$C_{13}H_{36}F_3O_3NSSn_4$ (817.8) (%): C 19.1, H 4.4, N 1.7; found: C 19.2, H 4.2, N 1.4. The mass spectrum showed only signals from fragments of the Me_3Sn group; ^1H NMR ([D$_8$]THF, 28 °C): $\delta = 0.36$ (s, $w_{1/2} = 75$ Hz); $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 28 °C): $\delta = -1.3$ (s, $w_{1/2} = 40$ Hz); $^{119}Sn\{^1H\}$ NMR ([D$_8$]THF, 25 °C): $\delta = 88.5$ (s, $w_{1/2} = 430$ Hz); ^{19}F NMR ([D$_8$]THF, 28 °C): $\delta = -79.6$ (s).

2: $(Me_3Sn)_3P$ (1.29 g, 2.47 mmol) was slowly added dropwise to a solution of Me_3SnOTf (0.77 g, 2.46 mmol) in toluene (ca. 20 mL) at room temperature. A colorless precipitate formed immediately and was crystallized from THF (ca. 10 mL) by cooling. This afforded cubic colorless crystals of **2** which were sparingly soluble in THF, insoluble in nonpolar solvents, and completely stable in air and towards hydrolysis (1.69 g, 2.02 mmol, 82 %). Elemental analysis calcd for $C_{13}H_{36}F_3O_3PSSn_4$ (834.8) (%): C 18.7, H 4.3; found: C 18.7, H 4.2. The mass spectrometric investigations (EI) gave signals corresponding to the cleavage of $(Me_3Sn)_3P$ and $(Me_3Sn)_2PH$; ^1H NMR: $\delta = 0.43$ (s, $w_{1/2} = 7$ Hz); ^{31}P NMR: $\delta = -325.5$ (s, $w_{1/2} = 50$ Hz); $^{13}C\{^1H\}$ NMR: $\delta = -3.3$ (s), CF_3 signal not observed; $^{119}Sn\{^1H\}$ NMR: $\delta = 37.6$ (s, $w_{1/2} = 430$ Hz); ^{19}F NMR: $\delta = -79.5$ (s).

2′: A solution of $NaBPh_4$ (2.01 g, 5.88 mmol) in THF (ca. 10 mL) was added to a suspension of Me_3SnF (1.16 g, 6.35 mmol) and $(Me_3Sn)_3P$ (3.37 g, 6.45 mmol) in THF (ca. 20 mL) at room temperature . The mixture was stirred for 24 h at 45 °C. The solution was separated by centrifugation from the NaF formed and the solvent removed under vacuum. The resulting powder was crystallized from a small amount of THF to give compound **2** which is very soluble in THF and only slightly air and moisture sensitive (3.29 g, 3.27 mmol, 56 %). Elemental analysis calcd for $C_{36}H_{56}BPSn_4$ (1004.6) (%): C 43.0, H 5.6; found: C 42.8, H 5.3; ^1H NMR ([D$_8$]THF): $\delta = 7.35$ (m, 8H, *o*-CH), 6.94 (pseudo-t, ^3J(H,H) = 7.2 Hz, 8H, *m*-CH), 6.80 (m, 4H, *p*-CH), 0.40 (s, $w_{1/2} = 4$ Hz, 36H); ^{31}P NMR ([D$_8$]THF): $\delta = -323.6$ (s, $w_{1/2} = 90$ Hz); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): $\delta = 164.3$ (q, C(1), ^1J(C,B) = 49.4 Hz), 136.6 (q, C(3), ^3J(C,B) = 1.2 Hz), 125.1 (q, C(2), ^2J(C,B) = 3.0 Hz), 121.3 (s, C(4)), −4.2 (s, $w_{1/2} = 11$ Hz); $^{119}Sn\{^1H\}$ NMR ([D$_8$]THF): $\delta = 38.4$ (s, $w_{1/2} = 180$ Hz).

