Dual Supermesityl Stabilization: 1-Alkyl-1*H*-[1,2,4]triphospholes, with Among the Most Planar and Least Sterically Hindered σ^3,λ^3-Phosphorus Atoms, and Novel $C_2P_3S_4$ Folded Heterocycles†

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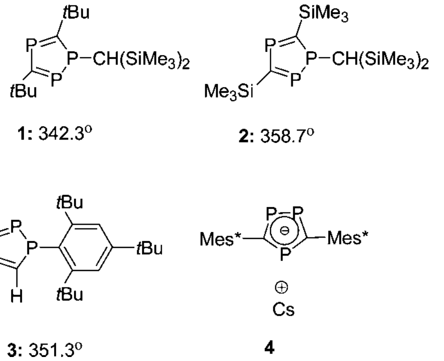
Received June 6, 2008

1-Methyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**6**) and 1-benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**7**) were synthesized and isolated with among the most planar and least sterically hindered σ^3,λ^3-phosphorus atoms, which are an indication of the aromaticity of this heterocycle. The sums of the bond angles at the σ^3,λ^3-phosphorus atoms in **6** and **7** are close to 360°. σ^3,λ^3-Phosphorus atoms in **6** and **7** have substantial deshielded chemical shifts at 151.86 and 161.71 ppm in the ^{31}P NMR spectra. The parental trimethylphosphine and tribenzylphosphine with pyramidal phosphorus atoms have chemicals shifts at −62.0 and −10.4 ppm. There are large P−P coupling constants: $^1J_{PP} = 549.7$ Hz for **6** and 553.3 Hz for **7**. This is further evidence of a significant delocalization of the electron density in these polyphosphorus heterocycles. Compound **7** reacts with sulfur to afford 3-benzyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-6,7-dithia-1,3λ^5,5-triphosphabicyclo[3.1.1]hepta-2,3-diene 1,5-disulfide (**8**), which is the first example of a $C_2P_3S_4$ folded heterocycle. The formation of **8** involves an unusual 1,3-benzyl shift with oxidation of all λ^3-phosphorus atoms to λ^5-phosphorus atoms.

Introduction

The majority of known tervalent tricoordinated phosphorus compounds are pyramidal. In these compounds, the phosphorus lone pair of electrons has a large "s" character and is unable to participate in conjugation with π-systems.[1] The introduction of sterically hindered groups at the σ^3,λ^3-phosphorus was shown to increase the degree of planarity of the phosphorus atom incorporated in ring systems with two-coordinated phosphorus atoms, e.g., in 1,2,4-triphospholes **1** and **2** and 1,2-diphosphole **3** (Scheme 1).[2] However, these sterically hindered groups have to be among the largest ones available for synthetic chemists to make a substantial effect. Ionic cesium 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-4*H*-[1,2,4]triphospholide (**4**), with a planar ring, was described recently with two supermesityl groups at positions 3 and 5.[3] The repulsive interactions of two supermesityl groups in the 3 and 5 positions of the ring contribute to the planarity of **4**, along with other factors, such as the delocalization of negative charge in the aromatic system.[4] Keeping two supermesityl groups in the 3 and 5 positions of the ring can be a useful synthetic tool for flattening the pyramidal σ^3,λ^3-phosphorus atom, moving from anionic to the neutral system. In this heterocycle the decreased pyramidality can be expected even with sterically less hindered groups at the σ^3,λ^3-phosphorus atom than in phosphole derivatives **1**−**3**. Neutral planar phos-

Scheme 1. Planarity of the σ^3,λ^3-Phosphorus Atoms in Selected Phospholes (1−3) Calculated by the Sum of Bond Angles at That Phosphorus and the Structure of Ionic Triphospholide (4)[a]



[a] Mes* is a supermesityl group (2,4,6-tri-*tert*-butylphenyl).

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† This is DuPont contribution #8849.

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(1) (a) Dillon, K. D.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998. (b) Quin, L. D. *A Guide to Organophosphorus Chemistry*; John Wiley & Sons, Inc.: New York, 2000. (c) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Georg Thieme Verlag: Stuttgart, 1990.

