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Synthesis and Structure of 1,2-Diphosphacyclopentenes

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ABSTRACT

Treatment of titanacyclobutenes with two equivalents of dichlorophenylphosphine affords diphosphacyclopentenes, two examples of which were structurally characterized by single-crystal X-ray diffraction analysis. The analogous reaction of a titanacyclobutene with dichlorophenylstibine affords the corresponding distibacyclopentene as well as a stibacyclobutene.

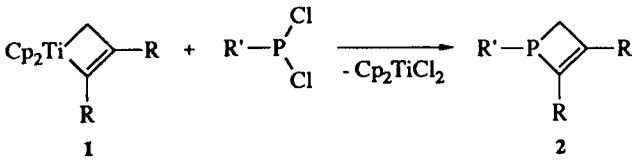
INTRODUCTION

Phosphorus heterocycles continue to attract wide-ranging interest, with studies focusing on unusual structural and conformational effects imparted by the introduction of phosphorus into cyclic structures, potential aromaticity involving the phosphorus lone pair, and unusual reactivity highlighting a few of the significant differences between phosphorus heterocycles and their nitrogen-containing or all-carbon analogs [1]. Small-ring phosphorus heterocycles remain rather scarce, despite the fact that a growing body of literature evidence suggests them to display a unique and diverse reaction chemistry.

In the course of our studies of the synthesis of 1,2-dihydrophosphetes (phosphacyclobutenes) via transmetalation reactions of titanacyclobutenes [2–4], we have discovered and characterized several members of an uncommon and only very recently reported [5] class of small-ring phosphorus heterocycles, the 1,2-diphosphacyclopentenes. Herein we report the synthesis, physical and spectroscopic characterization, and X-ray structural analysis of two simple members of this unusual class of heterocycles, as well as the synthesis of two antimony analogs of the phosphorus heterocycles, a stibacyclobutene and a 1,2-distibacyclopentene.

RESULTS AND DISCUSSION

As we have previously reported [2], treatment of 1,1-bis(cyclopentadienyl)-2,3-disubstituted-1-titanacyclobut-2-enes (1) with one equivalent of various dichlorophosphines affords the corresponding 1-phosphacyclobut-2-enes (1,2-dihydrophosphetes) (2) in moderate to good yield.



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However, when 1,1-bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene (**1a**) is treated with two equivalents of dichlorophenylphosphine, a product (**3a**) is obtained (in up to 27% yield) that by mass spectral analysis has clearly incorporated two PhP units.

This article is dedicated to Louis Quin, an outstanding and inspirational phosphorus chemist.

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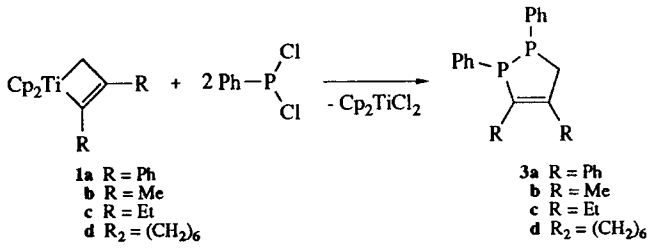


^{31}P-NMR spectroscopy clearly indicates the presence of two inequivalent phosphorus nuclei, with the ca. 220 Hz coupling constant consistent with the presence of a direct P–P bond. The chemically inequivalent hydrogens of the methylene group in **3a** appear as well-resolved, highly characteristic multiplets, one an upfield doublet of pseudotriplets due to coupling to the geminal hydrogen ($^2J_{HH} \sim 18$ Hz) and coincidentally equivalent coupling to the two phosphorus centers ($^2J_{PH} \sim {}^3J_{PH} \sim 3$ Hz), the other a downfield pseudotriplet due to coincidentally equivalent coupling to the geminal hydrogen and one phosphorus ($^2J_{HH} \sim {}^2J_{PH} \sim 18$ Hz) and no observable coupling to the second phosphorus. The large differences in $^2J_{PH}$ and $^3J_{PH}$ for the two methylene hydrogens are noteworthy but not surprising given both similar coupling differences seen in the 1,2-dihydrophosphetes [2] and the well-known, often dramatic stereospecificity of ^{31}P-element coupling [6]. Only a single $^1J_{PC}$ (ca. 25 Hz) is resolved in the ^{13}C-NMR spectrum for the methylene group of **3a**. Although considerable phosphorus coupling, perhaps holding the key to revealing the stereochemistry of **3a**, is evident in the remainder of the ^{13}C spectrum, the spectrum is sufficiently complex to preclude unambiguous assignment of resonances and thus leaves stereochemical issues unresolved. Single-crystal X-ray diffraction analysis, however, quickly demonstrated the 1,2-*trans*-diphenyl stereochemistry and also confirmed the formulation of **3a** as a diphosphacyclopentene (Figure 1).

