

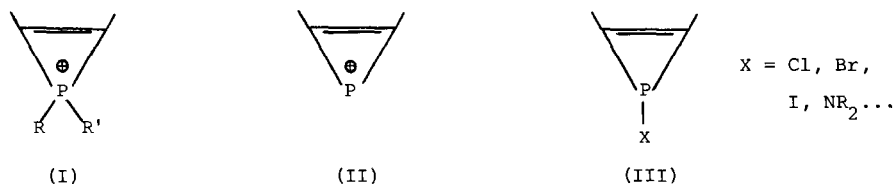
SYNTHESIS OF 1-CHLOROPHOSPHIRENES IN THE COORDINATION SPHERE OF TUNGSTEN

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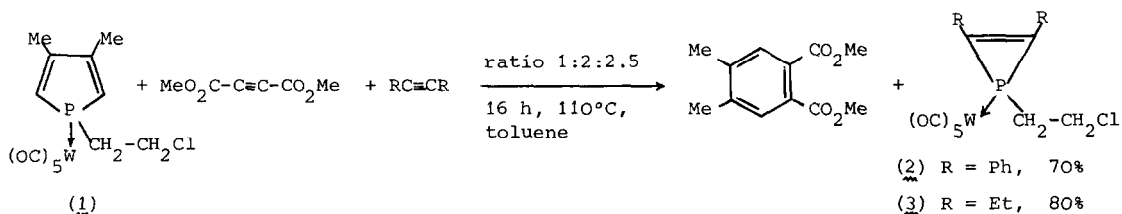
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Summary : Upon treatment with AlCl_3 , 1- β -chloroethylphosphirene $\text{P-W}(\text{CO})_5$ complexes lose ethylene and yield the corresponding 1-chlorophosphirene complexes.

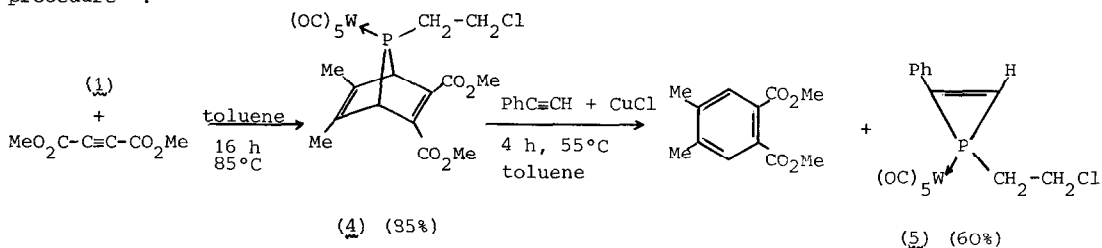
Apparently, the recently synthesized phosphirenium salts (I)¹⁻³ have not an "aromatic" behaviour⁴ probably because the (3d-2p) π interaction between the phosphorus atom and the C=C double bond remains weak as in the isoelectronic silirenes⁵. However, the situation is entirely different for the still unknown phosphirenium cations (II) in which a powerful (3p-2p) π interaction might take place between the electron-deficient heteroatom and the double bond. In such a case, these cations would be the first genuine 2 π -aromatic species containing phosphorus. In practice, the synthesis of such cations requires an access to 1-halo- or 1-amino-phosphirenes (III). In this communication, we wish to describe a route to such compounds.



The synthesis starts from [1- β -chloroethyl-3,4-dimethylphosphole]pentacarbonyltungsten (1)⁶. According to a simplified procedure described elsewhere³, complex (1) is heated with a mixture of dimethyl acetylenedicarboxylate and tolan or 3-hexyne, thus directly producing [1- β -chloroethylphosphirene]pentacarbonyltungsten complexes (2) and (3) in good yields :