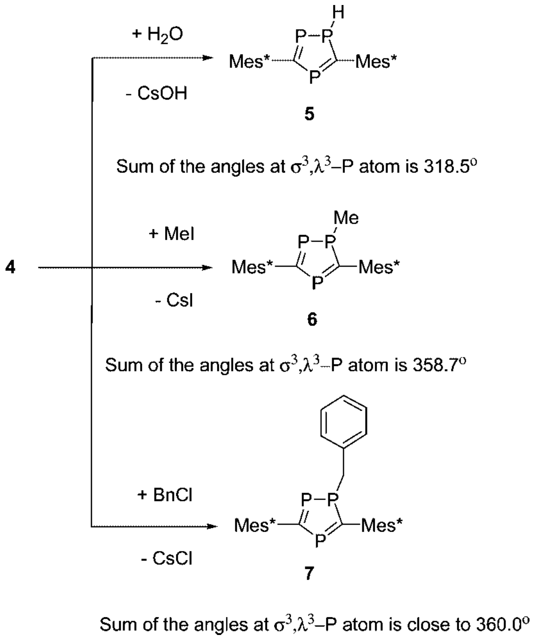
(2) (a) Dransfeld, A.; Nyulászi, L.; Schleyer, P. v. R. *Inorg. Chem.* **1998**, *37*, 4413. (b) Nyulászi, L.; Nixon, J. F. *J. Organomet. Chem.* **1999**, *588*, 28. (c) Egan, W.; Tang, R.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 1443. (d) Andose, J. D.; Rauk, A.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 6904. (e) Nyulászi, L. *Chem. Rev.* **2001**, *101*, 1229. (f) Nyulászi, L. *Tetrahedron* **2000**, *56*, 79. (g) Caliman, V.; Hitchcock, P. B.; Nixon, J. F. *Chem. Commun.* **1995**, 1661. (h) Nyulászi, L.; Bergsträsser, U.; Regitz, M.; Schleyer, P. v. R. *New J. Chem.* **1998**, 651. (i) Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 555. (k) Nyulászi, L.; Soós, L.; Keglevich, G. *J. Organomet. Chem.* **1999**, *588*, 28.

(3) Ionkin, A. S.; Marshall, W. J.; Fish, B. M.; Marchione, A. A.; Howe, L. A.; Davidson, F.; McEwen, C. N. *Eur. J. Inorg. Chem.* **2008**, 2386.

(4) (a) Quin, L. D.; Keglevich, G.; Ionkin, A. S.; Kalgutkar, R.; Szalontai, G. *J. Org. Chem.* **1996**, *61*, 7801. (b) Keglevich, G.; Bocskei, Z.; Keseru, G. M.; Ujszaszy, K.; Quin, L. D. *J. Am. Chem. Soc.* **1997**, *119*, 5095. (c) Keglevich, G.; Farkas, R.; Ludanyi, K.; Kudar, V.; Hanusz, M.; Simon, K. *Heteroat. Chem.* **2005**, *64*, 104. (d) Cloke, F. G. N.; Hitchcock, P. B.; Hunnable, P.; Nixon, J. F.; Nyulászi, L.; Niecke, E.; Thelen, V. *Angew. Chem., Int. Ed.* **1998**, *37*, 1083. (e) Ionkin, A. S.; Marshall, W. J.; Fish, B. M.; Schiffhauer, M. F.; Davidson, F.; McEwen, C. N.; Keys, D. E. *Organometallics* **2007**, *26*, 5050.

10.1021/om800528g CCC: $40.75

Scheme 2. Planarity of the σ^3,λ^3-Phosphorus Atoms in Triphospholes (5−7) Calculated by the Sum of Bond Angles at That Phosphorus



pholes are expected to be highly aromatic, and therefore the chemical reactivity, spectral, and geometrical properties should be different from nonplanar phospholes.[2,4]