The diphosphacyclopentene ring is nearly planar, with the methylene group only slightly displaced from the plane defined by the remaining ring atoms [e.g., the P(2)–C(3)–C(2)–C(1) torsion angle is −5.4(4)°]. Bond lengths and angles (Tables 1 and 2) are largely within the anticipated ranges. Constraints imposed by the five-membered ring are revealed by comparatively slight reductions in the intraring bond angles at each phosphorus atom (ca. 94°) from that expected in unstrained systems and by distortion of the bond angle at the saturated carbon of the ring (113.5°). The corresponding 1,2-dihydrophosphete, while maintaining quite similar bond lengths for comparable structural elements, displays considerably smaller intraring bond angles

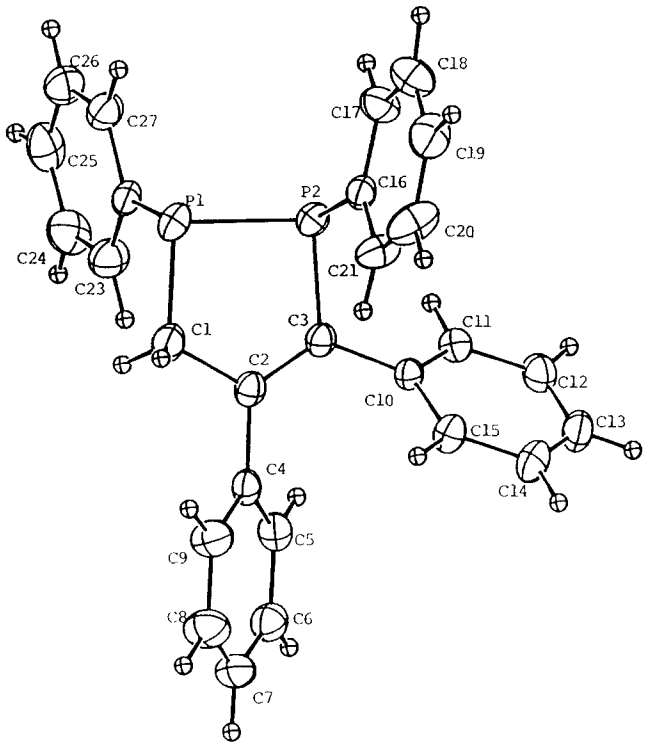


FIGURE 1 Molecular structure of tetraphenyldiphosphacyclopentene (**3a**), showing atom numbering scheme.

at phosphorus (74°) and at the saturated carbon (88°) due to the more dramatic geometric constraints of the smaller ring [4].

Dichlorophenylphosphine reacts analogously with 1,1-bis(cyclopentadienyl)-2,3-dimethyl-1-titanacyclobut-2-ene (**1b**), affording the corresponding diphosphacyclopentene (**3b**). Mass and NMR spectral analysis again were consistent with this formulation; as for **3a**, the magnitude of $^1J_{PP}$, $^2J_{PC}$, $^2J_{PH}$, and $^3J_{PH}$ and the coupling patterns displayed by the geminal hydrogens of the ring methylene group were particularly diagnostic. As for the tetraphenyl deriv-

TABLE 1 Key Bond Lengths (Å) in Tetraphenyldiphosphacyclopentene (**3a**) and Dimethyldiphenyldiphosphacyclopentene (**3b**)

Bond	**3a**	**3b**
P(1)–P(2)	2.205(1)	2.209(7)
P(1)–C(1)	1.854(3)	1.85(2)
P(1)–C(exocyclic)	1.832(3)	1.84(2)
C(1)–C(2)	1.514(4)	1.46(2)
C(2)–C(3)	1.342(3)	1.33(2)
P(2)–C(3)	1.835(2)	1.84(2)
P(2)–C(exocyclic)	1.836(2)	1.85(2)
C(2)–C(exocyclic)	1.484(3)	1.52(2)
C(3)–C(exocyclic)	1.493(3)	1.49(2)

TABLE 2 Key Bond Angles (deg) in Tetraphenyldiphosphacyclopentene (**3a**) and Dimethyldiphenyldiphosphacyclopentene (**3b**)

