Enhancing the Dienic Reactivity of Phospholes: An Improved Access to Trivalent 7-Phosphanorbornenes

Eric Mattmann, David Simonutti, Louis Ricard, François Mercier, and François Mathey*

Laboratoire "Hétéroéléments et Coordination" UMR CNRS 7653, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

francois.mathey@polytechnique.fr

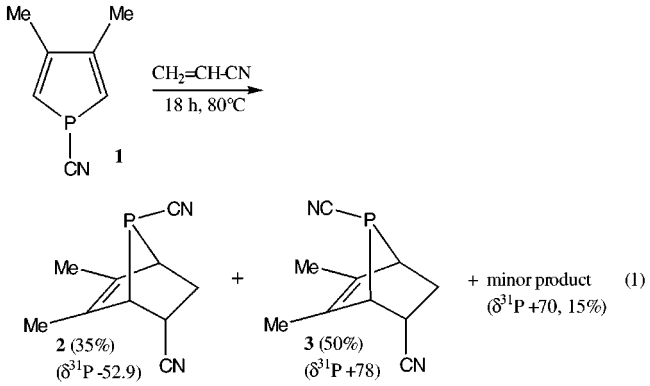
Received July 19, 2000

A structural comparison of 1-cyano- and 1-alkoxy-3,4-dimethylphospholes with 1-benzylphosphole has led to some unexpected conclusions. There is no univocal relationship between phosphole aromaticity and pyramidality at phosphorus. It has been found that both the highly pyramidal 1-cyanophosphole **1** (∑(CPC angles) = 290°), and the much less pyramidal 1-alkoxyphosphole **6** (∑(CPC angles) = 310°) have a low Bird aromaticity index (27 for both molecules), when compared to 1-benzylphosphole (∑(CPC angles) = 303°, BI = 35.5). This low aromaticity is correlated with a high reactivity of the diene in both **1** and **7** (similar to **6**) toward acrylonitrile. Good stereochemical control is observed with **7**, which gives exclusively the *anti,endo* [4 + 2] cycloadducts with acrylonitrile and diethyl vinylphosphonate.

PennPhos has recently been developed as an exceptionally powerful bis-phosphine for the rhodium-catalyzed enantioselective hydrogenation of ketones,[1] cyclic enol acetates,[2] and cyclic enamides.[3] In structural terms, PennPhos is built around a 7-phosphanorbornane skeleton. Similarly, a large number of enantiopure 7-phosphanorbornenes for asymmetric catalysis have been described.[4] These two series of results cast some light on the catalytic potential of the related 7-phosphanorbornane and norbornene structures. From a synthetic standpoint, the most straightforward route to 7-phosphanorbornenes is the direct [4 + 2] cycloaddition between trivalent phospholes and appropriate dienophiles. In practice, this route has found limited application[5] because the ability of phospholes to react as conjugated dienes is diminished by a degree of aromaticity within the ring (the aromatic stabilization energy of parent phosphole is estimated to be ca. 7 kcal·mol^{-1} [6]), and by side-reactions which sometimes occur between the phosphole lone pair and the dienophiles. In this work, we describe our attempts to generalize this direct route to 7-phosphanorbornenes by using P-substituents which have been chosen for their ability to reduce the aromaticity of the phosphole ring. In that respect, our approach is precisely the opposite to that employed by others who have employed P-substituents which induce a planarization of phosphorus and an increase in lone pair delocalization.[7]

