at elucidating the mechanism of these TCNE-induced bond-selective insertion reactions are under way. Currently, we are investigating the applicability of this ring-expansion protocol to $\pi$ systems other than nitriles and to other three-membered heterocycle complexes.

## 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 $^{31}P$) using [D]chloroform and [D$_6$]benzene as solvent and internal standard; shifts are given relative to external tetramethylsilane ($^1H$, $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). Mass spectra were recorded on a Finigan Mat 8430 (70 eV); apart from *m/z* values of the molecular ions, only *m/z* values are given that have intensities greater than 20%. 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 $\kappa P$-notation differentiates between P- and N-coordination of the appropriate heterocycle to the metal.

**{{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,4-tetracyano-5-(1-piperidino)-$\Delta^5$–1,2-azaphospholene-$\kappa P$]}tungsten(0)} (2c)**: A solution of 2*H*-azaphosphirene tungsten complex **1c** (0.62 g, 1 mmol), 1-piperidinonitrile (0.2 mL, ca. 2 mmol) and tetracyanoethylene (TCNE) (0.26 g, 2 mmol) in toluene (3 mL) was heated at 75 °C for 1.5 h with slow stirring. After complete reaction ($^{31}P$ NMR control) the solution was concentrated in vacuo (ca. 0.1 mbar) to dryness and the residue washed several times with small amounts of *n*-pentane (0 °C). Complex **2c** was obtained after drying in vacuo as a light-brown amorphous solid. Yield: 135 mg (18%), m.p. 116 °C (decomp). $^1H$ NMR ($CDCl_3$): $\delta = 0.39$ (s, 9H; $SiMe_3$), 0.44 (s, 9H; $SiMe_3$), 1.76 (s br, 6H; $NCH_2CH_2CH_2$), 2.23 (d, $^2J(P,H) = 17.1$ Hz, 1H; $CH(SiMe_3)_2$), 3.79 (m br, 4H; $NCH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 2.9 (d, $^3J(P,C) = 4.0$ Hz; $SiMe_3$), 3.5 (d, $^3J(P,C) = 1.8$ Hz; $SiMe_3$), 23.6 (s; $NCH_2CH_2CH_2$), 25.2 (s br; $NCH_2CH_2CH_2$), 32.6 (d, $^1J(P,C) = 29.0$ Hz; $CH(SiMe_3)_2$), 49.4 (d, $^{(2+3)}J(P,C) = 20.6$ Hz; PC*C*), 50.4 (s; $NCH_2CH_2CH_2$), 54.1 (d, $^1J(P,C) = 27.6$ Hz; *P*CC), 107.4 (s; *C*N), 108.5 (s; *C*N), 109.1 (s; *C*N), 111.5 (s; *C*N), 144.9 (d, $^{(2+3)}J(P,C) = 10.7$ Hz; PN*C*), 195.6 (d, $^2J(P,C) =$ 7.2 Hz; *cis*-CO), 196.1 (d, $^2J(P,C) = 32.8$ Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 158.5$ (s, $^1J(P,W) = 306.7$ Hz); IR (KBr): $\tilde{\nu} = 2091$ (s), 1998 (s), 1954 (vs, br) $cm^{-1}$ (CO); 1625 (s br) (C=N) $cm^{-1}$; MS (70 eV, EI; $^{184}W$); *m/z* (%): 752 (10) $[M]^+$, 640 (20) $[M - 4CO]^+$, 612 (40) $[M - 5CO]^+$, 468 (40) $[(CO)_4WPCH(SiMe_3)_2]^+$, 402 (40) $[M - W(CO)_5 - CN]^+$, 73 (100) $[SiMe_3]^+$; elemental analysis for $C_{24}H_{29}N_6O_5PSi_2W$ (752.1) (%): calcd: C 38.31, H 3.88, N 11.17; found: C 38.09, H 3.99, N 11.04.