Bond	**3a**	**3b**
P(1)–P(2)–C(3)	93.8 (1)	94.9 (6)
P(2)–P(1)–C(1)	94.1 (1)	91.8 (6)
P(1)–C(1)–C(2)	113.5 (2)	114.8 (13)
C(1)–C(2)–C(3)	119.1 (2)	121 (2)
C(2)–C(3)–P(2)	118.9 (2)	116 (2)
C(1)–P(1)–C(exocyclic)	103.7 (1)	103.0 (8)
P(2)–P(1)–C(exocyclic)	98.3 (1)	97.5 (6)
C(3)–P(2)–C(exocyclic)	102.1 (1)	103.1 (7)
P(1)–P(2)–C(exocyclic)	99.4 (1)	100.8 (6)
C(1)–C(2)–C(exocyclic)	116.8 (2)	114 (2)
C(3)–C(2)–C(exocyclic)	124.2 (2)	124 (2)
C(2)–C(3)–C(exocyclic)	125.9 (2)	127 (2)
P(2)–C(3)–C(exocyclic)	115.1 (2)	116.7 (12)

ative, single-crystal X-ray diffraction analysis confirmed the formulation as a diphosphacyclopentene and displayed the 1,2-*trans*-diphenyl stereochemistry (Figure 2). The rather large standard deviations in bond length and angle data, resulting from low crystal quality, suggest that a detailed discussion of such data would be inappropriate. However, qualitative comparison with the tetraphenyl derivative (Tables 1 and 2) reveals a close structural analogy between the two derivatives.

Diphosphacyclopentenes are also formed in the reactions of other titanacyclobutenes with dichlorophenylphosphine, including the diethyl derivative, forming **3c**, and the 2,3-cycloocteno derivative, forming the cycloannelated diphosphacyclopentene (**3d**). In addition, treatment of 1,1-bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene (**1a**) with dichlorophenylstibine appears to form both the stibacyclobutene (**4**) and the distibacyclopentene (**5**) competitively.

As in the case of the phosphorus derivatives, it is interesting to note the downfield shift (ca. 1 ppm) and enhanced two-bond coupling constant (16.7 vs. 13.3 Hz) for the methylene protons in the ^{1}H-NMR spectrum of **5** vs. **4**, consistent with the easing of ring strain in the larger-ring derivatives [7]. In contrast to the relative air stability of the 1,2-dihydrophosphetes, the stibacyclobutene in benzene solution undergoes extensive decomposition upon exposure to air.

Given our earlier studies of the reactivity of the metal–carbon bonds in titanacyclobutenes [8], we originally speculated that the diphosphacyclopentenes were formed either through reaction of two equivalents of the dichlorophosphine with the metallacycle, followed by reductive ring closure via P–P bond formation, or through reductive coupling before the transmetalation step.

It appears most likely, however, that the diphosphacyclopentenes are simply formed through a follow-up reaction of the dihydrophosphetes with excess dichlorophenylphosphine [9]. Analogous processes are presumably responsible for formation of the distibacyclopentene, which presents an interesting structural parallel to a series of stibathiolanes prepared through related transmetalation reactions of sulfur-containing zirconium metallacycles [10].

CONCLUSION

Transmetalation reactions from transition-metal metallacycles to main group elements, already well exploited for the synthesis of larger-ring main group heterocycles, appear to serve as an equally powerful synthetic tool for the synthesis of small-ring main group heterocycles. In phosphorus and antimony-based transmetalation reactions of titanacyclobutenes, both heterocyclobutenes and diheterocyclopentenes may be formed. Solid-state structural analysis of the diphosphacyclopentenes demonstrates their diastereoselective formation, with only the *trans* isomer obtained. The transmetalation route appears to offer ready access to a series of heterocycles bearing bonds between two group 15 elements, a class of materials of on-going chemical interest.

EXPERIMENTAL

All procedures were carried out under an inert atmosphere, either in a Vacuum Atmospheres glovebox or using standard benchtop inert atmosphere techniques. Although the diphosphacyclopentenes do not appear to be air-sensitive, they were handled under an inert atmosphere as a precautionary measure. The starting materials, 1,1-bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene [11], 1,1-bis(cyclopentadienyl)-2,3-dimethyl-1-titanacyclobut-2-ene [12], 1,1-bis(cyclopentadienyl)-2,3-diethyl-1-titanacyclobut-2-ene [13], and 1,1-bis(cyclopentadienyl)-2,3-cycloocteno-1-titanacyclobut-2-ene [14] were prepared as described. Dichlorophenylphosphine was distilled under inert atmosphere, then degassed by several freeze–pump–thaw cycles. Dichlorophenylstibine was prepared from antimony trichloride and triphenylantimony as described [15]. Toluene, diethyl ether, and deuterobenzene were dried and deoxygenated over sodium/benzophenone ketyl, vacuum transferred to sealed storage flasks, and stored under an inert atmosphere. NMR spectra were recorded on a Varian QE-300 spectrometer