Results and Discussion

Synthesis of neutral derivatives **5**−**7** from anionic **4** is shown in Scheme 2. The products were purified by the chromatography on silica gel and additionally by sublimation for **6** and **7**. The sum of bond angles method is used to evaluate the planarity of the three structures. Any heterocycle by definition is comprised of differently sized atoms and cannot be perfectly flat, per se. The accepted practice to evaluate the planarity of such heterocycles is to measure the sum of bond angles of the particular heteroatom in question. In the case of the triphospholes **5**−**7**, this will be the sum of bond angles at the σ^3,λ^3-phosphorus atom, and higher numbers (close to 360°) will correspond to greater phosphorus planarity.[2,4] The hydrogen derivative **5**, which is the first stable P−H triphosphole, shows pyramidal geometry, with a sum of bond angles of 318.5° (Figure 1, Scheme 2, and Table 1). This is likely because the hydrogen at position 1 is not bulky enough to prevent one supermesityl group from rotating away from the second supermesityl group. Replacement of this hydrogen by a methyl group in **6**, or a benzyl group in **7**, makes the triphosphole rings more planar (Figures 2 and 3). The crystal structure refinements for compounds **6** and **7** were plagued by disorder, with the heterocyclic ring flipping 180° along with the methyl group of compound **6** and benzyl group of compound **7**. *tert*-Butyl groups also showed typical rotational disorder. Compound **7** refines in space group *Cmca*, and the heterocyclic ring has been constrained to sit on a crystallographic mirror plane, causing the sum of the angles to be artificially 360°. An examination of the thermal ellipsoids shows the ring is slightly disordered above and below the mirror plane, meaning the planarity is less than perfect. So far, it has been necessary to place a bulky substituent such as a bis(trimethylsilyl)methyl group at the σ^3,λ^3-phosphorus atom of the triphosphole to achieve a planar system (sum of bond angles = 358.7°).[4d] **6** and **7** have tricoordinate tervalent phosphorus atoms, which are among the closest to planarity known for such heterocycles.

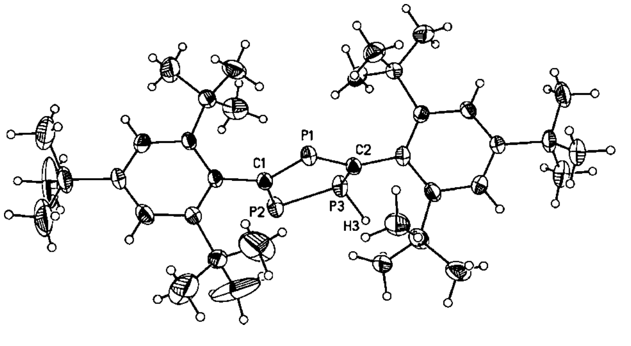
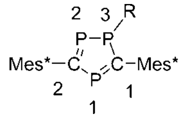


Figure 1. ORTEP drawing of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**5**). No hydrogen bonds were detected. Thermal ellipsoids are drawn at the 50% probability level. Disordered *tert*-butyl groups are omitted for clarity.

Table 1. Selected Bond Lengths and Sum of the Angles at the σ^3,λ^3-Phosphorus Atom for 3,5-Bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphospholes 5, 6, and 7 (Å and deg)



	P1−C1	P1−C2	P3−C1	P2−P3	P2−C2	sum of the angles at the σ^3,λ^3-phosphorus atom (P3)
5	1.703(4)	1.790(4)	1.775(4)	2.1188(14)	1.719 (4)	318.5
6	1.749(8)	1.751(8)	1.690(8)	2.042(2)	1.744(8)	358.7
7	1.709(9)	1.737(10)	1.718(9)	2.026(4)	1.729(10)	Close to 360.0°

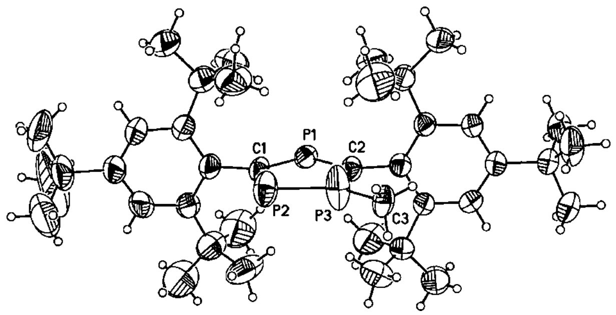


Figure 2. ORTEP drawing of 1-methyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**6**). Thermal ellipsoids are drawn at the 50% probability level. Disordered *tert*-butyl groups and methyl and heterocyclic ring atoms are omitted for clarity.