**General procedure for the synthesis of 2*H*-1,4,2-diazaphosphole complexes 3a–e**: To a solution of the 2*H*-azaphosphirene complexes **1a–c** (1 mmol each) in the appropriate nitrile (3 mL each) was added tetracyanoethylene (0.26 g, 2 mmol) (**1a**, **c**) or tetracyanoethylene (**1b**) (0.026 g, 0.2 mmol) and the mixture was stirred at ambient temperature for 1.5 h (**3a**, **c**), 3 d (**3d**), 30 h (**3e**) or heated at 75 °C for 1 h (**3b**) ($^{31}P$ NMR control). The brownish solutions were concentrated in vacuo (ca. 0.1 mbar), the residues separated by single (**3c–e**) or two-fold (**3a**, **b**) low-temperature column chromatography ($SiO_2$; **3c**, **d**: −50 °C, petrol ether (40/60); **3a**, **b**, **e**: ($SiO_2$; −50 °C, petrol ether (40/60)/diethyl ether 90:10), the eluates concentrated in vacuo (ca. 0.1 mbar) and the residues crystallised from small amounts of *n*-pentane at −20 °C.

**{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3-phenyl-5-(1-piperidino)-2*H*-1,4,2-diazaphosphole-$\kappa P$]chromium(0)} (3a)**: Yield: 125 mg (23%) orange crystals, m.p. 98 °C (decomp); $^1H$ NMR ($CDCl_3$): $\delta = 0.10$ (s, 9H; $SiMe_3$), 0.46 (s, 9H; $SiMe_3$), 1.05 (d, $^2J(P,H) = 3.1$ Hz, 1H; $CH(SiMe_3)_2$), 1,68 (s br, 6H; $NCH_2CH_2CH_2$), 3.81 (s br, 2H; $NCH_2CH_2CH_2$), 4.05 (s br, 2H; $NCH_2CH_2CH_2$), 7.51 (m br, 3H; $CH_{aromat.}$), 8.10 (m br, 2H; $CH_{aromat.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 3.6$ (d, $^3J(P,C) = 4.8$ Hz; $SiMe_3$), 3.9 (d, $^3J(P,C) = 2.1$ Hz; $SiMe_3$), 22.1 (d, $^1J(P,C) = 2.2$ Hz; $CH(SiMe_3)_2$), 24.7 (s; $NCH_2CH_2CH_2$), 25.6 (s br; $NCH_2CH_2CH_2$), 26.8 (s br; $NCH_2CH_2CH_2$), 46.6 (s br; $NCH_2CH_2CH_2$), 47.3 (s br; $NCH_2CH_2CH_2$), 128.6 (s; $CH_{aromat.}$), 129.6 (d, $^2J(P,C) = 5.2$ Hz; $C_{aromat.}$), 131.1 (d, $^3J(P,C) = 1.3$ Hz; $CH_{aromat.}$), 132.8 (s; $CH_{aromat.}$), 162.1 (s; PN*C*), 199.9 (d, $^1J(P,C) = 31.6$ Hz; P*C*N), 216.8 (d, $^2J(P,C) = 12.4$ Hz; *cis*-CO), 221.9 (d, $^2J(P,C) = 6.7$ Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 143.9$ (s); IR (KBr): $\tilde{\nu} = 2058$ (s), 1977 (s), 1950 (vs), 1923 (vs) (CO); 1587 (s, sh) $cm^{-1}$ (C=N); MS (CI, $NH_3$, positive-ion mode), ($^{52}Cr$): *m/z* (%): 486 (100) $[M - C_6H_{10}N + H]^+$, 383 (55) $[(CO)_5Cr\text{-}PCH(SiMe_3)_2 + H]^+$, 193 (45) $[(CO)_5CrH]^+$; MS (CI, $NH_3$, negative-ion mode), ($^{52}Cr$): *m/z* (%): 382 (60) $[(CO)_5CrPCH(SiMe_3)_2]^-$, 354 (35) $[(CO)_4CrPCH(SiMe_3)_2]^-$, 326 (30) $[(CO)_3CrPCH(SiMe_3)_2]^-$, 192 (100) $[Cr(CO)_5]^-$; elemental analysis for $C_{25}H_{34}N_3O_5PSi_2Cr$ (595.7) (%): calcd: C 50.41, H 5.75, N 7.05; found: C 50.05, H 5.75, N 6.20.