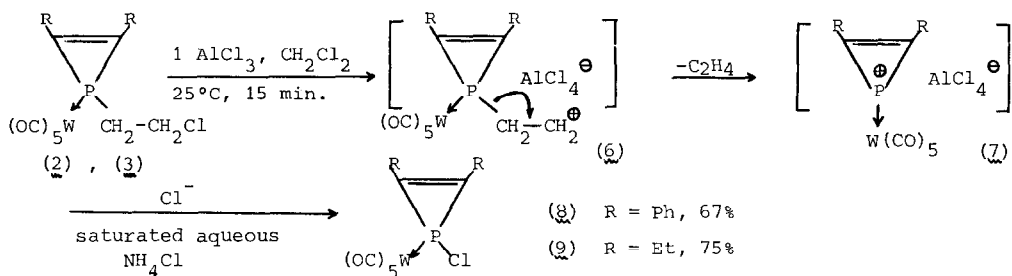


The reaction with 3-hexyne is run in a sealed tube. The phosphirene complexes are purified by chromatography on silica gel with hexane-benzene 80:20 and characterized by n.m.r. spectroscopy[†]. The less stable 1-β-chloroethyl-2-phenylphosphirene complex (5) is made in two steps through the 7-phosphanorbornadiene complex (4) according to the classical catalytic procedure⁷:



The phosphanorbornadiene complex (4)[†] and the phosphirene complex (5)[†] are both purified by chromatography on silica gel respectively with benzene and hexane-benzene 80:20.

When allowed to react with one equivalent of anhydrous aluminium trichloride, the 1-β-chloroethylphosphirene complexes (2) and (3) readily lose ethylene to afford the corresponding 1-chlorophosphirene complexes (8) and (9) in good yields:



Complex (8)[†] is purified by chromatography with hexane-benzene 80:20. Complex (9)[†] is more sensitive toward hydrolysis and is purified by extraction of the crude reaction product with pentane. A similar reaction attempted with complex (5) gives a more complicated product which has not been identified yet. It must be stressed here that neither the 7-phosphanorbornadiene complex (4) nor the phosphole complex (1) lose ethylene upon treatment with AlCl_3 . Thus, it is very likely that the driving force for the loss of ethylene in the transient cation (6) is the aromaticity of the complexed phosphirenyl cation (7). For the same reason, the P-Cl bond of complexes (8) and (9) has probably a strong ionic character ($\text{P}^+\dots\text{Cl}^-$). This high ionicity is reflected in the various mass spectra of (8) which show prominent peaks corresponding to the complexed and uncomplexed phosphirenyl cations. The increase of the intracyclic $^1\text{J}(\text{C}-\text{P})$ coupling constant when converting (3) into (9) also suggests an increase of the C-P bond order and hence, some aromaticity for (9).

† δ + for downfield shifts, references internal Me_4Si or external 85% H_3PO_4 .

(2) : m.p. 63°C ; $\delta(^1\text{H})$ n.m.r. (CDCl_3) 2.41 [dt, $^3\text{J}(\text{H-H}) \sim 7.3$ Hz, $^2\text{J}(\text{H-P})$ 1.5 Hz, CH_2P] and 3.43 p.p.m. [dt, $^3\text{J}(\text{H-P})$ 13.4 Hz, CH_2Cl] ; $\delta(^{13}\text{C})$ n.m.r. (CD_2Cl_2) 41.24 [d, $^1\text{J}(\text{C-P}) \sim 0.8$ Hz, CH_2P], 41.44 [d, $^2\text{J}(\text{C-P})$ 8.6 Hz, CH_2Cl], 196.91 [d, $^2\text{J}(\text{C-P})$ 8.5 Hz, cis CO], and 198.84 p.p.m. [d, $^2\text{J}(\text{C-P})$ 30.5 Hz, trans CO] ; $\delta(^{31}\text{P})$ n.m.r. (CH_2Cl_2) -162.5 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 263.7 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2070 m, 1983 w, and 1944 vs cm^{-1} .

(3) : $\delta(^{13}\text{C})$ n.m.r. (CD_2Cl_2) 12.82 [d, $^3\text{J}(\text{C-P})$ 4.9 Hz, Me], 20.97 [d, $^2\text{J}(\text{C-P})$ 6.1 Hz, Me- CH_2], 41.23 [d, $^1\text{J}(\text{C-P})$ 2.4 Hz, CH_2P], 42.11 [d, $^2\text{J}(\text{C-P})$ 8.5 Hz, CH_2Cl], 133.77 [d, $^1\text{J}(\text{C-P})$ 13.4 Hz, =C-P], 197.30 [d, $^2\text{J}(\text{C-P})$ 7.3 Hz, cis CO], and 199.42 p.p.m. [d, $^2\text{J}(\text{C-P})$ 29.3 Hz, trans CO] ; $\delta(^{31}\text{P})$ n.m.r. (CH_2Cl_2) -163.3 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 258.8 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2070 m, 1982 w, 1943 vs cm^{-1} .