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[9] **1**: Trigonal, space group $R3$, $a = b = 10.0939(1)$, $c = 21.655(4)$ Å, $Z = 3$, $V = 1910.7(5)$ Å^3. 1064 independent reflections ($I > 2\sigma(I)$), $R1 = 0.0332$ (observed reflections), $wR2 = 0.0895$ (all data). **2**: Tetragonal, space group $P4/nmm$, $a = b = 12.4613(19)$, $c = 8.885(2)$ Å, $Z = 2$, $V = 1379.7(4)$ Å^3, 658 independent reflections ($I > 2\sigma(\mathrm{I})$), $R1 = 0.0631$ (observed reflections), $wR2 = 0.1693$ (all data). Intensity data was collected with a Bruker-AXS-SMART diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71707$ Å, ω-Scan, $T = 203$ K). The structure was solved by direct methods (SHELXLS 97), the refinement against F^2 was with all the measured reflections (SHELXLS 97). The non-hydrogen atoms were refined anisotropically and the H atoms isotropically. The methyl groups in the $[P(SnMe_3)_4]^+$ ion of **2** are disordered, with an occupancy of 0.5, while the triflate anion is rotation disordered about a fourfold axis. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-145133 (**1**) and CCDC-145132 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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New and Facile Entry to Nitrilium Phosphane Ylide Complex Chemistry by Using 7-Phosphanorbornadiene Complexes[**]

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Ngoc Hoa Tran Huy, and François Mathey[*]

Dedicated to Professor Heinrich Vahrenkamp
on the occasion of his 60th birthday

It is known that nitrilium phosphane ylide complexes **II** can be efficiently generated by thermally[1] or photochemically[2] induced ring opening of 2*H*-azaphosphirene complexes **I** (Scheme 1) and subsequently trapped by electronically activated π systems such as alkynes,[3] nitriles,[4] or phosphaalkynes,[5] thus providing access to a variety of new unsaturated N,P-heterocyclic ring systems. To develop the synthetic potential of this methodology, it was necessary to find a novel access to nitrilium phosphane ylide complexes **II**, thus providing N,P-heterocycles with more ubiquitous substituents

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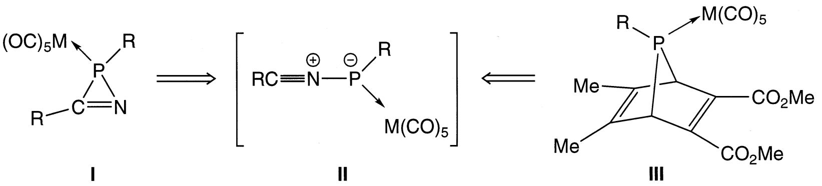


Scheme 1. 2*H*-azaphosphirene **I** and 7-phosphanorbornadiene complexes **III** as synthons for the generation of transient nitrilium phosphane ylide complexes **II** (R = alkyl, aryl; [M] = metal complex fragment).

at phosphorus such as methyl, phenyl, or even functional groups. Although it is now well established that 7-phosphanorbornadiene complexes **III** serve as efficient precursors for transient terminal phosphanediyl complexes and react with a wide variety of π systems,[6] giving cycloaddition products in most cases, no reactions of derivatives of **III** with nitriles have been reported. Nevertheless, there is also evidence for the transient formation of 1,3-dipole systems such as phosphacarbonyl ylide complexes in reactions of complexes of type **III** with carbonyl compounds.[7–9]

Here we report the synthesis of *P*-methyl- and *P*-phenyl-substituted 2*H*-1,2-azaphosphole complexes using three-component reaction conditions and 7-phosphanorbornadiene complexes, 1-piperidinonitrile, and dimethylacetylenedicarboxylate (DMAD) as components, as well as the structure of a *P*-methyl-substituted 2*H*-1,2-azaphosphole complex.