**{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3-phenyl-5-(1-piperidino)-2*H*-1,4,2-diazaphosphole-$\kappa P$]molybdenum(0)} (3b)**: Yield: 120 mg (19%)

orange brown crystals, m.p. 94 °C (decomp). $^1$H NMR ($CDCl_3$): $\delta = 0.11$ (s, 9H; $SiMe_3$), 0.46 (s, 9H; $SiMe_3$), 0.92 (d, $^2J$(P,H) = 2.6 Hz, 1H; C*H*($SiMe_3)_2$), 1.67 (s br, 6H; $NCH_2CH_2CH_2$), 3.81 (s br, 2H; $NCH_2CH_2CH_2$), 4.04 (s br, 2H; $NCH_2CH_2CH_2$), 7.51 (m br, 3H; $CH_{aromat.}$), 8.12 (m br, 2H; $CH_{aromat.}$), $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 3.0$ (d, $^3J$(P,C) = 1.3 Hz; $SiMe_3$), 3.7 (d, $^3J$(P,C) = 3.0 Hz; $SiMe_3$), 20.9 (d, $^1J$(P,C) = 12.2 Hz; *C*H($SiMe_3)_2$), 24.8 (s; $NCH_2CH_2CH_2$), 25.7 (s br; $NCH_2CH_2CH_2$), 26.9 (s br; $NCH_2CH_2CH_2$), 46.6 (s br; $NCH_2CH_2CH_2$), 47.3 (s br; $NCH_2CH_2CH_2$), 128.7 (s; $CH_{aromat.}$), 130.8 (d, $^3J$(P,C) = 2.2 Hz; $CH_{aromat.}$), 132.8 (s; $CH_{aromat.}$), 132.8 (d, $^2J$(P,C) = 20.6 Hz; $C_{aromat.}$), 163.1 (s; PN*C*), 200.8 (d, $^1J$(P,C) = 29.3 Hz; P*C*N), 205.9 (d, $^2J$(P,C) = 8.5 Hz; *cis*-*C*O), 211.1 (d, $^2J$(P,C) = 23.1 Hz; *trans*-*C*O); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = 120.0$ (s); IR (KBr): $\tilde{\nu}$ = 2071 (s), 1999 (s), 1989 (s), 1956 (vs), 1943 (vs) 1931 (vs), 1920 (vs, sh) (CO); 1588 (vs, sh) cm$^{-1}$ (C=N); MS (70 eV, EI), ($^{184}$W): *m/z* (%): 613 (45) [*M* − CO]$^+$, 585 (100) [*M* − 2CO]$^+$, 557 (50) [*M* − 3CO]$^+$, 447 (60) [*M* − 3CO − PhCN]$^+$, 73 (90) [$SiMe_3$]$^+$; elemental analysis for $C_{25}H_{34}N_3O_5PSi_2Mo$ (641.2) (%): calcd: C 46.94, H 5.36, N 6.57; found: C 46.79, H 5.45, N 6.45.

