Chemistry of 2*H*-Azaphosphirene Complexes, 10[◇]

Syntheses of 3-Heteroaryl-2*H*-Azaphosphirene Tungsten Complexes☆

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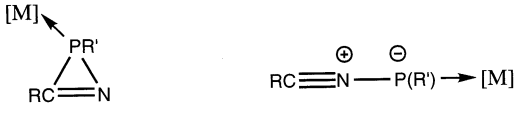
The syntheses of 3-heteroaryl-substituted 2*H*-azaphosphirene pentacarbonyltungsten complexes are reported. The products were characterized by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{15}N, ^{31}P, ^{183}W); the structure of the 3-*N*-methylpyrryl-substituted 2*H*-azaphosphirene complex was determined by single-crystal X-ray structure analysis.

2*H*-azaphosphirene tungsten complexes (**I**) are of current synthetic interest because of their widespread applicability in heterocycle synthesis. For example, we very recently demonstrated that 2*H*-azaphosphirene tungsten complexes provide a new access to five-membered heterocyclic complexes, through trapping reactions of transiently formed nitrilium phosphane ylide tungsten complexes (**II**) with an acetylene[2] and a nitrile derivative.[3] Therefore, we were interested in the synthesis of 3-heteroaryl-substituted 2*H*-azaphosphirene tungsten complexes. We also wished to test the limits of our initial synthetic approach[4] to 2*H*-azaphosphirene complexes.

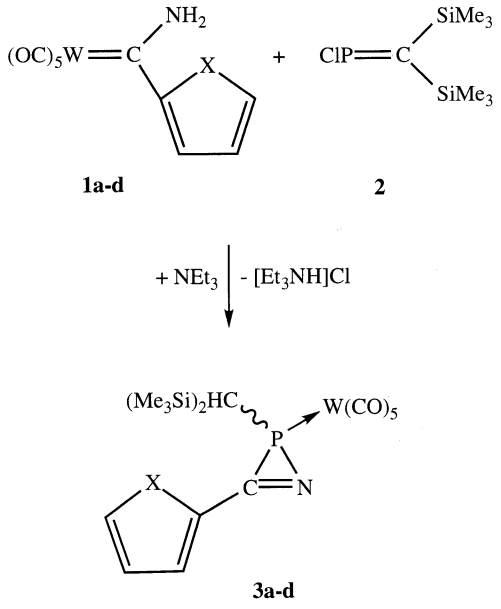
Scheme 1. 2*H*-azaphosphirene tungsten complexes (**I**) and nitrilium phosphane ylide tungsten complexes (**II**) (**I**, **II**: R, R′ = alkyl, aryl; [M] = metal complex fragment)



I **II**

Heteroaryl-substituted aminocarbene tungsten complexes **1a−c** were synthesized according to standard procedures[5] and reacted with [bis(trimethylsilyl)methylene]-chlorophosphane (**2**)[6] in the presence of triethylamine. In a similar way to our previously reported reactions of aryl-substituted aminocarbene complexes,[1][7] these reactions proceeded smoothly to give the 2*H*-azaphosphirene tungsten complexes **3a−c** (Scheme 2). These compounds were isolated in moderate to good yields after low-temperature column chromatography.

Scheme 2. Synthesis of 2*H*-azaphosphirene tungsten complexes **3a−c**



1a,3a: X = NMe; **1b,3b**: X = O; **1c,3c**: X = S; **1d,3d**: HC=CH

The proposed structures of the 2*H*-azaphosphirene tungsten complexes **3a−c** are unambiguously confirmed by their typical NMR data. The assignment of the ^{1}H- and ^{13}C-NMR resonances of the aromatic substituents in **3a−c** is based on a comparison with the corresponding data of 2-formyl-substituted heteroarenes.[8] The chemical shift of the

[◇] Part 9: See ref.[7].