Results and Discussion

Assuming that an electron-withdrawing substituent at phosphorus would reduce the delocalization of the lone pair into the diene of the phosphole, we first focused upon the crystalline 1-cyano-3,4-dimethylphosphole (**1**).[8] The X-ray crystal structure analysis of **1** (Table 1) clearly shows that cyclic delocalization within the phosphole ring is rather poor. For a phosphole, the pyramidality of phosphorus is very high: ∑(CPC angles) = 290.3°, as opposed to 302.7° for 1-benzylphosphole [9] and 292.4° for 1-phenyl-2,5-bis(phenylethynyl)-3,4-dimethylphosphole,[10] the most pyramidal phosphole known to date. The degree of C−C bond alternation is very high in **1**, which shows a Cβ−Cβ' bond length of 1.484(3) Å (cf. only 1.438 Å in 1-benzylphosphole[9]). More quantitatively, the Bird aromaticity index[11] is only 27.0 for **1** as against 35.5 for 1-benzylphosphole.[7] Consistent with these structural data, phosphole **1** reacts quantitatively with acrylonitrile at 80 °C over 18 h to provide a nonseparable mixture comprising mainly the two 1:1 adducts (m/z = 190) **2** and **3** (eq 1).



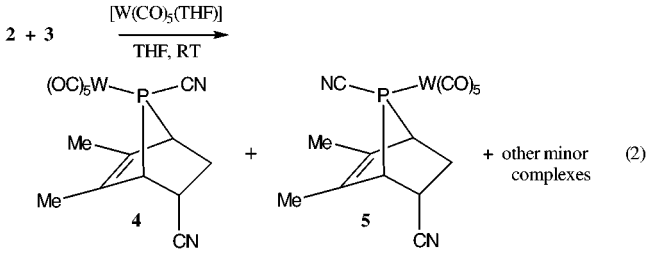
(1) Jiang, Q.; Jiang, Y.; Xiao, D.; Cao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **1998**, *37*, 1100−1103.
(2) Jiang, Q.; Xiao, D.; Zhang, Z.; Chao, P.; Zhang, X. *Angew. Chem., Int. Ed.* **1999**, *38*, 516−518.
(3) Zhang, Z.; Zhu, G.; Jiang, Q.; Xiao, D.; Zhang, X. *J. Org. Chem.*, **1999**, *64*, 1774−1775.
(4) Leung, P.-H.; He, G.; Lang, H.; Liu, A.; Loh, S.-K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7. He, G.; Qin, Y.; Mok, K. F.; Leung, P.-H. *Chem. Commun.* **2000**, 167−168.
(5) Isaacs, N. S.; El-Din, G. N. *Tetrahedron* **1989**, *45*, 7083−92. Keglevich, G.; Trecska, M.; Dajka, B.; Pete, B.; Dobo, A.; Toke, L. *Heteroat. Chem.* **2000**, *11*, 271−275. Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 319−322.
(6) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337−40.

10.1021/jo001096i CCC: $20.00
Published on Web 01/23/2001

Table 1. Some Structural Parameters of Phosphole 1

significant bond distances (Å)		significant bond angles (deg)	
P−C_α	1.794(1)	C_α−P−$C_{\alpha'}$	90.9(1)
P−CN	1.801(2)	C_α−P−CN	99.68(6)
C_α−C_β	1.347(2)	C_β−C_α-P	110.5(1)
C_β−$C_{\beta'}$	1.484(3)	C_α−C_β−$C_{\beta'}$	113.47(7)
C−N	1.151(3)	N−C−P	177.1(2)

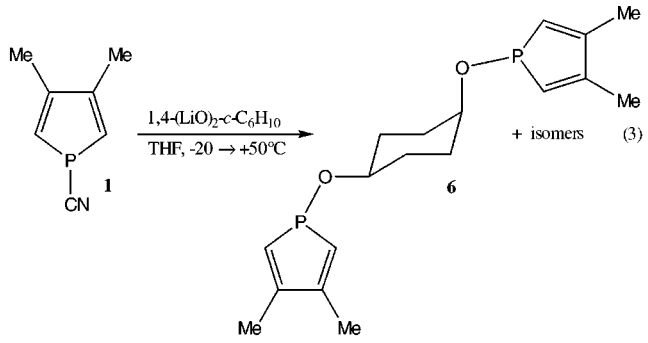
The ^{31}P resonance for syn isomers of trivalent 7-phosphanorbornenes (those having the P−R functionality syn to the C=C double bond) is invariably found at extremely low field.[12] On that basis, it is clear that **3** displays a syn stereoselectivity whereas **2** is anti. Other, previously described trivalent phospholes have invariably reacted with dienophiles to yield exclusively or very predominantly the anti isomers, even when bulky substituents are present at phosphorus.[5] Why the cyano substituent should induce the formation of syn isomers is unclear at present. For further characterization, the crude mixture **2**+**3** was treated with [W(CO)$_5$(THF)] to give mainly the corresponding P−W(CO)$_5$ complexes **4** and **5** (eq 2).