The thermal decomposition of 7-phosphanorbornadiene complexes **1a**,**b**,[10] 1-piperidinonitrile, and DMAD in toluene at 120 °C yielded selectively the 2*H*-1,2-azaphosphole complexes **5a**, **b** as main products (crude product yields >80 %) (Scheme 2); two by-products (≤5 %) were detected by ^{31}P NMR spectroscopy (reaction to give **5a**: $\delta = 124.4$, $|{}^1J(^{31}\mathrm{P},^{183}\mathrm{W})| = 262.6$ Hz; reaction to give **5b**: $\delta = 125.3$, $|{}^1J(^{31}\mathrm{P},^{183}\mathrm{W})| = 270.1$ Hz), but could not be isolated. The 2*H*-1,2-azaphosphole complexes **5a**, **b** are isolated by low-temperature chromatography and crystallization from *n*-pentane/toluene. The suggested structures of the complexes **5a**, **b** are based on solution NMR-spectroscopic and MS data[11] and are confirmed in the case of **5a** by a single-crystal X-ray structure analysis.[12]

The product formation is readily explained by assuming that nitrilium phosphane ylide complexes **4a**, **b** are transiently formed, by reaction of the terminal phosphanediyl complexes **2a**, **b** with 1-piperidinonitrile, and undergo [3+2] cycloaddition reactions with DMAD to yield complexes **5a**, **b**. This interpretation is strongly supported by observations, made earlier, on nitrile/nitrile exchange processes of nitrilium phosphane ylide complexes.[4b] Interestingly, cycloaddition reactions of **4a**, **b** to the C–O π system of DMAD, which would give Δ^3-1,3,2-oxazaphospholene complexes, were not observed.[4b] The complexes **5a**, **b** display ^{31}P NMR signals in the range of $\delta = 75-80$ with $|{}^1J(^{31}\mathrm{P},^{183}\mathrm{W})|$ values of about 250 Hz and characteristic ^{13}C chemical shifts of the carbon atoms of the five-membered rings in the range $\delta = 140-160$.[1, 3]

As also observed for pentacarbonyl[2-bis(trimethylsilyl)methyl-3,4-bis(methoxycarbonyl)-5-dimethylamino-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (**6**),[13] the molecular structure of complex **5a** (Figure 1) shows a planar five-membered ring (mean deviation 3 pm) with N1–C8 and C7–C6 bond lengths of 131.9(2) and of 135.0(2) pm, respectively, which are similar to those of complex **6** (N–C: 131.2(5); C–C: 133.8(6)[13]). The different steric situation in the $(OC)_5WPR$ structural units of **5a** (R = Me) and **6** (R = $CH(SiMe_3)_2$) correlates with shortened bond lengths in **5a** (W–P 249.96(5) and C9–P 181.4(2) pm; **6**: W–P 252.37(11) and C–P 183.6(4) pm[13]) and a narrowing of the W-P-C6 bond angle in **5a** (114.97(6)° vs 119.26(14)° in **6**[13]).

