[10] Preliminary calculations (PM3/RHF) indicate, that the elimination of phenol from the hydrazine derivative formed by insertion of **2** in the N–H bond of diethylamine should be distinctly endothermic (by about 24 kcal mol^{-1}). A thermal elimination of phenol, as suggested by a referee, therefore seems unlikely. Such a reaction should also preferentially yield the *anti* isomers of the iminoquinone methides.
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Formation and Structure of the First 7-Aza-1-phosphanorbornadiene Complex**

Udo Rohde, Frank Ruthe, Peter G. Jones, and Rainer Streubel*

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

The chemistry of the norbornadienes (bicyclo[2.2.1]hepta-2,5-dienes) displays a variety of interesting aspects. One of these is the photochemical isomerization of norbornadienes to quadricyclanes[1] and its catalytic reversal.[2] Another is the synthesis, stability, and reactivity of heterocyclic analogues bearing a nitrogen or phosphorus atom at the 1- and/or 7-position (**I**–**III** in Figure 1); particularly noteworthy results from this area concern the differences in stability between 7-aza-[3] and 7-phosphanorbornadienes (Type **II**),[4] (the latter can be stabilized and isolated by coordination of the phosphorus to a metal[5]), and catalytic reactions[6] using 1-phosphanorbornadienes[7] (Type **I**) as novel ligands.

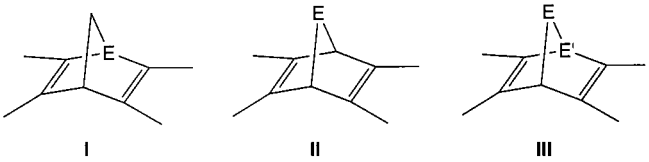

Figure 1. Heteronorborna-2,5-dienes **I**–**III** (exocyclic lines denote arbitrary substituents; E,E′ = N, NR and/or P, PR).

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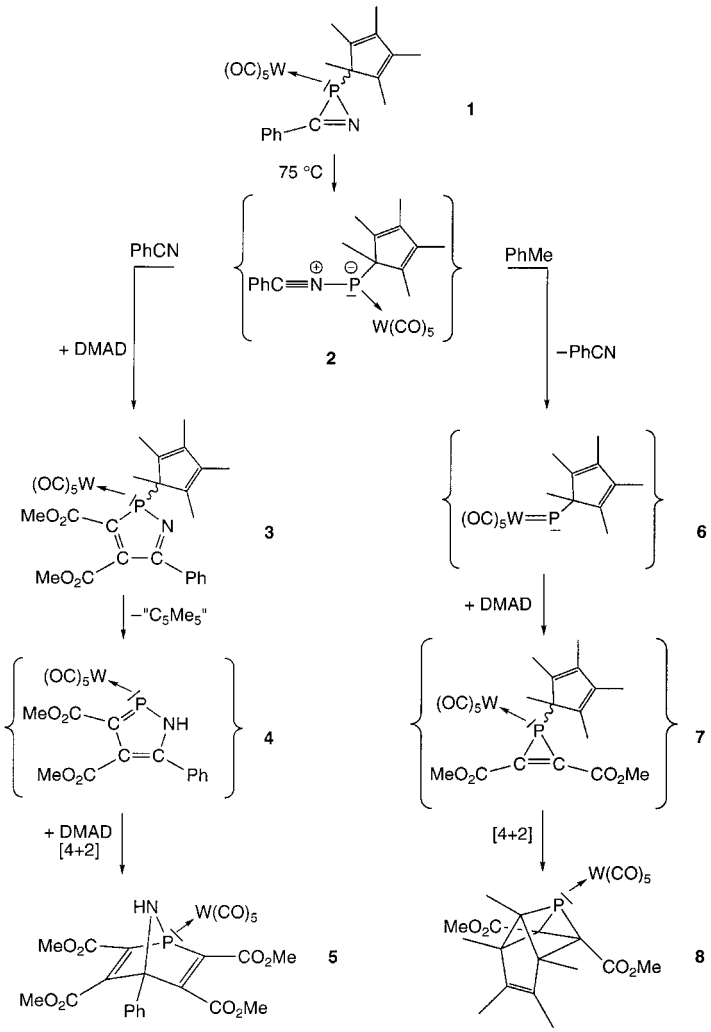
Here we report the synthesis and structural characterization of a tungsten complex of the novel 7-aza-1-phosphanorbornadiene ring system.[8] This is formed by a trapping reaction of an intermediate, a PC_5Me_5-substituted nitrilium phosphane ylide tungsten complex,[9] with dimethylacetylene dicarboxylate (DMAD) and subsequent reaction with DMAD, which leads to cleavage of an exocyclic P–C bond. We also present a highly efficient synthesis of a novel phosphorus–carbon cage compound.[10]