These complexes could be separated by chromatography. Complex **4** displays two significant spectroscopic features. As expected, the ^{31}P resonance occurs at high field $\delta(^{31}P) = -1.2$ ppm. Moreover the sp^2 carbon atoms are highly coupled to phosphorus (17.3 and 16.6 Hz) whereas the CH_2 and CHCN sp^3 carbon atoms are not (0 and 9.7 Hz). All these features are characteristic of anti stereochemistry at P. For complex ***5***, where quite different features are observed: $\delta(^{31}P) = +96$ ppm, ^2J(C−P) = 0 Hz for the two sp^2 carbon atoms, 24.3 Hz for CH_2 and 42.8 Hz for CHCN, the syn stereochemistry is clearly established. The endo stereochemistry (C−CN) was not proven directly, but is most likely by analogy with **8** and **9** (see later).

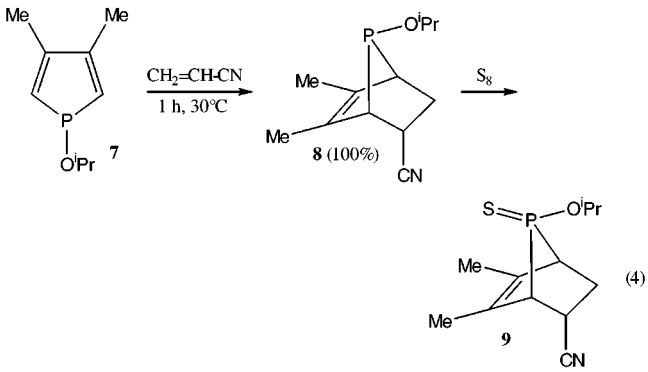
This first series of results was encouraging because it tended to support our working hypothesis that the dearomatization of phospholes increases the reactivity of the dienic system. Consistently, 1-phenyl-3,4-dimethylphosphole is completely unreactive toward acrylonitrile under similar conditions. However, from a practical standpoint, the isolation of an intractable mixture of *syn*−*anti* and endo−exo (C−CN) isomers was disappointing. Hence, we decided to look for another weakly aromatic phosphole. In a phosphole such as **1**, it seems certain that the overlap between the lone pair at phosphorus and the (CN) π-system is poor as a consequence of the high pyramidality at phosphorus. The dearomatization resulting from the introduction of the CN substituent is thus probably mainly due to an electron-withdrawing inductive effect. On that basis, we turned our attention toward 1-alkoxyphospholes. The crystalline phosphole **6** was prepared as shown in eq 3.

A mixture of axial−axial, equatorial−equatorial, and axial−equatorial isomers was thus obtained. The axial−



equatorial isomer **6** crystallized from pentane. The structural parameters of the axial and equatorial phospholyloxy groups are very similar, and those of the equatorial group are given in Table 2. The phosphorus atom is far closer to planarity in **6** than in **1**: $\sum$(CPC angles) = 309.5° in **6**. Nevertheless, as with **1**, both the long P−C (ring) bonds (1.800(1) and 1.798(2) Å) and the Bird index (27.0) point to poor delocalization. Thus, the comparison between **6** and 1-benzylphosphole [7] shows clearly that there is no direct relationship between pyramidality at phosphorus and aromaticity within the ring.

