Notes

Simple Access to a 2,4-Diphosphabicyclobutane

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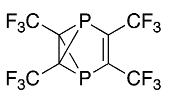
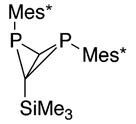
Summary: A 2-(phosphirenyl)ethylphosphinidene [W(CO)$_5$]$_2$ complex undergoes an original phosphinidene + phosphirene self-condensation to yield the tricyclic compound **5** *with an unusual 2,4-diphosphabicyclobutane "butterfly" structure. The product has been characterized by X-ray crystal structure analysis and its formation studied from a theoretical standpoint at the B3LYP/6-311+G(d,p) level.*

Introduction

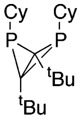
The long-known bicyclobutane structure has been of special interest due to the similarity between the chemical reactivity of its central bond and that of a π-bond in alkenes. This similarity is underlined by the recent development of original polycyclobutane polymers obtained by radical or anionic polymerization of bicyclobutanes.[1] In view of the fruitful analogy which exists between phosphorus and carbon chemistry,[2] it was obviously tempting to synthesize and study phospha-substituted bicyclobutanes. Adequate routes are known for the synthesis of 1,3-diphospha structures.[3] In contrast, as far as we know, only three 2,4-diphosphabicyclobutane derivatives, **1a**−**c**, have been previously reported and their syntheses involve nontrivial transformations.[4] We wish to describe in this paper a simpler access to a 2,4-diphosphabicyclobutane and its characterization by X-ray crystal structure analysis.



1a



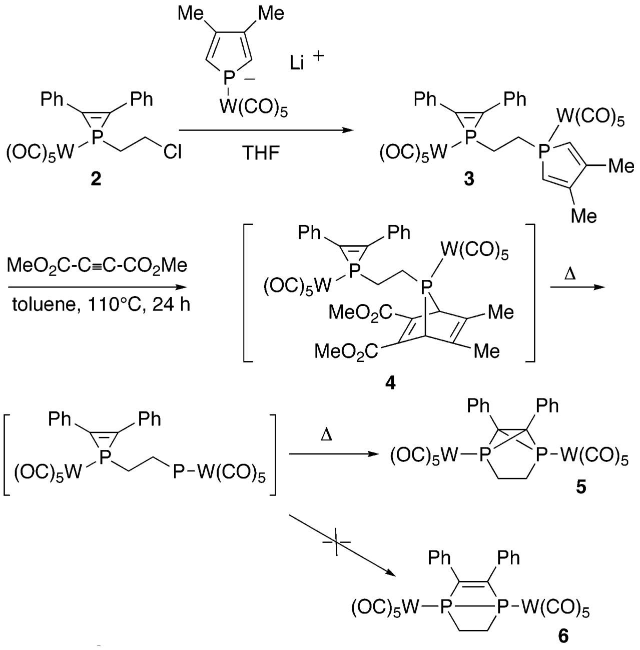
1b (Mes*= 2,4,6-*t*-Bu$_3$ C$_6$H$_2$)



1c

Results and Discussion

Scheme 1



An obvious approach to 2,4-diphosphabicyclobutanes involves the cycloaddition of a phosphinidene unit onto the C=C double bond of a phosphirene ring. Such an approach has never been described in the literature, and in our laboratory and others, numerous attempts to condense a terminal phosphinidene complex with a phosphirene complex have either failed or led to an insertion into one of the P−C ring bonds to give a diphosphetene derivative.[5] A related chemistry has also been developed with phosphirene imines and iminophosphanes.[6] In the course of a program aiming at the synthesis of new chelating ligands using the versatile chemistry of electrophilic terminal phosphinidene complexes,[7] we have discovered the first case where a phosphirene + phosphinidene condensation leads to a

