Articles

Thermal [2 + 2] Cycloadditions between Diphosphene Complexes and Alkynes

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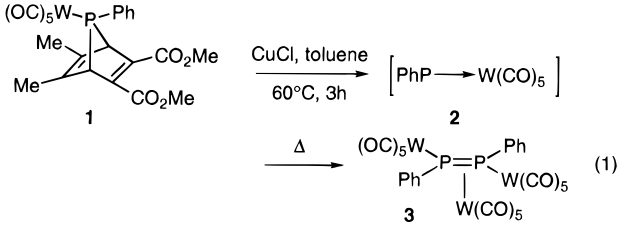
According to the experimental conditions, the thermal decomposition of the 7-phenyl-7-phosphanorbornadiene−W(CO)$_5$ complex **1** affords the diphosphene complex **3** (60 °C, CuCl as a catalyst), the triphosphirane complex **4** (120 °C, 8 h), or the tetraphosphetane complex **5** (120 °C, 15 h). The reaction of **3** with alkynes at 120 °C in toluene gives the corresponding 1,2-dihydro-1,2-diphosphete complexes **6**−**8** in modest yield (ca. 25%) *via* a [2 + 2] cycloaddition. This result gives some insight into the reaction of cyclopolyphosphines with alkynes.

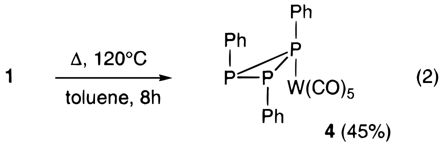
A great deal of work has already been done on the synthesis of 1,2-dihydro-1,2-diphosphetes by thermal reaction of cyclopolyphosphines (RP)$_n$ with alkynes.[1] Whereas the mechanism of this synthesis has never been investigated, one possible explanation[2] would be a direct P═P + C≡C [2 + 2] cycloaddition. We thus decided to evaluate this possibility. In fact, the problem is not trivial, since very bulky substituents are needed to provide diphosphenes with a sufficient kinetic stability. This may be the reason why only a few [2 + 2] cycloadditions of diphosphenes have been described in the literature, including the classical cyclodimerization[2] and the condensation of metallodiphosphenes [Fe]−P═P−R with electron-poor alkenes.[3] Alternatively, it is possible to stabilize unhindered diphosphenes by complexation. The reactivity of the P═P bond of such complexes has already been investigated in some depth by Huttner.[4] We decided to select this approach, which parallels our work with phosphaalkenes.[5]

Results and Discussion

All our work has been done with the diphosphene complex **3**, resulting from the dimerization of the unstable terminal phosphinidene complex [PhP→W(CO)$_5$] (**2**) as generated from the appropriate 7-phosphanorbornadiene precursor **1** (eq 1).[6]



Optimization of the reaction conditions allowed the synthesis of **3** in 46% yield (based on P) from **1**. While optimizing the synthesis of **3** *via* the CuCl-catalyzed decomposition of **1**, we also investigated the uncatalyzed thermal splitting of the bicyclic skeleton. At 120 °C in toluene, the only detectable organophosphorus product was the mono complex of the triphosphirane **4** (eq 2). Most of the tungsten was recovered as W(CO)$_6$.



Complex **4** displays a characteristic ABX ^{31}P {^{1}H} NMR spectrum which implies a *trans* stereochemistry for the PhP−PPh unit. The two uncomplexed phosphorus atoms resonate at δ −126.8 (A) and −133.2 (B). The complexed phosphorus appears at δ −94.1 (X). As expected, the ^1J(P−P) coupling increases when the tetracoordinated phosphorus is involved: ^1J(AB) = 146.5 Hz, ^1J(AX) = 220.3 Hz, and ^1J(BX) = 231.6 Hz.

Since the π-bonded [W(CO)$_5$] group is known to be labile in **3**,[4] we suspected that **4** was formed *via* the reaction of the phosphinidene complex **2** with the diphosphene complex. We verified this hypothesis by a ^{31}P NMR study of the reaction of the precursor **1** with 1 equiv of **3** (eq 3).

$$\mathbf{1} + \mathbf{3} \xrightarrow[\text{toluene, 5h}]{120°\text{C}} \mathbf{4} \qquad (3)$$

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

[1] (a) Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306. (b) Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453. (c) Charrier C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3. (d) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623. (e) Phillips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1988**, *27*, 2269.

