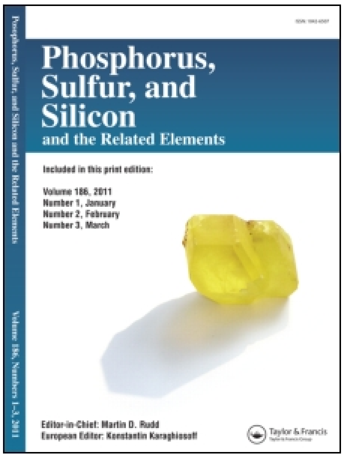


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF TERMINAL PHOSPHINIDENE COMPLEXES WITH ELECTRON-RICH ALKYNES: A NEW APPROACH TO THE PHOSPHOLE RING

Ngoc Hoa Tran Huy[a]; Francois Mathey[a]
[a] Laboratoire de Chimie du Phosphore et des Métaux de Transition DCPH, Ecole Polytechnique, Palaiseau, Cedex, France

To cite this Article Huy, Ngoc Hoa Tran and Mathey, Francois(1990) 'THE REACTION OF TERMINAL PHOSPHINIDENE COMPLEXES WITH ELECTRON-RICH ALKYNES: A NEW APPROACH TO THE PHOSPHOLE RING', Phosphorus, Sulfur, and Silicon and the Related Elements, 47: 3, 477 — 481

To link to this Article: DOI: 10.1080/10426509008038004

URL: http://dx.doi.org/10.1080/10426509008038004

Phosphorus, Sulfur, and Silicon, 1990, Vol. 47, pp. 477–481
Reprints available directly from the publisher
Photocopying permitted by license only

THE REACTION OF TERMINAL PHOSPHINIDENE COMPLEXES WITH ELECTRON-RICH ALKYNES: A NEW APPROACH TO THE PHOSPHOLE RING

NGOC HOA TRAN HUY and FRANÇOIS MATHEY

Laboratoire de Chimie du Phosphore et des Métaux de Transition DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

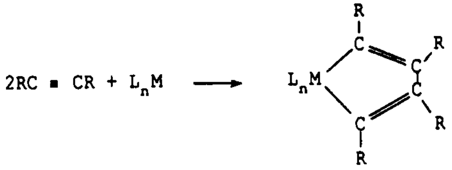
(Received July 17, 1989; in final form August 3, 1989)

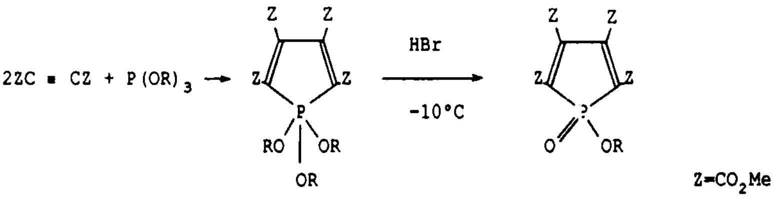
The reaction of electron-rich alkynes such as ethoxyacetylene or propynyldiethylamine with a transient terminal phosphinidene complex such as [PhP=W(CO)$_5$] directly yields the corresponding phosphole complexes via a formal [2 + 2 + 1] cycloaddition involving two molecules of alkyne and one phosphorus center.

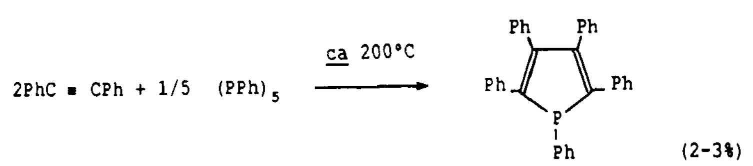
Key words: Phosphinidenes; phospholes; [2 + 2 + 1] cycloadditions; (phosphine)pentacarbonyltungsten complexes.