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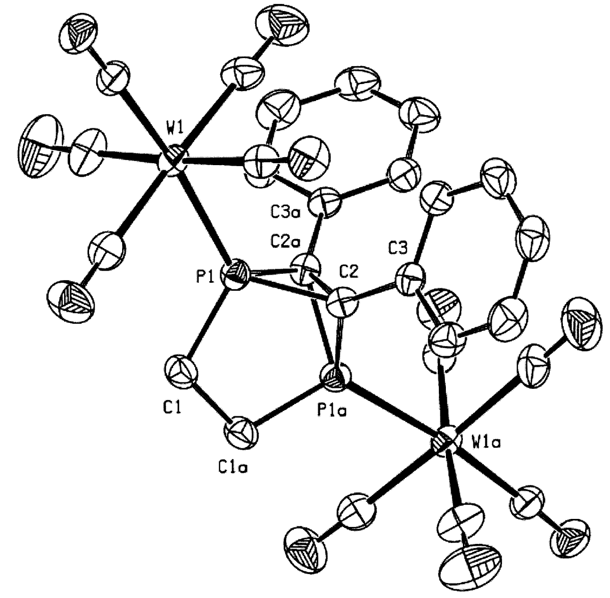


Figure 1. Crystal structure of complex **5**. Significant bond distances (Å) and angles (deg): W(1)−P(1) = 2.4541(8), P(1)−C(2) = 1.821(3), P(1)−C(2a) = 1.802(3), P(1)−C(1) = 1.843(3), C(1)−C(1a) = 1.532(6), C(2)−C(2a) = 1.570(6); C(2)−P(1)−C(2a) = 51.3(2), C(2)−P(1)−C(1) = 103.7(1), C(2)−P(1)−W(1) = 127.9(1), P(1)−C(2)−P(1a) = 97.8(2), C(1)−P(1)−W(1) = 122.5(1); folding angle P(1)C(2)C(2a)/P(1a)C(2)C(2a) 113.44.

Table 1. Geometry and Energy of 2,4-Diphosphabicyclobutanes

	product			
	A	B	C	D
P−C (Å)	1.836	1.841−1.850	1.861	1.832[b]
C−C (Å)	1.507	1.484	1.465	1.516[b]
P···P (Å)	2.996	2.902	2.856	2.882
folding (deg)	126.9	118.4	113.1	119.6
energy (au)[a]	−761.265 872	−761.265 990	−761.262 330	−838.690 238

[a] ZPE correction included. [b] P-CH_2 1.878 Å, H_2C-CH_2 1.541 Å.

2,4-diphosphabicyclobutane structure. Our starting point has been the 1-(β-chloroethyl)phosphirene complex **2**.[8] The lithium 3,4-dimethylphospholide−pentacarbonyltungsten complex[9] reacts with **2** as a weak base and a good nucleophile to give the substitution product **3**. Complex **3** then reacts with dimethyl acetylenedicarboxylate via its phosphole dienic system to give the intermediate 7-phosphanorbornadiene complex **4**, which collapses in situ to give the final product **5** (Scheme 1).

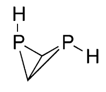
Product **5** displays a ^{31}P resonance at −6.9 ppm, and thus, we initially believed that it had the expected bicyclic structure **6**. However, its ^{13}C spectrum shows two sp^3-carbon resonances at 34.01 (s, CH_2) and 33.35 ppm (pseudo-triplet, *C*−Ph), and a X-ray analysis demonstrated that it has in fact the tricyclic “butterfly” structure **5** (Figure 1). This structure is characterized by a long C−C bridge bond at 1.570(6) Å and a high folding (as measured by the angle between the two PCC planes) around that bond at 113.4°. Otherwise, the structure of the phosphirane rings appears to be normal. Finally, the endo,endo configuration of the 2,4-diphosphabicyclobutane moiety explains the abnormal ^{31}P chemical shift, as shown previously.[4c]

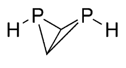
Table 2. Geometry and Energy of 1,2-Diphosphetenes

