

Rearrangement of Chloromethylphosphinidene into Methylenechlorophosphine in the Co-ordination Sphere of Tungsten. Stabilization of an Unhindered P=C Double Bond without Deactivation by π -Complexation

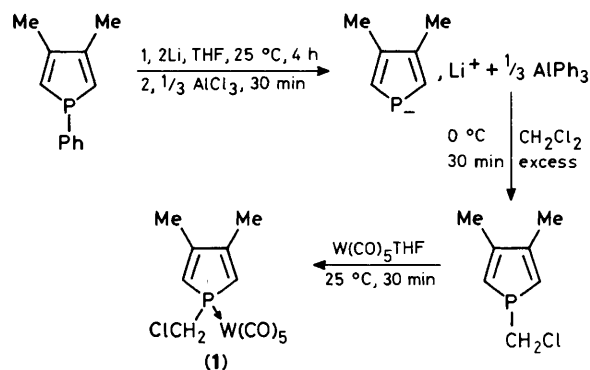
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Transient $[\text{ClCH}_2\text{-P=W(CO)}_5]$ rearranges into stable $(\eta^2\text{-CH}_2\text{=P=Cl})\text{W(CO)}_5$ which can be characterized in solution by i.r., ^1H n.m.r., and ^{31}P n.m.r. spectroscopy and reacts readily with alcohols and conjugated dienes as a σ -P-co-ordinated species.

In a series of preceding papers, we demonstrated that it was possible to generate terminal phosphinidene complexes such as R-P=W(CO)_5 by thermolysis of the appropriate 7-phosphanorbornadiene complexes. The formation of these unstable transient species was proven by chemical trapping^{1,2} and kinetic measurements.³ All our experiments were conducted with non-functional R substituents such as methyl and phenyl. In a subsequent step, it was interesting to install a reactive functionality within the R group in order to study its interaction with the phosphinidene phosphorus. Hereafter we describe our first experiments on chloromethylphosphinidene complexes.

The necessary starting material (1) was prepared in a one pot reaction (overall yield ca. 40%) from 1-phenyl-3,4-dimethylphosphole⁴ according to Scheme 1.



Scheme 1

The chloromethylphosphole complex (1) was purified by chromatography on silica gel with hexane-benzene (80:20) as eluant and mainly characterized by ^1H , ^{13}C , and ^{31}P n.m.r. spectroscopy.† According to our previous work,⁵ the reaction of (1) with dimethyl acetylenedicarboxylate then afforded the expected 7-phosphanorbornadiene complex (2) (35–50%) which was purified by chromatography with benzene and also mainly characterized by n.m.r. spectroscopy.† The magnitudes of the $^2J(\text{Me}-\text{C} \cdots \text{P})$ and $^2J(\text{MeO}_2\text{C}-\text{C} \cdots \text{P})$ couplings are strictly equal for (2) and for the analogous $\text{Ph}-\text{P} \rightarrow \text{Cr}(\text{CO})_5$ complex⁶ thus suggesting similar structures with $\text{W}(\text{CO})_5$ *syn* to the $\text{MeC}=\text{CMe}$ double bond.⁵ A minor by-product [$\delta(^{31}\text{P}) + 207.9$ p.p.m.] is probably the isomer with the reverse stereochemistry.

Following the described procedure,² we then studied the thermal cleavage of the phosphorus bridge of (2) in the presence of copper(I) chloride as a catalyst around 55 °C. The decomposition was run in the presence of various trapping reagents and the results are summarized in Scheme 2.