If the 2*H*-azaphosphirene tungsten complex **1**[11] is heated in benzonitrile at 75 °C in the presence of DMAD, the 2*H*-1,2-azaphosphole tungsten complex **3** is formed (Scheme 1); however, **3** ($\delta(^{31}P) = 119.1$, $^1J(^{31}P,^{183}W) = 249$ Hz[9]) is not stable under these conditions, and undergoes cleavage of the exocyclic P–C bond (presumably by a radical mechanism) to form the transient intermediate 1*H*-1,2-azaphosphole complex **4**, which finally yields complex **5** by [4+2] cycloaddition with DMAD;[7, 12, 13] the source of the H atom is still unclear. Since this reaction also provided a product with a ^{31}P NMR resonance signal at high field, ($\delta(^{31}P) = -66.8$, ca. 10%), we decided to repeat the reaction in toluene.[9] This led, after formation of a short-lived intermediate ($\delta(^{31}P) = -100.1$) to benzonitrile and, as sole phosphorus-containing product, the



Scheme 1. Suggested reaction courses for the formation of complexes **5** and **8**.

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complex **8**; our suggestion[9] as to how **8** is formed is shown in Scheme 1. The complexes **5** and **8** are isolated by low-temperature chromatography and crystallization. The suggested structures of **5** and **8** are based on NMR-spectroscopic data in solution (Table 1) and MS data[14] and are in both cases supported by X-ray structure analysis.[15]

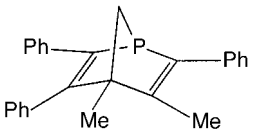
Table 1. Selected NMR-spectroscopic data of the complexes **5** and **8**.[a]

5: $^{13}C\{^1H\}$ NMR: $\delta = 52.8$ (s; OCH_3), 53.0 (s; OCH_3), 88.6 (d, $J(P,C) = 5.4$ Hz; C4), 126.1 (s; Ph), 129.0 (s; Ph), 129.6 (s; Ph), 132.5 (d, $J(P,C) = 5.3$ Hz; *i*-C(Ph)), 148.5 (d, $J(P,C) = 13.3$ Hz; C2/6), 162.3 (d, $J(P,C) = 16.3$ Hz; C3/5), 164.4 (d, $J(P,C) = 9.7$ Hz; C3/5-CO_2Me), 166.7 (d, $^2J(P,C) = 2.1$ Hz; C2/6-CO_2Me), 194.2 (d, $^2J(P,C) = 8.2$ Hz; *cis*-CO), 196.6 (d, $^2J(P,C) = 32.9$ Hz; *trans*-CO); ^{1}H-NMR: $\delta = 3.72$ (s, 6H; OCH_3), 3.76 (d, $^2J(P,H) = 5.1$ Hz, 1H; NH), 3.85 (s, 6H; OCH_3), 7.45 (m_c, 3H; $H_{arom.}$), 7.62 (m_c, 2H, $H_{arom.}$)

