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Preliminary Investigation of the [3+2] Cycloaddition Reactions of 2-Alkylidenephosphiranes

Ngoc Hoa Tran Huy,*,†,‡ Louis Ricard,† and François Mathey*,‡

Laboratoire "Hétéroéléments et Coordination" UMR CNRS 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France, and UCR-CNRS Joint Research Chemistry Laboratory, Department of Chemistry, University of California Riverside, California 92521-0403

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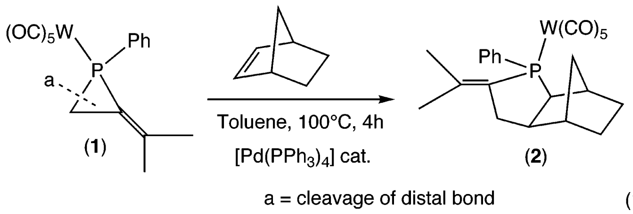
*Summary: The 2-alkylidenephosphirane complex **1** reacts with norbornene and dimethyl acetylenedicarboxylate at 100 °C in toluene to give the corresponding [3+2] cycloadducts. With norbornene, only the P−C distal bond is involved, whereas with acetylenedicarboxylate, both the P−C distal and proximal bonds react.*

Introduction

The high and varied reactivity of alkylidenecyclopropanes has led to numerous applications of these molecules in organic synthesis. The most classical methodology based on these species involves their transition metal-catalyzed [3+2] cycloaddition reactions with alkenes and alkynes, leading to five-membered rings.[1] However, the scope of their transformations is much broader, as shown by the recent discovery that they isomerize into cyclobutenes in the presence of $PtCl_2$ as a catalyst[2] or cycloadd with two molecules of alkynes in the presence of a nickel catalyst to give seven-membered rings.[3] In the organometallic field, their most spectacular reaction is their conversion into trimethylenemethane complexes.[4] All of this chemistry is under the control of the ring strain and can be, a priori, transposed with the heteroatomic analogues of alkylidenecyclopropanes. Until now, however, attention has been mainly focused on the synthesis of heteroatomic analogues of the trimethylenemethane complexes with sulfur,[5] silicon,[6] and phosphorus.[7] In our group, besides the transformation of alkylidenephosphiranes into η^4-1-phosphatrimethylenemethane complexes,[7] we have also studied their ring opening upon metalation at the ring sp^3-carbon[8] and the cycloaddition of a second phosphinidene unit onto their exocyclic C═C double bond.[9] Along the same vein, we decided to investigate their cycloaddition chemistry. Our preliminary results are reported hereafter.

Results and Discussion

Our starting product has been the alkylidenephosphirane pentacarbonyltungsten complex **1** obtained by cycloaddition of the transient terminal phosphinidene complex [PhP−W(CO)$_5$] with the appropriate allene following the work of Lammertsma.[10] The preferential cleavage of one of the P−C ring bonds of **1** during the cycloaddition reactions was taken for granted. They are indeed substantially weaker than the C−C ring bond. But what about the choice between the distal and the proximal P−C bond? Since the X-ray crystal structure of **1** as determined by Lammertsma[10] showed that the distal bond is much longer than the proximal bond (1.85(1) vs 1.776(8) Å) probably due to the strain at the olefinic ring carbon, we felt that a preferential distal cleavage was likely. The reaction of the strained and reactive norbornene with **1** gave us a first answer (eq 1).



(1)

Under palladium catalysis at 100 °C, the reaction proceeds in high yield and exclusively takes place at the distal P−C bond as expected. The two most significant data from the ^{13}C NMR spectrum of **2** are the α ring carbon resonances at 139.82 ($^1J_{C-P}$ = 33.0 Hz) and 56.42 ppm ($^1J_{C-P}$ = 25.5 Hz). The structure was fully established by X-ray analysis (Figure 1). The exo junction between the norbornane and the phospholane rings is not surprising, but the stereochemistry at phosphorus with the tungsten on the same side as the norbornane bridge was not expected. That some steric repulsion exists between the bulky phosphorus ligand and the complexing group is shown by the fact that the P−W bond is elongated from 2.500(2) in **1**[10] to 2.5444(8) Å in **2**.

