Chemistry of 2*H*-Azaphosphirene Complexes, 9[◇]

Syntheses of 3-Phenyl-2*H*-Azaphosphirene Chromium and Molybdenum Complexes – First Evidence for Reaction Intermediates[☆]

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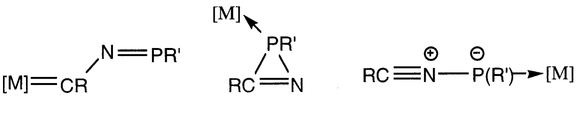
The synthesis of 3-phenyl-substituted 2*H*-azaphosphirene pentacarbonylchromium and pentacarbonylmolybdenum complexes is reported. New information on the rearrangement cascade, which finally leads to 2*H*-azaphosphirene ring formation, has been obtained through isolation of a reactive intermediate. A comparison of the ^{13}C-, ^{15}N-, ^{31}P-NMR, and UV/vis spectroscopic data and single crystal X-ray structural data of 3-phenyl-substituted 2*H*-azaphosphirene chromium, molybdenum, and tungsten complexes is presented.

Over the last three years we have focussed our attention on the synthesis and chemistry of 2*H*-azaphosphirene tungsten complexes (**II**) (Scheme 1).[2] These complexes show a fascinating reactivity upon ring opening to give, depending on the reaction conditions, nitrilium phosphane ylide tungsten complexes (**III**)[1][3] and/or an electrophilic terminal phosphanediyl tungsten complex.[4] Meanwhile, both reactive intermediates have found several applications in the synthesis of heterocycles.[5]

Scheme 1. 2-Aza-1-phospha-4-metallabutadienes **I**, 2*H*-azaphosphirene metal complexes **II** and their acyclic isomers, the nitrilium phosphane ylide metal complexes **III**; **I**, **II**, **III**: R, R′ = alkyl, aryl; [M] = metal complex fragment



I **II** **III**

Our first synthetic route to 2*H*-azaphosphirene tungsten complexes used a rearrangement cascade in which transiently formed metallaheterobutadienes **I**, which are isomeric to **II** and **III**, were assumed to be key intermediates.[2a] The elucidation of the reaction course was an intriguing problem for us and, therefore, we decided to investigate the reaction of the aminobenzylidene chromium **1a**[6] and molybdenum complex **1b**[7] with [bis(trimethylsilyl)methylene]chlorophosphane (**2**).[8]

When we first carried out the reaction of complex **1a** with methylenechlorophosphane **2** in ether at ambient temperature and in the presence of triethylamine, we obtained a complicated product mixture. According to ^{31}P-NMR spectroscopic measurements the mixture contained approximately ten products, most of them appearing as singuletts in the spectra. Although these products could not be separated by column chromatography, the chromium complex **5** and the 2*H*-azaphosphirene chromium complex **6a**, the latter formed only in small amounts, were easily identified by their typical ^{31}P-nuclear magnetic resonances [**5**: δ = 95.4 (s) and **6a**: δ = −54.3 (s)]. Three other products showed chemical shift values at low field [δ = 518.6 (s)/425.4 (s), and δ = 476.3 (d)/445.1 (d), the latter with a ^{31}P,^{31}P coupling constant of 515 Hz]. Because of these typical chemical shift and coupling constant values, their identification was achieved by comparison with the data of compounds known in literature as bis[bis(trimethylsilyl)methyl]diphosphene [δ = 517 (s)][9] and the corresponding mono- and dinuclear diphosphene pentacarbonylchromium complexes, $[\{(Me_3Si)_2HCP{=}PCH(SiMe_3)_2\}Cr(CO)_5]$: δ = 475.8 and 444.3, ^1J(P,P) = 516 Hz and $[\{(Me_3Si)_2HCP{=}PCH(SiMe_3)_2\}[Cr(CO)_5]_2]$: δ = 425.9 (s).[10]

