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Conversion of 2-alkylidenephosphiranes into 1,4-diphosphaspiropentanes

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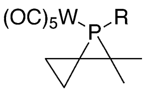
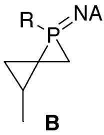
Abstract—The bis-condensation of [MeP-W(CO)$_5$] with 3-methyl-1,2-butadiene yields two stereoisomers of the corresponding 1,4-diphosphaspiropentane, one of which has been characterized by X-ray crystal structure analysis. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

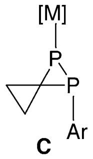
Spiropentane has been known for over a century and has been the subject of intensive theoretical and chemical studies.[1] According to a recent theoretical estimate, the replacement of one carbon of the ring by a phosphorus leads to a reduction of the strain energy of spiropentane by ca 10 kcal mol^{-1}.[2] On that basis, it is not surprising to find that several phosphaspiropentanes have been already synthesized including the monophosphorus species (**A**), (**B**)[3,4] and the 1,2-diphospha-(**C**)[5] and 1,2,4,5-tetraphospha-spiropentanes (**D**).[6]



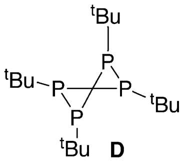
A



B



C

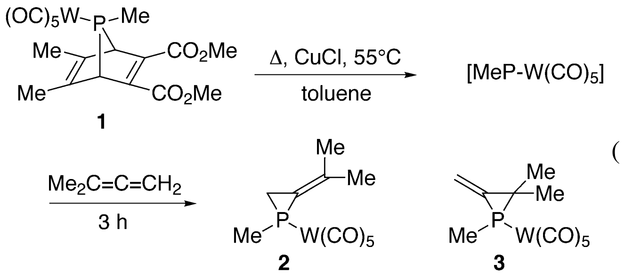


D

In such a context, we were somewhat puzzled to find a report by Lammertsma and coworkers mentioning unsuccessful attempts to prepare 1,4-diphosphaspiropentanes from alkylidenephosphiranes.[7] We thus decided to reinvestigate this problem.

2. Results and discussion

The carbene-like chemistry of transient terminal phosphinidene complexes [RP-M(CO)$_5$] is well established.[8] The attempts of Lammertsma were based on the reaction of [PhP-W(CO)$_5$] with allenes and cumulenes. In all cases, the reaction stopped after the first condensation leading to alkylidenephosphiranes. Suspecting some kind of steric problems, we decided to investigate the reaction of the less bulky [MeP-W(CO)$_5$] with allenes. The appropriate 7-phosphanorbornadiene precursor (**1**) was thus allowed to react with an excess of 3-methyl-1,2-butadiene (Eq. (1)):

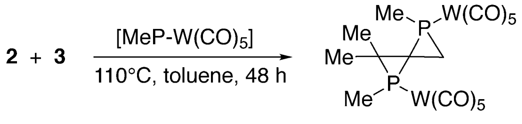


(**2**:**3** ratio 58:42)

(1)

The two alkylidenephosphiranes were separated by recrystallization. In the ^{1}H NMR spectra, the two methyl carbon substituents appear as singlets in **2**, whereas they are coupled to ^{31}P in **3**. It must be recalled that [PhP-W(CO)$_5$] exclusively cycloadds onto the unsubstituted C═C double bond of this allene.[9] This convincingly demonstrates that [MeP-W(CO)$_5$] is less sensitive to steric hindrance than its phenyl analogue.

Encouraged by this favorable observation, we then allowed the precursor (**1**) to react with the crude mixture (**2**)+(**3**) under more drastic conditions (Eq. (2)):



4a,b (55%)

(2)

The desired 1,4-diphosphaspiropentane was obtained as a mixture of only two among the three possible isomers.[10] These two isomers can be separated by chromatography and distinguished by their ^{31}P NMR data: **4a** (eluted first): δ ^{31}P -152.3 and -122.2; **4b**: δ ^{31}P -145.4 and -130.6. The

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Keywords: allenes; phosphiranes; phosphinidenes; spiro compounds.