We also investigated the reaction of **1** with dimethyl acetylenedicarboxylate. Unexpectedly the reaction gives two

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* Corresponding author. E-mail: francois.mathey@ucr.edu.

† Laboratoire "Hétéroéléments et Coordination".

‡ UCR-CNRS Joint Research Chemistry Laboratory.

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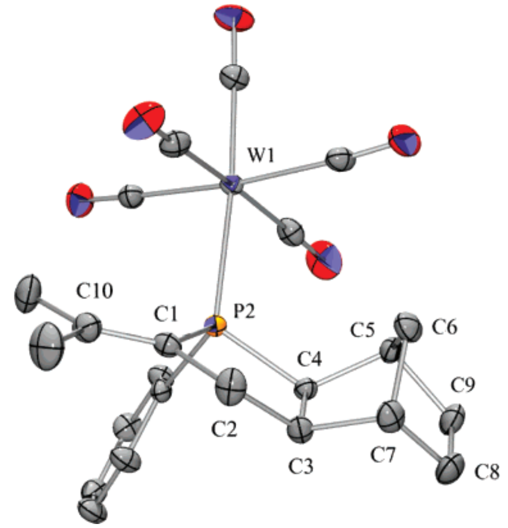
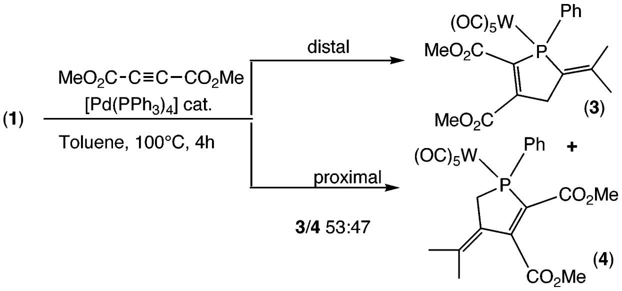


Figure 1. X-ray crystal structure of the norbornene adduct (**2**). Main bond lengths (Å) and angles (deg): P−W 2.5444(8), P−C1 1.830(2), P−C4 1.858(2), P−C13 1.841(2), C1−C2 1.513(3), C1−C10 1.339(3), C2−C3 1.533(3), C3−C4 1.570(3); C1−P−C4 94.9(1), C1−P−C13 103.8(1), C13−P−C4 99.8, C4−P−W 119.93(7).

products resulting from the insertion of the C≡C triple bond into the P−C distal and proximal bonds (eq 2).



(2)

The two products could not be separated, but, fortunately, **3** proved to be unstable in basic medium and was selectively destroyed by ^{t}BuOK without leaving any well-defined product. Apparently, **3** is more easily deprotonated than **4**. We were thus able to get **4** in the pure state. The most informative datum is the P−CH$_2$ resonance in the ^{13}C NMR spectrum at 41.68 ppm ($^1J_{C-P}$ = 30.0 Hz). The data for **3** were obtained from the mixture. The CH$_2$ resonance appears at 40.80, and the P−C coupling is much weaker than for **4** ($^2J_{C-P}$ = 11.0 Hz). The resonance for the Me$_2$C═*C* carbon appears at 127.39 with the expected huge P−C coupling ($^1J_{C-P}$ = 47.1 Hz).

We have no obvious explanation for the fact that the reaction of acetylenedicarboxylate involves both the distal and proximal P−C bonds. Anyhow, these experiments clearly illustrate the synthetic potential of alkylidenephosphirane complexes. We plan to explore other transformations of these species.

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H$_3$PO$_4$(^{31}P). Elemental analyses were performed by the Service de microanalyse du CNRS, Gif-sur-Yvette, France.