In contrast, the molybdenum complex **1b** gave the 2*H*-azaphosphirene molybdenum complex **6b** straight away, but only in low yields (28%). This reaction behavior underlines the close relationship between aminobenzylidene molybdenum and tungsten complexes. Significantly better yields of **6a** (30%) and **6b** (67%) were obtained if the reactions of **1a** and **1b** with **2** were carried out at low temperature (**1a**: −40°C; **1b**: −10°C). Apart from triethylammonium chloride, the 2*H*-azaphosphirene metal complexes **6a**, **b** and the phosphanediyl-bridged dinuclear chromium carbene complex **5a** were obtained in good yields after low-temperature column chromatography. The nature of complex **5a** as a long-lived intermediate was determined by reacting a pure sample of it with triethylamine under similar reaction conditions. Therefore we assume that the overall reaction pro-

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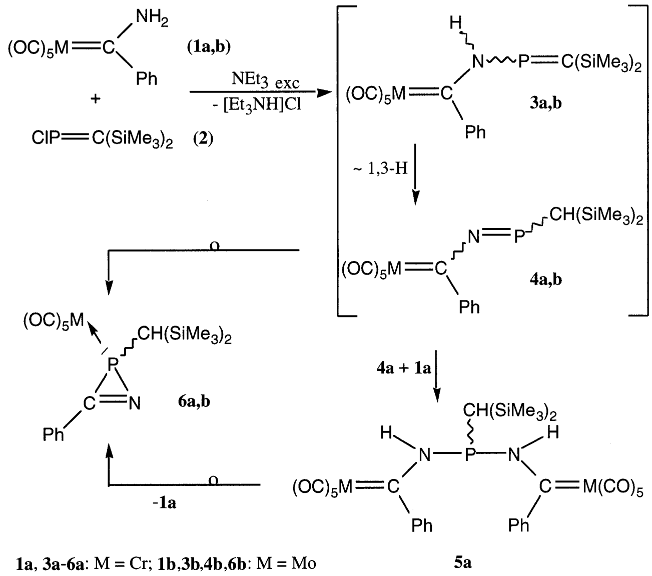
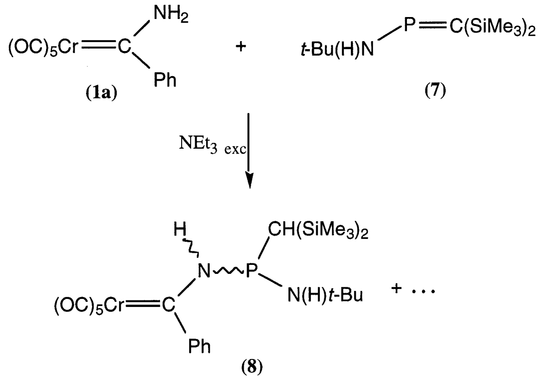
Scheme 2. Synthesis of $2H$-azaphosphirene metal complexes **6a**, **b**



Scheme 3



ceeds through the rearrangement cascade depicted in Scheme 2.

An additional experiment was carried out to shed more light on the formation of complex **5a**, which can a priori proceed through 1,2-addition reactions of aminobenzylidene chromium complex **1a** to the P−C and/or P−N double bond of the reactive intermediates **3a** and/or **4a**. In order to distinguish between these two pathways, we mimicked the hypothetical reaction of the first intermediate, **3a**, with the aminobenzylidene chromium complex **1a** by reacting **1a** with [bis(trimethylsilyl)methylene](*tert*-butylamino)phosphane **7**[11] under similar reaction conditions. After approximately one day at ambient temperature, only 18% of **7** was consumed, leading predominantly to one product, **8**, with a chemical shift at $\delta = 96.8$ (Scheme 3). Unfortunately, we could not isolate this product because of subsequent chemical transformations and the lack of stability of **8** precluding chromatography. By comparison of the phosphorus chemical shift of **8** ($\delta = 96.8$) with that of complex **5** ($\delta = 95.4$), and because of the reaction selectivity, we tentatively assign the structure of complex **8** to this product. Nevertheless, the finding that complex **1a** reacted very slowly with compound **7** to give complex **8**, supports the interpretation that complex **5** resulted from a trapping of the 2-aza-1-phospha-4-chromabutadiene **4a**.