[2] For a review on the chemistry of diphosphenes, see: Weber, L. *Chem. Rev.* **1992**, *92*, 1839.

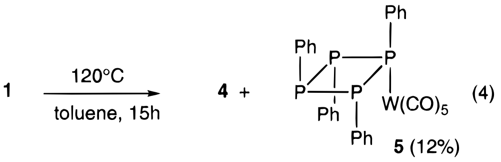
[3] Weber, L.; Frebel, M.; Boese, R. *Chem. Ber.* **1990**, *123*, 733.

[4] Borm, J.; Huttner, G.; Orama, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 53. Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *304*, 309.

[5] Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90.

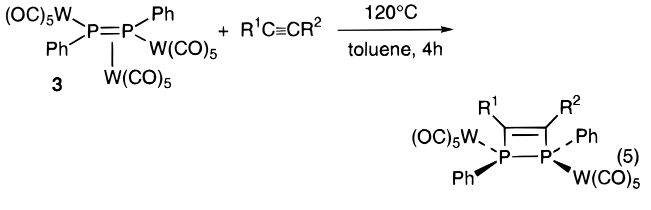
[6] Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134.

Upon longer heating of **1** alone, we observed the formation of **4** as expected, but the four-membered ring **5** was the other major product of the reaction (eq 4).



Complex **5** was also obtained by reaction of the precursor **1** with the triphosphirane complex **4** under similar experimental conditions. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows three types of phosphorus atoms at δ −70.6 (1P), −21.9 (2P) and +0.06 (1P), respectively. Its formulation was established by an X-ray crystal structure analysis (Figure 1). The P−P bond lengths are normal, between 2.226 and 2.241(1) Å. The phenyl groups display an *all-trans* disposition. The four-membered ring is folded around the P_2-P_4 axis by 51.24 + 0.05°.

Having established the experimental conditions for obtaining the various oligomers of [PhP→W(CO)$_5$], we came back to our initial problem. Heating complex **3** with various alkynes in refluxing toluene led to the corresponding 1,2-dihydro-1,2-diphosphetes, as expected (eq 5).



6 $R^1 = R^2 = Ph$ (25%)
7 $R^1 = Ph, R^2 = H$ (27%)
8 $R^1 = Me, R^2 = CO_2Me$ (27%)

Complex **6** was identified by comparison of its ^1H, ^{13}C, and ^{31}P NMR spectra with those of an authentic sample prepared by reaction of [W(CO)$_5$(THF)] with *trans*-1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete. Particularly significant is the ^{13}C resonance corresponding to the ring carbons, which appears as a pseudotriplet at δ 148.57 ($CDCl_3$). Due to their lack of symmetry, the identification of the original complexes **7** and **8** was easier. Both complexes **7** and **8** give rise to characteristic ^{31}P AX spectra: **7**, δ 27.73 and 46.64, $\sum J(P-P) = 23.9$ Hz; **8**, δ 37.92 and 41.92, $\sum J(P-P) = 27.6$ Hz. The low P···P couplings result from the superimposition of ^1J and ^3J couplings of opposite signs.[1d]

Since we have checked that **3** is stable upon heating in refluxing toluene for 4 h, it is reasonable to admit that the first step of the reaction is a reversible unmasking of the P=P double bond followed by a [2 + 2] P=P + C≡C cycloaddition. Thus, this series of experiments suggests that a similar mechanism is at work in the synthesis of 1,2-dihydro-1,2-diphosphetes from alkynes and cyclopolyphosphines. However, the experimental conditions depicted in eq 4 are much milder than those of the $R^1C{\equiv}CR^2 + (RP)_n$ route. For example, the reaction of PhC≡CPh with $(PhP)_5$ is performed at 240 °C for 6 h and affords the corresponding dihydrodiphosphete in only 15% yield.[1c] Besides, this earlier route gives no access to partially unsubstituted or functional derivatives such as **7** and **8**. Thus, working with protected diphosphenes offers new synthetic opportunities, since it is possible to recover free dihydrodiphosphetes from their complexes.[7]