  1434−1948/98/0505−0575 $ 17.50+.50/0

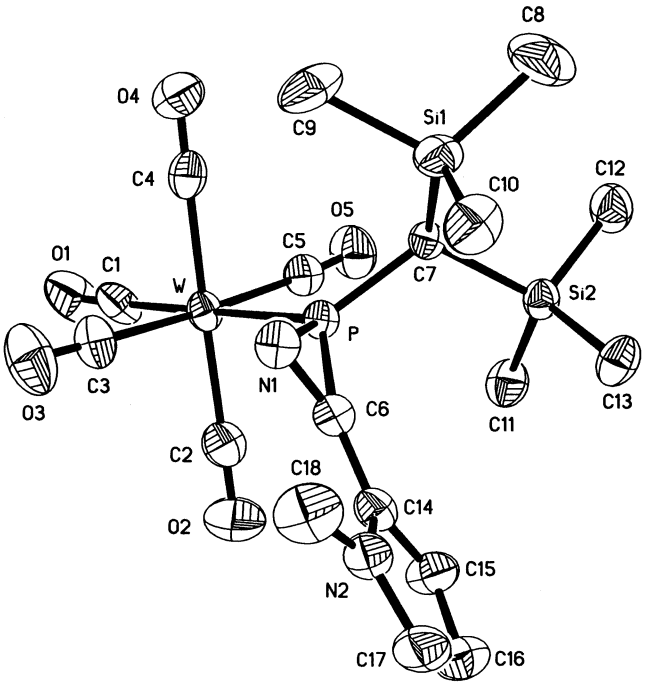
pyrryl nitrogen atom in **3a** compares to reported values of *N*-alkyl pyrroles.[9] The chemical shifts of the atoms in the three membered rings of **3b,c** match those of the phenyl substituted derivative, **3d**, [1] while for the *N*-methylpyrryl-substituted compound, **3a**, both the ^{31}P and ^{15}N resonances display marked shifts to higher field (Table 1). The origin of this phenomenon arises presumably from π-interactions between the five- and three-membered rings and is in accord with the higher π-donor capability of a pyrryl as compared to a thienyl or phenyl substituent. The magnitudes of the carbon-phosphorus coupling constants in **3a−c** [$^{(1+2)}J_{PC}$ = 4.0−8.2 Hz] are larger than in **3d** and related *para*-substituted derivatives (1−3 Hz, ref.[7]) and increase in the same order (**3c** < **3b** < **3a**) as [$^{(1+2)}J_{PN}$]. The values of $\delta^{183}W$ and $^1J_{WP}$ for **3a−c** are essentially constant and lie in the known range for complexes of the type $[W(CO)_5(PR_3)]$.[10] CI EI mass spectrometric experiments revealed that, although only the [(M + H)$^+$] and not the [(M − H)$^-$] ions were detected, these 2*H*-azaphosphirene complexes preferentially show PCN-ring cleavage subsequent to the ionisation processes; this was observed in the positive and negative CI mode. Additionally, the resulting fragment ions indicate subsequent loss of carbon monoxide.

Table 1. Comparison of selected ^{13}C[a], ^{15}N[b], ^{31}P[b], ^{183}W[b] NMR data (δ values, *J*[Hz]) of 3-heteroaryl-2*H*-azaphosphirene tungsten complexes **3a−c**, **d**[7] (exclusively atoms of the three-membered ring and tungsten)

	δ ^{31}P	$^1J_{W,P}$	δ ^{13}C	$^{(1+2)}J_{C,P}$	δ ^{15}N	$^{(1+2)}J_{N,P}$	δ ^{183}W
3a	−127.9	294	179.2	8.2	−85.3	40.1	3249.8
3b	−108.3	298	181.7	7.0	−60.7	39.7	3252.5
3c	−103.0	296	185.0	4.0	−62.6	38.7	3255.3
3d	−108.8	294	192.3	1.3	−53.9	36.7	3255.9

[a] $CDCl_3$, room. temp. − [b] CH_2Cl_2, room. temp.