The Diels−Alder experiments were conducted with the simple 1-isopropoxy-3,4-dimethylphosphole **7**,[13] which proved to be extremely reactive toward acrylonitrile (eq 4). Furthermore, only one product was obtained.



The anti stereochemistry of **8** was established by X-ray crystal structure analysis of its P-sulfide **9**. Anti stereochemistry at P has been systematically found for C=C + phosphole [4 + 2] cycloadducts in previous experiments.[5]

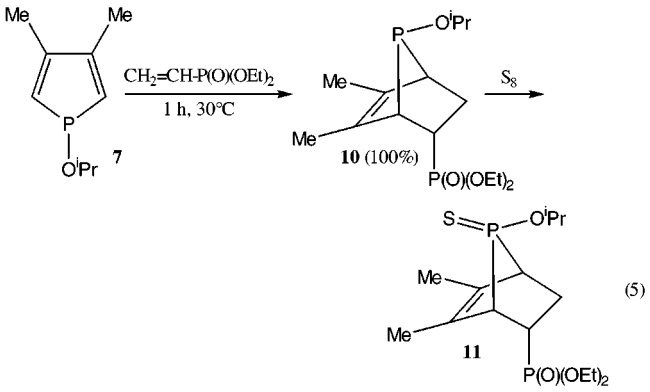
Once again, the most useful spectroscopic features come from the ^{13}C NMR spectrum of **8**. The ^2J(C−P) couplings are large for the ring sp^2 carbon atoms (19.9 and 20.2 Hz, respectively) and small for the CH_2 and CHCN sp^3 carbon atoms (2.9 and 4.0 Hz, respectively). As seen above, this is characteristic of anti stereochemistry at the P−O^{i}Pr bond.

(7) Keglevich, G.; Bocskei, Z.; Keseru, G. M.; Ujszaszy, K.; Quin, L. D. *J. Am. Chem. Soc.* **1997**, *119*, 5095−5099.
(8) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796−801.
(9) Coggon, P.; McPhail, A. T. *J. Chem. Soc., Dalton Trans.* **1973**, 1888−91.
(10) Holand, S.; Gandolfo, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1996**, *133*, 33−7.
(11) Bird, C. W. *Tetrahedron* **1990**, *46*, 5697−702.
(12) Quin, L. D.; Caster, K. C.; Kisalus, J. C.; Mesch, K. A. *J. Am. Chem. Soc.*, **1984**, *106*, 7021−32. Chesnut, D. B.; Quin, L. D.; Moore, K. D. *J. Am. Chem. Soc.*, **1993**, *115*, 11984−90.
(13) Laporte, F.; Mercier, F.; Ricard, L.; Mathey, F. *Bull. Soc. Chim. Fr.* **1993**, *130*, 843−850.

Table 2. Some Structural Parameters of Phosphole 6

significant bond distances (Å)		significant bond angles (deg)	
P−O	1.624(1)	O−P−C_α	109.81(7)
P−C_α	1.800(1)	C_α−P−$C_{\alpha'}$	89.93(8)
P−$C_{\alpha'}$	1.798(2)	C_β−C_α−P	110.0(1)
C_α−C_β	1.343(2)	C_α−C_β−$C_{\beta'}$	113.8(2)
C_β−$C_{\beta'}$	1.474(2)	$C_{\alpha'}$−$C_{\beta'}$−C_β	113.0(2)
$C_{\alpha'}$−$C_{\beta'}$	1.349(2)	$C_{\beta'}$−$C_{\alpha'}$−P	110.5(1)

The high reactivity of the diene in **7** has some interesting practical applications. It readily reacts with diethyvinylphosphonate (eq 5).