Where possible [compounds (4), (5), (7), and (9)], the products were isolated in the pure state by chromatography on silica gel with hexane. In all cases, they were mainly characterized by n.m.r. spectroscopy.†

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

(1): $\delta(^1\text{H})$ n.m.r. (CDCl_3) 2.17 [dd, $^4J(\text{H}-\text{H}) \sim ^4J(\text{H}-\text{P}) \sim 0.9$ Hz, Me], 3.78 [d, $^2J(\text{H}-\text{P})$ 1.5 Hz, CH_2Cl], and 6.27 [dd, $^2J(\text{H}-\text{P})$ 37.1 Hz, $=\text{CH}-\text{P}$]; $\delta(^{13}\text{C})$ n.m.r. (CDCl_3) 17.30 [d, $^3J(\text{C}-\text{P})$ 11 Hz, Me], 41.35 [d, $^1J(\text{C}-\text{P})$ 18.3 Hz, CH_2Cl], 126.35 [d, $^1J(\text{C}-\text{P})$ 42.7 Hz, CH], 153.55 [d, $^2J(\text{C}-\text{P})$ 8.5 Hz, C], 195.35 [d, $^2J(\text{C}-\text{P})$ 6.1 Hz, *cis*-CO], and 198.29 [d, $^2J(\text{C}-\text{P})$ 19.5 Hz, *trans*-CO]; $\delta(^{31}\text{P})$ n.m.r. (CDCl_3) +11.5 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 220 Hz].

(2): $\delta(^1\text{H})$ n.m.r. (CDCl_3) 1.99 [d, $^4J(\text{H}-\text{P})$ 1.5 Hz, Me], 3.70 [d, $^2J(\text{H}-\text{P})$ 2 Hz, CH_2Cl], 3.84 [s, OMe], and 4.01 [d, $^2J(\text{H}-\text{P})$ 2.2 Hz, CH]; $\delta(^{13}\text{C})$ n.m.r. (CDCl_3) 15.93 [d, $^3J(\text{C}-\text{P})$ 2.4 Hz, Me], 45.22 [d, $^1J(\text{C}-\text{P})$ 6.1 Hz, CH_2Cl], 52.58 [s, OMe], 58.76 [d, $^1J(\text{C}-\text{P})$ 19.5 Hz, CH], 138.19 [d, $^2J(\text{C}-\text{P})$ 17.1 Hz, C-Me], 144.79 [d, $^2J(\text{C}-\text{P})$ 4.9 Hz, C-CO₂Me], 164.66 [d, $^3J(\text{C}-\text{P})$ 2.4 Hz, -CO₂-], and 195.32 [d, $^2J(\text{C}-\text{P})$ 7.3 Hz, *cis*-CO]; $\delta(^{31}\text{P})$ n.m.r. (toluene) +194.36 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 244.1 Hz].

(3): $\delta(^1\text{H})$ n.m.r. (C_6D_6) 3.04 [d, $^3J(\text{H}-\text{P})$ 12.7 Hz, CH_3O], 3.26 [m, $^2J(\text{H}-\text{P}) \sim 1$ Hz, CH_2Cl], 6.75 [dt, $^1J(\text{H}-\text{P})$ 352 Hz, $^3J(\text{H}-\text{H})$ 4.1 Hz, H-P]; $\delta(^{31}\text{P})$ n.m.r. (tetrahydrofuran, THF) +104.8 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 283.2 Hz].

(4): $\delta(^1\text{H})$ n.m.r. (C_6D_6) 1.33 [d, $^2J(\text{H}-\text{P})$ 3.9 Hz, CH_3P], 2.99 [d, $^3J(\text{H}-\text{P})$ 12.2 Hz, CH_3O]; $\delta(^{31}\text{P})$ n.m.r. (MeOH) +162.7 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 322.3 Hz]; mass [electron impact (E.I.), ^{184}W] m/z 432 (M , 47%), 348 ($M-3\text{CO}$, 100%).