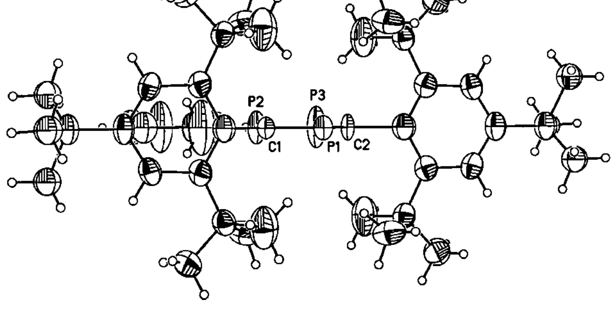


Figure 3. ORTEP drawing of 1-benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**7**). Thermal ellipsoids are drawn at the 50% probability level. Disordered *tert*-butyl groups and methyl and heterocyclic ring atoms are omitted for clarity.

Table 2. ^{31}P NMR Spectra of 3,5-Bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphospholes 5−7

	δ P4 (ppm)	δ P2 (ppm)	δ P1 (ppm)	$^1J_{PP}$ (Hz)	$^2J_{PP}$ (Hz)
5	310.22 (s)	299.20 (d)	76.40 (dd)*	405.9	N/A
6	282.73 (d)	199.08 (dd)	151.86 (d)	549.7	38.8
7	281.90 (d)	197.20 (dd)	161.71 (d)	553.3	38.0

* Sample was run at − 80 °C, $^1J_{PH}$ = 128.2 Hz.[3]

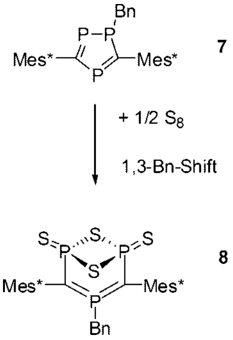
As seen from Table 1, there is an averaging of C═P and C−P bond lengths in these triphosphole systems, indicating electron delocalization. The P−P distances (2.042 Å for **6** and 2.026(4) Å for **7**) are closer to the value of Yoshifuji's original diphosphene, with a P═P double bond of 2.034(2) Å, than for a P−P single bond (2.22 Å).[1c] The structures are disordered, and this is why we are not comparing in more detail the structural features.

The ^{31}P NMR spectra of **5**, **6**, and **7** contain very similar chemical shifts for the tri- and dicoordinated phosphorus atoms, suggesting a delocalization of electron density in these 1*H*-[1,2,4]triphosphole rings. Tricoordinated phosphorus atoms in **6** and **7** with methyl and benzyl groups have chemical shifts at 151.86 and 161.71 ppm (Table 2). Those are substantially deshielded resonances from the chemical shifts of parental trimethylphosphine (−62.0 ppm) and tribenzyl phosphine (−10.4 ppm) with pyramidal phosphorus atoms (for example, the sum of bond angles at the σ^3,λ^3-phosphorus atom for trimethylphosphine is 297.3°, and 296.4° for tribenzylphosphine).[5] Dicoordinated phosphorus atoms in **6** and **7** have chemicals shifts that range from 310.22 to 197.20 ppm and are typical of dicoordinated phosphorus atoms in a triphosphole environment. The direct phosphorus−phosphorus coupling constants in **5**, **6**, and **7** are rather large (from 405.9 Hz for **5** to 553.3 Hz for **7**), which is a further indication of the delocalization of electron density in this triphosphole system.[4d] There is a vicinal coupling between two dicoordinated phosphorus atoms in **6** and **7** with normal values of 38.8 and 38.0 Hz.

The room-temperature ^{31}P NMR spectrum of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**5**) shows only one broad peak at 314.21 ppm. A series of successive [1,5]-sigmatropic hydrogen shifts between P1 and P2 is occurring so quickly that only the P4 is manifested in the ^{31}P NMR spectrum. Slowing down the exchange by cooling to −80 °C produces the expected spectrum for **5** containing three chemical shifts: a singlet at 310.22 ppm (P4), a doublet at 299.20 ppm ($^1J_{PP}$ = 405.9 Hz) (P2), and a doublet at 76.40 ppm (P1) with the same coupling constant. Details are shown in our previous communication.[3]

The carbon atoms for the five-membered ring of **6** have the typical ^{13}C NMR downfield signals for carbon−phosphorus double bonds at 185.24 ppm as a triplet of doublets with average (P4 and P2) $^1J_{PC}$= 70.0 Hz and $^2J_{PC}$ = 27.6 Hz and at 171.83 ppm as a doublet of triplets with average (P4 and P1) $^1J_{PC}$= 69.2 Hz and $^2J_{PC}$ = 10.4 Hz.