Figure 1. Molecular structure of **3a** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity). Selected bond lengths [A] and angles [°]: P−C(6) 1.760(4), P−N(1) 1.789(3), N(1)−C(6) 1.296(5), W−P 2.4741(13); C(6)−P−N(1) 42.8(2), C(6)−N(1)−P 67.4(2), N(1)−C(6)−P 69.8(2), N(1)−C(6)−C(14) 138.0(4).



The molecular structure of complex **3a** was confirmed for the solid state by X-ray crystallography (Figure 1).[11] One of the most interesting structural features of **3a** is the almost coplanar arrangement of the two ring systems (interplanar angle 6.4°) which allows an effective π-electron interaction between the *N*-methylpyrryl group (π-donor) and the PCN-ring (π-acceptor). This is strongly supported by the observed bond length equalization of the carbon−carbon bonds in the pyrryl ring [C14−C15 1.389(5), C15−C16 1.385(6), C16−C17 1.396(6) Å] and the inter-ring bond [C6−C14 1.404(5) Å]. The latter is also significantly shorter than the corresponding distance in **3d** [1.457(7) Å][7], while at the same time the C−N double bond [N1−C6 1.296(5) Å] is longer than there [1.272(7) Å[7]].

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Experimental Section

General: All operations were carried out under deoxygenated dry nitrogen as inert gas, solvents were dried according to standard procedures. − NMR spectra were recorded on a Bruker AC-200 or a Bruker AMX-300 spectrometer (AC-200: 200 MHz for ^1H; 50.3 MHz for ^{13}C; 81 MHz for ^{31}P; AMX-300: 30.4 MHz for ^{15}N; 12.5 MHz for ^{183}W) using [D]chloroform and dichloromethane as solvent and internal standard; shifts are given relative to ext. tetramethylsilane (^1H, ^{13}C), H_3CNO_2 (^{15}N), 85% H_3PO_4 (^{31}P) and WO_4^{2-} (^{183}W). ^{15}N-NMR spectra were recorded using ^{31}P- and ^1H-based polarisation transfer techniques (INEPT); ^{183}W-NMR data were obtained from two dimensional ^{31}P-detected ^{31}P, $^{183}W\{^1H\}$ HMQC spectra. − MS: Finigan Mat 8430 (70 eV). − Elemental analyses: Carlo Erba analytical gas chromatograph. − IR: Biorad FT-IR-165.

General Procedure for the Preparation of Amino(heteroaryl)carbene Tungsten Complexes: The ethoxy(heteroaryl)-carbene tungsten complexes were prepared according to ref.[5] and reacted, without purification, with ammonia. A gentle flow of ammonia was bubbled through a solution of 5 mmol of the ethoxy-(heteroaryl)carbene tungsten complexes in 60 ml of ether until a yellow colour persisted and thin layer chromatography (SiO_2) indicated that all starting material had reacted. All volatile compounds were removed under reduced pressure (0.1 mbar) and the yellow residue was purified by column chromatography. The assignment of the ^1H and ^{13}C resonances of the aromatic heterocyclic substituents of **1a−c** accords with related chromium complexes.[12]

{[Amino(1-methyl-2-pyrryl)carbene]pentacarbonyltungsten(0)} (**1a**): 1.7 g of **1a** (79%) was obtained as a yellow powder after low temperature chromatography (SiO_2, −10°C; hexane/ether 1:1). M.p. 120°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3451 (m) cm^{-1}, 3351 (m), 3256 (m), (NH), 2061 (m), 1978 (m), 1903 (s), (CO). − ^1H NMR ($CDCl_3$): δ = 3.80 (s, 3 H, N−CH_3), 6.22 (dd, $^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 2.6 Hz, 1 H, pyrryl-C4-*H*), 6.85−6.91 (m, 2 H, pyrryl-C3/5-*H*), 8.07 (br, 2 H, NH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 37.1 (s, N−*C*H_3), 110.3 (s, pyrryl-*C4*), 123.7 (s, pyrryl-*C5*), 132.0 (s, pyrryl-*C3*), 143.6 (s, pyrryl-*C2*), 198.9 (s, $^1J_{CW}$ = 127.6 Hz, *cis*-*C*O), 202.9