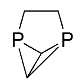
	product		
	E	F	G
P−C (Å)	1.846	1.851	1.845−1.926
C−C (Å)	1.341	1.338	1.342−1.536
P−P (Å)	2.289	2.313	2.316
folding (deg)			100.8
energy (au)	−761.296253	−761.293270	−838.688407

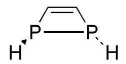
At this point, we were wondering why, in this precise case, the phosphinidene + phosphirene condensation leads to a butterfly structure **5** instead of the more conventional 1,2-diphosphetene structure **6**. The study was carried out at the B3LYP/6-311+G(d,p) level[10] on the noncomplexed parent structures A−G. The results

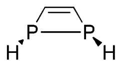

A (*endo,endo*)

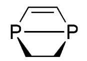

B (*endo,exo*)


C (*exo,exo*)


D


E (*trans*)


F (*cis*)


G

are summarized in Tables 1 and 2 (energy and geometry). Compound B has already been studied at the MP2/6-31G* level, and our geometrical parameters are very similar to those reported for **1b**[4b] and those found in the earlier theoretical study.[11] The endo,exo (B) and endo,endo (A) 2,4-diphosphabicyclobutane isomers are almost isoenergetic, while the exo,exo isomer (C) is the least stable by 2.2 kcal mol^{-1}. In the same vein, the trans form (E) is favored over the *cis*-diphosphetene (F) by 1.9 kcal mol^{-1}.[12] This result agrees nicely with the slow isomerization of the *cis*-diphosphetene into the corresponding *trans*-diphosphetene upon heating.[13] However, the most significant result is that both *cis*- and *trans*-1,2-diphosphetenes are substantially more stable than the 2,4-diphosphabicyclobutanes. Isomer B is higher in energy than E and F by 19.0 and 17.1 kcal mol^{-1}, respectively. This explains why the isolation of a 2,4-diphosphabicyclobutane is normally difficult. In contrast, the introduction of the P−CH_2CH_2−P bridge leads to an inversion of stability. The tricyclic structure D becomes slightly more stable than the bicyclic structure G by 1.15 kcal mol^{-1}. Even though the experiments

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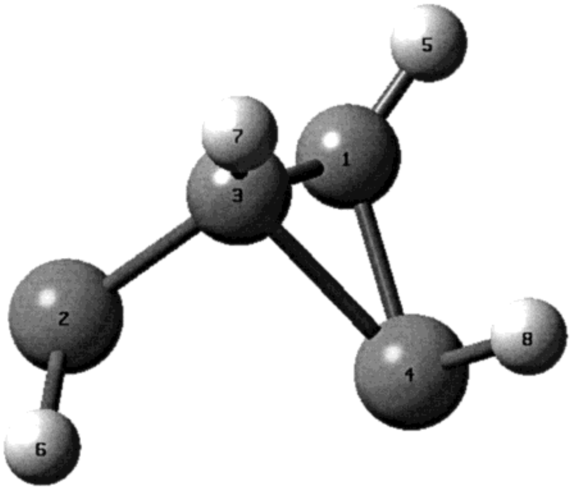

Figure 2. Computed structure of the (B−F) transition state. Significant bond distances (Å) and angles (deg): P(2)−C(1) = 2.511, P(2)···P(4) = 2.780, P(2)−C(3) = 1.823, P(4)−C(3) = 2.033, P(4)−C(1) = 1.804, C(1)−C(3) = 1.406; P(2)−C(3)−P(4) = 92.1, P(2)−C(3)−C(1) = 101.3, P(2)−C(3)−C(1)−P(4) = −81.9, H(6)−P(2)···P(4)−H(8) = −66.7.

have been carried out on the $W(CO)_5$-complexed species, the trend revealed by the calculations is consistent with the successful isolation of complex **5**.