Scheme 3. Reaction of 1-Benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (7) with Elemental Sulfur



Planar triphospholes are not expected to be chemically inert. The destruction of the aromatic system of such triphospholes in any chemical reaction can be compensated by the energetically favorable pyramidalization of the tricoordinated phosphorus or an oxidation reaction of the phosphorus lone pair of electrons.[2b,4e] In order to test the reactivity of planar 1*H*-[1,2,4]triphosphole (**7**), the reaction with elemental sulfur was undertaken. No reaction was observed at room temperature, pointing to the relative stability of **7** toward oxidation. However, heating of **7** with elemental sulfur in toluene resulted in the oxidative expansion of the five-membered ring across of the P−P bond and, second, an oxidative 1,3-shift of the benzyl group affording **8** (Scheme 3). The cleavage of the P−P bond was expected since the reaction of triphosphole **1** with elemental sulfur was known to result in oxidative cleavage of this bond.[6] However, the 1,3-shift of the benzyl group was unexpected: no 1,3-shift of a bis(trimethylsilyl)methyl group was reported in the reaction of sulfur with **1**.[6] The benzyl group has more propensity to migrate than the bis(trimethylsilyl)methyl group. For example, a 1,3-shift of the benzyl group in the Claisen rearrangement is probably the most prominent case by far in organic chemistry.[7] There are a few cases of 1,3-shifts of benzyl groups in organophosphorus chemistry.[8] Notably, the reaction in Scheme 3 represents the first example of a 1,3-shift of a benzyl group in triphospholes. Moreover, compound **8** is the first example of a $C_2P_3S_4$ folded heterocycle. The folded six-membered rings with two phosphorus atoms, not with three phosphorus atoms, have been described.[9]

The ^{31}P NMR spectrum of **8** consists of a triplet at 140.83 ppm with $^2J_{PP}$ = 58.9 Hz, which is characteristic for tricoordinate five-valent phosphorus atoms, and a doublet at 28.25 ppm with the same coupling constant for the P_2S_4 moiety of the ring.[9] The chemical shift of tricoordinate five-valent phosphorus atoms of **8** is within the range of chemical shifts (84.7 to 204.5 ppm) of bis(methylene)phosphoranes stabilized by four trimethylsilyl groups.[10] The mass spectrum of **8** is also consistent with the structure showing the expected MH$^+$ ion at 827.32, corresponding to $C_{45}H_{66}P_3S_4$. The structure of **8** was proven by X-ray analysis. However, due to low resolution, the structure serves only to establish the connectivity for this study.

In conclusion we present here a synthesis of neutral 1*H*-[1,2,4]triphospholes **6** and **7** with σ^3,λ^3-phosphorus atoms, which

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(5) (a) Tong, J.; Liu, S.; Zhang, S.; Li, S. Z. *Spectrochim. Acta, Part A* **2007**, *67A*, 837. (b) Bruckmann, J.; Krüger, C. *Acta Crystallogr.* **1995**, *C51*, 1155.

(6) Caliman, V.; Hitchcock, P. B.; Nixon, J. F.; Sakarya, N. *Bull. Soc. Chim. Belg.* **1996**, *105*, 675.

(7) (a) Burger, K.; Hennig, L.; Tsouker, P.; Spengler, J.; Albericio, F.; Koksch, B. *Amino Acids* **2006**, *31*, 55. (b) Tietze, L. F.; Schulz, G. *Chem.−Eur. J.* **1997**, *3*, 523.

(8) Chen, Y.; Sun, X.; Fu, H.; Liu, X.; Zhao, Y. *J. Mass Spectrom.* **2004**, *39*, 730.

