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Synthesis of a Doubly Complexed Bisphosphirenyl Ether and Generation of Phosphirenylium Cations Complexed with Pentacarbonyltungsten[1]

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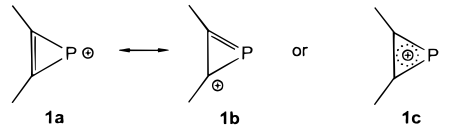
*Summary: Reaction of the 1-β-chloroethyl-substituted 1H-phosphirene complex **2** with silver salts results in formation of the acceptor-substituted 1H-phosphirene complexes **3**; decomposition of the latter furnishes the doubly complexed bisphosphirenyl ether **4**. Treatment of the acceptor-substituted 1H-phosphirene complexes **3** or, respectively, the bisphosphirenyl ether **4** with the strong Lewis acid boron tris(trifluoromethanesulfonate) leads to the corresponding salts **6** or **7** of the pentacarbonyltungsten-substituted phosphirenylium cation.*

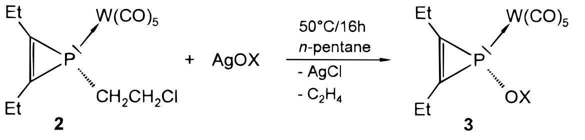
Although numerous representatives of the cyclopropenylium cation including the parent compound have been prepared and characterized,[2,3] salts of the analogous phosphirenylium cation **1** are as yet a sparsely investigated class of compounds (Scheme 1).

In numerous substitution reactions of 1-chloro-1*H*-phosphirenes[4] phosphirenylium cations have been postulated as intermediates.[5−7] The first ever characterization of a phosphirenylium cation **1** was reported by Laali and Regitz et al.; the compound was prepared by reaction of a trifluoromethanesulfonyloxy-substituted 1*H*-phosphirene with the strong Lewis acid boron tris(trifluoromethanesulfonate) in liquid sulfur dioxide at low temperature.[8] The NMR spectroscopic data of **1** confirmed the complete delocalization of the positive charge over the entire ring system.

Scheme 1



Scheme 2



3a: X = SO_2CF_3
b: X = $C(O)CF_3$

Concomitantly Nixon and co-workers described the first preparation of a transition metal-complexed phosphirenylium cation obtained by condensation of atomic nickel with *tert*-butylphosphaalkyne.[9] The relatively high-field position of the ^{31}P NMR of the phosphorus atom ($\delta = -161$) was attributed to a strong backbonding effect. Attempts to prepare pentacarbonyltungsten-complexed phosphirenylium cations by displacement reactions from 1-β-chloroethyl-substituted 1*H*-phosphirene complexes have so far been unsuccessful.[10]

We now report on the preparation of acceptor-substituted 1*H*-phosphirene complexes. The synthesis of pentacarbonyltungsten-complexed phosphirenylium cations should then be possible by abstraction of the acceptor substituent with a strong Lewis acid.

The reaction of the 1-β-chloroethyl-1*H*-phosphirene complexes **2** with silver trifluoromethanesulfonate or silver trifluoroacetate, respectively, leads selectively to the acceptor-substituted 1*H*-phosphirene complexes **3a**,**b** in almost quantitative yields (Scheme 2).[11] However, these compounds could not be completely characterized by spectroscopy on account of their extreme instability.

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[1] This communication is part 133 of the series of papers on *Organophosphorus Compounds*. For part 132, see: Mack, A.; Regitz, M. In *Carbocyclic and Heterocyclic (P, As, N) Cage Compounds and their Building Blocks: Synthesis, Structure, Mechanism and Theory*; JAI Press Inc.: Greenwich, Ct, in press.

[2] Garratt, P. J. *Aromaticity*; Wiley: New York, 1986; pp 137−141.

[3] Billups, W. E.; Moorehead, A. W.; In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; pp 1533−1574.

[4] Wagner, O.; Ehle, M.; Regitz, M. *Angew. Chem.* **1989**, *101*, 227−229; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 225.

[5] Wagner, O.; Ehle, M.; Birkel, M.; Hoffmann, J.; Regitz, M. *Chem. Ber.* **1991**, *124*, 1207−1213.