Norbornene Cycloadduct 2. Phosphirane **1** (0.5 g, 1 mmol), norbornene (0.2 g, 2 mmol), and 0.02 g of [Pd(PPh$_3$)$_4$] in toluene (8 mL) were heated at 100 °C for 4 h. The product was purified by chromatography on silica gel (hexane/CH$_2$Cl$_2$, 9:1). A total of 0.45 g of alkylidenephospholane **3** was isolated as beige microcrystals (75% yield). ^{31}P NMR (CDCl$_3$): δ 25.27, $^1J_{P-W}$ 231 Hz. ^{1}H NMR (CDCl$_3$): δ 1.10 (d, 1H, gem J_{H-H} = 2.1 Hz, bridge CH); 1.14 (d, gem J_{H-H} = 2.1 Hz, bridge CH); 1.18 (d, 1H, $^1J_{Hexo-Hendo}$ = 10.6 Hz endo H); 1.60 (m, 3H, 2 exo H and 1 endo H); 1.66 (br s, 3H, Me); 1.92 (br s, 3H, Me); 2.03 (t, 1H, $^3J_{P-H}$ = 7.2 Hz, $^3J_{H-endoH}$ = 9.2 Hz, junction CH), 2.2 (m, 2H, bridgehead CH$_2$); 2.44, 2.54 (m, 2H, phospholane CH$_2$); 3.06 (sextuplet, 1H, $^3J_{H-endoH}$ = 9.1 Hz, $^3J_{P-H}$ = 17.8 Hz, $^3J_{H-H}$ = 16.8 Hz); 7.3−7.6 (m, 5H, Ph). ^{13}C NMR (CDCl$_3$): δ 23.40 (d, $^3J_{C-P}$ = 8.8 Hz, CH$_3$); 26.68 (d, $^3J_{C-P}$ = 9.0 Hz,CH$_3$); 27.97 (s, bridge CH$_2$); 31.19 (d, $^3J_{C-P}$ = 13.1 Hz, norbornane CH$_2$); 35.86 (s, norbornane CH$_2$); 40.05 (d, $^2J_{C-P}$ = 22.0 Hz, phospholane CH$_2$); 42.50 (s, bridgehead CH); 43.41 (d, $^2J_{C-P}$ = 9.7 Hz, bridgehead CH); 50.45 (d, $^2J_{C-P}$ = 2.5 Hz, phospholane CH); 56.45 (d, $^1J_{C-P}$ = 25.5 Hz, phospholane CH); 129.16, 130.01, 131.94 (Ph C), 134.51 (d, $^1J_{C-P}$ = 40.0 Hz, ipso C); 139.84 (d, $^1J_{C-P}$ = 33.0 Hz, ring sp$_2$ C); 140.94 (d, $^2J_{C-P}$ = 10.7 Hz,═*C*Me$_2$); 197.98 (d, $^2J_{P-C}$ = 6.9 Hz,*cis* CO); 199.45 (d, $^2J_{P-C}$ = 20.7 Hz, *trans* CO). MS (^{184}W): *m/z* 594 (M, 18%); 566 (M − CO, 12%); 538 (M − 2 CO, 19%); 510 (M − 3 CO, 83%); 452 (M − 2 − 5 CO, 100%). Anal. Calcd for C$_{23}$H$_{23}$O$_5$PW: C, 46.49; H, 3.90. Found: C, 46.39; H, 3.89.

Cycloadducts with Dimethyl Acetylenedicarboxylate, 3 and 4. Phosphirane **1** (0.5 g, 1 mmol), DMAD (0.25 mL, 2 mmol), and [Pd(PPh$_3$)$_4$] (0.02 g, 0.2 mmol) in toluene (8 mL) were heated at 100 °C for 4 h. **3** and **4** were purified by chromatography on silica gel (hexane/CH$_2$Cl$_2$, 1:2), giving a yellow oil, yield 0.51 g (80%). ^{31}PNMR (CDCl$_3$): δ 12.9, $^1J_{P-W}$ 245 Hz (**4**); 28.4, $^1J_{P-W}$ 239 Hz (**3**).

A mixture of **3** and **4** (0.2 g, 0.3 mmol) and ^{t}BuOK (0.05 g, 0.5 mmol) in THF (3 mL) were stirred at room temperature for 0.5 h. After hydrolysis, extraction with hexane and purification on silica gel with hexane/CH$_2$Cl$_2$, 1:2, gave 0.06 g of **4** (60% recovery).