(5)

The anti (P−O^{i}Pr), endo (PO_3Et_2) stereochemistry of **10** and **11** was easily proven through ^{31}P NMR spectroscopy. It is well established that the ^{31}P resonance of trivalent 7-phosphanorbornenes is strongly shifted to low fields when converting an anti into a syn isomer.[12] The ^{31}P resonance of the bridge phosphorus of **10** appears at 66.5 ppm (vs 72.3 ppm for **8**). Compound **11** can be compared to well-characterized endo and exo phosphole sulfide dimers. The ^3J(P−P) coupling is known to be close to 0 Hz for the exo dimers and very large for the endo dimers.[14] The observed ^3J(P−P) coupling for **11** is huge: 62.0 Hz.

Finally, whereas 1-halo-3,4-dimethylphospholes are unstable and 1-phenoxy-3,4-dimethylphosphole is difficult to prepare, the readily available 1-dialkylamino-3,4-dimethylphospholes were shown to react with acrylonitrile by their phosphorus lone pair, thus forming ylidic products.

The preceding series of experiments clearly demonstrates that it is possible to fine-tune the reactivity of phospholes by choosing the appropriate substituents at phosphorus. They nicely complement the data for bulky substituents, which induce a planarization of phosphorus and an increase in cyclic delocalization by comparison with 1-benzylphosphole.[7] The comparison between 1-cyano (Bird index 27, ∑(CPC angles) = 290°), 1-alkoxy (Bird index 27, ∑(CPC angles) = 309°), and 1-benzylphospholes (Bird index 35, ∑(CPC angles) = 302°) shows that cyclic delocalization within the phosphole ring does not depend exclusively on the pyramidality at phosphorus. More theoretical work is needed to determine which other parameters are involved.[15] From another standpoint, preliminary experiments have shown that alkyllithiums react with 7-phosphanorbornenes such as **2** and **3** to give the corresponding 7-alkyl-7-phosphanorbornenes. Thus, it appears possible to prepare chelating bis-7-phosphanorbornenes of potential use in catalysis with an appropriate choice of dilithio derivatives. This work will be described in due course.

(14) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809−15.

(15) Delaere, D.; Dransfeld, A.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Org. Chem.* **2000**, *65*, 2631−2636. Dransfeld, A.; Nyulaszi, L.; Schleyer, P. v. R. *Inorg. Chem.* **1998**, *37*, 4413−4420. Nyulaszi, L. *J. Phys. Chem.* **1995**, *99*, 586−91.

Experimental Section

All reactions were performed under argon. The solvents were purified, dried and degassed by standard techniques. Compounds **1**[8] and **7**[13] were prepared according to previously reported procedures and characterized, for **1**, by NMR and the X-ray diffraction structure, and for **7**, by NMR, mass spectrum, and the full characterization of the borane complex. Cyclohexane-1,4-diol, diethylvinylphosphonate, and acrylonitrile were purchased from Aldrich and used without further purification. Elemental analyses were performed by the Service de Microanalyze ICSN, CNRS, Gif sur Yvette.

1,4-Bis(3,4-dimethylphospholyl-1-oxy)cyclohexane(axial−equatorial) 6. To cyclohexane-1,4-diol (1.16 g. 10 mmol) stirred in 20 mL of THF at −40 °C was added dropwise BuLi solution (12.5 mL of 1.6 M in hexane, 20 mmol). The reaction mixture was then allowed to warm to room temperature. After standing for 30 min, it was cooled to −78 °C. A solution of **1** (2.74 g. 20 mmol) in 20 mL of THF was slowly added, and the resulting mixture was heated to 50 °C for 1 h. After aqueous workup, the crude reaction mixture was extracted with ether. The ether extracts were dried over magnesium sulfate and concentrated under reduced pressure. A mixture of isomers was obtained: **6** was isolated by pentane extraction and crystallized by solvent evaporation (low yield, mp 102 °C): ^{31}P NMR ($CDCl_3$) δ 96.5 and 97.6; ^{1}H NMR ($CDCl_3$) δ 1.2−1.9 (m, 8H), 2.02 (t, 6H), 2.04 (t, 6H), 3.18 (br, 1H), 3.72 (br, 1H), 6.11 (d, J = 38.5 Hz, 2H), 6.13 (d, J = 38.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ17.8, 29.9, 30.7, 78.8 (m), 127.5 (m), 148.4 (m).