INTRODUCTION

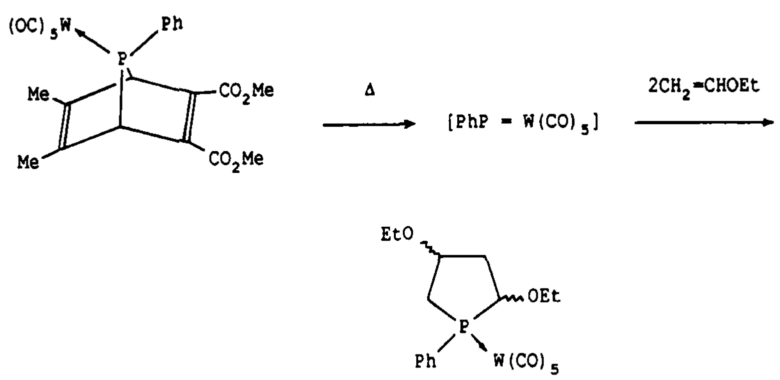
The synthesis of metallacyclopentadienes via the [2 + 2 + 1] cyclodimerization of alkynes onto a transition metal center is a well-known and rather general reaction (Equation (1)).[1] On the contrary, the synthesis of phospholes via the [2 + 2 + 1] cyclodimerization of alkynes onto a phosphorus center has little precedent. The cyclodimerization of dimethyl acetylenedicarboxylate with trialkyl phosphites [Equation (2)][2–4] or with dialkyl alkyl- or aryl-phosphonites[5] gives 2,3,4,5-tetrakis-methoxycarbonyl-phosphole oxides:







Minute amounts of pentaphenylphosphole have also been obtained in the reaction of pentaphenylcyclopentaphosphine with tolane [Equation (3)].[6] In one instance, we have shown that transient terminal phosphinidene complexes as generated from the appropriate 7-phosphanorbornadiene complexes were able to promote the cyclodimerization of enol ethers in the same way as a transition metal center [Equation (4)][7].

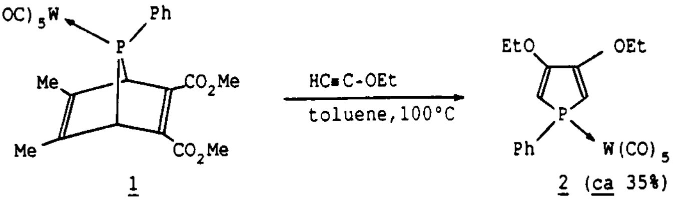


In view of these results from the literature and from our laboratory, we were led to attempt the cyclodimerization of electron-rich alkynes with terminal phosphinidene complexes as a possible route to the phosphole ring.

RESULTS AND DISCUSSION

The reaction of precursor **1**[8] with an excess of ethoxyacetylene was carried out in toluene at 100°C. It gave the phosphole **2** as the only major product [Equation (5)]. If we except trace products, no other compound than **1** and **2** was detected by ^{31}P NMR spectroscopy in the reaction mixture. The modest yield of **2** may be due to some decomposition of **2** during the reaction and during the work up or to a rapid loss of ethoxyacetylene at 100°C via elimination of ethylene (see later).

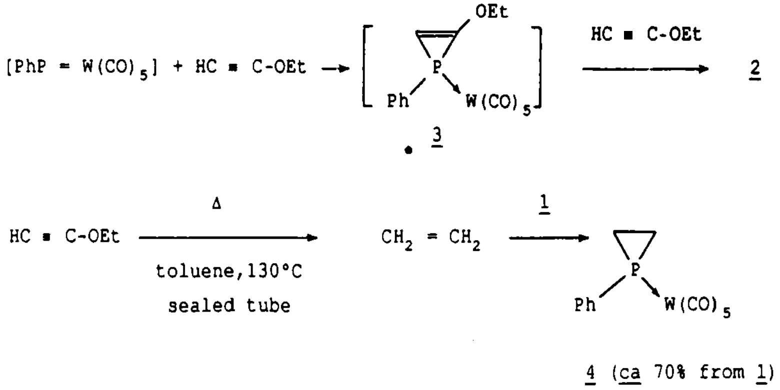
The mass spectrum of complex **2** (EI, 20 eV, ^{184}W) displays a molecular peak at *m/z* 572 which demonstrates that the cyclodimerization has indeed taken place. The unexpected symmetrical structure of **2** was established beyond any doubt by ^{1}H and ^{13}C NMR spectroscopy. The α-C$\underline{H}$ protons give a characteristic resonance at 5.39 ppm with a ^{2}J(H—P) coupling constant of 27 Hz. We suppose that the formation of **2** involves two separate steps, the first one being the formation of the phosphirene complex **3** [Equation (6)]. Indeed, phosphirene complexes are the normal products of the reaction of terminal phosphinidene complexes with alkynes[9] and we have also shown that it is possible to insert monosubstituted