Interestingly, the NMR parameters of the carbon and nitrogen atoms of the three-membered ring of the $2H$-azaphosphirene metal complexes **6a**, **b** and **9**[2b] vary very little with respect to metal exchange (Table 1). This is not the case with the phosphorus resonances, which differ significantly on going from chromium to the tungsten complex; this is a common feature of coordinated tervalent phosphorus compounds.[12] In order to obtain information about the electronic situation of the complexes **6a**, **b**, and **9**, UV/visible spectra were measured and λ_{max} values determined (Table 2). λ_{max} values of 200 and 240 nm should be attributable to π-π^* electron transitions related to the phenyl groups. Bands appearing as shoulders with λ_{max} values of 330 (**6b**) and 350 nm (**9**), with significantly lower lg ε values, are tentatively assigned to π-π^*-electron transitions of the C−N double bonds. It should be noted that some metal carbonyl complexes also show charge-transfer transitions in the range of 300−350 nm.[13] A comparison of the values obtained for **6a**, **b**, and **9** with those of a mixture of related 3-phenyl-$1H$-thiazirene and benzonitrile sulfide (bands with λ_{max} values of 335, 324, 295, and 240 nm) is interesting.[14] This interpretation of these UV/visible spectra remains somewhat unsatisfactory because the bands of benzonitrile sulfide had been assigned unambigously, but those of 3-phenyl-$1H$-thiazirene had not.[14] EI-mass spectrometry experiments have shown that all of these $2H$-azaphosphirene metal complexes predominantly undergo ring cleavage subsequent to the ionisation process.

Figure 1. Molecular structure of **6a** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity)

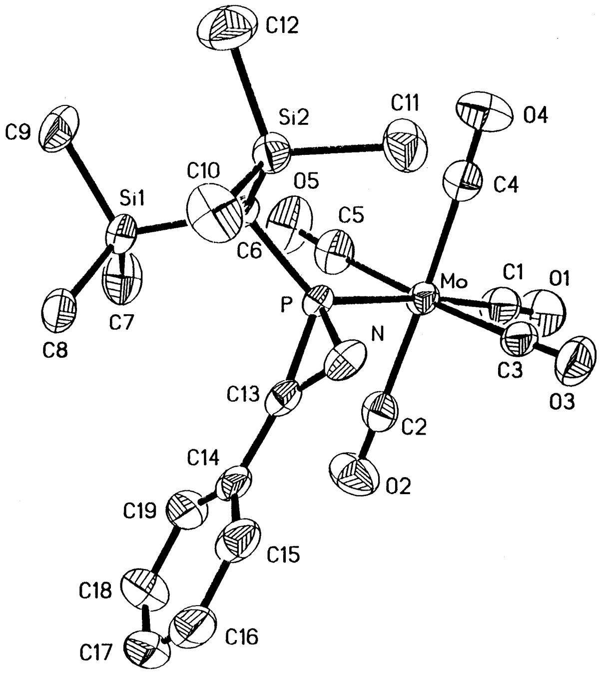


Table 1. Selected $^{13}C^{[a]}$, $^{15}N^{[b]}$, $^{31}P^{[a]}$ NMR data (δ/[ppm], *J*/[Hz]) of 3-phenyl-2*H*-azaphosphirene metal complexes **6a**, **b**, and **9** (exclusively ring atoms of the 2*H*-azaphosphirene ring system)

complex	metal	$\delta^{13}C$	$\delta^{15}N$	$\delta^{31}P$	$^{(1+2)}J(PC)$	$^{(1+2)}J(PN)$
6a	Cr	193.3	−55.3	−54.3	1.7	38.3
6b	Mo	192.1	−56.3	−84.5	3.4	36.7
9	W	192.4	−53.2	−111.0	1.7	36.9

[a] C_6D_6, room temp. − [b] CD_2Cl_2, room temp.