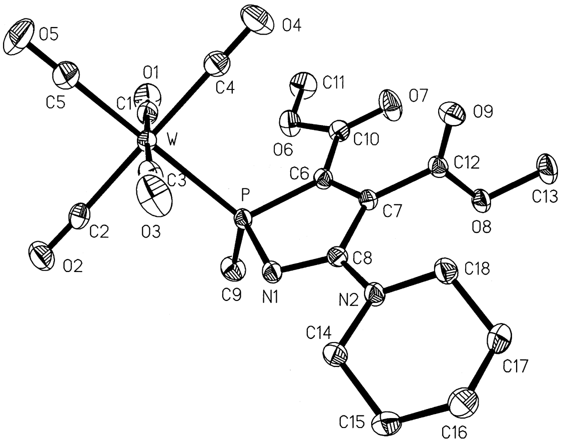
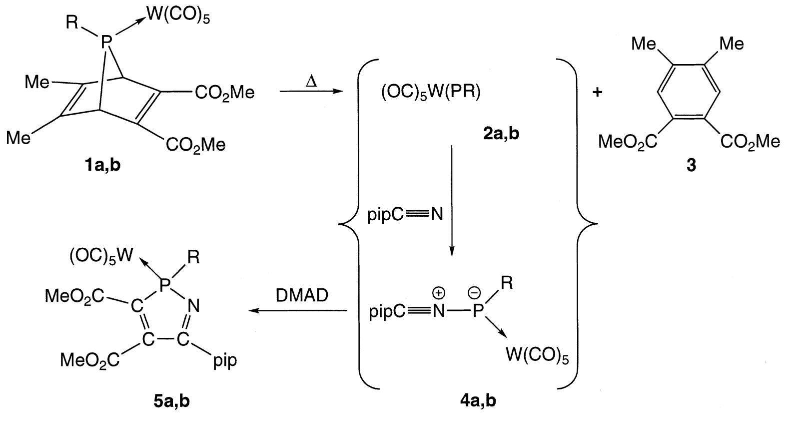


Figure 1. Molecular structure of complex **5a** in the crystal (ellipsoids represent 30% probability levels; H atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: W-P 249.96(5), P-N1 168.22(15), N1-C8 131.9(2), C8-C7 151.3(2), C7-C6 135.0(2), C6-P 181.51(17), C9-P 181.4(2); N1-P-C6 93.6(2), P-C6-C7 108.36(12), C6-C7-C8 111.10(14), C7-C8-N1 114.74(15), C8-N1-P 111.60(12).



Scheme 2. Proposed reaction course for the formation of 2*H*-1,2-azaphosphole complexes **5a**, **b**. R = Me (**a**), Ph (**b**); pip = 1-piperidino; DMAD = $MeO_2CC{\equiv}CCO_2Me$.

Experimental Section

5a, **b**: DMAD (0.5 mL, 3 mmol) and 1-piperidinonitrile (0.5 mL, 4.7 mmol) were added to a solution of **1a** (0.80 g, 1.3 mmol) or **1b** (0.90 g, 1.3 mmol) in toluene (10 mL) and the reaction mixture was stirred for 3.5–4 h at 120 °C. When the reaction was complete (as monitored by ^{31}P NMR), the solution was evaporated to dryness in vacuo (ca. 0.1 mbar), and the residue subjected to low-temperature column chromatography on silica (−32 °C, *n*-hexane/diethyl ether