1

2 (ca 35%)

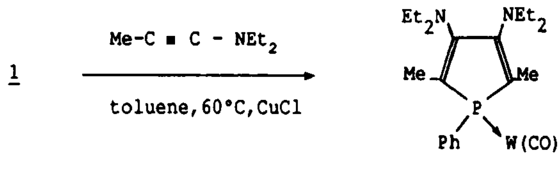
acetylenes into the ring of phosphirene complexes in the presence of a palladium catalyst.[10] However, we have never been able to detect the transient formation of **3**. Indeed, the stability of ethoxyacetylene is minimal at 100°C and we were obliged to use an excess of this alkyne. On the other hand, when working at 130°C in a sealed tube, the decomposition of the alkyne proceeds so fast that we were only able to isolate the phosphirane complex **4** which results from the condensation of the terminal phosphinidene complex with ethylene [Equation (7)].



3

4 (ca 70% from 1)

The same cyclodimerization reaction also takes place with propynyldiethylamine [Equation (8)]. Copper (I) chloride was used as a catalyst to promote the decomposition of **1** at 60°C.[7] As for **2**, ^{1}H and ^{13}C NMR spectroscopy demonstrate that the structure of **5** is symmetrical. The two α-CH$_3$ groups give rise to one ^{1}H resonance at 1.88 ppm with a ^3J(H—P) coupling constant of 12.8 Hz. On the other hand, the inspection of the crude reaction mixture by ^{31}P NMR before the completion of the reaction indicates the presence of another product (δ^{31}P-133 ppm) which is probably the postulated phosphirene intermediate. Whatever the experimental conditions used, we have never been able to



5 (54%)

synthesize this product in sufficient quantity so as to allow its separation. It is also interesting to note that the palladium catalyzed insertion of alkynes into phosphirene complexes[10] is only operative with monosubstituted acetylenes. Finally, the β,β' dialkoxy and -diamino substitution schemes of **2** and **5** are unique and may impart special properties to their phosphole rings.

EXPERIMENTAL

All reactions were performed under argon. NMR spectra were recorded on multinuclear WP 80 SY and AC 200 SY Bruker spectrometers operating at 80.13 and 200.13 (^{1}H), 20.15 and 50.32 (^{13}C), and 32.44 (^{31}P) MHz. Chemical shifts are in ppm downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P), and coupling constants are in Hz. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 instrument at 70 eV under electronic impact. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, France. Silica gel (70–230 mesh) was used for the chromatographic separations. All commercially available reagents were used as received from the suppliers.

(1-Phenyl-3,4-diethoxyphosphole)pentacarbonyltungsten **2**. The 7-phosphanorbornadiene complex **1**[11] (1 g, 1.53×10^{-3} mol) and ethoxyacetylene (1 mL at 40% in hexane) were heated at 100°C for 3.5 h in 10 mL of toluene. After evaporation of the solvent, the residue was chromatographed with hexane/CH_2Cl_2 2/1 as eluent. Yield of **2** 0.3 g (*ca* 35%). ^{31}P NMR ($CDCl_3$): δ −9.5 ppm, $^{1}J(^{31}\text{P}—^{183}\text{W}) = 224.6$ Hz; ^{1}H NMR ($CDCl_3$): δ 1.36 (t, 6H, Me), 4.00 (q, 4H, OCH_2), 5.39 (d, 2H, $^{2}J(\text{H—P}) = 27$ Hz, =CH), 7.27–7.50 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 14.15 (s, Me), 66.32 (s, OCH_2), 97.60 (d, $^{1}J(\text{C—P}) = 47$ Hz, =CH), 158.01 (d, $^{2}J(\text{C—P}) = 15.6$ Hz, Cβ) ppm; IR (CH_2Cl_2): ν(CO) 2070 and 1940 cm^{-1}; mass spectrum (20 eV, ^{184}W): *m/z* 572 (M^+, 13%), 570 (M^+—2H, 41%), 544 (M^+—CO, 100%). The compound is too unstable to give reliable analytical data.