(9) (a) Eleftheriou, M. E.; Novosad, J.; Williams, D. J.; Woollins, J. D. *Chem. Commun.* **1991**, *2*, 116–17. (b) Slawin, A. M. Z.; Williams, D. J.; Wood, P. T.; Woollins, J. D. *Chem. Commun.* **1987**, *22*, 1741. (c) Grossmann, G.; Beckmann, H.; Rademacher, O.; Krueger, K.; Ohms, G. *Dalton Trans.* **1995**, *17*, 2797–803. (d) Foreman, M.; St, J.; Novosad, J.; Slawin, A. M.Z.; Woollins, J. D. *Dalton Trans.* **1997**, *8*, 1347–1350. (e) Kilian, P.; Philp, D.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2003**, *2*, 249–254. (f) Fei, Z.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2001**, *20*, 2577–2581. (g) Foreman, M. St. J.; Slawin, A. M. Z.; Woollins, J. D. *Heteroat. Chem.* **1999**, *10*, 651–657.

(10) Becker, P.; Brombach, H.; David, G.; Leuer, M.; Metternich, J.; Niecke, E. *Chem. Ber.* **1992**, *125*, 771.

are among the phosphorus atoms with the least deviations from planarity known for such heterocycles. It is likely that the repulsive interactions of two supermesityl groups in the 3 and 5 positions of the ring contribute to the planarity of **6** and **7** to some degree. Novel phosphorus−sulfur heterocycle **8**, with more heteroatoms than carbons in the ring, was synthesized and characterized by X-ray crystallography. The use of **6** and **7** in homogeneous catalysis will be further investigated and reported in due time.

Experimental Section

All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Dioxane, iodomethane, benzyl chloride, methanol, and THF were purchased from Aldrich. Melting points are uncorrected. The mass spectra were collected on an Orbitrap mass spectrometer (ThermoFisher Scientific Breman, Germany). All NMR experiments were run on a Bruker 500 Avance DRX spectrometer.

3,5-Bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (5). A 0.50 g (0.457 mmol) sample of the cesium salt of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-4 *H*-[1,2,4]triphosphole (**4**)[3] and 0.01 mL of water in 20 mL of dioxane were stirred for 5 min at ambient temperature. The reaction mixture was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The yield of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**5**) was 0.23 g (81%) as orange crystals with a mp of 240 °C (dec). ^{1}H NMR (500 MHz, toluene-d_8, TMS): δ 1.30 (s, 18H, Me), 1.42 (s, 36H, Me), 6.90 (d, $^5J_{PH} = 1.0$ Hz, 2H, Ar−H), 7.10 (d, $^5J_{PH} = 1.0$ Hz, 2H, Ar−H). ^{31}P NMR (500 MHz, toluene-d_8, 30 °C): δ 314.21 (br). ^{31}P NMR (500 MHz, toluene-d_8, −81 °C): δ 310.22 (s, 1P), 299.20 (d, $^1J_{PP} = 405.9$ Hz, 1P), 76.40 (dd, $^1J_{PP} = 405.9$ Hz, $^1J_{PH} = 128.2$ Hz, 1P). 3,5-Bis-(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**5**) was identified by mass spectrometry (ASAP method), which gave an MH$^+$ ion at 608.38, corresponding to $C_{38}H_{59}P_3$. The structure was determined by X-ray analysis.

1-Methyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (6). A 0.60 g (0.549 mmol) sample of the cesium salt of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-4*H*-[1,2,4]triphosphole (**4**) and 0.16 g (1.13 mmol) of iodomethane in 20 mL of dioxane were stirred for 12 h at ambient temperature. The reaction mixture was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The yield of 1-methyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**6**) was 0.26 g (75%) as golden crystals with a mp of 215−216 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 1.42 (s, 18H, Me), 1.44 (s, 18H, Me), 1.49 (s, 9H, Me), 1.50 (s, 9H, Me), 2.23 (dd, $^2J_{PH} = 13.0$ Hz, $^3J_{PH} = 3.6$ Hz, 3H, P−Me), 7.80 (br, 4H, Ar−H). ^{31}P NMR (500 MHz, C_6D_6): δ 282.73 (d, $^2J_{PP} = 38.8$ Hz, 1P), 199.08 (dd, $^1J_{PP} = 549.7$ Hz, $^2J_{PP} = 38.8$ Hz, 1P), 151.86 (d, $^1J_{PP} = 549.7$ Hz, 1P). The structure was determined by X-ray analysis.