[6] Hoffmann, J. Ph.D. Dissertation, University of Kaiserslautern, 1990.

[7] Wagner, O. Ph.D. Dissertation, University of Kaiserslautern, 1989.

[8] Laali, K. K.; Geissler, B.; Wagner, O.; Hoffmann, J.; Armbrust, R.; Eisfeld, W.; Regitz, M. *J. Am. Chem. Soc.* **1994**, *116*, 9407−9408.

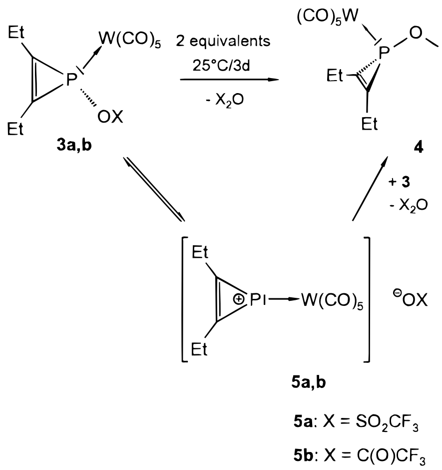
[9] Avent, A. G.; Cloke, F. G. N.; Flower, K. R.; Hitchcock, P. B.; Nixon, J. F.; Vickers, D. M. *Angew. Chem.* **1994**, *106*, 2406−2408; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2330.

[10] Deschamps, B.; Mathey, F. *Tetrahedron Lett.* **1985**, *26*, 4595−4598.

[11] For **3a**: ^{31}P NMR ($CDCl_3$, 81 MHz) −35.4 (s, $^{1}J_{P,W} = 343.8$ Hz); MS (EI, 70 eV) $m/z = 586$ (M^+, 5), 113 ($C_6H_{10}P^+$, 100). For **3b**: ^{31}P NMR (C_6D_6, 81 MHz) −66.3 (s, $^{1}J_{P,W} = 330.6$ Hz); ^{1}H NMR (C_6D_6, 200 MHz) 1.09 (t, 6H, $^{3}J_{H,H} = 7.4$ Hz, CH_3), 2.26−2.48 (m, 4H, CH_2); ^{13}C NMR (C_6D_6, 50 MHz) 11.5 (d, $^{3}J_{C,P} = 3.8$ Hz, CH_3), 20.1 (d, $^{2}J_{C,P} = 3.8$ Hz, CH_2), 115.4 (dq, $^{1}J_{C,F} = 286.6$ Hz, $^{3}J_{C,P} = 2.3$ Hz, CF_3), 151.4 (d, $^{1}J_{C,P} = 20.6$ Hz, C=C), 156.2 (dq, $^{2}J_{C,F} = 43.5$ Hz, $^{2}J_{C,P} = 6.9$ Hz, *C*(O)-CF_3), 194.5 (d, $^{2}J_{C,P} = 9.2$ Hz, $^{1}J_{C,W} = 125.9$ Hz, *cis*-CO), 198.1 (d, $^{2}J_{C,P} = 45.8$ Hz, *trans*-CO); MS (EI, 70 eV) $m/z = 550$ (M^+, 2), 113 ($C_6H_{10}P^+$, 100).

10.1021/om980723f CCC: $18.00

Scheme 3



A mechanism involving cleavage of ethylene can be postulated for the formation of the acceptor-substituted 1*H*-phosphirene complexes **3**, similar to that formulated by Mathey et al. for other examples.[10] The formation of **3** is reflected in the ^{31}P NMR spectrum by a significant shift to low field of the signal in comparison to that of the alkyl-substituted starting material **2**. The larger shift to low field of the trifluoromethanesulfonyloxy-substituted 1*H*-phosphirene complex **3a** in comparison to **3b** is in accord with the known data for the uncomplexed species.[6,7] The ^{13}C NMR spectrum of **3b** demonstrates the substitution of the chloroethyl group by the trifluoroacetyloxy substituent unequivocally. Accordingly, the carbon atoms of the acceptor group experience coupling not only with the fluorine atoms but also with the phosphorus atom, thus providing concrete evidence for the direct bonding of the substituent to the phosphorus atom.