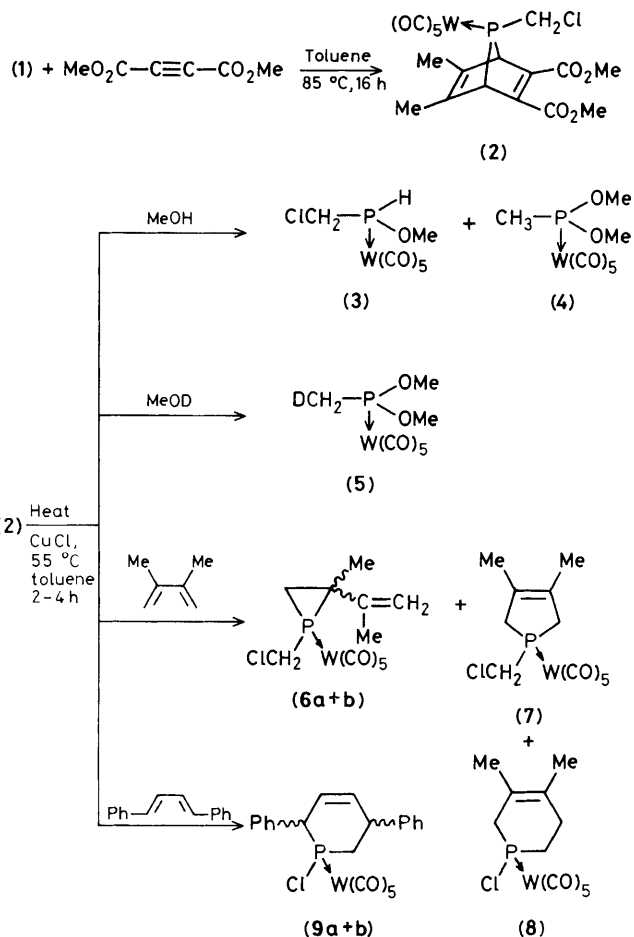
(5): $\delta(^1\text{H})$ n.m.r. (C_6D_6) 1.30 [m, 2H, DCH_2P], 2.98 [d, $^3J(\text{H}-\text{P})$ 12.2 Hz, 6H, CH_3O]; mass (E.I., ^{184}W) m/z 433 (M , 67%), 349 ($M-3\text{CO}$, 100%).

(6a+b): $\delta(^{31}\text{P})$ n.m.r. (toluene) -145.4 (major) and -140.1 p.p.m. (minor).

(7): $\delta(^1\text{H})$ n.m.r. (CDCl_3) 1.75 [s.br., CH_3], 2.86 [s.br., CH_2], 3.71 [d, $^2J(\text{H}-\text{P})$ 1.2 Hz, ClCH_2]; $\delta(^{13}\text{C})$ n.m.r. (CDCl_3) 16.0 [d, $^3J(\text{C}-\text{P})$ 7.3 Hz, Me], 41.32 [d, $^1J(\text{C}-\text{P})$ 26.9 Hz, CH_2], 43.25 [d, $^1J(\text{C}-\text{P})$ 14.6 Hz, ClCH_2], 129.47 [s, C(sp²)], 196.0 [d, $^2J(\text{C}-\text{P})$ 7.3 Hz, *cis*-CO]; $\delta(^{31}\text{P})$ n.m.r. (toluene) +1.5 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 239 Hz].

(8): $\delta(^{13}\text{C})$ n.m.r. (CDCl_3) 20.05 [s, $\text{Me}-\text{C}(4)$], 21.38 [d, $^3J(\text{C}-\text{P})$ 7.3 Hz, $\text{Me}-\text{C}(3)$], 28.65 [d, $^2J(\text{C}-\text{P})$ 4.9 Hz, CH_2], 34.44 [d, $^1J(\text{C}-\text{P})$ 19 Hz, CH_2P], 42.80 [d, $^1J(\text{C}-\text{P})$ 15.9 Hz, CH_2P], 119.68 [d, $^3J(\text{C}-\text{P})$ 6.1 Hz, $=\text{C}(4)$], 127.59 [d, $^2J(\text{C}-\text{P})$ 12.2 Hz, $=\text{C}(3)$], 195.50 [d, $^2J(\text{C}-\text{P})$ 7.3 Hz, *cis*-CO]; $\delta(^{31}\text{P})$ n.m.r. (CDCl_3) +79.6 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 273.4 Hz].