Pentacarbonyltungsten Complexes of (*endo*)-2-Cyano-5,6-dimethyl-(*anti*)- and (*syn*)-7-cyano-7-phosphabicyclo-[2.2.1]hept-5-enes (4 and 5). Phosphole **1** (1.4 g, 10 mmol) and acrylonitrile (1 mL) were heated for 8 h in a sealed tube at 80 °C. Excess acrylonitrile was removed under vacuum. The crude product was treated with a solution of [$W(CO)_5$, THF], prepared by irradiation of [$W(CO)_6$] (3.5 g, 10 mmol) in THF (250 mL) for 1.5 h at room temperature. The THF was removed in vacuo, and the residue was chromatographed. The byproducts were removed using hexane/CH_2Cl_2 (4:1) and isomer **4** was obtained as a pale yellow solid after elution with CH_2Cl_2 (1.8 g, 35% yield), mp 220 °C (dec): ^{31}P NMR ($CDCl_3$) δ −1.2 (J_{W-P} = 257.2 Hz); ^{1}H NMR ($CDCl_3$) δ 1.90 (s, 3H), 1.97 (s, 3H), 2.15 (m, J = 13.4 Hz, 1H), 2.97 (dt, J = 12.5 Hz and J = 1.7 Hz, 1H), 3.17 (d, J = 1.7 Hz, 1H), 3.35 (d, J = 1.7 Hz, 1H), 3.78 (dt, J = 9.5 Hz and J = 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 16.2, 30.1 (d, J = 9.7 Hz), 33.4, 49.7 (d, J = 15.3 Hz), 52.8 (d, J = 18.3 Hz), 119.3, 120.4 (d, J = 11.2 Hz), 129.9 (d, J = 17.3 Hz), 133.9 (d, J = 16.6 Hz), 194.3 (d, J = 7.4 Hz), 195.7 (d, J = 33.7 Hz); mass spectrum m/z (relative intensity) 514 (M^+, 20), 164 (M − [$W(CO)_5$ + CN], 100); infrared (CH_2Cl_2) 2082 (m), 1955 (s). Anal. Calcd. For $C_{15}H_{11}N_2O_5PW$: C, 35.05; H, 2.16; N, 5.45; P, 6.02; W, 35.77; Found: C, 35.11; H, 2.16; N, 5.41; P, 5.66; W, 35.66.

Complex **5** was eluted using CH_2Cl_2/AcOEt 80/20 as a green solid (1.3 g, 25% yield), mp 120 °C (dec): ^{31}P NMR (CDCl3) δ 96.0 (t, J_{P-W} = 239.1 Hz); ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 3H), 2.0 (s, 3H), 2.05 (d, J = 38.0 Hz, 1H), 2.73 (dt, J = 11.7 Hz, 1H), 3.20 d, J = 1.7 Hz, 1H), 3.38 (d, J = 1.7 Hz, 1H), 3.51 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.8, 16.0, 27.2 (d, J = 42.8 Hz), 29.9 (d, J = 24.3 Hz), 53.0 (d, J = 27.0 Hz), 55.6 (d, J = 30.3 Hz), 118.0, 120.1 (d, J = 20.4 Hz), 139.0, 142.7, 194.3 (d, J = 6.0 Hz), 195.9 (d, J = 27.5 Hz); mass spectrum m/z (relative intensity) 514 (M^+, 20), 164 (M − [$W(CO)_5$ + CN], 100); infrared (CH_2Cl_2) 2083 (m), 1955 (s). Anal. Calcd for $C_{15}H_{11}N_2O_5PW$: C, 35.05; H, 2.16; N, 5.45; P, 6.02; W, 35.77. Found: C, 35.29; H, 2.21; N, 5.24; P, 5.65; W, 35.50.