(1-Phenylphosphirane)pentacarbonyltungsten **4** The same reaction as for the synthesis of **2** was performed in a sealed tube at 130°C for 3 h. The residue was chromatographed with pentane/CH_2Cl_2 9/1 as eluent. Yield of **4** 0.5 g (*ca* 70%). ^{31}P NMR ($CDCl_3$): δ −190.1 ppm, $^{1}J(^{31}\text{P}—^{183}\text{W}) = 258.8$ Hz; ^{1}H NMR ($CDCl_3$): δ 0.80–0.94 (m, 4H, CH_2), 6.82–7.06 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 11.12 (d, $^{1}J(\text{C—P}) = 12.2$ Hz, CH_2), 195.7 (d, $^{2}J(\text{C—P}) = 8.2$ Hz, *cis* CO), 197.9 (d, $^{2}J(\text{C—P}) = 30.7$ Hz, *trans* CO) ppm; IR (CH_2Cl_2): ν(CO) 2070 and 1940 cm^{-1}; mass spectrum (^{184}W): *m/z* 460 (M^+, 50%), 348 (M^+—4CO, 100%). Anal. Calcd. for $C_{13}H_9O_5PW$: C, 33.92; H, 1.96. Found: C, 34.51; H, 1.84.

[1-Phenyl-2,5-dimethyl-3,4-bis-(diethylamino)phosphole]pentacarbonyltungsten **5** The 7-phosphanorbornadiene complex **1** (1.5 g, 2.3×10^{-3} mol), propynyl-diethylamine (0.5 mL), and CuCl (50 mg) were heated at 60°C for 0.5 h in 10 mL of toluene. After evaporation of the solvent, the residue was chromatographed as usual. Yield of **5** 0.8 g (*ca* 54%); white crystals, mp 86°C. ^{31}P NMR (CH_2Cl_2): δ +21.7 ppm, $^{1}J(^{31}\text{P}—^{183}\text{W}) = 224.6$ Hz; ^{1}H NMR ($CDCl_3$): δ 1.07 (t, 12H, Me of Et_2N), 1.88 (d, 6H, $^{3}J(\text{H—P}) = 12.8$ Hz, αMe), 3.25 (q, 8H, NCH_2), 7.41 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): δ 13.23 (*s*, Me of Et_2N), 13.53 (αMe), 45.16 (s, NCH_2), 123.78 (d, $^{1}J(\text{C—P}) = 44.4$ Hz, αC), 152.39 (d, $^{2}J(\text{C—P}) = 17.8$ Hz, βC), 196.95 (d, $^{2}J(\text{C—P}) = 7$ Hz, *cis* CO) ppm; IR (CH_2Cl_2): ν(CO) 2070 and 1935 cm^{-1}; mass spectrum (^{184}W): *m/z* 654 (M^+, 22%), 514 (M^+—5CO, 100%). Anal. Calcd. for $C_{23}H_{27}N_2O_5PW$: C, 45.87; H, 4.74. Found: C, 45.99; H, 4.88.

REFERENCES

1. J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry* (University Science Books, Mill Valley, CA, 1987), Chap. 9, pp. 509–512.
2. J. C. Tebby, S. E. Willetts, and D. V. Griffiths, *J. Chem. Soc., Chem. Commun.*, 420 (1981).
3. J. C. Caesar, D. V. Griffiths, J. C. Tebby, and S. E. Willets, *J. Chem. Soc., Perkin Trans. I*, 1627 (1984).
4. R. Burgada, Y. Leroux, and Y. O. El Koshnieh, *Tetrahedron Lett.*, **22**, 3533 (1981).
5. J. C. Caesar, D. V. Griffiths, and J. C. Tebby, *Phosphorus Sulfur*, **29**, 123 (1987); *J. Chem. Soc., Perkin Trans. I*, 175 (1988).

6. C. Charrier, J. Guilhem, and F. Mathey, *J. Org. Chem.*, **46,** 3 (1981).
7. A. Marinetti and F. Mathey, *Organometallics*, **3,** 456 (1984).
8. The use of 7-phosphanorbornadiene complexes as precursors of terminal phosphinidene complexes has been reviewed, see: F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **26,** 275 (1987).
9. A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, **104,** 4484 (1982).
10. A. Marinetti, F. Mathey, *Tetrahedron Lett.*, **28,** 5021 (1987).
11. A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Chem. Soc., Chem. Commun.* 668 (1982).