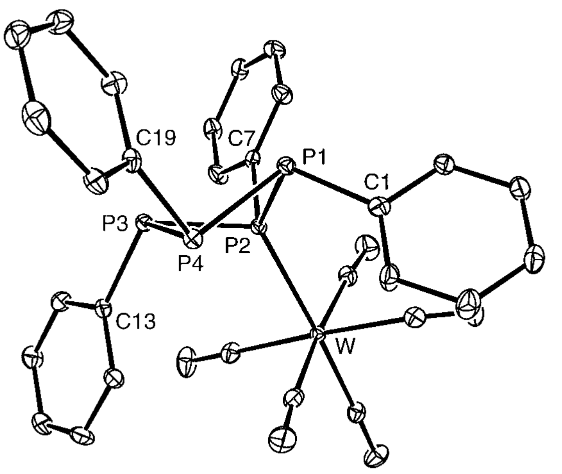


Figure 1. ORTEP drawing of one molecule of **5**, as determined by a single-crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W−P(2) = 2.520(1), P(1)−P(2) = 2.229(1), P(1)−P(4) = 2.226(1), P(1)−C(1) = 1.832(4), P(2)−P(3) = 2.241(1), P(2)−C(7) = 1.832(4), P(3)−P(4) = 2.227(1), P(3)−C(13) = 1.816(4), P(4)−C(19) = 1.846(4); P(2)−P(1)−P(4) = 85.58(5), P(2)−P(1)−C(1) = 106.0(1), P(4)−P(1)−C(1) = 105.5(1), W−P(2)−P(1) = 124.51(5), W−P(2)−P(3) = 125.08(5), W−P(2)−C(7) = 113.7(1), P(1)−P(2)−P(3) = 82.79(5), P(1)−P(2)−C(7) = 104.9(1), P(3)−P(2)−C(7) = 100.0(1), P(2)−P(3)−P(4) = 85.26(5), P(2)−P(3)−C(13) = 107.3(1), P(4)−P(3)−C(13) = 107.1(1), P(1)−P(4)−P(3) = 83.19(5), P(1)−P(4)−C(19) = 101.1(1), P(3)−P(4)−C(19) = 100.1(1).

Experimental Section

All reactions were performed under nitrogen; the solvents were purified, dried, and degassed by standard techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32, and 81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

[1,2,3-Triphenyltriphosphirane]pentacarbonyltungsten (4). A solution of complex **1** (1 g, 15 × 10^{-4} mol) in toluene (10 mL) was refluxed at 120 °C for 8 h. After evaporation, the residue was chromatographed on silica gel with hexane. The triphosphirane complex **4** was thus obtained as a light yellow powder in 45% yield (0.15 g). ^{31}P NMR: see text. Mass spectrum (^{184}W): *m/z* 648 (M^+, 2%), 620 ($M^+ - CO$, 7%), 592 ($M^+ - 2CO$, 7%), 564 ($M^+ - 3CO$, 14%), 536 ($M^+ - 4CO$, 9%), 508 ($M^+ - 5CO$, 45%), 262 (64%), 183 (100%). Anal. Calcd for $C_{23}H_{15}O_5P_3W$: C, 42.59; H, 2.31. Found: C, 42.23; H, 2.18.

[1,2,3,4-Tetraphenyltetraphosphetane]pentacarbonyltungsten (5). A solution of complex **1** (3 g, 45 × 10^{-4} mol) in toluene (20 mL) was refluxed at 120 °C for 15 h. Chromatography of the residue, first with hexane as the eluent, afforded **4** (0.4 g) and then with hexane/CH_2Cl_2 (10:1) gave **5** as a yellow powder (0.4 g, 12%). ^{31}P NMR ($CDCl_3$): δ −70.6 (1 P_C), −21.9 (2 P_B), +0.06 (1 P_A, complexed), $^1J_{AB} \approx 155$ Hz, $^1J_{AC} \approx 75$ Hz, $^1J_{BC} \approx 100$ Hz. Mass spectrum (^{184}W):

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[7] Maigrot, N.; Ricard, L.; Charrier, C.; Le Goff, P.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 76.

m/*z* 728 ($M^+ - CO$, 4%), 700 ($M^+ - 2CO$, 2%), 672 ($M^+ - 3CO$, 12%), 644 ($M^+ - 4CO$, 6%), 616 ($M^+ - 5CO$, 25%), 262 (100%), 183 (95%). The base peak probably corresponds to Ph_3P, which could be formed by dismutation of the [PhP] units.