We were eager to shed some light on a curious feature of the insertion of phosphinidenes into phosphirenes. In the complexed series, it gives exclusively or predominantly the *cis*-diphosphetenes.[5] The proposed explanation involved the attack of the phosphinidene at the C═C double bond of the phosphirene from the less hindered side of the ring opposite to the P substituent. This type of condensation corresponds to a endo,exo stereochemistry, as in B. Thus, we decided to investigate the potential rearrangement of B into F. The QST2 procedure yielded a transition state (B−F) (one imaginary frequency), which is depicted in Figure 2. The optimized structure of this transition state is remarkably similar to that of the transient geometry proposed for the formation of *cis*-1,2-diphosphetenes in our earlier paper.[5] One of the P−C bonds of B is broken (P···C separation 2.511 Å), while the other P−C bond into which the phosphinidene will insert is already elongated at 2.037 Å. At 1.406 Å, the C−C bond lies halfway between a single and a double bond, and the P···P separation has decreased from 2.902 in B to 2.780 Å in the TS. The folding is reduced from 118.4° in B to 81.9° in the TS. Finally, the (B−F) transition state lies 46.3 kcal mol^{-1} above B, which shows that the reaction is not easy under purely thermal conditions. It must be stressed here that bicyclobutanes are known to rearrange thermally to give the corresponding butadienes via one disrotatory and one conrotatory opening of the two three-membered rings.[14] Cyclobutenes are not intermediates in this rearrangement. In the 2,4-diphosphabicyclobutane series, however, the 1,4-diphosphabutadienes are certainly destabilized by comparison with 1,2-diphosphetenes, except when very bulky substituents are bonded to the two phosphorus atoms.[4b] In any event, these results give some credence to the mechanism of formation of *cis*-1,2-diphosphetenes, as proposed in our earlier work. It must be stressed, however, that the actual reaction takes place on the $W(CO)_5$-complexed species under mild conditions (60 °C) with a catalyst (CuCl) and a alkynyl activating group on C_3. The role of the activating group is to weaken the P_4-C_3 bond as already established.[5] We think that the role of CuCl is to facilitate the cleavage of the P_2-C_1 bond by inserting into this bond. The insertion of d^{10} metallic centers into the P−C ring bonds of phosphiranes is indeed a well-known process.[15]

Experimental Section

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 MHz for ^{1}H, 75.47 MHz 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_3PO_4 (^{31}P). Elemental analyses were performed by the Service de microanalyse du CNRS, Gif-sur-Yvette, France.

[1-(2-Chloroethyl)-2,3-diphenylphosphirene]pentacarbonyltungsten (2). [1-(2-Chloroethyl)-3,4-dimethylphosphole]-pentacarbonyltungsten[8] (6.0 g, 12 mmol), dimethyl acetylenedicarboxylate (3.0 mL, 24 mmol), and diphenylacetylene (5 g, 28 mmol) were dissolved in toluene (35 mL) and heated to 110 °C for 48 h. The solvent was then removed under reduced pressure and the residue separated by flash chromatography (2% diethyl ether in hexane). Recrystallization from dichloromethane/hexane gave the product **2** as pale yellow crystals (3.4 g, 47%). ^{31}P NMR ($CDCl_3$): δ −161.98 ppm (d, $^1J_{P-W}$ = 265.3 Hz). ^{1}H NMR ($CDCl_3$): δ 2.33 (2H, t, J = 7.3 Hz, $P-CH_2$), 3.35 (2H, dt, $^3J_{P-H}$ = 13.3, J = 7.3 Hz, CH_2Cl), 7.43−7.53 (6H, m, Ph), 7.84 (4H, d, J = 6.9 Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 40.57 (d, $^1J_{C-P}$ = 1.7 Hz, $P-CH_2$), 40.98 (d, $^2J_{C-P}$ = 7.0 Hz, CH_2-Cl), 127.95 (d, $^1J_{C-P}$ = 6.8 Hz, P−C), 128.94 (d, J_{C-P} = 11.0 Hz, Ph), 129.79 (s, Ph), 130.62 (d, J_{C-P} = 5.3 Hz, Ph), 131.25 (s, Ph), 196.15 (dt, $^1J_{C-W}$ = 108.7 Hz, $^2J_{C-P}$ = 8.3 Hz, *cis*-CO), 198.05 (d, $^2J_{C-P}$ = 30.9 Hz, *trans*-CO) MS (EI; *m/z* (ion, relative abundance)): 596 (M^+, 87), 512 ($M^+ - (CO)_3$, 46), 484 ($M^+ - (CO)_4$, 93), 748 ($M^+ - (CO)_5 + 1$, 100). Anal. Calcd for $C_{21}H_{14}ClO_5PW$: C, 42.48; H, 2.37. Found: C, 42.42; H, 2.31.