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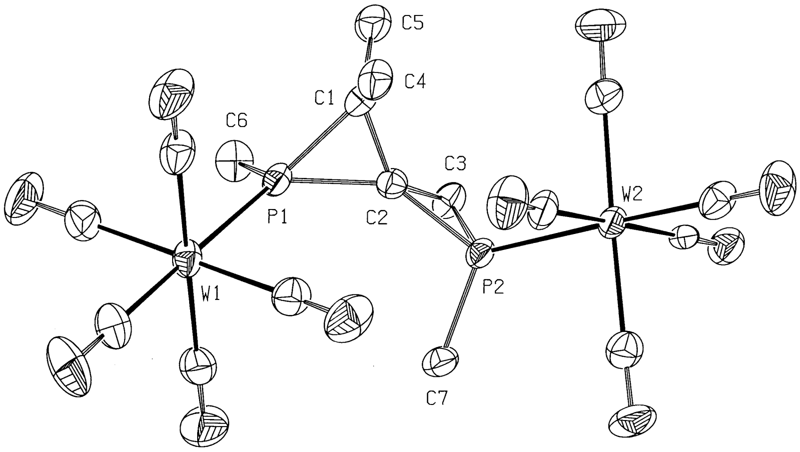

Figure 1. ORTEP drawing of one molecule of **4b**. Selected bond distances (Â) and angles (°): $P_1{-}C_1$ 1.858(7), $P_1{-}C_2$ 1.809(6), $P_1{-}C_6$ 1.833(6), $P_1{-}W_1$ 2.483(2), $C_1{-}C_2$ 1.502(8), $P_2{-}C_2$ 1.805(6), $P_2{-}C_3$ 1.836(6), $C_2{-}C_3$ 1.521(8), $P_2{-}C_7$ 1.809(6), $P_2{-}W_2$ 2.496(2); $C_1{-}P_1{-}C_2$ 48.4(3), $C_1{-}P_1{-}W_1$ 128.5(2), $C_1{-}P_1{-}C_6$ 108.4(3), $C_2{-}P_1{-}W_1$ 127.2(2), $C_2{-}P_1{-}C_6$ 106.5(3), $P_1{-}C_1{-}C_2$ 64.1(3), $C_1{-}C_2{-}P_1$ 67.5(3), $C_1{-}C_2{-}P_2$ 136.0(4), $C_1{-}C_2{-}C_3$ 127.6(6), $P_1{-}C_2{-}C_3$ 131.4(4), $P_1{-}C_2{-}P_2$ 140.1(4), $P_2{-}C_2{-}C_3$ 66.4(3), $P_2{-}C_3{-}C_2$ 64.3(3), $C_2{-}P_2{-}C_3$ 49.4(3), $C_2{-}P_2{-}C_7$ 107.1(3), $C_2{-}P_2{-}W_2$ 128.7(2), $C_3{-}P_2{-}C_7$ 106.0(3), $C_3{-}P_2{-}W_2$ 125.4(2).

second isomer was recrystallized in dichloromethane/petroleum ether and characterized by X-ray crystal structure analysis (Fig. 1). The angle between the planes of the two rings is normal at 89.5°. The geometry of both rings is very similar to that found in complex A (R=Ph).[3] According to the nomenclature of Gajewski and Burka,[10] the two P-W(CO)$_5$ groups adopt a *medial*, *anti* disposition which minimizes the steric repulsion. That the choice of the P-methyl group is crucial for a successful bis-condensation onto allenes is demonstrated by the fact that the replacement of P-Me by P-Ph in **2** suffices to cause the failure of the second condensation. This successful bis-condensation can be explained by both the lower steric bulk and the higher reactivity[11] of [MeP-W(CO)$_5$] in comparison with [PhP-W(CO)$_5$]. It must be also noticed that all our attempts with [MeP-Mo(CO)$_5$] have given untractable mixtures. Apparently, the thermal stability of the molybdenum complexes is somewhat lower than that of their tungsten analogues.

The relative weakness of the P–C bonds in the phosphirane ring[12] suggests that **4** will have a rich chemistry that we plan to investigate in the near future.

3. Experimental

3.1. General

All reactions were performed under an inert atmosphere (nitrogen or argon). NMR spectra were measured on a multinuclear Bruker 300 MHz spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C) or external 85% H_3PO_4(^{31}P); coupling constants are expressed in Hz. Mass spectra (Electron Impact, unless otherwise noted) were measured at 70 eV by the direct inlet method. Elemental analysis were performed at the Service de Microanalyse du CNRS, Gif sur Yvette, France.