(9a+b): $\delta(^{31}\text{P})$ n.m.r. (THF) +88.8 and +94.4 p.p.m. [$^1J(^{31}\text{P}-^{183}\text{W})$ 273.4 and 283.2 Hz]; mass (chemical ionisation, CH_4^+ , ^{184}W , ^{35}Cl) m/z 611 ($M+1$, 34%); (E.I.) m/z 610 (M , 0.7%), 470 ($M-5\text{CO}$, 25%).

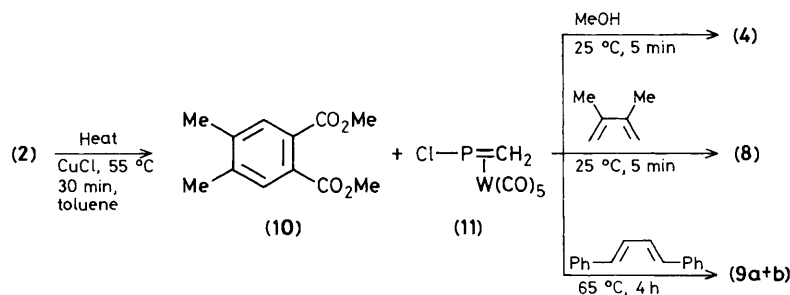


Scheme 2

In the first case, variable amounts of (3) and (4) were obtained according to the concentrations of the reagents. In pure methanol (no toluene), almost pure (4) was obtained. The reaction with MeOD was also run without toluene. In the third case, on performing the reaction in boiling toluene and without catalyst overnight, only (7) was formed.

Complexes (3) and (6) + (7) were the normal products expected from the reactions of transient $[\text{ClCH}_2-\text{P}=\text{W}(\text{CO})_5]$ with methanol⁶ and 2,3-dimethylbutadiene.² However, the formation of complexes (4), (5), (8), and (9) shows that chloromethylphosphinidene rearranged into methylenechlorophosphine $\text{Cl}-\text{P}=\text{CH}_2$ in the co-ordination sphere of tungsten: CuCl might play a role in this rearrangement. Thus, we studied the thermal decomposition of (2) without trapping reagents, Scheme 3.

The decomposition took place very cleanly around 55 °C with CuCl as the catalyst and gave only one phosphorus-containing product according to the ^{31}P n.m.r. spectrum of the crude reaction mixture. This product was far too reactive to allow its separation from the organic by-product and we were obliged to characterize it as a mixture with the phthalate. Nevertheless, n.m.r. and i.r. spectroscopy allowed us to establish unambiguously its formula as (11). The ^{31}P n.m.r. spectrum is the X part of an ABX system: $\delta(^{31}\text{P})$ (toluene) +84.1 (307 K), +89.8 (223), +90.9 p.p.m. (183), [$^1J(^{31}\text{P}-^{183}\text{W})$ not visible, $^2J(\text{P}-\text{H}_A)$ 49, $^2J(\text{P}-\text{H}_B)$ 7 Hz (307 K)]. The ^1H n.m.r. spectrum is the AB part of the same ABX system: $\delta(^1\text{H})$ (C_6D_6) 2.73 [ABX, $^2J(\text{A}-\text{B})$ 8.3 Hz, CH_2], 3.38 [ABX, CH_2]. The i.r. spectrum recorded in decaline [$\nu(\text{CO})$ 2092m, 1992vs, 1986s, 1970vs, 1944m (broad) cm^{-1}] excludes the