The acceptor-substituted 1*H*-phosphirene complexes **3** are unstable compounds: they decompose on storage at room temperature or in solution (diethyl ether) with formation of the bisphosphirenyl ether **4** (Scheme 3).

The composition and constitution of **4** are elucidated by NMR and mass spectroscopic measurements.[12] The NMR data reveal close agreement with the values for the uncomplexed bisphosphirenyl ether.[7,13]

On account of the presence of several isotopomers, the ^{31}P NMR spectrum of **4** contains several component sets for which analysis as an AA′X spin system according to reported methods is possible.[14,15]

The crystal structure analysis of the complex **4** confirmed the proposed structure (Figure 1).[16] In the solid state the two pentacarbonytungsten fragments and, respectively, the phosphirene units have a syn arrangement to each other. The intracyclic bond parameters are all in the expected ranges for complexed 1*H*-phosphirenes.[17]

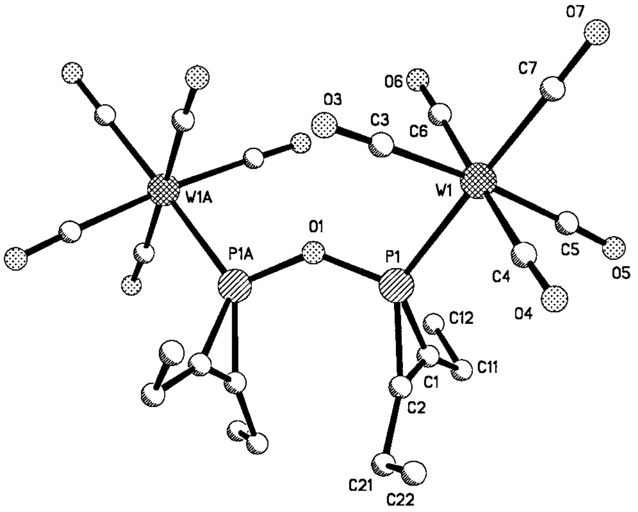
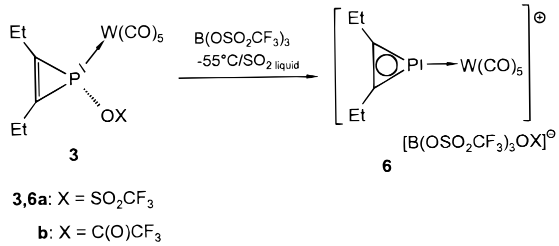


Figure 1. XP plot of **4**. Selected bond lengths (Å) and angles (deg): W(1)–P(1) 2.4792(14), P(1)–O(1) 1.642 (2), P(1)–C(1) 1.757(6), P(1)–C(2) 1.767(5), O(1)–P(1A) 1.642(2); O(1)–P(1)–C(1) 111.5(3), O(1)–P(1)–C(2) 113.1(3), C(1)–P(1)–C(2) 43.2(3), P(1)–O(1)–P(1A) 138.0(3), C(2)–C(1)–P(1) 68.8(4), C(1)–C(2)–P(1) 68.0(3).

Scheme 4



It is very likely that the formation of **4** from **3** proceeds through the phosphirenylium species **5**. Thus, in addition to the ^{31}P NMR signals for **3a** and **4** another signal is seen at $\delta = +217$, which may be assigned to the complexed phosphirenylium cation **5** on the basis of its extremely low-field position.

Similar to the generation of noncomplexed phosphirenylium cations,[8] treatment of the acceptor-substituted 1*H*-phosphirene complexes **3a**,**b** with the strong Lewis acid boron tris(trifluoromethanesulfonate) in liquid sulfur dioxide at −55 °C leads to salts **6a**,**b** of the complexed phosphirenylium cation (Scheme 4).