3.1.1. [1-Methyl-2-isopropylidenephosphirane]pentacarbonyltungsten (2) and [1,3,3-trimethyl-2-methylidenephosphirane]pentacarbonyltungsten (3). A solution of the precursor **1**[13] (5 g, 8.5 mmol) and an excess of 3-methyl-1,2-butadiene (1.5 mL), CuCl (100 mg) in toluene (20 mL) was heated at 55°C for 3 h. After evaporation of the solvent, the residue was chromatographed on silica gel with hexane/CH_2Cl_2 10/0.5 as the eluent. Alkylidenephosphiranes were isolated as a mixture of **2** and **3** (oil, 2.2 g, ≃60% yield). **2** and **3** were separated by recrystallization in petroleum ether.

2. ^{31}P NMR ($CDCl_3$): δ −174.1, $^1J_{P-W}$=245.9 Hz. ^{1}H NMR ($CDCl_3$): δ 1.43 (d, $^2J_{H-P}$=7.7 Hz, P–CH_3), 1.59 (m, CH_2), 1.93 (s, CH_3), 2.0 (s, CH_3). ^{13}C NMR ($CDCl_3$): δ 12.84 (d, $^1J_{C-P}$=1.4 Hz, CH_2), 17.54 (d, $^1J_{C-P}$=9.5 Hz, P–CH_3), 22.59 (d, $^3J_{C-P}$=9.3 Hz, CH_3), 24.14 (d, $^3J_{C-P}$=6.2 Hz, CH_3), 116.48 (d, $^2J_{C-P}$=3.8 Hz, =CMe_2), 140.78 (d, $^1J_{C-P}$=3.0 Hz, =C–P), 195.28 (d, $^2J_{C-P}$=8.35 Hz, *cis*-CO), 198.00 (d, $^2J_{C-P}$=28.0 Hz, *trans*-CO). Mass (^{184}W): *m/z* 439 (M^++1H, 100%), 381 (M^+−1H−2CO, 47%), 323 (M^+−3H−4CO, 41%), 296 (M^+−2H−5CO, 63%).

3. ^{31}P NMR ($CDCl_3$): δ −150.8, $^1J_{P-W}$=244.0 Hz. ^{1}H NMR ($CDCl_3$): δ 1.36 (d, $^3J_{H-P}$=19.3 Hz, CH_3), 1.50 (d, $^3J_{H-P}$=12.7 Hz, CH_3), 1.52 (d, $^2J_{H-P}$=7.1 Hz, P–CH_3), 5.98 (d, $^3J_{H-P}$=12.5 Hz, HC=), 6.06 (d, $^3J_{H-P}$=28.4 Hz, HC=). ^{13}C NMR ($CDCl_3$): δ 15.25 (d, $^1J_{C-P}$=10.6 Hz, P–CH_3), 21.54 (d, $^2J_{C-P}$=2.7 Hz, CH_3), 27.0 (ring C), 27.26 (s, CH_3), 117.18 (s, =CH_2), 145.29 (d, $^1J_{C-P}$=4.4 Hz, =C–P), 196.24 (d, $^2J_{C-P}$=8.0 Hz, *cis*-CO), 198.47 (d, $^2J_{C-P}$=28.4 Hz, *trans*-CO). Mass (^{184}W): *m/z* 439 (M^++1H, 57%), 381 (M^+−1H−2CO, 37%), 354 (M^+−3CO, 48%), 324 (M^+−2H−4CO, 68%), 296 (M^+−2H−5CO, 100%).

3.1.2. [1,2,2,4-Tetramethyl-1,4-diphosphaspiropentane]decacarbonylditungstens 4a,b. A solution of the mixture **2**+**3** (1.5 g, 3.4 mmol), of **1** (1.2 equiv.) in toluene (10 mL) was heated at 110°C for 48 h. After evaporation, the residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 4/1 as the eluent (55% yield).