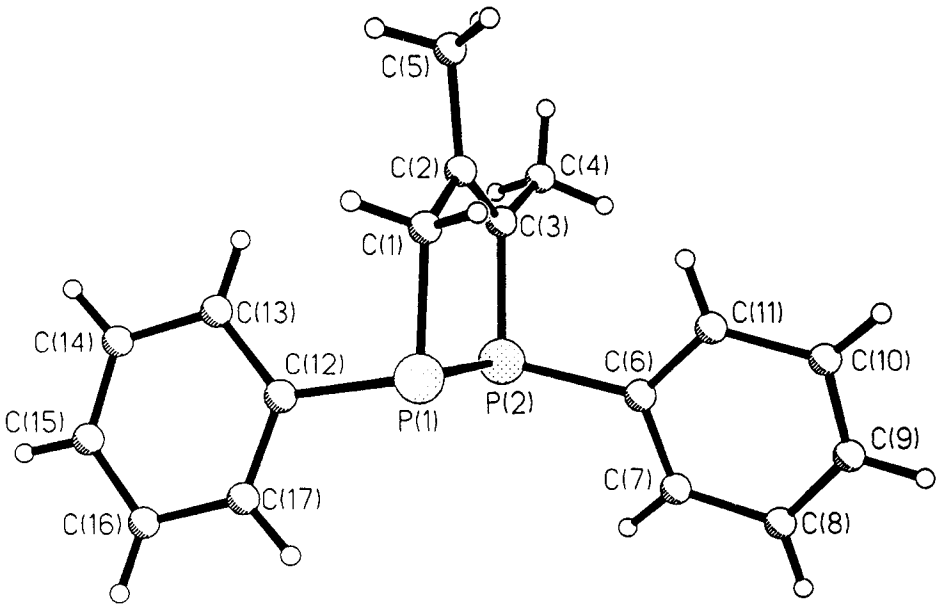
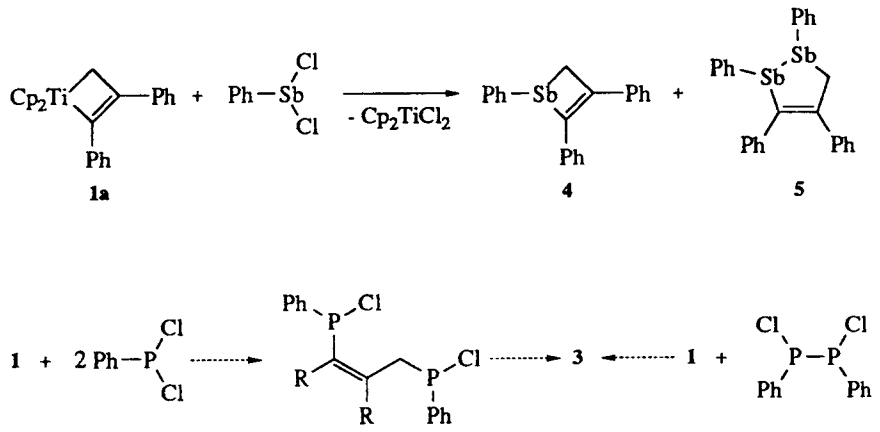


FIGURE 2 Molecular structure of dimethyldiphenyldiphosphacyclopentene (**3b**), showing atom numbering scheme.



(300 MHz for ^{1}H, 75.48 MHz for ^{13}C) or a home-built 360 MHz spectrometer (145.731 MHz for ^{31}P).