Scheme 3

formulation of (11) as a classical P-W(CO)₅ complex. The ABX pattern of the ¹H and ³¹P n.m.r. spectra indicates that (11) is monomeric. The low P-metal coupling constant and the high field shifts of the protons and phosphorus of (11) are characteristic of an η²-P,C-complexation.⁷⁻¹⁰ Indeed, using the data of Appel on free CH₂=P=Cl,¹¹ we calculate a co-ordination chemical shift of -151 p.p.m. for (11). This is far too high for a classical P-W(CO)₅ co-ordination which causes upfield shifts of ca. -30 p.p.m. for P^{II} species (see for example ref. 12). On the other hand, the methylene protons of a free Ar-P=CH₂ species have been found at δ +6.77 and +7.05.¹³ Since free methylenechlorophosphine is a very unstable species only transiently characterized in the dehydrochlorination of methyldichlorophosphine either by heat¹⁴ or by nitrogen bases,¹¹ obviously π-co-ordination of the P=C double bond drastically stabilizes the molecule: (11) can be heated without decomposition up to 65 °C. Nevertheless, this π-complexation does not suppress the reactivity of the P=C double bond since (11) reacts instantly at room temperature with methanol and 2,3-dimethylbutadiene¹⁵ and at 65 °C with 1,4-diphenylbutadiene¹⁵ to give (4), (8), and (9) respectively. Compound (8) was isolated in the pure state by this method. These observations can be explained by assuming that there is an equilibrium between σ-P- and η²-P,C-co-ordination. This type of equilibrium has already been described in the literature for some platinum-phospha-alkene complexes.¹⁶⁻¹⁸ In our case, this equilibrium is completely shifted toward η²-co-ordination in solution. Nevertheless, it explains conveniently why the co-ordinated P=C double bond of (11) retains high reactivity.

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References

- 1 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.
- 2 A. Marinetti and F. Mathey, *Organometallics*, 1984, **3**, 456.
- 3 A. Marinetti, C. Charrier, F. Mathey, and J. Fischer, *Organometallics*, 1985, **4**, in the press.
- 4 A. Brèque, F. Mathey, and Ph. Savignac, *Synthesis*, 1981, 983.
- 5 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 1982, 667.
- 6 A. Marinetti and F. Mathey, *Organometallics*, 1982, **1**, 1488.
- 7 A. H. Cowley, R. A. Jones, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H. M. Zhang, *J. Am. Chem. Soc.*, 1983, **105**, 3737.
- 8 S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1983, 930.
- 9 T. A. van der Knaap, L. W. Jenneskens, H. J. Meeuwissen, F. Bickelhaupt, D. Walther, E. Dinjus, E. Uhlig, and A. L. Spek, *J. Organomet. Chem.*, 1983, **254**, C33.
- 10 A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H. M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015.
- 11 R. Appel and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 556.
- 12 A. Brèque, C. C. Santini, F. Mathey, J. Fischer, and A. Mitschler, *Inorg. Chem.*, 1984, **23**, 3463.
- 13 R. Appel, C. Casser, M. Immenkeppel, and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 895.
- 14 M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513.
- 15 Some [4 + 2] cycloadditions of stable hindered chlorophospha-alkenes have been described in the literature: G. Märkl, G. Yu Jin, and E. Silbereisen, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 370; Y. Y. C. Yeung Lam Ko and R. Carrié, *J. Chem. Soc., Chem. Commun.*, 1984, 1640.
- 16 T. A. van der Knaap, F. Bickelhaupt, H. van der Poel, G. van Koten, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 1756.
- 17 T. A. van der Knaap, F. Bickelhaupt, J. G. Kraaykamp, G. van Koten, J. P. C. Bernards, H. T. Edzes, W. S. Veeman, E. de Boer, and E. J. Baerends, *Organometallics*, 1984, **3**, 1804.
- 18 H. W. Kroto, S. I. Klein, M. F. Meidine, J. F. Nixon, R. K. Harris, K. J. Packer, and P. Reams, *J. Organomet. Chem.*, 1985, **280**, 281.