[1-(2-(2,3-Diphenylphosphiren-1-yl)ethyl)-3,4-dimethylphosphole]bis(pentacarbonyltungsten) (3). Lithium 3,4-dimethylphospholide−pentacarbonyltungsten[9] (2.2 mmol) in THF (5 mL) was cooled to 0 °C, and [1-(2-chloroethyl)-2,3-diphenylphosphirene]pentacarbonyltungsten (**2**; 1.25 g, 2.1 mmol) was added. The solution was allowed to warm to room temperature and then the solvent was removed under reduced pressure. The resulting residue was separated by flash chromatography (3% diethyl ether in hexane), and recrystallization from dichloromethane/hexane gave the product **3** as pale yellow crystals (0.6 g, 28%). ^{31}P NMR ($CDCl_3$): δ −153.41 ppm (dd, $^3J_{P-P}$ = 25.2 Hz, $^1J_{P-W}$ = 262.8 Hz), 6.80 ppm (dt, $^3J_{P-P}$ = 25.2 Hz, $^1J_{P-W}$ = 211.7 Hz). ^{1}H NMR ($CDCl_3$): δ 1.97 (4H, br s, $P-CH_2$), 2.23 (6H, s, Me), 6.24 (2H, d, $^2J_{P-H}$ = 37.2 Hz, 2 × CH−P), 7.4−7.7 (6H, m, Ph), 7.97 (4H, d, J = 8.0 Hz, Ph). ^{13}C NMR ($CDCl_3$): δ 17.73 (d, $^3J_{C-P}$ = 11.1 Hz, Me), 27.03 (dd, $^2J_{C-P}$ = 3.8 Hz, $^1J_{C-P}$ = 19.6 Hz, $P-CH_2$), 33.88 (dd, $^2J_{C-P}$ = 4.5 Hz, $^1J_{C-P}$ = 8.7 Hz, $P-CH_2$), 127.82 (d, $^1J_{C-P}$ = 40.8 Hz, P−CH), 128.16 (s, Ph), 129.49 (d, $^1J_{C-P}$ = 11.5 Hz, Ph−C), 129.86 (s, Ph), 130.52 (d, J_{C-P} = 5.0 Hz, Ph), 131.28 (s, Ph), 152.81 (d, $^2J_{C-P}$ = 5.8 Hz, Me−C), 196.17 (m, *cis*-CO), 196.26 (m, *trans*-CO). MS (EI; *m/z* (ion, relative abundance)): 996 (M^+, 4), 828 ($M^+ - (CO)_6$, 9), 772 ($M^+ - (CO)_8$, 34), 744 ($M^+ - (CO)_9$, 100), 716 ($M^+ - (CO)_{10}$, 40), 532 ($M^+ - W(CO)_{10}$, 19). Anal. Calcd for $C_{32}H_{22}O_{10}P_2W_2$: C, 38.58; H, 2.23. Found C, 38.45; H, 2.25.