1,2,3,4-Tetraphenyl-1,2-diphosphacyclopent-3-ene. To a solution of 200 mg of 1,1-bis(cyclopentadienyl)-2,3-diphenyl-1-titanacyclobut-2-ene (0.540 mmol) in 3 mL of toluene was added 147 μL of dichlorophenylphosphine (0.194 g, 1.08 mmol), resulting in an immediate color change from dark burgundy to a lighter red and precipitation of titanocene dichloride. After having been stirred at room temperature for 1.5 hours, the solvent was removed in vacuo, affording a red residue. This material was dissolved/suspended in diethyl ether, then passed through a 10 × 1 cm column of basic alumina (Brockman Activity 1, 50–200 mesh), eluting with ca. 60 mL of diethyl ether, leaving the titanocene dichloride as a red band at the top of the column. Removal of solvent from the eluent in vacuo afforded the crude product as a slightly yellow oil. This oil was dissolved in a minimum amount of diethyl ether, and the resulting solution was cooled in a −30°C freezer for ca. 12 hours. Decantation afforded 0.060 g of the diphosphacyclopentene (27%) as an off-white crystalline solid, mp 122–126°C. IR (CCl_4): 3060 (m), 3027 (mw), 2965 (w), 1561 (m), 1495 (m), 1438 (m), 1262 (s), 1102 (ms), 1029 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.32 (d"t", 1H, $^2J_{HH} \sim 18$ Hz, $^2J_{PH} \sim {}^3J_{PH} \sim 3$ Hz), 3.87 ("t", 1H, ^{2}JHH $\sim {}^2J_{PH} \sim 18$ Hz, $^3J_{PH} \sim 0$), 6.7–7.3 (m, 17H, aromatic), 7.72 ("t", 3H, J = 7 Hz, aromatic). ^{13}C[^{1}H] NMR (C_6D_6): δ 43.3 (d, J_{PC} = 25.4 Hz, CH_2), 126.6 (s), 127.0 (s), 127.5 (s), 127.7 (s), 128.1

(s), 128.4 (s), 128.5 (d, J_{PC} = 7.3 Hz), 129.0 (s), 129.9 (d, J_{PC} = 6.1 Hz), 131.9 (d, J_{PC} = 7.3 Hz), 132.0 (s), 132.2 (s), 132.7 (dd, J_{PC} = 18.3, 6.1 Hz), 136.2 (dd, J_{PC} = 26.2, 11.6 Hz), 138.5 (d, J_{PC} = 29.3 Hz), 138.8 (d, J_{PC} = 2.4 Hz), 139.8 (d, J_{PC} = 2.5 Hz), 149.1 (dd, J_{PC} = 6.2, 3.5 Hz). ^{31}P NMR (C_6D_6): δ −30 (d, J_{PP} = 220 Hz), 31 (d, J_{PP} = 220 Hz). MS (EI): *m/z* = 408 (M^+, 100%), 331 (M–Ph, 7%), 299 (M–PhP–H, 20%), 286 (M–PhPCH$_2$, 4%), 223 ($Ph_2C_3H_2P$, 61%), 221 (78%), 216 (Ph_2P_2, 8%), 209 (33%), 191 (Ph_2C_3H, 82%), 183 (59%), 178 (Ph_2C_2, 91%), 165 (53%), 125 (18%), 115 (PhC_3H_2, 32%), 108 (PhP, 44%), 107 (PhP–H, 48%), 103 (43%), 95 (41%), 91 (57%), 85 (29%). Anal. calcd for $C_{27}H_{22}P_2$: C, 79.40; H, 5.43; P, 15.17. Found: C, 79.27; H, 5.50; P, 15.26.

3,4-Dimethyl-1,2-diphenyl-1,2-diphosphacyclopent-3-ene. This compound was prepared analogously from 105 mg of 1,1-bis(cyclopentadienyl)-2,3-dimethyl-1-titanacyclobut-2-ene (0.426 mmol) in 2 mL of toluene through the addition of 117 μL of dichlorophenylphosphine (0.154 g, 0.860 mmol). Chromatography of the crude product as described above afforded only a low yield of the purified compound due to its rather low solubility in diethyl ether, but it did allow partial characterization as well as successful crystallization (vide infra). ^{1}H NMR (C_6D_6): δ 1.56 (s, 3H, CH_3), 1.72 (d, 3H, J_{PH} = 11 Hz, CH_3), 2.74 (d″t″, 1H, $^2J_{HH} \sim 18$ Hz, $^2J_{PH} \sim {}^3J_{PH} \sim 2$ Hz), 3.15 (″t″, 1H, ^2JHH ~ $^2J_{PH} \sim 18$ Hz, $^3J_{PH} \sim 0$), 6.7–7.2 (m, 7H, aromatic), 7.5–7.8 (m, 3H, aromatic). MS (EI): *m/z* = 284 (M^+, 100%), 269 (M–CH_3, 12%), 207 (M–Ph, 5%), 183 (17%), 108 (PhP, 8%), 107 (PhP–H, 14%), 99 (22%), 77 (Ph, 14%).