(4) : m.p. 96°C ; $\delta(^{13}\text{C})$ n.m.r. (CDCl_3) 15.51 [d, $^3\text{J}(\text{C-P})$ 2.4 Hz, Me], 38.35 and 39.80 [2s, P- CH_2 - CH_2Cl], 52.16 [s, OMe], 59.49 [d, $^1\text{J}(\text{C-P})$ 19.5 Hz, CH-P], 138.52 [d, $^2\text{J}(\text{C-P})$ 15.9 Hz, CMe], 145.10 [d, $^2\text{J}(\text{C-P})$ 4.9 Hz, C-CO₂Me], 164.57 [d, $^3\text{J}(\text{C-P})$ 3.7 Hz, CO₂], 195.50 [d, $^2\text{J}(\text{C-P})$ 7.3 Hz, cis CO], and 196.83 p.p.m. [d, $^2\text{J}(\text{C-P})$ 26.9 Hz, trans CO] ; $\delta(^{31}\text{P})$ n.m.r. (toluene) +204.4 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 239.3 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2070 m, 1985 w, 1945 vs cm^{-1} .

(5) : $\delta(^{13}\text{C})$ n.m.r. (CD_2Cl_2) 40.99 [d, $^1\text{J}(\text{C-P})$ 2.4 Hz, $\text{CH}_2\text{-P}$], 41.87 [d, $^2\text{J}(\text{C-P})$ 4.1 Hz, CH_2Cl], 119.05 [d, $^1\text{J}(\text{C-P})$ 8.5 Hz, =CH-P], 196.78 [d, $^2\text{J}(\text{C-P})$ 8.5 Hz, cis CO], and 198.93 p.p.m. [d, $^2\text{J}(\text{C-P})$ 31.7 Hz, trans CO] ; $\delta(^{31}\text{P})$ n.m.r. (CH_2Cl_2) -157.4 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 268.6 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2072 m, 1983 w, 1947 vs cm^{-1} .

(6) : m.p. 154°C ; $\delta(^{13}\text{C})$ n.m.r. (CD_2Cl_2) 143.20 [d, $^1\text{J}(\text{C-P})$ 22 Hz, =C-P] and 195.91 p.p.m. [d, $^2\text{J}(\text{C-P})$ 9.8 Hz, cis CO] ; $\delta(^{31}\text{P})$ n.m.r. (CH_2Cl_2) -109.7 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 327 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2077 m, 1993 w, 1957 vs cm^{-1} ; mass (E.I., 70 eV, ^{35}Cl , ^{184}W) m/z 428 (M-5CO, 11%), 209 (M-Cl-W(CO)₅, 100%) ; (C.I., CH_4^+) m/z 533 (M-Cl, 5%), 209 (M-Cl-W(CO)₅, 100%) ; (C.I. NH_3^+) m/z 533 (M-Cl, 100%), 209 (M-Cl-W(CO)₅, 24%).

(7) : $\delta(^{13}\text{C})$ n.m.r. (CD_2Cl_2) 12.43 [d, $^3\text{J}(\text{C-P})$ 3.7 Hz, Me], 20.97 [d, $^2\text{J}(\text{C-P})$ 3.7 Hz, CH_2], 150.38 [d, $^1\text{J}(\text{C-P})$ 25.6 Hz, =C-P], and 196.33 p.p.m. [d, $^2\text{J}(\text{C-P})$ 9.8 Hz, cis CO] ; $\delta(^{31}\text{P})$ n.m.r. (CH_2Cl_2) -97.1 p.p.m., $^1\text{J}(^{31}\text{P}-^{183}\text{W})$ 317.4 Hz ; i.r. (decalin), $\nu(\text{CO})$ 2078 m, 1993 w, 1953 vs cm^{-1} .

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(Received in France 5 July 1985)