1-Benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (7). A 0.40 g (0.366 mmol) sample of the cesium salt of 3,5-bis(2,4,6-tri-*tert*-butylphenyl)-4*H*-[1,2,4]triphosphole (**4**) and 0.093 g (0.731 mmol) of benzyl chloride in 20 mL of dioxane were stirred for 12 h at ambient temperature. The reaction mixture was purified by chromatography on silica gel, starting with hexane as eluent and increasing the polarity of the eluent to 20% ethyl ether and 80% hexane. The yield of 1-benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**7**) was 0.16 g (63%) as golden crystals with a mp of 252−253 °C. ^{1}H NMR (500 MHz, C_6D_6, TMS): δ 1.10 (s, 9H, Me), 1.19 (s, 9H, Me), 1.22 (s, 9H, Me), 1.24 (s, 9H, Me), 1.33 (s, 9H, Me), 1.38 (s, 9H, Me), 3.28 (dd, $^2J_{PH} = 13.7$ Hz,$^3J_{PH} = 3.0$ Hz, 2H, CH_2−Ph), 6.48 (br, 1H, Ph), 6.70 (br, 2H, Ph), 6.81 (br, 2H, Ph), 7.30 (br, 2H, Ar−H), 7.53 (s, 1H, Ar−H), 7.59 (s, 1H, Ar−H). ^{31}P NMR (500 MHz, C_6D_6): δ 281.90 (d, $^2J_{PP} = 38.0$ Hz, 1P), 197.20 (dd, $^1J_{PP} = 553.3$ Hz, $^2J_{PP} = 38.0$ Hz, 1P), 161.71 (d, $^1J_{PP} = 553.3$ Hz, 1P). The structure was determined by X-ray analysis. 1-Benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**7**) was identified by mass spectrometry (ASAP method), which gave an M$^+$ ion at 698.43, corresponding to $C_{45}H_{65}P_3$.

3-Benzyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-6,7-dithia-1,3λ^5,5-triphospha-bicyclo[3.1.1]hepta-2,3-diene 1,5-Disulfide (8). A 0.05 g (0.0715 mmol) sample of 1-benzyl-3,5-bis(2,4,6-tri-*tert*-butylphenyl)-1*H*-[1,2,4]triphosphole (**4**) and 0.00916 g (0.286 mmol) of elemental sulfur in 5 mL of toluene were refluxed for 30 min. Upon cooling the reaction mixture to rt, orange crystals were formed. The yield of 3-benzyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-6,7-dithia-1,3λ^5,5-triphosphabicyclo[3.1.1]hepta-2,3-diene 1,5-disulfide (**8**) was 0.0402 g (68%) as orange crystals, mp 196−197 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, TMS): δ 1.37 (s, 9H, Me), 1.39 (s, 9H, Me), 1.43 (s, 18H, Me), 1.45 (s, 9H, Me), 1.52 (s, 9H, Me), 3.20 (br, 2H, CH_2−Ph), 6.80 (br, 1H, Ph), 6.85 (br, 2H, Ph), 7.12 (br, 2H, Ph), 7.40 (br, 2H, Ar−H), 7.90 (s, 2H, Ar−H). ^{31}P NMR (500 MHz, CD_2Cl_2): δ 140.83 (t, $^2J_{PP} = 58.9$ Hz, 1P), 28.25 (d, $^2J_{PP} = 58.9$ Hz, 2P). The structure was determined by X-ray analysis. 3-Benzyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-6,7-dithia-1,3λ^5,5-triphosphabicyclo[3.1.1]hepta-2,3-diene 1,5-disulfide (**8**) was identified by mass spectrometry (ASAP method), which gave an MH$^+$ ion at 827.32, corresponding to $C_{45}H_{66}P_3S_4$.

Acknowledgment. The authors thank Prof. Barry Trost for helpful discussions of this study and Karin Karel for proofreading the manuscript.

Supporting Information Available: Crystallographic information (CIF file) for compounds **5**−**8**. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM800528G