8: $^{13}C\{^1H\}$ NMR: $\delta = 5.9$ (d, $^3J(P,C) = 5.8$ Hz; C8-CH_3), 14.0 (s; C3/6-CH_3), 14.1 (d, $^4J(P,C) = 2.6$ Hz; C4/5-CH_3), 52.1 (s; OCH_3), 56.5 (d, $^4J(P,C) = 9.2$ Hz; C3/6), 66.5 (d, $J(P,C) = 32.2$ Hz; C8), 70.4 (d, $J(P,C) = 5.2$ Hz; C2/7), 141.7 (d, $J(P,C) = 10.4$ Hz; C4/5), 168.7 (s; CO_2CH_3), 193.6 (d; $^2J(P,C) = 8.1$ Hz; *cis*-CO), 197.4 (s; *trans*-CO); ^{1}H NMR: $\delta = 0.58$ (d, $^3J(P,H) = 19.0$ Hz, 3H; C8-CH_3), 1.52 (s, 6H; C3/6-CH_3), 1.71 (s, 6H; C4/5-CH_3), 3.62 (s, 6H; CO_2CH_3)

[a] $CDCl_3$, 20 °C; ^{13}C NMR: 50.3 MHz; ^{31}P NMR: 81.0 MHz. The deuterated solvent was used as internal standard, 85 % H_3PO_4 as external standard.

Complex **5** shows a ^{31}P NMR resonance ($\delta = 63.0$) that is considerably low-field shifted compared to that of 3,4-dimethyl-2,5,6-triphenyl-1-phosphabicyclo[2.2.1]heptadiene[7] (**9**) ($\delta = -8.4$). The magnitude of the coupling constant $|J(^{183}W,^{31}P)|$, 294.8 Hz, indicates not only the direct bond to the phosphorus atom, but also that the latter is bonded to nitrogen (further NMR data in Table 1). The highly symmetrical structure of the heterocyclic ligand in complex **8** is demonstrated by the symmetry-related reduction in the number of cage carbon signals and those of the directly bonded methyl groups. As expected,[16] the ^{31}P NMR resonance of complex **8** is observed at high field ($\delta = -67.2$), although this is low-field shifted in comparison to that for {[(2,3-bis-(methyloxycarbonyl)-1-bis(trimethylsilyl)methyl-1*H*-phosphirene]pentacarbonyltungsten(0)}[17] ($\delta = -74.6$, $^1J(^{183}W,^{31}P) = 281.1$ Hz[17]) and also has a lower coupling constant $|J(^{183}W,^{31}P)|$ of 242.0 Hz.



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The molecular structure of complex **5** in the crystal (Figure 2) shows the characteristic norbornadiene-type ring system; two molecules are linked by hydrogen bonds (Figure 2 bottom). The P–C bonds in the six-membered ring are markedly lengthened at about 187 pm, and the C-P-C and P-N-C angles are widened (ca. 96 and 100.7(3)°, respectively); this is similar to the situation in the uncoordinated 1-phosphanorborna-2,5-diene derivative **9** (P–C 186.9(4) and 186.9(3) pm; C-P-C 96.1(2) and P-C-C 97.6(2)° [7]). The structure of complex **8** (Figure 3) displays notably narrow endocyclic angles in the phosphirane ring system, a considerably lengthened P–C8 bond (192.4(3) pm), and a P–W bond considerably shorter than expected at 245.69(8) pm.[16]

