

Easy Access to *C,C'*-Bifunctionalized 1*H*-Phosphirene–Tungsten Complexes: Evidence for Ambiphilic Reaction Behaviour of a Phosphanediyl–Tungsten Complex

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The 2*H*-azaphosphirene–tungsten complex **1** reacts with ethoxyacetylene **2a** or dimethyl acetylenedicarboxylate **2b** to yield *C,C'*-bifunctionalized 1*H*-phosphirene–tungsten complexes **4a,b**; compounds **4a,b** are characterized by NMR spectroscopy (¹³C, ³¹P) and complex **4a** by single-crystal X-ray diffraction.

The chemistry of three-membered, unsaturated phosphorus heterocycles has been extensively investigated in the last decade.¹ For example, the synthetic potential of 1*H*-phosphirene derivatives in heterocyclic chemistry may be illustrated by their ring-enlargement reactions leading to a variety of four- and five-membered heterocycles.^{1b,2} Despite all previous attempts, no access to *C,C'*-bifunctionalized 1*H*-phosphirene complexes has been reported up to now; *e.g.* the reaction of terminal phosphanediyl–tungsten complexes³ with ethoxyacetylene leads directly to 1*H*-phosphole complexes via 1*H*-phosphirene complexes as assumed intermediates,⁴ whereas with dimethyl acetylenedicarboxylate no trapping reaction was observed.⁵ We now report the synthesis of *C,C'*-bifunctionalized 1*H*-phosphirene complexes by thermal decomposition of the 2*H*-azaphosphirene–tungsten complex **1**⁶ in the

presence of electron-rich and electron-poor alkyne derivatives.

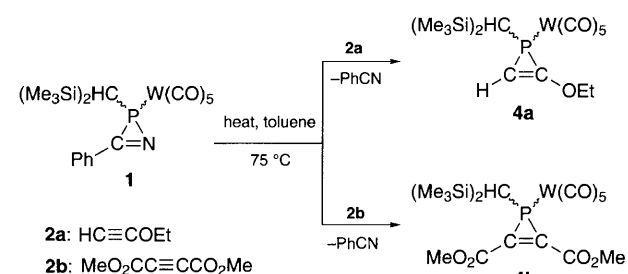
Complex **1** reacts on heating in solution with ethoxyacetylene **2a** and dimethyl acetylenedicarboxylate **2b** to give the corresponding 1*H*-phosphirene–tungsten complexes **4a,b** in good yields (Scheme 1). Both reactions probably proceed by thermally induced ring-cleavage of the 2*H*-azaphosphirene complex with formation of benzonitrile, determined by IR spectroscopy, and the phosphanediyl–tungsten complex [(CO)₅W=PCH(SiMe₃)₂] **3**.⁷ The assumption of a short-lived phosphanediyl complex is further supported by the results of kinetic investigations on the reactivity of complex **1** using phenylacetylene as trapping reagent and the stereospecific trapping reaction of **3** with *trans*-stilbene.⁸

The composition and constitution of **4a,b** are confirmed by NMR spectroscopic and mass spectrometric investigations.† In comparison to the *C*-phenyl substituted 1*H*-phosphirene derivatives,⁷ achieved by the same reaction pathway, the bifunctionalized complexes **4a,b** show significant low-field shifted resonances of the phosphorus nucleus at δ –90.8 (**4a**) and –74.6 (**4b**). The resonance values of the ring carbon atoms in **4a** are remarkable; the hydrogen substituted carbon atom is shifted up-field (δ 88.1), whereas the C–O-ring carbon atom is highly deshielded (δ 158.8). These findings probably reflect a π-electron interaction of the oxygen lone pair with the double-bond system. The ¹J_{PC} coupling constants of the ring carbon atoms of **3a** are smaller than observed for previously known 1*H*-phosphirene complexes.^{1b,7}

The X-ray crystal structure analysis of the complex **4a** confirms the molecular structure (Fig. 1).‡ The P–C bond lengths of **4a** [P–C(7) 179.2(8), P–C(6) 175.3(8) pm] exhibit significant differences in comparison to the triphenyl-1*H*-phosphirene–tungsten complex⁹ [179.0(4), 178.7(4) pm].

We are currently investigating the reactivity of **4a,b**. This work was supported by a grant to R. S. from the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft.