**{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3-phenyl-5-(1-piperidino)-2*H*-1,4,2-diazaphosphole-κ*P*]tungsten(0)} (3c)**: Yield: 125 mg (41%) yellow orange crystals, m.p. 111 °C (decomp). $^1$H NMR ($CDCl_3$): $\delta = 0.10$ (s, 9H; $SiMe_3$), 0.47 (s, 9H; $SiMe_3$), 1.06 (d, $^2J$(P,H) = 3.7 Hz, 1H; C*H*($SiMe_3)_2$), 1,68 (s br, 6H; $NCH_2CH_2CH_2$), 3.82 (s br, 2H; $NCH_2CH_2CH_2$), 4.06 (s br, 2H; $NCH_2CH_2CH_2$), 7.51 (m br, 3H; $CH_{aromat.}$), 8.16 (m br, 2H; $CH_{aromat.}$); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 3.1$ (d, $^3J$(P,C) = 2.7 Hz; $SiMe_3$), 3.8 (d, $^3J$(P,C) = 2.7 Hz; $SiMe_3$), 21.6 (d, $^1J$(P,C) = 6.4 Hz; *C*H($SiMe_3)_2$), 24.7 (s; $NCH_2CH_2CH_2$), 25.7 (s br; $NCH_2CH_2CH_2$), 26.9 (s br; $NCH_2CH_2CH_2$), 46.7 (s br; $NCH_2CH_2CH_2$), 47.3 (s br; $NCH_2CH_2CH_2$), 128.6 (s; $CH_{aromat.}$), 131.2 (d, $^3J$(P,C) = 1.9 Hz; $CH_{aromat.}$), 132.6 (d, $^2J$(P,C) = 20.8 Hz; $C_{aromat.}$), 132.9 (s; $CH_{aromat.}$), 163.4 (s; PN*C*), 198.1 (d, $^2J$(P,C) = 6.9 Hz, $^1J$(C,W) = 127.0 Hz, *cis*-*C*O); 199.9 (d, $^1J$(P,C) = 22.5 Hz; P*C*N), 200.0 (d, $^2J$(P,C) = 24.7 Hz; *trans*-*C*O); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = 100.1$ (s, $^1J$(P,W) = 240.5 Hz); IR (KBr): $\tilde{\nu}$ = 2069 (s), 1990 (s), 1980 (s), 1948 (vs), 1936 (vs), 1926 (vs), 1913 (vs) (CO); 1589 (s) cm$^{-1}$ (C=N); MS (70 eV, EI), ($^{184}$W): *m/z* (%): 727 (5) [*M*]$^+$, 699 (50) [*M* − CO]$^+$, 671 (55) [*M* − 2CO]$^+$, 533 (30) [*M* − 3CO − $C_5H_{10}N$]$^+$, 403 (45) [*M* − W(CO)$_5$]$^+$, 330 (40) [*M* − W(CO)$_5$ − $SiMe_3$]$^+$, 73 (100) [$SiMe_3$]$^+$; elemental analysis for $C_{25}H_{34}N_3O_5PSi_2W$ (727.6) (%): calcd: C 41.26, H 4.68, N 5.78; found: C 41.27, H 4.72, N 5.80.

**{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,5-diphenyl-2*H*-1,4,2-diazaphosphole-κ*P*]tungsten(0)} (3d)**: For NMR, IR and MS data see reference [8]. Yield: 435 mg (62%) red crystals, m.p.: 92 °C (decomp).

**{Pentacarbonyl[2-bis(trimethylsilyl)methyl-3-phenyl-5-methyl-2*H*-1,4,2-diazaphosphole-κ*P*]tungsten(0)} (3e)**: Yield: 345 mg (54%) orange crystals, m.p. 62 °C (decomp). $^1$H NMR ($CDCl_3$): $\delta = -0.09$ (s, 9H; $SiMe_3$), 0.51 (s, 9H; $SiMe_3$), 1.05 (d, $^2J$(P,H) = 4.6 Hz, 1H; C*H*($SiMe_3)_2$), 2.69 (s, 3H; $CH_3$), 7.53 (m br, 3H; $CH_{aromat.}$), 8.12 (m br, 2H; $CH_{aromat.}$); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 2.9$ (d, $^3J$(P,C) = 1.7 Hz; $SiMe_3$), 3.7 (d, $^3J$(P,C) = 2.7 Hz; $SiMe_3$), 17.5 (d, $^1J$(P,C) = 4.5 Hz; *C*H($SiMe_3)_2$), 22.3 (d, $^3J$(P,C) = 11.3 Hz; $CH_3$), 128.9 (s; $CH_{aromat.}$), 131.1 (d, $^3J$(P,C) = 1.9 Hz; $CH_{aromat.}$), 131.9 (d, $^2J$(P,C) = 23.2 Hz; $C_{aromat.}$), 133.4 (s; $CH_{aromat.}$), 173.3 (d, $^{(2+3)}J$(P,C) = 7.3 Hz; PN*C*), 197.1 (d, $^2J$(P,C) = 6.5 Hz, $^1J$(C,W) = 126.8 Hz; *cis*-*C*O), 197.9 (d, $^2J$(P,C) = 22.5 Hz; *trans*-*C*O), 202.3 (d, $^1J$(P,C) = 21.8 Hz; P*C*N); $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta = 109.3$ (s, $^1J$(P,W) = 228.2 Hz); IR (KBr): $\tilde{\nu}$ = 2071 (s), 1980 (m), 1936 (vs, sh), 1921 (vs) (CO); 1571 (w), 1561 (w) cm$^{-1}$ (C=N); MS (70 eV, EI): *m/z* (%): 658 (10) [*M*]$^+$, 602 (50) [*M* − 2CO]$^+$, 533 (20) [*M* − 3CO − $C_2H_3N$]$^+$, 477 (50) [*M* − 5CO − $C_2H_3N$]$^+$, 73 (100) [$SiMe_3$]$^+$; elemental analysis for $C_{21}H_{27}N_2O_5PSi_2W$ (658.5) (%): calcd: C 38.31, H 4.13, N 4.25; found: C 38.23, H 4.24, N 4.22.