Table 2. UV/vis spectroscopic data (hexane, r.t.; λ_{max}/[nm]) of 3-phenyl-2*H*-azaphosphirene metal complexes **6a**, **b**, and **9**

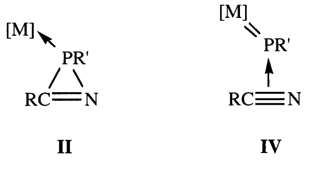
complex	metal	λ_{max} (lg ε)	λ_{max} (lg ε)	λ_{max} (lg ε)	λ_{max} (lg ε)
6a	Cr	–	208 (4.637)	240 (4.599)	–
6b	Mo	198 (4.625)	206 (4.610)	240 (4.697)	330 (3.394)
9	W	198 (4.655)	216 (4.657)	254 (4.590)	350 (3.544)

The molecular structures of the complexes **6a**, **b** were determined by X-ray crystallography (Figure 1 and Table 3).[15] The dimensions of the isostructural complexes **6a**, **b** (therefore, only **6a** is depicted in Figure 1) and the corresponding tungsten complex **9**[2b] differ mainly in their metal-phosphorus bond distances [**6a**: 2.3125(6), **6b**: 2.4772(12), and **9**: 2.470(2) Å] and, as a consequence of this, in the distance between the metal atom and the geometrical center of the C−N double bond (**6a**: 3.542, **6b**: 3.670, and **9**: 3.659 Å). These and previously reported findings[2b] seem to underline that the bonding situation of the heterocyclic ligand of 2*H*-azaphosphirene pentacarbonylmetal complexes should be described as a resonance hybrid of a three-membered ring system with a covalent bonding (**II**) and a π-electron donor-acceptor complex of benzonitrile and the phosphorus atom of the terminal phosphanediyl complex unit (**IV**) (Scheme 4).

Table 3. Selected bond lengths [pm] and angles [°] of complexes **6a**, **b**, and **9**

complex	P−C13	P−N	N−C13	C13−C14	M−P
6a	1.755(2)	1.811(2)	1.274(3)	1.458(3)	2.3125(6)
6b	1.762(4)	1.802(3)	1.273(5)	1.457(5)	2.4772(12)
9	1.759(5)	1.795(4)	1.272(7)	1.457(7)	2.470(2)
	C13−P−N	C13−N−P	N−C13−P	N−C13−C14	C6−P−M
6a	41.82(8)	66.75(11)	71.43(11)	133.3(2)	124.13(6)
6b	41.8(2)	67.4(2)	70.8(2)	134.4(3)	124.57(12)
9	41.9(2)	67.5(3)	70.6(3)	134.2(5)	124.3(2)

Scheme 4



II **IV**

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Experimental Section

General: All operations were carried out under an inert atmosphere of deoxygenated dry nitrogen. 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 MHz for ^{31}P) using [D_6]chloroform and [D_6]benzene as solvents, the latter as internal standard, or a Bruker AMX-300 (30.4 MHz for ^{15}N) using dichloromethane as solvent and nitromethane as external standard; shifts are given relative to tetramethylsilane (^1H, ^{13}C), to nitromethane (^{15}N) and 85% H_3PO_4 (^{31}P). − MS: Finigan Mat 8430 (70 eV). − Elemental analyses: Carlo Erba analytical gas chromatograph. − IR: Biorad FT-IR-165; UV/vis: Hewlett Packard 8452A.