9/1). The eluates were evaporated to dryness in vacuo (ca. 0.1 mbar), and the residues recrystallized from *n*-pentane/toluene (9/1). Selected physical and NMR spectroscopic data for **5a**, **b** (the deuterated solvents were used as internal and 85% H_3PO_4 as external standards). **5a**: yellow powder, yield: 180 mg (34%), m.p. 113°C (decomp). **5a**: $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25°C): $\delta = 20.3$ (d, $^1J(P,C) = 27.1$ Hz; P*C*H$_3$), 24.2 (s; NCC*C*H$_2$), 25.7 (s; NC*C*CH$_2$), 48.5 (s; N*C*CCH$_2$), 52.3 (s; OMe), 52.8 (s; OMe), 141.6 (d, $^{(2+3)}J(P,C) = 21.1$ Hz; PC*C*), 159.7 (d, $^{(1+4)}J(P,C) = 8.4$ Hz; P*C*C), 160.2 (d, $^{(2+3)}J(P,C) = 5.4$ Hz; PN*C*), 161.4 (d, $J(P,C) = 11.1$ Hz; *C*O$_2$Me), 165.6 (d, $J(P,C) = 15.4$ Hz; *C*O$_2$Me), 196.5 (d, $^2J(P,C) = 7.6$ Hz; *cis*-CO), 199.8 (d, $^2J(P,C) = 21.7$ Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25°C): $\delta = 76.0$ (s, $^1J(P,^{183}W) = 248.7$ Hz). **5b**: yellow powder, yield: 80 mg (13%), m.p. 124°C (decomp). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25°C): $\delta = 24.3$ (s; NCC*C*H$_2$), 25.9 (s; NC*C*CH$_2$), 48.9 (s; N*C*CCH$_2$), 52.8 (s; OMe), 53.4 (s; OMe), 128.7 (d, $^2J(P,C) = 10.6$ Hz; *o*-Ph), 130.8 (d, $^3J(P,C) = 14.1$ Hz; *m*-Ph), 131.2 (d, $^4J(P,C) = 2.9$ Hz; *p*-Ph), 131.9 (d, $^1J(P,C) = 42.1$ Hz; *i*-Ph), 140.0 (d, $^{(2+3)}J(P,C) = 20.4$ Hz; PC*C*), 159.3 (d, $^{(1+4)}J(P,C) = 7.6$ Hz; P*C*C), 160.9 (d, $^{(2+3)}J(P,C) = 5.4$ Hz; PN*C*), 161.4 (d, $J(P,C) = 10.8$ Hz; *C*O$_2$Me), 165.6 (d, $J(P,C) = 15.3$ Hz; *C*O$_2$Me), 196.0 (d, $^2J(P,C) = 6.4$ Hz; *cis*-CO), 199.0 (d, $^2J(P,C) = 22.8$ Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25°C): $\delta = 78.8$ (s, $^1J(P,^{183}W) = 254.0$ Hz).

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[11] Crystal structure analysis of complex **5a**: $C_{18}H_{19}N_2O_9PW$, $M_r = 622.17$; monoclinic, space group $P2_1/c$: $a = 1046.17(10)$, $b = 993.21(10)$, $c = 2167.5(2)$ pm, $\beta = 97.627(3)°$, $V = 2.2322(4)$ nm^3; $Z = 4$, $\rho_{calcd} = 1.851$ Mg m^{-3}, $\lambda = 0.71073$ pm, $T = 143$ K. A crystal (0.27 × 0.20 × 0.17 mm) was mounted in perfluoropolyether at −130°C on a Bruker SMART 1000 CCD. Intensities were registered to $2\theta = 60°$. Of 40121 reflections, 6787 were independent ($R_{int} = 0.0524$). An absorption correction was based on multiple scans. The structure was solved by direct methods and refined against F^2 (SHELXL-97) (SHELXL-97: G. M. Sheldrick, Universität Göttingen, **1997**). Methyl H atoms were included using rigid groups, all other H atoms with a riding model. Final $wR2 = 0.0461$ based on F^2 for all data, conventional $R(F) = 0.0206$, for 283 parameters; max. $\Delta\rho = 722$ e nm^{-3}. 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-143302. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Spin Frustration in a Dimeric Mn^{II} Complex with a Metallocene-Substituted α-Nitronyl Nitroxide Radical**

Daniel Ruiz-Molina, Christian Sporer, Klaus Wurst, Peter Jaitner,* and Jaume Veciana*

The synthesis of new molecular magnetic materials that combine paramagnetic metal ions and pure organic radicals as ligating sites has attracted much more attention in the last few years.[1] Such systems enhance the diversity and/or dimensionality of magnetic systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. So far, different types of stable organic radicals have been studied although one of the families most extensively used is that of α-nitronyl nitroxides (NIT). Since the nitroxyl groups are only weakly coordinating, α-nitronyl nitroxides bearing different coordinating functionalities have been reported.[2, 3] Variation of the coordination ability provided access to new complexes, whose diversity ranged from discrete molecules[4] to high-spin clusters[5] and to extended two- or three-dimensional systems.[6] Another approach successfully used to expand the dimensionality of the systems, ensuring the presence of large exchange interactions, has been the use of multicoordinating polyradical ligands. For instance, Iwamura et al. reported complexes with such polyradicals and manganese(II) hexa-

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