3,4-Diethyl-1,2-diphenyl-1,2-diphosphacyclopent-3-ene. This compound was prepared analogously from 544 mg of 1,1-bis(cyclopentadienyl)-2,3-diethyl-1-titanacyclobut-2-ene (1.998 mmol) in 15 mL of benzene through the addition of 269 μL of dichlorophenylphosphine (0.355 g, 1.98 mmol). Chromatography of the crude product as described above, using silica in place of alumina, afforded the diphosphacyclopentene as a pale-yellow oil. ^{1}H NMR (C_6D_6): δ 0.86 (t, 3H, CH_3), 0.99 (t, 3H, CH_3), 1.9–2.2 (m, 4H, CH_2), 2.80 (d″t″, 1H, $^2J_{HH} \sim 18$ Hz, $^2J_{PH} \sim {}^3J_{PH} \sim 2$ Hz), 3.20 (″t″, 1H, ^2JHH ~ $^2J_{PH} \sim 18$ Hz, $^3J_{PH} \sim 0$), 6.9–7.3 (m, 7H, aromatic), 7.5–7.8 (m, 3H, aromatic). ^{13}C[^{1}H] NMR (C_6D_6): δ 13.4 (s), 14.8 (d, J_{PC} = 4.9 Hz), 24.1 (d, J_{PC} = 23.5 Hz), 25.3 (d, J_{PC} = 3.4 Hz), 40.8 (d, J_{PC} = 24.9 Hz), 127–129 (m, aromatic), 132–134 (aromatic). ^{31}P NMR (C_6D_6): δ −29.9 (d, J_{PP} = 220 Hz), 17.2 (d, J_{PP} = 220 Hz). High-resolution MS (EI): Calcd for $C_{19}H_{22}P_2$: 312.1197. Found: 312.1189.

3,4-Cycloocteno-1,2-diphenyl-1,2-diphosphacyclopent-3-ene. This compound was prepared analogously from 1,1-bis(cyclopentadienyl)-2,3-cycloocteno-1-titanacyclobut-2-ene and dichlorophenylphosphine. Chromatographic purification was unsuccessful (the major contaminant being the corresponding 1,2-dihydrosphosphete), but the following spectral characterization data were recorded. ^{1}H NMR (C_6D_6): δ 1.2–1.7 (m, 8H, CH_2), 2.1–2.4 (m, 4H, allylic CH_2), 2.65 (d″t″, 1H, $^2J_{HH} \sim 18$ Hz, $^2J_{PH} \sim {}^3J_{PH} \sim 2$ Hz), 3.20 (″t″, 1H, ^2JHH ~ $^2J_{PH} \sim 18$ Hz, $^3J_{PH} \sim 0$), 7.0–7.3 (m, 7H, aromatic), 7.5–7.8 (m, 3H, aromatic). ^{13}C[^{1}H] NMR (C_6D_6): δ 42.0 (d, J_{PC} = 25.2 Hz). ^{31}P NMR (C_6D_6): δ −25.6 (d, J_{PP} = 221 Hz), 22.0 (d, J_{PP} = 221 Hz). High-resolution MS (EI): Calcd for $C_{21}H_{24}P_2$: 338.1353. Found: 338.1348.

1,2,3-Triphenyl-1-stibacyclobut-2-ene and 1,2,3,4-Tetraphenyl-1,2-distibacyclopent-3-ene. The diphenyltitanacyclobutene (0.0370 g, 0.100 mmol) was dissolved in ca. 2 mL of diethyl ether. To the resulting deep-red solution was added a solution of 0.0270 g of dichlorophenylstibine (0.100 mmol) in ca. 2 mL of diethyl ether, resulting in an immediate change to a cloudy purple-brown solution. After having been stirred for ca. 5 minutes, the solution became transparent and red, then changed to a rust-colored suspension. After an additional 5 minutes of stirring, the mixture was allowed to settle, and the supernatant was passed through a ca. 1 cm plug of alumina, eluting with diethyl ether. Removal of solvent in vacuo afforded the stibacyclobutene (4) as a pale-yellow solid. Vacuum sublimation afforded a very low yield of purified material as a white solid. ^{1}H NMR (C_6D_6): δ 1.72 (d, 1H, $^2J_{HH}$ = 13.3 Hz), 2.05 (d, 1H, $^2J_{HH}$ = 13.3 Hz), 6.8–7.2 (m, 9H), 7.24 (d, 2H, $^3J_{HH}$ = 7.5 Hz), 7.37 (d, 2H, $^3J_{HH}$ = 6.9 Hz), 7.75 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz). MS (EI): *m/z* = 392 (M^+ for ^{123}Sb, 4%), 390 (M^+ for ^{121}Sb, 5%), 314 (M–PhH for ^{123}Sb, 25%), 312 (M–PhH for ^{121}Sb, 31%), 200 (Ph^{123}Sb, 32%), 198 (Ph^{121}Sb, 41%), 191 (M–PhSb–H, 100%). High-resolution MS (EI): Calcd for $C_{21}H_{17}{}^{121}$Sb: 390.0367. Found: 390.0351. The progress of this reaction appears extremely sensitive to experimental conditions and often provides the product as a mixture with the distibacyclopentene (5). In several cases, the reaction afforded the pure distibacyclopentene, allowing the following characterization data to be recorded for this compound. ^{1}H NMR (C_6D_6): δ 3.52 (d, 1H, $^2J_{HH}$ = 16.7 Hz), 3.81 (d, 1H, $^2J_{HH}$ = 16.7 Hz), 6.7–7.2 (m, 16H), 7.65 (d, 2H, $^3J_{HH}$ = 6.3 Hz), 7.70 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz). MS (EI): *m/z* = 592 (M^+ for $^{123}Sb_2$, 2.4%), 590 (M^+ for ^{123}Sb^{121}Sb, 5.0%), 588 (M^+ for $^{121}Sb_2$, 3.4%).