(s, *trans*-*C*O), 240.6 (s, W=*C*R_2). − MS (70 eV), (^{184}W) *m*/*z* (%): 432 (8) [M^+], 404 (11) [M^+ − CO], 352 (53) [M^+ − C_5H_6N], 296 (40) [M^+ − 2 × CO − C_5H_6N], 268 (100) [M^+ − 3 × CO − C_5H_6N], 240 (41) [M^+ − 4 × CO − C_5H_6N], 212 (43) [M^+ − 5 × CO − C_5H_6N], 184 (33) [M^+ − 5 × CO − C_5H_6N − CNH_2]. − $C_{11}H_8N_2O_5W$ (432.0): calcd. C 30.58, H 1.87, N 6.48; found C 30.67, H 1.90, N 6.48.

{[Amino(2-furyl)carbene]pentacarbonyltungsten(0)} (**1b**): 1.5 g of **1b** (71%) was obtained as a yellow-orange powder after low temperature chromatography (SiO_2, −10°C; hexane/ether 1:1). M.p. 95°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3457 (m) cm^{-1}, 3341 (m), 3256 (m), (NH), 2064 (m), 1976 (m), 1928 (s), 1888 (s), (CO). − ^{1}H NMR ($CDCl_3$): δ = 6.56 (dd, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, furyl-C4-*H*), 7.45−7.47 (m, 1 H, furyl-C3-*H*), 7.54−7.55 (m, 1 H, furyl-C5-*H*), 7.91 (br, 1 H, NH_2), 8.94 (br, 1 H, NH_2). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 114.5 (s, furyl-*C4*), 129.4 (s, furyl-*C3*), 145.6 (s, furyl-*C5*), 159.0 (s, furyl-*C2*), 198.4 (s, $^1J_{CW}$ = 129.9 Hz, *cis*-*C*O), 202.6 (s, *trans*-*C*O), 229.8 (s, W=*C*R_2). − MS (70 eV), (^{184}W); *m*/*z* (%): 419 (56) [M^+], 391 (18) [M^+ − CO], 335 (55) [M^+ − 3 × CO], 307 (51) [M^+ − 4 × CO], 279 (100) [M^+ − 5 × CO], 252 (56) [M^+ − 3 × CO − NH_2 − C_4H_3O], 224 (35) [M^+ − 4 × CO − NH_2 − C_4H_3O]. − $C_{10}H_5NO_6W$ (419.0): calcd. C 28.67, H 1.20, N 3.34; found C 28.73, H 1.21, N 3.32.

{[Amino(2-thienyl)carbene]pentacarbonyltungsten(0)} (**1c**): 1.8 g of **1c** (84%) was obtained as a yellow powder after low temperature chromatography (SiO_2, −10°C; hexane/ether 1:1). M.p. 101°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3426 (m) cm^{-1}, 3343 (m), 3266 (m), (NH), 2064 (m), 1969 (m), 1922 (vs), 1911 (vs), 1888 (s), 1872 (vs), (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.16 (dd, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 3.9 Hz, 1 H, thienyl-C4-*H*), 7.60 (dd, $^3J_{HH}$ = 3.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1 H, thienyl-C3-*H*), 7.66 (dd, $^3J_{HH}$ = 5.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1 H, thienyl-C5-*H*), 8.02 (br, 1 H, NH_2), 8.52 (br, 1 H, NH_2). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 129.0 (s, thienyl-*C4*), 132.7 (s) and 133.2 (s) (thienyl-*C3*/*C5*), 153.5 (s, thienyl-*C2*), 198.4 (s, $^1J_{CW}$ = 127.2 Hz, *cis*-*C*O), 202.6 (s, *trans*-*C*O), 243.8 (s, W=*C*R_2). − MS (70 eV), (^{184}W); *m*/*z* (%): 435 (49) [M^+], 407 (30) [M^+ − CO], 351 (28) [M^+ − 3 × CO], 295 (100) [M^+ − 5 × CO], 268 (41) [M^+ − 3 × CO − C_4H_3S]. − $C_{10}H_5NO_5SW$ (435.1): calcd. C 27.61, H 1.16, N 3.22, S 7.37; found C 27.68, H 1.16, N 3.15, S 7.40.