The formation of **6a**,**b** is reflected in the ^{31}P NMR spectra by a dramatic shift to low field of the signals by about 300 ppm in comparison to those of the starting compounds. A chemical shift change of the same order

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[12] For **4**: ^{31}P NMR (C_6D_6, 81 MHz) −77.3 (s, $^1J_{P,W} = 326.3$ Hz, $^2J_{P,P} = 47.8$ Hz, $^3J_{P,W} = 0.3$ Hz); ^{1}H NMR (C_6D_6, 200 MHz) 1.26 (t, 12H, $^3J_{H,H} = 7.4$ Hz, CH_3), 2.60–2.83 (m, 8H, CH_2); ^{13}C NMR (C_6D_6, 50 MHz) 12.0 (s, CH_3), 21.2 (s, CH_2), 154.6 (dd, $^1J_{C,P} = 10.6$ Hz, $^3J_{C,P} = 8.0$ Hz, C=C), 196.0 (*pseudo*-t, $^2J_{C,P} + {}^4J_{C,P} = 5.0$ Hz, $^1J_{C,W} = 126.3$ Hz, *cis*-CO), 199.0 (*pseudo*-t, $^2J_{C,P} + {}^4J_{C,P} = 20.4$ Hz, $^1J_{C,W} = 148.8$ Hz, *trans*-CO); MS (EI, 70 eV) *m*/*z* = 890 (M^+, 97), 409 [$C_6H_{10}PW(CO)_4{}^+$, 100].

[13] Deschamps, B.; Mathey, F. *New. J. Chem.* **1988**, *12*, 755–759.

[14] Hoffmann, R. A.; Forsen, S.; Gestblom, B. *NMR* **1971**, *5*, 65–78.

[15] Schmidpeter, A.; Zirzow, K.-H. *Phosphorus Sulfur* **1988**, *36*, 15–21.

[16] Crystallographic data for **4**: $C_{22}H_{20}O_{11}P_2W_2$; *M* = 890.02 g/mol; orthorhombic; space group *Pbcn*; *a* = 10.127(2) Å, *b* = 18.890(4) Å, *c* = 15.409(3) Å, *V* = 2947.8(10) Å^3; *Z* = 4; $D_c = 2.005$ Mg/m^3; $\mu = 7.958$ mm^{-1}; *F*(000) = 1672. Crystal dimensions 0.30 × 0.18 × 0.15 mm^3. Total reflections collected = 17525 and 2238 with $I > 2\sigma(I)$. Goodness-of-fit on F^2 1.374; R ($I > 2\sigma(I)$) = 0.0415, *wR2* = 0.0977; *R* (all data) = 0.0455, *wR2* = 0.0998; maximum residual density 2.822 e Å^{-3}. Data were collected on an STOE imaging plate diffraction system at room temperature with Mo Kα radiation ($\lambda = 0.71073$ Å). Full details of the crystallographic analysis of **4** are described in the Supporting Information.

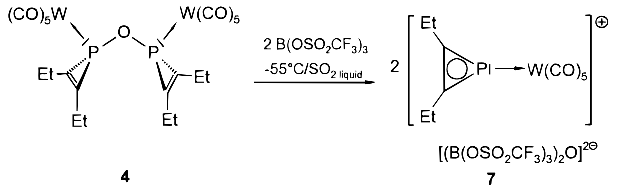
[17] (a) Mathey, F. *Chem. Rev.* **1990**, *90*, 997–1025. (b) Mathey, F.; Regitz, M. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; p 227.

of magnitude was also observed in the synthesis of the noncomplexed phosphirenylium cation.[8] The NMR spectroscopic data of **6** exhibited close resemblance to the corresponding values for the noncomplexed species.[8,18] The large shifts to low field of the signals of all ring atoms in comparison to those of the starting materials are indicative of a complete delocalization of the positive charge over the ring system. The high-field shifts of all NMR signals of **6** in comparison to those of the staring materials result from back-bonding of the metal fragment to the phosphorus atom.

A definite conclusion with regard to coordination of the pentacarbonyltungsten fragment to the cationic three-membered ring system is possible: not only η^1- but also η^3-coordination is feasible. Ab initio calculations on an analogous $Cr(CO)_5$ complex favor η^3-coordination;[19] however, the large $^1J_{P,W}$ coupling constant of 392 Hz is more suggestive of η^1-coordination.