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[1,6-Diphenyl-2,5-diphosphatricyclo(3.1.0.0^{2,6})hexane]bis(pentacarbonyltungsten) (5). [1-(2-(2,3-Diphenylphosphiren-1-yl)ethyl)-3,4-dimethylphosphole]bis(pentacarbonyltungsten) (**3**; 0.55 g, 0.55 mmol) and dimethyl acetylenedicarboxylate (0.27 mL, 2.2 mmol) were dissolved in toluene (35 mL) and heated to 110 °C for 24 h. The solution was then cooled to room temperature, and the solvent was removed under vacuum. The residue was extracted with hexane (2 × 8 mL), and the combined extracts were filtered, concentrated to approximately 5 mL under vacuum, and left to stand under nitrogen, whereupon the product **5** precipitated as colorless crystals (60 mg, 12%). ^{31}P NMR (CDCl$_3$): δ −6.93 ppm (dd, $^3J_{\mathrm{P-W}} = 31.2$ Hz, $^1J_{\mathrm{P-W}} = 235.3$ Hz). ^{1}H NMR (CDCl$_3$): δ 2.20 (4H, t, $J = 4.4$ Hz, CH$_2$), 7.2−7.3 (10H, m, Ph). ^{13}C NMR (CDCl$_3$): δ 33.35 (pseudo-t, Ph−C), 34.01 (s, CH$_2$), 128.51 (s, Ph), 128.69 (t, $J_{\mathrm{C-P}} = 10.9$ Hz, Ph), 129.22 (s, Ph), 131.47 (t, $J_{\mathrm{C-P}} = 7.3$ Hz, Ph), 194.11 (m, *cis*-CO), 196.2 (m, *trans*-CO). MS (EI; *m*/*z* (ion, relative abundance)): 916 (M$^+$, 39), 805 (M$^+$ − (CO)$_4$ + 1, 76), 776 (M$^+$ − (CO)$_5$, 55), 748 (M$^+$ − (CO)$_6$, 54), 720 (M$^+$ − (CO)$_7$, 100), 692 (M$^+$ − (CO)$_8$, 47), 636 (M$^+$ − (CO)$_{10}$, 84), 451 (M$^+$ − W(CO)$_{10}$ − 1, 63), 268 (M$^+$ − W$_2$(CO)$_6$, 36). Anal. Calcd for $C_{26}H_{14}O_{10}P_2W_2$: C, 34.09; H, 1.54. Found: C, 34.14; H, 1.57.

Intermediate Compound 4 (Not Isolated). ^{31}P NMR (toluene): δ −152.62 (dd, $^3J_{\mathrm{P-P}} = 19.9$ Hz, $^1J_{\mathrm{P-W}} = 261.7$ Hz), 212.63 (dt, $^3J_{\mathrm{P-P}} = 19.0$ Hz, $^1J_{\mathrm{P-W}} = 236.6$ Hz).

Crystallographic Data for 5: $C_{26}H_{14}O_{10}P_2W_2$: M_r = 916.01; orthorhombic; space group *Pbcn*; $a = 10.450(1)$ Å, $b = 15.079(10)$ Å, $c = 18.567(1)$ Å, $V = 2925.7(4)$Å^3; $Z = 4$; $D = 2.080$ g cm^{-3}; $\mu = 8.019$ cm^{-1}; $F(000) = 1712$; crystal dimensions 0.20 × 0.20 × 0.20 mm; 17 413 total reflections collected and 3412 with $I > 2\sigma(I)$; goodness of fit on F^2 1.056; R1 = 0.0285 ($I > 2\sigma(I)$), wR2 = 0.0814 (all data); maximum/minimum residual density 2.522(0.147)/−1.538(0.147) e Å^3. Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Full details of the crystallographic analysis are described in the Supporting Information.

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Supporting Information Available: Tables giving crystallographic data for **5** and *Z* matrixes for A−G and the (B−F) transition state. This material is available free of charge via the Internet at http://pubs.acs.org.

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