The first fraction was **2**+**3** (300 mg). The second fraction was **4a** (350 mg). ^{31}P NMR ($CDCl_3$): δ −152.29,

$^1J_{P-W}$=256.3 Hz; −122.22, $^1J_{P-W}$=258.4 Hz. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, $^3J_{H-P}$=18.4 Hz, CH_3), 1.42 (m, CH_2), 1.63 (d, J_{H-P}=7.0 Hz, CH_3), 1.64 (d, J_{H-P}=10.3 Hz, CH_3), 1.65 (d, J_{H-P}=8.9 Hz, CH_3), 1.71 (m, CH_2). ^{13}C NMR ($CDCl_3$): δ 14.64 (d, $^1J_{C-P}$=11.6 Hz, P–CH_3), 18.94 (d, $^1J_{C-P}$=15.0 Hz, P–CH_3), 18.19 (d, $^1J_{C-P}$=6.1 Hz, ring CH_2), 20.37 (s, CH_3), 22.98 (d, $^2J_{C-P}$=5.1 Hz, CH_3), 29.44 (d, $^1J_{C-P}$=8.0 Hz, CMe_2), 36.56 (dd, $^1J_{C-P}$=21.6, 18.1 Hz, spiro C), 195.66 (d, $^2J_{C-P}$=7.9 Hz, *cis*-CO), 195.81 (d, $^2J_{C-P}$=8.0 Hz, *cis*-CO), 197.0 (d, $^2J_{C-P}$=30.3 Hz, *trans*-CO). Mass (^{184}W): *m/z* 809 (M^++1H, 24%), 726 (M^++2H−3CO, 81%), 670 (M^++2H−5CO, 53%), 642 (M^++2H−6CO, 100%). Anal. calcd for $C_{17}H_{14}O_{10}P_2W_2$: C, 25.27; H, 1.75. Found: C, 25.27; H, 1.51.

The third fraction was a mixture of **4a** and **4b** (600 mg). The fourth fraction was **4b** (250 mg). ^{31}P NMR ($CDCl_3$): δ −145.44, $^1J_{P-W}$=257.9 Hz; −130.56, $^1J_{P-W}$=259.9 Hz. ^{1}H NMR ($CDCl_3$): δ 1.35 (d, $^3J_{H-P}$=11.9 Hz, CH_3), 1.50 (m, CH_2), 1.55 (m, 2CH_3), 1.69 (d, $^2J_{H-P}$=6.6 Hz, P–CH_3). ^{13}C NMR ($CDCl_3$): δ 14.54 (d, $^1J_{C-P}$=8.5 Hz, P–CH_3), 15.63 (s, CH_3), 19.07 (s, CH_2), 19.62 (d, $^1J_{C-P}$=14.1 Hz, P–CH_3), 26.00 (s, CH_3), 30.43 (d, $^1J_{C-P}$=7.6 Hz, CMe_2), 36.45 (dd, $^1J_{C-P}$=26.3, 20.8 Hz, spiro C), 195.37 (d, $^1J_{C-P}$=8.0 Hz, *cis*-CO), 195.73 (d, $^1J_{C-P}$=7.9 Hz, *cis*-CO), 196.77 (d, $^1J_{C-P}$=20.7 Hz, *trans*-CO), 197.18 (d, $^1J_{C-P}$=20.9 Hz, *trans*-CO). Mass (^{184}W): *m/z* 809 (M^++1H, 15%), 726 (M^++2H−3CO, 96%), 670 (M^++2H−5CO, 58%), 640 (M^+−6CO, 100%), 612 (M^+−7CO, 79%). Anal. calcd for $C_{17}H_{14}O_{10}P_2W_2$: C, 25.27; H, 1.75. Found: C, 25.53; H, 1.52. Single crystals of **4b** were obtained by recrystallization in CH_2Cl_2/petroleum ether.

3.2. X-ray crystal structure analysis of 4b

4b, $C_{17}H_{14}O_{10}P_2W_2$: M=807.92 g mol^{-1}; monoclinic; space group $P2_1/c$; a=30.7754(3) Å, b=9.7907(1) Å, c=16.3111(1) Å, β=104.2170(10)°, V=4764.21(7) Å^3; Z=8; D=2.253 g cm^{-3}; μ=9.832 cm^{-1}; F(000)=2992. Crystal dimensions 0.26×0.16×0.03 mm. Total reflections collected 30775 and 10011 with $I>2\sigma(I)$. Goodness of fit on F2 1.029; $R(I>2\sigma(I))$=0.0426, $wR2$=0.1161 (all data); maximum/minimum residual density 2.778(0.310)/−3.353(0.310) e Å^{-3}. Data were collected on a KappaCCD diffractometer at 150.0(10) K with Mo Kα radiation (λ=0.71073 Å). Full details of the crystallographic analysis are described in the Supporting Information.

3.3. Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number CCDC 177641.

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