TABLE 3 Crystallographic Data for Tetraphenyldiphosphacyclopentene (**3a**) and Dimethyldiphenyldiphosphacyclopentene (**3b**)

	3a	**3b**
Chem formula	$C_{27}H_{22}P_2$	$C_{17}H_{18}P_2$
fw	408.4	284.25
Space group	P1̄	P2(1)/c
a, Å	8.049 (2)	11.158 (2)
b, Å	11.296 (2)	6.2050 (10)
c, Å	13.445 (2)	22.913 (2)
α, deg	110.68 (1)	90
β, deg	93.99 (1)	91.150 (10)
γ, deg	105.28 (2)	90
V, Å^3	1085.3 (9)	1586.1 (4)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.250	1.190
T (K)	297	293
λ (Å)	0.71073	1.54178
μ, cm^{-1}	2.05	23.45
Rel trans coeff	0.96–1.00 (ψ)	
$2\theta_{max}$ (deg)	50	56.78
Index range	$0 \le n \le 9, -12 \le k \le 12, -15 \le l \le 14$	$0 \le h \le 4, 0 \le k \le 6, -22 \le l \le 22$
No. of collected reflecns	3811	1070
No. of obsd reflecns	2640 [$I > 2.5\sigma(I)$]	943 [$I > 2\sigma(I)$]
Parameters refined	350	90
$R(F_o)$[a]	0.037	0.0912
$wR(F_o)$[a]	0.038	0.1540

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $wR(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 4 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) [$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$] for Tetraphenyldiphosphacyclopentene (**3a**)[a]

Atom	*x*	*y*	*z*	B_{eq}
P(1)	2124.6 (9)	3423.8 (7)	6468.7 (6)	4.04 (2)
P(2)	82.1 (8)	3732.1 (6)	7455.6 (6)	3.57 (2)
C(1)	1988 (4)	1781 (3)	6516 (3)	4.5 (1)
C(2)	801 (3)	1422 (2)	7260 (2)	3.39 (8)
C(3)	−185 (3)	2194 (2)	7692 (2)	3.13 (8)
C(4)	802 (3)	207 (2)	7455 (2)	3.43 (8)
C(5)	973 (3)	207 (3)	8482 (2)	4.0 (1)
C(6)	1032 (3)	−908 (3)	8666 (3)	4.5 (1)
C(7)	894 (4)	−2060 (3)	7812 (3)	5.2 (1)
C(8)	718 (5)	−2096 (3)	6786 (3)	6.0 (1)
C(9)	678 (4)	−968 (3)	6612 (3)	5.2 (1)
C(10)	−1566 (3)	1901 (2)	8332 (2)	3.07 (8)
C(11)	−1616 (3)	2836 (3)	9314 (2)	3.8 (1)
C(12)	−2960 (4)	2584 (3)	9871 (3)	4.6 (1)
C(13)	−4274 (4)	1394 (3)	9452 (3)	4.9 (1)
C(14)	−4246 (4)	460 (3)	8483 (3)	5.0 (1)
C(15)	−2901 (3)	700 (3)	7927 (2)	4.1 (1)
C(16)	−1788 (3)	3239 (2)	6374 (2)	3.45 (8)
C(17)	−2182 (4)	4240 (3)	6144 (3)	4.9 (1)
C(18)	−3506 (4)	3974 (4)	5322 (3)	5.9 (1)
C(19)	−4514 (4)	2701 (4)	4725 (3)	5.6 (1)
C(20)	−4151 (4)	1701 (4)	4949 (3)	6.1 (1)
C(21)	−2799 (4)	1953 (3)	5760 (2)	4.8 (1)
C(22)	4038 (3)	4568 (2)	7501 (2)	3.58 (8)
C(23)	4911 (4)	4294 (3)	8269 (3)	5.1 (1)
C(24)	6388 (4)	5229 (4)	8971 (3)	6.0 (1)
C(25)	7021 (4)	6440 (3)	8911 (3)	5.8 (1)
C(26)	6169 (4)	6750 (3)	8178 (3)	5.5 (1)
C(27)	4682 (4)	5825 (3)	7479 (3)	4.5 (1)