Procedure for the Preparation of 2H-Azaphosphirene Pentacarbonylmetal(0) Complexes: 0.34 g (1.5 mmol) of **2** and 5 ml of NEt_3 were added at −40°C or −10°C, respectively, to a solution of 1.5 mmol of aminobenzylidene chromium or molybdenum complex **1a**, **b** in 15 ml of diethyl ether. The reaction mixtures were stirred for approximately 40 and 48 hours, respectively, and allowed to warm up slowly to ambient temperature. The yellow/orange reaction mixtures were evaporated to dryness under reduced pressure (0.1 mbar). The residues were extracted with 30 ml of pentane and filtered. The filtration residues were washed twice with 5 ml of pentane, the organic phases combined and the solvent removed under reduced pressure. The residues were purified by column chromatography.

{[2-Bis(trimethylsilyl)methyl-3-phenyl-2H-azaphosphirene-κP]-pentacarbonylchromium(0)} (**6a**): separation by low-temperature chromatography (SiO_2, −40°C; hexane/ether, 9:1) afforded 0.22 g of **6a** (30%) as a yellow powder after removal of the solvent from the first yellow phase. M.p. 104°C (decomp.). − IR (KBr) $\tilde{\nu}$ = 2065 (s) cm^{-1}, 1988 (m), 1968 (vs), 1942 (vs), 1942 (vs) (CO), 1625 (s), 1618 (vw) (CN). − ^1H NMR (C_6D_6): δ = −0.01 (s, 9 H, $SiMe_3$), 0.27 (s, 9 H, $SiMe_3$), 0.57 [d, $^2J(P,H)$ = 3.97 Hz, 1 H, PC*H*], 7.01 (m_c, 3 H, *m,p*-Ph−*H*), 7.91 (m_c, 2 H, *o*-Ph−*H*). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 1.2 [d, $^3J(P,C)$ = 3.1 Hz, $SiMe_3$], 2.1 [d, $^3J(P,C)$ = 2.9 Hz, $SiMe_3$], 28.3 [d, $^1J(P,C)$ = 29.8 Hz, P*C*H], 127.1 [d, $^2J(P,C)$ = 14.8 Hz, Ph−*C*1], 129.6 (s, Ph−*C*3/3′), 129.7 (s, Ph−*C*2/2′), 134.0 (s, Ph−C4), 193.3 [d, $^{(1+2)}J(P,C)$ = 1.7 Hz, P*C*N], 215.9 [d, $^2J(P,C)$ = 16.8 Hz, *cis*-*C*O], 219.8 [d, $^2J(P,C)$ = 4.7 Hz, *trans*-*C*O]. − ^{15}N NMR (CH_2Cl_2): δ = −55.3 [d, $^{(1+2)}J(P,N)$ = 38.3 Hz]. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −54.3 (s). − UV/vis (hexane, *c* = $2.06 \cdot 10^{-5}$ M): λ_{max} (lg ε) = 208 (4.637), 240 (4.599). − MS (70 eV), [pos.-CI (NH_3)], (^{52}Cr); *m*/*z* (%): 486 (100) [$(M + H)^+$], 338 (40) [$(M + H) - PhCN)^+$]. − $C_{19}H_{24}CrNO_5PSi_2$ (485.5) calcd. C 47.00, H 4.98, N 2.88; found C 46.95, H 5.04, N 2.81.