General Procedure for the Preparation of 2H-Azaphosphirene-(pentacarbonyl)tungsten Complexes: To a solution of 1.5 mmol of amino(heteroaryl)carbene tungsten complexes **1a−c** in 15 ml of ether was added 0.34 g (1.5 mmol) of **2** and 5 ml of NEt_3 at 0°C. The reaction mixture was stirred at ambient temp. until **2** was consumed (^{31}P-NMR control). The yellow-orange reaction mixture was evaporated to dryness under reduced pressure (0.1 mbar). The residue was extracted with 30 ml of pentane and filtered. The filtration residue was washed twice with 5 ml of pentane, the organic phases combined and the solvent removed under reduced pressure. The residue was purified, if necessary, by low temperature column chromatography (SiO_2, −10°C; hexane/ether 10:1).

{[2-Bis(trimethylsilyl)methyl-3-(1-methyl-2-pyrryl)-2H-azaphosphirene-κP]pentacarbo-nyltungsten(0)} (**3a**): 0.35 g of **3a** (56%) was obtained, after stirring for 20 hours, as a yellow powder. M.p. 112°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2073 (m) cm^{-1}, 1990 (m), 1952 (s, sh), 1936 (s), 1919 (vs), (CO), 1618 (w) (CN). − ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.58 (d, $^2J_{HP}$ = 2.9 Hz, 1 H, PC*H*), 4.01 (d, $^4J_{HH}$ = 0.5 Hz , 3 H, N−CH_3), 6.37 (dd, $^3J_{HH}$ = 4.1 Hz, $^3J_{HH}$ = 2.5 Hz, 1 H, pyrryl-C4-*H*), 7.04−7.06 (m, 1 H, pyrryl-C3-*H*), 7.10 (m, 1 H, pyrryl-C5-*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 1.3 (d, $^3J_{CP}$ = 3.5 Hz, $SiMe_3$), 2.2 (d, $^3J_{CP}$ = 3.1 Hz, $SiMe_3$), 27.2 (d, $^1J_{CP}$ = 24.2 Hz, P*C*H), 36.2 (s, N−*C*H_3), 111.0 (s, pyrryl-*C4*), 120.2 (d, $^2J_{CP}$ = 19.2 Hz, pyrryl-*C2*), 122.3 (s, pyrryl-*C3*), 132.6 (s, pyrryl-*C5*), 179.2 (d, $^{(1+2)}J_{PC}$ = 8.2 Hz, P*C*N), 196.0 (d, $^2J_{CP}$ = 8.9 Hz, *cis*-*C*O), 198.1 (d, $^2J_{CP}$ = 35.6 Hz, *trans*-*C*O). − ^{15}N NMR (CH_2Cl_2): δ = −85.3 (d, $^{(1+2)}J_{NP}$ = 40.1 Hz, PC*N*), −224.3 (d, $^3J_{NP}$ = 1.4 Hz, pyrryl-*N*). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −125.8 (s, $^1J_{PW}$ = 293.1 Hz). − ^{31}P{^{1}H} NMR (CH_2Cl_2): δ = −127.9 (s, $^1J_{PW}$ = 294.0 Hz). − ^{183}W NMR (CH_2Cl_2): δ = −3249.8 (d, $^1J_{PW}$ = 294.0 Hz). − MS (pos.-CI, NH_3), (^{184}W) *m*/*z* (%): 621 (100) [(M + H)$^+$], 515 (18) [(M + H)$^+$ − $C_6H_6N_2$], 106 (5) [$C_6H_6N_2^+$]. − MS (neg.-CI, NH_3), (^{184}W) *m*/*z* (%): 513 (100) [(M − H)$^-$ − $C_6H_6N_2$], 485 (18) [(M − H)$^-$ − $C_6H_6N_2$ − CO], 457 (2) [(M − H)$^-$ − $C_6H_6N_2$ − 2 × CO]. − $C_{18}H_{25}N_2O_5PSi_2W$ (620.4): calcd. C 34.85, H 4.06, N 4.52; found C 35.08, H 4.03, N 4.62.