Reaction of the doubly complexed bisphosphirenyl ethers **4** with boron tris(trifluoromethanesulfonate) in liquid sulfur dioxide provides further access to the class of transition metal-complexed phosphirenylium cations (Scheme 5).

Scheme 5



The formation of **7** is unequivocally confirmed by a comparison of its NMR data with those of the analogous compounds **6a**,**b**.[20]

Acknowledgment. We thank the Landesregierung von Rheinland-Pfalz for a post graduate grant (to J.S.) and the Fonds der Chemischen Industrie for generous financial support.

Supporting Information Available: Text giving synthesis details and characterization data for **3a**,**b**, **4**, **6a**,**b**, and **7** and tables giving X-ray structural information for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] For **6a**: ^{31}P NMR (acetone-d_6, 81 MHz) 232.6 (s, $^1J_{P,W} = 392.8$ Hz); ^1H NMR (acetone-d_6, 200 MHz) 1.55 (t, 6H, $^3J_{H,H} = 7.3$ Hz, CH_3), 3.14−3.35 (m, 4H, CH_2); ^{13}C NMR (acetone-d_6, 50 MHz) 12.2 (d, $^3J_{C,P} = 4.2$ Hz, CH_3), 26.2 (s, CH_2), 119.2 (q, $^1J_{C,F} = 317.0$ Hz, OSO_2CF_3), 190.5 (d, $^2J_{C,P} = 7.1$ Hz, $^1J_{C,W} = 119.8$ Hz, *cis*-CO), 193.0 (d, $^2J_{C,P} = 49.1$ Hz, *trans*-CO), 197.2 (d, $^1J_{C,P} = 40.5$ Hz, C═C). For **6b**: ^{31}P NMR (acetone-d_6, 81 MHz) 232.7 (s, $^1J_{P,W} = 392.4$ Hz); ^1H NMR (acetone-d_6, 200 MHz) 1.63 (t, 6H, $^3J_{H,H} = 7.0$ Hz, CH_3), 3.22−3.46 (m, 4H, CH_2); ^{13}C NMR (acetone-d_6, 50 MHz) 12.2 (d, $^3J_{C,P} = 5.0$ Hz, CH_3), 26.2 (s, CH_2), 115.6 (q, $^1J_{C,F} = 284.0$ Hz, C(O)*C*F$_3$), 119.3 (q, $^1J_{C,F} = 317.3$ Hz, OSO_2CF_3), 160.7 (q, $^2J_{C,F} = 42.4$ Hz, *C*(O)CF$_3$), 190.2 (d, $^2J_{C,P} = 8.5$ Hz, *cis*-CO), 192.6 (d, $^2J_{C,P} = 57.6$ Hz, *trans*-CO), 198.4 (d, $^1J_{C,P} = 42.4$ Hz, C═C).

[19] Nyulászi, L. Department of Inorganic Chemistry, Technical University of Budapest, Budapest XI, Gellért tér 4, H-1521 Budapest, Hungary, personal communication.

[20] For **7**: ^{31}P NMR (acetone-d_6, 81 MHz) 231.3 (s, $^1J_{P,W} = 392.2$ Hz); ^1H NMR (acetone-d_6, 200 MHz) 1.59 (t, 12H, $^3J_{H,H} = 7.3$ Hz, CH_3), 3.18−3.40 (m, 8H, CH_2); ^{13}C NMR (acetone-d_6, 50 MHz) 12.2 (d, $^3J_{C,P} = 5.0$ Hz, CH_3), 26.2 (s, CH_2), 119.2 (q, $^1J_{C,F} = 316.4$ Hz, OSO_2CF_3), 190.4 (d, $^2J_{C,P} = 9.3$ Hz, $^1J_{P,W} = 125.0$ Hz, *cis*-CO), 192.8 (d, $^2J_{C,P} = 51.7$ Hz, *trans*-CO), 198.2 (d, $^1J_{C,P} = 41.5$ Hz, C═C).