1-Isopropoxy-3,4-dimethylphosphole 7. Additional data, which has not previously been reported is given here: ^{13}C NMR

($CDCl_3$) (17.9 (s), 24.8 (s), 74.6 (d, J = 7.6 Hz), 127.8 (d, J = 16.8 Hz), 148.3 (d J = 12.3 Hz); mass spectrum m/z (relative intensity) 170 (M^+, 21), 128 (M − propene, 100).

(*endo*)-2-Cyano-5,6-dimethyl-(*anti*)-7-isopropoxy-7-phosphabicyclo[2.2.1]hept-5-ene 8. A solution of **7** (1.7 g, 10 mmol) in 2 mL (1.59 g, 30 mmol) of acrylonitrile was stirred at RT for 30 min in a closed tube. The product was obtained by evaporation of acrylonitrile and washing with hexane (70% yield): ^{31}P NMR ($CDCl_3$) 72.3; ^{1}H NMR ($CDCl_3$) 1.15 (d, J = 6.15 Hz, 6H), 1.77 (s, 3H), 1.84 (s, 3H), 1.8 (m, 1H,) 2.41 (m, 2H), 2.48 (br, 1H), 3.18 (m, 1H), 4.02 (m, 1H); ^{13}C NMR 14.8, 15.7, 24.8 (d, J = 4.0 Hz), 28.4, 32.0 (d, J = 2.9 Hz), 49.8 (d, J = 15.3 Hz), 52.8 (d, J = 18.4 Hz), 71.3 (d, J = 15.5 Hz), 123.8, 129.9 (d, J = 20.2 Hz,) 133.9 (d, J = 19.9 Hz); mass spectrum m/z (relative intensity) 223 (M^+, 15), 132 (M − (P bridge) 100), 107 (xylene 83).

(*endo*)-2-Cyano-5,6-dimethyl-*(anti)*-7-isopropoxy-7-phosphabicyclo[2.2.1]hept-5-ene *P*-Sulfide *9*. To a solution of **8** in dichloromethane were added 1/8 equiv of S_8 and 0.1% equiv of *N*-methylimidazole. After 2 h stirring at room temperature, the crude product was obtained by removal of the solvent. The product **9** was purified by crystallization from hexane (70% yield): ^{31}P NMR ($CDCl_3$) δ 104.9; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 3.7 Hz, 3H), 1.27 (d, J = 3.7 Hz, 3H), 1.70 (ddd, J = 31.1 Hz, J = 12.4 Hz and J = 4.3 Hz, 1H), 1.87 (s, 3H),1.92 (s, 3H), 2.57 (ddd, J = 12.4 Hz, J = 9.6 Hz and J = 3 Hz, 1H), 2.69 (m, 1H), 2.88 (m, 1H), 3.35 (ddd, J = 4.3 Hz, J = 3 Hz and J = 9.6 Hz, 1H), 4.88 (dd, J = 9.4 Hz and J = 3.7 Hz, 1H), (coupling and attributions were made on the basis of 400 MHz ^{1}H, {^{31}P}^{1}H, and COSY); ^{13}C NMR ($CDCl_3$) δ 15.8 (d, J = 5.7 Hz), 16.7 (d, J = 3.1 Hz), 24.4, 28.0 (d, J = 25.7 Hz), 31.7 (d, J = 10.7 Hz), 50.4 (d, J = 64.1 Hz), 52.7 (d, J = 66.9 Hz), 73.6 (d, J = 8.9 Hz), 121.8 (d, J = 16.7 Hz), 132.3 (d, J = 10.6 Hz), 136.4 (d, J = 10.6 Hz); mass spectrum m/z (relative intensity) 255 (M^+, 15) 133 (M − P bridge, 100) 118 (133 − Me, 81). Anal. Calcd for $C_{12}H_{18}NOPS$: C, 56.45; H, 7.11; P, 12.13. Found: C, 56.42; H, 7.07, P, 12.28.