{[2-Bis(trimethylsilyl)methyl-3-(2-furyl)-2H-azaphosphirene-κP]pentacarbonyltungsten(0)} (**3b**): 0.35 g of **3b** (58%) was obtained, after stirring for 25 hours, as a yellow powder. M.p. 106°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2074 (s) cm^{-1}, 1991 (m), 1965 (s), 1945 (vs), 1935 (s), 1923 (vs), 1907 (vs) (CO), 1636 (w) (CN). − ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.65 (d, $^2J_{HP}$ = 3.8 Hz, 1 H, PC*H*), 6.74 (dd, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, furyl-C4-*H*), 7.42 (d, $^3J_{HH}$ = 3.5 Hz, 1 H, furyl-C3-*H*), 7.88 (d, $^3J_{HH}$ = 1.8 Hz,1 H, furyl-C5-*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 1.0 (d, $^3J_{CP}$ = 3.4 Hz, $SiMe_3$), 2.0 (d, $^3J_{CP}$ = 3.2 Hz, $SiMe_3$), 28.0 (d, $^1J_{CP}$ = 23.6 Hz, P*C*H), 113.6 (s, furyl-*C3*), 120.6 (s, furyl-*C4*), 143.3 (d, $^2J_{CP}$ = 17.1 Hz, furyl-*C2*), 149.2 (s, furyl-*C5*), 181.7 (d, $^{(1+2)}J_{CP}$ = 7.0 Hz, P*C*N), 195.6 (d, $^2J_{CP}$ = 8.9 Hz, *cis*-*C*O), 197.6 (d, $^2J_{CP}$ = 37.0 Hz, *trans*-*C*O). − ^{15}N NMR (CH_2Cl_2): δ = −60.7 (d, $^{(1+2)}J_{NP}$ = 39.7 Hz). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −105.4 (s, $^1J_{PW}$ = 297.9 Hz). − ^{31}P{^{1}H} NMR (CH_2Cl_2): δ = −108.3 (s, $^1J_{PW}$ = 298.0 Hz). − ^{183}W NMR (CH_2Cl_2): δ = −3252.5 (d, $^1J_{PW}$ = 298.0 Hz). − MS (pos.-CI, NH_3), (^{184}W); *m*/*z* (%): 608 (100) [(M + H)$^+$], 515 (4) [(M + H)$^+$ − C_5H_3NO]. MS (neg.-CI, NH_3), (^{184}W); *m*/*z* (%): 513 (100)[(M − H)$^-$ − C_5H_3NO], 485 (8) [(M − H)$^-$ − C_5H_3NO − CO]. − $C_{17}H_{22}NO_6PSi_2W$ (607.4): calcd. C 33.56, H 3.64, N 2.30; found C 33.78, H 3.55, N 2.28.