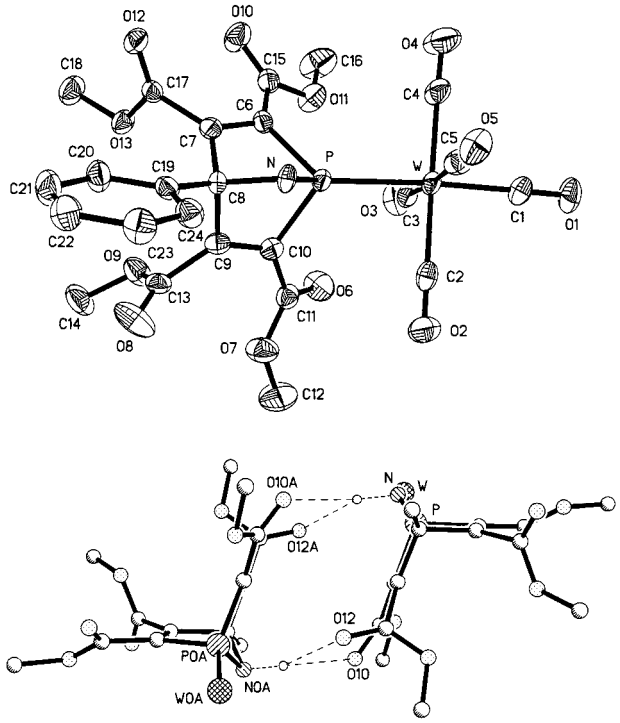

Figure 2. a) Molecular structure of complex **5** in the crystal. View direction from 'above' onto the nitrogen atom. Ellipsoids represent 50 % probability levels; H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: P–N 172.2(4), P–C6 187.3(5), P–C10 185.7(5), N–C8 148.1(6), C6–C7 133.4(7), C7–C8 156.1(7), C8–C9 155.2(7), C9–C10 133.3(7), W–P 245.25(13); C6-P-C10 95.6(2), N-P-W 124.8(2), C10-P-W 120.3(2), C6-P-W 128.6(2), C8-N-P 100.7(3). b) The hydrogen-bonded dimer of complex **5** in the crystal.

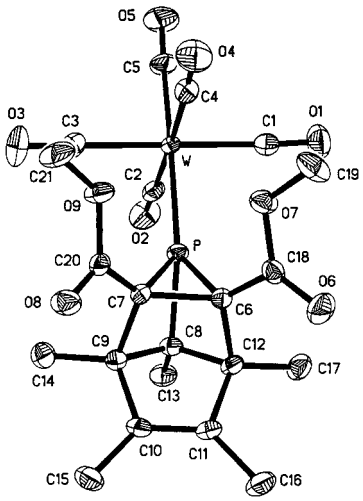

Figure 3. Molecular structure of complex **8** in the crystal. View direction from 'below' onto the six-membered ring. Ellipsoids represent 50 % probability levels; H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: P–C6 183.6(3), P–C7 183.0(3), C6–C7 155.9(3), P–C8 192.4(3), C10–C11 133.6(4), P–W 245.69(8); C7-P-C6 50.34(11), C6-C7-P 65.04(13), C6-C7-P 64.63(13), C6-P-C8 72.21(12).

Experimental Section

Preparation of complexes **5** and **8**: 2*H*-azaphosphirene tungsten complex **1** (0.3 g, 0.5 mmol) and DMAD (0.5 mL, 0.6 mmol) were stirred for 25 min in benzonitrile (3 mL; **5**) or toluene (3 mL; **8**) at 75 °C. The solution was concentrated to dryness in vacuo (ca. 0.01 mbar), and the residue subjected

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to low-temperature column chromatography on silica (−20 °C, hexane/diethyl ether 99/1). The eluents were concentrated to dryness in vacuo, and the residues crystallized from pentane at −20 °C. **5**: Pale yellow crystals, yield 0.18 g (51 %), m.p. 128 °C (decomp). **8**: Pale yellow crystals, yield 0.25 g (81 %), m.p. 89 °C (decomp).