Synthesis of 1,2-Dihydro-1,2-diphosphete Complexes 6−8. A solution of complex **3** (0.45 g, 3.8×10^{-4} mol) and alkyne (3.8×10^{-4} mol) was refluxed in toluene (5 mL) at 120 °C for 4 h. After evaporation, the residue was chromatographed on silica gel to give **6**−**8** as yellow powders.

Complex **6**: eluent hexane/CH_2Cl_2 9:1, yield 0.1 g (25%). ^{31}P NMR ($CDCl_3$): δ 46.34, $^1J(P-W) = 231.9$ Hz. Mass spectrum (^{184}W): *m*/*z* 1042 (M^+, 38%), 958 ($M^+ - 3CO$, 52%), 874 ($M^+ - 6CO$, 100%), 762 ($M^+ - 10CO$, 79%). IR (CH_2Cl_2): ν(CO) 2069 (m), 1949 (vs) cm^{-1}.

Complex **7**: eluent hexane/CH_2Cl_2 (7:3) yield 0.1 g (27%). ^{31}P NMR ($CDCl_3$): see text. ^{13}C NMR ($CDCl_3$): δ 153.79 (dd, $^1J(P-C) = 30.25$ Hz, $^2J(P-C) = 11.5$ Hz, $=CPh$). Mass spectrum (^{184}W): *m*/*z* 965 (M^+, 42%), 881 ($M^+ - 3CO$, 64%), 770 ($M^+ - 7CO$, 75%), 685 ($M^+ - 10CO$, 100%). IR (CH_2Cl_2): ν(CO) 2069 (m), 1951 (vs) cm^{-1}. Anal. Calcd for $C_{30}H_{16}O_{10}P_2W_2$: C, 37.26; H, 1.65. Found: C, 37.88; H, 1.78.

Complex **8**: eluent hexane/CH_2Cl_2 (1:1), yield 0.1 g (27%). ^{31}P NMR ($CDCl_3$): see text. ^1H NMR ($CDCl_3$): δ 2.72 (dd, $^3J(P-H) = 11.0$ Hz, $^4J(P-H) = 1.6$ Hz, 3H, CH_3), 3.86 (s, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 20.46 (t, $^2J(C-P) = 15.1$ Hz, $^3J(C-P) = 6.6$ Hz, CH_3), 53.11 (s, CO_2CH_3), 163.12 (dd, $^2J(C-P) = 21.4$ Hz, $^3J(C-P) = 12.4$ Hz, CO), 168.51 (dd, $^1J(C-P) = 27.6$ Hz, $^2J(C-P) = 12.4$ Hz, $=CMe$). IR (CH_2Cl_2): ν(CO) 2070 (m), 1952 (vs), 1716 (w) cm^{-1}. Anal. Calcd for $C_{27}H_{16}O_{12}P_2W_2$: C, 33.69; H, 1.66. Found: C, 33.65; H, 1.79.

X-ray Structure Determination for 5. Crystals of **5**, $C_{29}H_{20}O_5P_4W$, were grown from a dichloromethane/pentane solution of the compound. Data were collected at -150 ± 0.5 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf-Nonius MOLEN package. The compound crystallizes in space group $P2_1/n$ (No. 14), with $a = 10.315(1)$ Å, $b = 22.604(3)$ Å, $c = 12.892(1)$ Å, $\beta = 106.41(1)°$, $V = 2883.5(1.0)$ Å^3, $Z = 4$, $d_{calc} = 1.742$ g/cm^3, $\mu = 43.5$ cm^{-1}, and $F(000) = 1472$. A total of 7560 unique reflections were recorded in the range $2° \le 2\theta \le 56.1°$, of which 2538 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 5022 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.03. The final agreement factors were $R = 0.025$, $R_w = 0.029$, and GOF = 1.02.

Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **5** (8 pages). Ordering information is given on any current masthead page.

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