(*endo*)-2-(Diethoxyphosphoryl)-5,6-dimethyl-*(anti)*-7-isopropoxy-7-phosphabicyclo[2.2.1]hept-5-ene 10. A mixture of **7 (**1.0 g, 5.8 mmol) and 2 mL (2.14 g, 13 mmol) of diethylvinylphosphonate was stirred at 40 °C for 2 h in a closed tube. The pure product was extracted from the crude solution by cyclohexane: ^{31}P NMR ($CDCl_3$) δ 35.3 (d, J = 7 Hz), 66.5 (d, J = 7 Hz); ^{1}H NMR ($CDCl_3$) δ 0.96 (d, J = 6.2 Hz, 6H), 1.13 (m, 6H),1.53 (s, 3H), 1.57 (s, 3H),1.5−2.1 (m, 1H), 2.2 (m, 1H), 2.24 (br, 1H), 2.46 (br, 1H), 2.4−2.6 (m, 1H), 3.8−4.0 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.0, 16.1, 17.1 (d, J = 5.0 Hz), 25.3, 27.6, 34.3, 37.2, 50.5 (dd, J = 9.6 Hz and J = 13.8 Hz), 51.5 (dd, J = 4.9 Hz and J = 18 Hz), 61.7 (d, J = 8.0 Hz), 62.1 (d, J = 7.9 Hz), 71.0 (d, J = 15.8 Hz), 130.8 (d, J = 20.1 Hz), 131.9 (d, J = 21.7 Hz). Complete characterization of **10** was made on the *P*-sulfide form **11** due to instability of the unprotected product.

(*endo*)-2-(Diethoxyphosphoryl)-5,6-dimethyl-*(anti)*-7-isopropoxy-7-phosphabicyclo[2.2.1]hept-5-ene *P*-Sulfide 11. To a solution of **10** in dichloromethane was added 1.1 equiv of sulfur and 5% equiv of *N*-methylimidazole. After 2 h stirring at 40 °C, the solvent was evaporated under vacuum, and the product was purified by chromatography on silica with dichloromethane as eluent (70% yield): ^{31}P NMR ($CDCl_3$) δ 28.1 (d, J = 61 Hz), 102.7 (d, J = 64 Hz); ^{1}H NMR ($CDCl_3$) δ 1.29 (d, J = 7.0 Hz, 6H), 1.28 (t, J = 7.2 Hz, 6H), 1.65 (m, 1H), 1.78 (s, 3H), 1.83 (s, 3H), 2.37 (m, 1H), 2.62 (m, 1H), 2.7−2.9 (m, 2H), 4.04 (m, J = 7.2 Hz and J = 7.2 Hz, 4H), 4.89 (m, J = 9.2 Hz and J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.2 (d, J = 4.6 Hz), 16.5 (d, J = 4.6 Hz), 16.9 (d, J = 5.9 Hz), 24.1 (d, J = 9.0 Hz), 26.8 (d, J = 13.5 Hz), 34.3 (dd, J = 154 Hz and J = 17.1 Hz), 50.5 (dd, J = 44.1 Hz and J = 4.1 Hz), 51.7 (dd, J = 41.6 Hz and J = 3.8 Hz), 62.0 (d, J = 7.2 Hz), 62.3 (d, J = 7.0 Hz), 72.8 (d, J = 8.8 Hz), 132.3 (d, J = 4.7 Hz), 133.6 (d, J = 9.0 Hz); mass spectrum m/z (relative intensity) 366 (M^+, 10) 244 (M − P bridge, 26) 111 (phospholyl, 100). Anal. Calcd for $C_{15}H_{28}O_4P_2S$: C, 49.18; H, 7.70. Found: C, 48.79; H, 7.64.

Supporting Information Available: Crystal data of compounds **1**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001096I