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[14] Selected MS data (pos. CI, NH_3, 70 eV, ^{184}W): **5**: *m/z* (%): 761 (100) $[(M+NH_4)^+]$; **8** : *m/z* (%): 632 (42) $[M^+]$; correct C,H elemental analyses for **5** and **8**.
[15] Crystal structure analyses: The crystals (**5:** 0.70 × 0.50 × 0.30 mm; **8:** 0.58 × 0.48 × 0.40 mm) were mounted in inert oil at −100 °C on a Siemens P4 diffractometer. Intensities were registered by using ω scans in the 2θ region 6–50°. Absorption corrections were based on Ψ scans). The structures were solved by direct methods (SHELXS-86) and refined against F^2 using SHELXL-93 (G. M. Sheldrick, Universität Göttingen). Hydrogen atoms were refined by using a riding model, with the exception of methyl H (rigid groups) and the nitrogen-bonded H0 in **5** (freely refined). **5**: $C_{24}H_{18}NO_{13}PW$, M_r = 743.21, monoclinic, space group C2/c, a = 2513.1(3), b = 1455.1(2), c = 1552.6(2) pm, β = 108.941(10)°, V = 5.3699(10) nm^3, Z = 8, ρ_{calcd} = 1.839 Mg m^{-3}, λ = 0.71073 pm, T = 173 K. Of a total of 9431 reflections, 4720 were independent (R_{int} = 0.0497). Final $wR2$ = 0.0620 for all data, conventional $R(F)$ ($R1$) = 0.0307, for 369 parameters and 265 restraints; max. $\Delta\rho$ −798 and 913 e nm^{-3}. **8**: $C_{21}H_{21}O_9PW$, M_r = 632.20, triclinic, space group $P\bar{1}$, a = 966.5(2), b = 985.2(2), c = 1322.9(3) pm, α = 111.29(2), β = 91.12(2), γ = 92.00(2)°, V = 1.1722(4) nm^3; Z = 2, ρ_{calcd} = 1.791 Mg m^{-3}, λ = 0.71073 pm, T = 173 K. Of a total of 6336 reflections, 3989 were independent (R_{int} = 0.0101). Final $wR2$ = 0.0428 for all data, conventional $R1$ = 0.0165, for 296 parameters and 217 restraints; max. $\Delta\rho$ −890 and 660 e nm^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Canbridge Crystallographic Data Centre as supplementary publication nos. CCDC-102463 and CCDC-102464. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Synthesis and Crystal Structure of the Bis(allyl)calcium Complex $[Ca\{C_3(SiMe_3)_2H_3\}_2\cdot(thf)_2]$**

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The cyclopentadienyl ring and its substituted derivatives are the most frequently encountered ligands in organocalcium, -strontium, and -barium chemistry.[1, 2] Alkaline-earth metal complexes containing other carbanionic groups (e.g., alkyls,[3, 4] indenyl,[5] pentadienyl,[6] or fluorenyl[7]) are described, but as a class have received far less attention. The allyl anion represents the simplest π-delocalized ligand, and although some allylbarium compounds are known,[8, 9] the allyl–(Ca,Sr,Ba) bond has never been structurally authenticated. By applying the methods of steric stabilization that allowed the isolation of a bis(pentadienyl)calcium compound,[6] we now describe the synthesis of the first crystallographically characterized bis(allyl)calcium complex.

In order to improve the solubility and crystallinity of the final compound, we selected 1,3-bis(trimethylsilyl)propene as the ligand precursor. This was converted into its lithium salt,[10] and then transmetalated with KO*t*Bu in hexane at room temperature to yield $K[C_3(SiMe_3)_2H_3]$ in quantitative yield. Reaction of slightly more than two equivalents of $K[C_3(SiMe_3)_2H_3]$ with CaI_2 in THF at −78 °C produces the colorless complex $[Ca\{C_3(SiMe_3)_2H_3\}_2(thf)_2]$ in high yield. It has good solubility in THF and aromatic hydrocarbons. The ^1H NMR spectrum of the complex in [D$_8$]THF contains a singlet for the trimethylsilyl protons, a doublet at $\delta = 2.98$ ($^3J = 16$ Hz) corresponding to the protons on the carbon atoms adjacent to the $SiMe_3$ groups, and a triplet at $\delta = 6.87$ from the unique hydrogen atom on the center carbon atom. The spectrum is invariant from room temperature to

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