N,N′-Bis{amino[(phenyl)carbene]pentacarbonylchromium(0)}bis(trimethylsilyl)methylphosphane (**5a**): Separation by low-temperature chromatography (SiO_2, −40°C; hexane/ether, 9:1) afforded 0.22 g of **5a** (20%) as a yellow orange powder after removal of the solvent from the second yellow phase. M.p. 106°C (decomp.). − IR (KBr) $\tilde{\nu}$ = 2061 (m) cm^{-1}, 1929 (vs, br), 1906 (vs, br) (CO). − ^1H NMR ($CDCl_3$): δ = 0.30 [d, $^4J(P,H)$ = 0.8 Hz, 18 H, $SiMe_3$], 0.39 [d, $^2J(P,H)$ = 1.8 Hz, 1 H, PC*H*], 6.52 (m_c, 8 H, *m*-Ph−*H*), 7.26 (m_c, 12 H, *o*-,*p*-Ph−*H*), 9.95 (br, 2 H, N*H*). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.2 [d, $^3J(P,C)$ = 4.6 Hz, $SiMe_3$], 21.8 [d, $^1J(P,C)$ = 49.0 Hz, P*C*H], 119.5 [d, $^3J(P,C)$ = 5.7 Hz, Ph−*C*2/2′], 127.6 (s, Ph−*C*4), 128.4 (s, Ph−*C*3/3′), 151.9 [d, ^3J(P,C) = 11.8 Hz, Ph−*C*1], 216.3 (s, *cis*-*C*O), 223.4 (s, *trans*-*C*O), 311.3 [d, ^2J(P,C) = 3.2 Hz, Cr=*C*R$_2$]. − ^{15}N NMR (CH$_2$Cl$_2$): δ = −161.1 [dd, ^1J(P,N) = 84, ^1J(N,H) = 84 Hz]. − ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 95.4 (s). − ^{31}P{^{1}H} NMR (Et$_2$O/C$_6$D$_6$): δ = 92.8 (s). − MS (70 eV), [pos.-CI (NH$_3$)], (^{52}Cr); *m*/*z* (%): 727 (100) [(M + H)$^+$], 653 (6) [(M + H)$^+$ − Me$_3$SiH], 535 (14) {[M − (Me$_3$Si)$_2$HCPH$_2$)]$^+$}. − $C_{31}H_{31}Cr_2N_2O_{10}P$ (726.6): calcd. C 47.57, H 3.99, N 3.58; found C 47.00, H 3.79, N 3.46.

{[2-Bis(trimethylsilyl)methyl-3-phenyl-2H-azaphosphirene-κP]-pentacarbonylmolybdenum(0)} (**6a**): Separation by low-temperature chromatography (SiO$_2$, −15°C; hexane/ether, 9:1) afforded 0.53 g of **6a** (67%) as yellow powder after removal of the solvent from the first yellow phase. M.p. 105°C (decomp.). − IR (KBr) $\tilde{\nu}$ = 2074 (s) cm^{-1}, 1994 (s), 1973 (vs), 1945 (vs), 1928 (vs) (CO), 1619 (w) (CN). − ^{1}H NMR (C$_6$D$_6$): δ = 0.1 (s, 9 H, SiMe$_3$), 0.29 (s, 9 H, SiMe$_3$), 0.48 [d, ^2J(P,H) = 4.74 Hz, 1 H, PC*H*], 7.63 (m$_c$, 3 H, *m*-, *p*-Ph−*H*), 8.02 (m$_c$, 2 H, *o*-Ph−*H*). − ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 1.4 [d, ^3J(P,C) = 3.7 Hz, SiMe$_3$], 2.2 [d, ^3J(P,C) = 3.1 Hz, SiMe$_3$], 27.9 [d, ^1J(P,C) = 30.6 Hz, P*C*H], 126.8 [d, ^2J(P,C) = 15.0 Hz, Ph−*C*1], 129.6 (s, Ph−*C*3/3′), 129.7 (s, Ph−*C*2/2′), 134.0 (s, Ph−*C*4), 192.1 [d, $^{(1+2)}J$(P,C) = 3.4 Hz, P*C*N], 204.5 [d, ^2J(P,C) = 11.5 Hz, *cis*-*C*O], 208.6 [d, ^2J(P,C) = 38.1 Hz, *trans*-*C*O]. − ^{15}N NMR (CH$_2$Cl$_2$): δ = −56.3 [d, $^{(1+2)}J$(P,N) = 36.7 Hz]. − ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = −84.5 [s, ^1J(Mo,P) = 166 Hz]. − UV/vis (hexane, c = 2.059·10^{-5} M): λ$_{max}$ (lg ε) = 198 (4.625), 206 (4.610), 240 (4.697), 330 (3.394). − MS (70 eV), (^{98}Mo); *m*/*z* (%): 531 (2) [M$^+$], 400 (100) [(M − PhCN − CO)$^+$], 103 (82) [PhCN$^+$], 73 (78) [Me$_3$Si$^+$]. − $C_{19}H_{24}MoNO_5PSi_2$ (529.5): calcd. C 43.09, H 4.58, N 2.65; found C 43.36, H 4.77, N 2.72.