Cycloadduct 4. ^{31}PNMR (CDCl$_3$): δ 12.9, $^1J_{P-W}$ 245 Hz. ^{1}HNMR (CDCl$_3$): δ 1.84 (s, Me); 1.85 (s, Me); 3.34 (m, 2H, PCH$_2$); 3.58 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), 7.40−7.55 (m, 5H, C$_6$H$_5$). ^{13}CNMR (CDCl$_3$): δ 21.7 (s, CH$_3$); 25.6 (s, CH$_3$); 41.6 (d, $^1J_{P-C}$ = 30.0 Hz, P*C*H$_2$); 52.7 (s, OCH$_3$); 53.4 (s, OCH$_3$); 131.0 (s, ═*C*Me$_2$); 132.7 (d, $^1J_{P-C}$ = 33.7 Hz, ipsoC); 135.2 (d, $^1J_{P-C}$ = 34.6 Hz, ring sp$_2$C); 145.0 (d, $^2J_{P-C}$ = 6 Hz, ringC), 153.8 (d, $^2J_{P-C}$ = 10 Hz, ring *C*═CMe$_2$); 164.2 (d, $^2J_{P-C}$ = 12.5 Hz, ester CO); 167.9 (d, $^3J_{P-C}$ = 11.4 Hz, ester CO); 196.7 (d, $^2J_{P-C}$ = 7.1 Hz, *cis* CO); 199.2 (d, $^2J_{P-C}$ = 23.5 Hz, *trans* CO).

The spectroscopic data of **3** were deduced from those of the mixture of **3** and **4** (ratio 53:47) and those of **4**.

Cycloadduct 3. ^{31}PNMR (CDCl$_3$): δ 28.4, $^1J_{P-W}$ = 239 Hz. ^{1}H NMR (CDCl$_3$): δ 1.61 (s, 6H, Me); 3.56 (s, 3H, OCH$_3$); 3.76 (s, 3H, OCH$_3$), 3.80 (m, 2H, PCH$_2$), 7.60 (m, 5H, C$_6$H$_5$). ^{13}CNMR (CDCl$_3$): δ 22.3 (d,$^3J_{P-C}$ = 9.8 Hz, CH$_3$); 25.4 (d, $^3J_{P-C}$ = 11.3 Hz, CH$_3$); 40.8 (d,$^2J_{P-C}$ = 11.2 Hz, P*C*H$_2$); 52.8 (d, $^4J_{P-C}$ = 3.1 Hz, OCH$_3$); 53.1 (s, OCH$_3$); 127.1 (d, $^1J_{P-C}$ = 47.1 Hz, ring *C*═CMe$_2$); 132.0 (s, ═*C*Me$_2$); 139.0 (d, $^1J_{P-C}$ = 35.5 Hz, ipsoC); 144.7 (d, $^1J_{P-C}$ = 32.0 Hz, ring sp$_2$C); 144.9 (d, $^2J_{P-C}$ = 11.5 Hz, ringC), 163.8 (d, $^2J_{P-C}$ = 14.4 Hz, ester CO); 165.4 (d, $^3J_{P-C}$ = 9.7 Hz, ester CO); 196.7 (d, $^2J_{P-C}$ = 9.7 Hz, *cis* CO); 199.4 (d, $^2J_{P-C}$ = 22.4 Hz, *trans* CO).

X-ray Structure Data. X-ray structure data: Nonius KappaCCD diffractometer, ϕ and ω scans, Mo Kα radiation (λ = 0.71073 Å), graphite monochromator, *T* = 150 K, structure solution with SIR97,[11] refinement against *F*^{2} in SHELXL97[12] with anisotropic

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thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. Data collection for **2**: colorless block, 0.20 × 0.20 × 0.20 mm; monoclinic, space group $P2_1/n$, $a = 11.325(5)$ Å, $b = 13.428(5)$ Å, $c = 15.724(5)$ Å, $\beta = 109.670(5)°$, $V = 2251.6(15)$ Å^3, $Z = 4$, $\rho_{calc} = 1.753$ g cm^{-3}, $\mu = 5.232$ cm^{-1}; $F(000) = 1160$, $\theta_{max} = 30.1°$, 13 292 data collected, 5943 unique data with $I > 2\sigma(I)$, 273 parameters refined, GOF(F^2) = 1.004, final R indices ($R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$): R1 = 0.0215, wR2 = 0.0540-(all data); max./min. residual electron density 1.733(0.103)/−1.878-(0.103) e$^-$ Å^{-3}.

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 639710. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223−336-033; e-mail deposit@ccdc.cam.ac.uk).

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