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Scheme 1 Reagents and conditions: 1 mmol of **1** was treated with 2 mmol **2a** or **2b** at 75 °C for 1.5 or 5 h, respectively. Work-up by column chromatography at low temperature afforded **4a,b** in good yields (**4a**: 58%, mp 88 °C; **4b**: 91%, mp 95 °C).

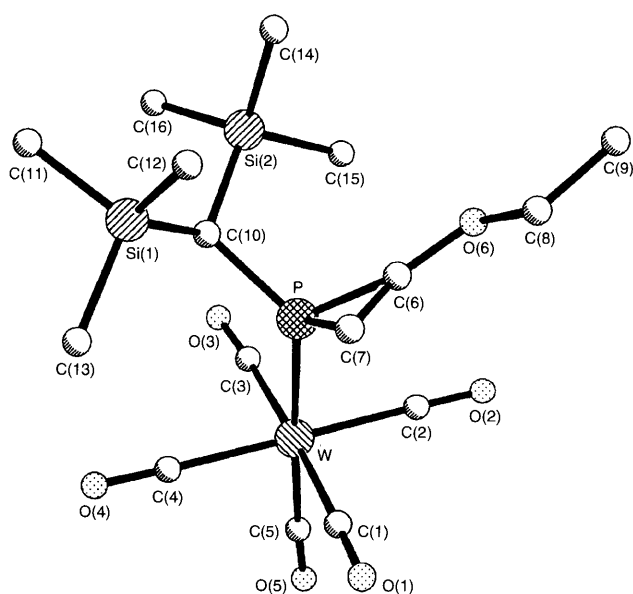


Fig. 1 Molecular structure of complex **4a** in the crystal. Selected bond lengths (pm) and angles (°) P–C(6) 175.3(8), P–C(7) 179.2(8), C(6)–C(7) 129.8(11), W–P 249.6(2), C(6)–O(6) 134.6(9); C(6)–C(7)–P 70.2(5), C(7)–P–C(6) 66.9(5), C(7)–P–C(6) 42.9(4).

Footnotes

† Satisfactory elemental analyses were obtained for all complexes reported. NMR data were recorded at room temperature in CDCl₃ solution at 50.3 MHz (¹³C) and 81.0 MHz (³¹P); *J*/Hz. Selected spectroscopic data for **4a**: ¹³C NMR δ 88.1 (d, ¹J_{PC} 4.9, P–CH=), 158.8 (d, ¹J_{PC} 2.0, P–COEt), 197.1 (dd, ¹J_{WC} 126.9, ²J_{PC} 8.4, *cis*-CO), 199.4 [d, ²J_{PC} 30.6, *trans*-CO]; ³¹P NMR δ –90.8 (d, ¹J_{WP} 268.0); MS (EI): M⁺ at *m/z* 584.

Selected data for **4b**: ¹³C NMR δ 143.2 (d, ¹J_{PC} 17.0, P–C=), 160.6 (d, ²J_{PC} 8.5, –CO₂Me), 194.7 (dd, ¹J_{WC} 124.5, ²J_{PC} 7.2, *cis*-CO), 196.8 (d, ²J_{PC} 34.0, *trans*-CO); ³¹P NMR δ –74.6 (d, ¹J_{WP} 281.1); MS (EI): M⁺ at *m/z* 656.

‡ Crystal data for **4a**: C₁₆H₂₅O₆PSi₂W, monoclinic, space group P2₁/c, *a* = 943.3(4), *b* = 1117.9(4), *c* = 2247.2(7) pm, β = 96.35(3)°, *U* = 2.3551(14) nm³, *Z* = 4, μ = 5.1 mm^{–1}, *T* = –130 °C. Pale brown tablet 0.4 × 0.4 × 0.08 mm, Mo-Kα radiation, Stoe STADI-4 diffractometer, 5911 intensities to 2θ_{max} 55°, 4151 unique (*R*_{int} 0.042) used for all calculations. Structure solution by direct methods, anisotropic refinement on *F*² (program SHELXL-93, G. M. Sheldrick, University of Göttingen).

Treatment of H atoms: rigid methyls, H(7) free, others riding. Final $wR(F^2)$ 0.103, conventional $R(F)$ 0.041 for 236 parameters. Full details may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the reference number CSD 404142, the names of the authors and the journal citation.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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