Reaction of [(Aminobenzylidene)pentacarbonylchromium(0)] (**1a**) *with [Bis(trimethylsilyl)methylene](tert-butylamino)phosphane* (**7**) *and Triethylamine*: To 150 mg (0.5 mmol) of **1a** in 6 ml of diethyl ether was added 130 mg (0.5 mmol) of **7** and 0.67 ml of triethylamine at −40°C with continuous stirring. The reaction mixture was allowed to warm up slowly and the reaction course was monitored after 24 h and 36 h by ^{31}P-NMR spectroscopy. The percentage of the compounds were estimated by signal integration, assuming that the relaxation times of the phosphorus nuclei are similar. The ratio of **7**/**8** (signal at δ = 96.8) was determined after 24 h as 82:18 and after 36 h as 64:29:7.

Crystal Structure Determination of **6a**[15]: $C_{19}H_{24}CrNO_5PSi_2$, M = 485.54, $P\bar{1}$, a = 9.1533(10), b = 10.7771(10), c = 13.5911(10) Å, α = 89.807(6)°, β = 85.161(8)°, γ = 64.298(8)°, V = 1202.9(2) Å^3, Z = 2, d_{calc} = 1.340 Mg/m^3, μ = 0.669 mm^{-1}, T = 173 K. A yellow needle (0.80 × 0.42 × 0.28 mm) was mounted in inert oil. 4502 intensities were measured (2Θ 6−50°, ω-scans, $-10 < h < 0$, $-12 < k < 11$, $-16 < l < 16$) using Mo-*K*α radiation (graphite monochromator) on a Siemens P4 diffractometer. After absorption correction (ψ-scans, min. and max. transmission: 0.847, 0.934), 4213 were unique (R_{int} = 0.0139) and 4208 used for all calculations (program SHELXL-93). The structure was solved by direct methods and refined anisotropically by full-matrix least squares on F^2. All hydrogen atoms (except rigid methyl groups) were refined with a riding model.The final $wR(F^2)$ was 0.0724 with conventional R(F) 0.0275 for 268 parameters and 100 restraints. Highest peak 0.293, hole −0.235 e/Å.

Crystal Structure Determination of **6b**[15]: $C_{19}H_{24}MoNO_5PSi_2$, M = 529.48, $P\bar{1}$, a = 9.158(2), b = 10.782(2), c = 13.816(3) Å, α = 89.17(2)°, β = 85.83(2)°, γ = 65.03(2)°, V = 1233.2(4) Å^3, Z = 2, d_{calc} = 1.426 Mg/m^3, μ = 0.721 mm^{-1}, T = 143 K. A pale yellow tablet (0.70 × 0.70 × 0.30 mm) was mounted in inert oil. 4577 intensities were measured (2Θ 6−50°, ω/Θ-scans, $-9 < h < 10$, $0 < k < 12$, $-10 < l < 10$) using Mo-*K*α radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. After absorption correction (ψ-scans, min. and max. transmission: 0.767, 0.878), 4330 were unique (R_{int} = 0.0214) and used for all calculations (program SHELXL-93). The structure was solved by heavy atom method and refined anisotropically by full-matrix least squares on F^2. All hydrogen atoms (except rigid methyl groups) were refined with a riding model.The final $wR(F^2)$ was 0.0926 with conventional $R(F)$ 0.0382 for 268 parameters and 98 restraints. Highest peak 0.510, hole −0.452 e/Å.

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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[15] 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-100668. 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(0)1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].

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