[a] B_{eq} defined by W. C. Hamilton, *Acta Crystallogr. 12*, 1959, 609–610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Crystallographic Analysis of 1,2,3,4-Tetraphenyl-1,2-diphosphacyclopent-3-ene. Slow evaporation of a solution of the diphosphacyclopentene in 4:1 diethyl ether/toluene afforded crystals suitable for X-ray structural analysis. A colorless block of dimensions 0.10 × 0.18 × 0.36 mm, cleaved from a larger crystal, was mounted on a glass fiber with epoxy. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $12.3° < \theta < 13.7°$. A summary of crystal parameters and the final residuals is provided in Table 3. The intensities of three standard reflections did not change significantly during data collection. The centric distribution of intensities indicated the space group P1̄. A MITHRIL [16] E-map showed the phosphorus and carbon atoms of the central ring and the attached carbon atoms. A cycle of DIRDIF [17] gave the positions of the remaining C atoms. Hydrogen atoms were located in a difference map after anisotropic refinement of the heavier atoms and were refined isotropically. Refinement of a secondary extinction parameter gave a value [1(1) × 10^{-8}] not significantly different from zero; this parameter was therefore fixed at zero in the last cycles. Final atomic coordinates are provided in Table 4. The final difference synthesis was featureless. The TEXSAN program suite [18], incorporating complex atomic scattering factors [19], was used in all calculations.

Crystallographic Analysis of 3,4-Dimethyl-1,2-diphenyl-1,2-diphosphacyclopent-3-ene. Slow evaporation of a solution of the diphosphacyclopentene in diethyl ether afforded clumps of fine needles, most of which appeared composite when viewed under high magnification between crossed polarizers. A data set adequate for resolution and confirmation of the structure was collected for a fiber-mounted fragment measuring approximately 0.02 × 0.04 × 0.20 mm on a Siemens P4 diffractometer equipped with a rotating anode. The structure was solved by direct methods. A summary of crystal parameters and the final residuals is provided in Table 3. Given the small size and poor quality of the crystals, the resulting

TABLE 5 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) [$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* \mathbf{a}_i^* \cdot \mathbf{a}_j$] for Dimethyldiphenyldiphosphacyclopentene (**3b**)[a]

Atom	*x*	*y*	*z*	B_{eq}
P(1)	2142 (5)	431 (7)	8339 (2)	5.2 (2)
P(2)	3252 (6)	2148 (9)	8999 (2)	6.8 (2)
C(1)	2149 (18)	4374 (27)	9041 (7)	4.8 (4)
C(2)	1008 (20)	3961 (26)	8743 (7)	5.4 (4)
C(3)	868 (18)	2299 (25)	8380 (6)	6.4 (5)
C(4)	−216 (16)	1755 (25)	8021 (6)	6.8 (5)
C(5)	53 (17)	5647 (29)	8851 (7)	9.2 (6)
C(6)	2883 (17)	1263 (24)	7660 (6)	4.5 (4)
C(7)	3562 (16)	−250 (26)	7384 (6)	5.4 (4)
C(8)	4148 (19)	190 (31)	6867 (7)	8.0 (6)
C(9)	3944 (19)	2163 (30)	6639 (7)	7.7 (6)
C(10)	3311 (18)	3766 (29)	6871 (7)	6.9 (5)
C(11)	2730 (16)	3265 (24)	7413 (6)	5.0 (4)
C(12)	2880 (19)	456 (25)	9630 (6)	5.1 (4)
C(13)	1805 (20)	667 (29)	9947 (7)	7.5 (6)
C(14)	1677 (21)	−802 (32)	10425 (8)	9.1 (6)
C(15)	2479 (20)	−2289 (30)	10550 (7)	6.7 (5)
C(16)	3502 (20)	−2575 (29)	10256 (7)	7.1 (6)
C(17)	3681 (18)	−1098 (25)	9786 (6)	6.0 (5)

limited data set permitted refinement of only the phosphorus atoms with anisotropic thermal parameters; carbon atoms were refined with isotropic parameters. Hydrogen atoms were included at calculated, updated positions. Final atomic coordinates are provided in Table 5. The final difference map was featureless.

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