{[2-Bis(trimethylsilyl)methyl-3-(2-thienyl)-2H-azaphosphirene-κP]-pentacarbonyltungsten(0)} (**3c**): 0.35 g of **3c** (56%) was obtained, after stirring for 22 hours, as a yellow powder. M.p. 110°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2072 (s) cm^{-1}, 1988 (m), 1963 (s), 1936 (vs, br), 1920 (vs), (CO), 1612 (w) (CN). − ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 0.70 (d, $^2J_{HP}$ = 3.3 Hz, 1 H, PC*H*), 7.34 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 3.8 Hz, 1 H, thienyl-C4-*H*), 7.87−7.94 (m, 2 H, thienyl-C3/5-*H*). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 1.3 (d, $^3J_{CP}$ = 3.5 Hz, $SiMe_3$), 2.1 (d, $^3J_{CP}$ = 3.3 Hz, $SiMe_3$), 28.2 (d, $^1J_{CP}$ = 24.3 Hz, P*C*H), 129.2 (s, thienyl-*C5*), 130.0 (d, $^2J_{CP}$ = 17.9 Hz, thienyl-*C2*), 134.9 (s) and 135.7 (s), thienyl-*C3*/*C4*, 185.0 (d, $^{(1+2)}J_{PC}$ = 4.0 Hz, P*C*N), 195.7 (d, $^2J_{CP}$ = 8.9 Hz, *cis*-*C*O), 197.7 (d, $^2J_{CP}$ = 36.7 Hz, *trans*-*C*O). − ^{15}N NMR (CH_2Cl_2): δ = −62.6 (d, $^{(1+2)}J_{PN}$ = 38.7 Hz). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −100.8 (s, $^1J_{PW}$ = 296.3 Hz). − ^{31}P{^{1}H} NMR (CH_2Cl_2): δ = −103.0 (s, $^1J_{PW}$ = 296.0 Hz). − ^{183}W NMR (CH_2Cl_2): δ = −3255.3 (d, $^1J_{PW}$ = 296.3 Hz). − MS (pos.-CI, NH_3), (^{184}W) *m*/*z* (%): 624 (50) [(M + H)$^+$], 515 (15) [(M + H)$^+$ − C_5H_3NS], 112 (100) [(C_5H_3NS + 3 H)$^+$], 74 (14) [($SiMe_3$ + H)$^+$]. − MS (neg.-CI, NH_3), (^{184}W) *m*/*z* (%): 513 (100) [(M − H)$^-$ − C_5H_3NS], 485 (44) [(M − H)$^-$ − C_5H_3NS − CO]. − $C_{17}H_{22}NO_5PSSi_2W$ (623.4): calcd. C 32.75, H 3.56, N 2.25, S 5.14; found C 32.82, H 3.61, N 2.11, S 5.17.

Crystal Structure Determination of **3a**[11]: $C_{18}H_{25}N_2O_5PSi_2W$, *M* = 620.40, $P\bar{1}$, *a* = 9.330(3), *b* = 9.522(3), *c* = 14.275(3) Å, α =

89.13(3), β = 83.66(3), γ = 79.80(3)°, V = 1240.5(5) Å^3, Z = 2, d_{calc} = 1.661 Mg/m^3, μ = 4.846 mm^{-1}, T = 143 K. A pale brown block (0.6 × 0.3 × 0.3 mm) was mounted in inert oil. 8349 intensities were measured (2Θ 6−50°) using Mo-*Kα* radiation on a Stoe STADI-4 diffractometer. After absorption correction (ψ-scans) 4383 were unique (R_{int} = 0.0256) and used for all calculations (program SHELXL-93). All hydrogen atoms (except rigid methyl groups) were refined with a riding model. The final $wR(F^2)$ was 0.052 with conventional $R(F)$ 0.023 for 269 parameters and 90 restraints. Highest peak 640, hole −969 e/nm^3.

☆ Dedicated to Professor *Hans Bock* on the occasion of his 70th birthday.

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[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100855. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, UK-Cambridge CB2 1EZ [fax: int. code +44(1223)336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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