**X-ray structure analysis of complex 3c**: empirical formula: $C_{25}H_{34}N_3O_5P$-$Si_2W$, $M_r$ = 727.55; triclinic, space group $P\bar{1}$; $a = 10.225(3)$, $b = 11.821(4)$, $c = 12.906(4)$ Å, $\alpha = 88.12(3)$, $\beta = 84.99(2)$, $\gamma = 76.44(3)°$; $V = 1510.6(8)$ Å$^3$; $Z = 2$; $\rho_{calcd} = 1.600$ Mg m$^{-3}$; $\lambda = 0.71073$ pm, $T = 143$ K. The crystal (0.55 × 0.40 × 0.15 mm) was mounted in inert oil. 8781 intensities were measured ($\omega/\theta$-scans, $2\theta$ 6–50°) using $Mo_{K\alpha}$ radiation on a Stoe STADI-4 diffractometer. After absorption correction (psi scans) 5329 were unique ($R_{int}$ = 0.0175) and used for all calculations (SHELXL-93) [15]. All hydrogen atoms (except rigid methyl groups) were refined with a riding model. Final $wR(F^2)$ was 0.0496 with conventional $R(F)$ 0.0214 for 340 parameters and 38 restraints; highest peak/hole 0.51/ − 0.42 e Å$^{-3}$.

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[1] R. Streubel, S. Priemer, F. Ruthe, P. G. Jones, *Eur. J. Inorg. Chem.* **2000**, 1253–1259.
[2] Reviews: a) A. J. Fatiadi, *Synthesis* **1986**, 249–284; b) A. J. Fatiadi, *Synthesis* **1987**, 959–978.
[3] L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, Berlin, **1987**.
[4] D. Astruc, *Electron-Transfer Processes in Transition Metal Chemistry*, VCH Publishers, New York, **1995**.
[5] Z. Yoshida, S. Yoneda, Y. Murata, *J. Org. Chem.* **1973**, *38*, 3537–3541.
[6] R. Appel in *Multiple Bonds and Low Coordination Chemistry in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 184.
[7] G. Märkl, P. Kreitmeier, R. Daffner, *Tetrahedron Lett.* **1993**, *34*, 7045–7048.
[8] a) 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; b) H. Wilkens, F. Ruthe, P. G. Jones, R. Streubel, *Chem. Eur. J.* **1998**, *4*, 1542–1553; b) H. Wilkens, A. Ostrowski, J. Jeske, F. Ruthe, P. G. Jones, R. Streubel, *Organometallics* **1999**, *18*, 5627–5642.
[9] R. Streubel, H. Wilkens, F. Ruthe, P. G. Jones, *Chem. Commun.* **1999**, 2127–2128.
[10] R. Streubel, U. Schiemann, N. Hoffmann, Y. Schiemann, P. G. Jones, D. Gudat, *Organometallics* **2000**, *19*, 475–481.
[11] R. Streubel, F. Ruthe, P. G. Jones, *Eur. J. Inorg. Chem.* **1998**, 571–574.
[12] R. Streubel, A. Ostrowski, S. Priemer, U. Rohde, J. Jeske, P. G. Jones, *Eur. J. Inorg. Chem.* **1998**, 257–261.
[13] K. Burger, K. Einhellig, *Chem. Ber.* **1973**, *106*, 3421–3430.
[14] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136733. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[15] G. M. Sheldrick, SHELXL-93, program for crystal structure refinement, Universität Göttingen, **1993**.

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