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Synthesis of New Tricyclic Phosphines and Phosphinites by Intramolecular Diels−Alder Reactions of Trivalent Phospholes

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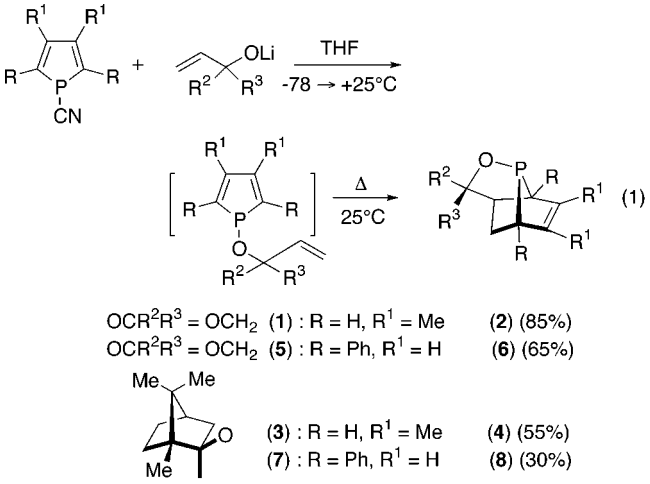
Abstract: Phospholes bearing an allyl-X substituent at phosphorus tend to undergo an intramolecular Diels−Alder cycloaddition (IMDA) leading to the corresponding tricyclic derivative. When X = O or NR, the IMDA easily takes place at room temperature. When X = CH_2, the IMDA slowly takes place around 110−140 °C, as a function to the substitution pattern of the dienic system. Two tricyclic derivatives (X = O and CH_2) have been characterized by X-ray crystal structure analysis of the *P*-sulfides.

From the little data presently available, it seems clear that polycyclic phosphines have a significant potential as ligands for transition metals in homogeneous catalysis. Striking examples are provided by PennPhos[1] and BIPNOR,[2] which have been used as enantiopure ligands for asymmetric catalysis. Against this background, we have already started a systematic investigation of the Diels−Alder reactions of trivalent functionalized phospholes, which can be used to prepare the versatile 7-phosphanorbornene bicyclic structure.[3] Due to their residual aromaticity,[4] phospholes act as rather poor dienes toward classic dienophiles.[5] Significant variations of reactivity are observed as a function of the substitution pattern of the dienic system and the heteroatom substituent.[3,6] The chemistry of furans led us to investigate the intramolecular versions of the Diels−Alder reactions of phospholes because, while furans are generally held as rather poor dienes, their intramolecular Diels−Alder reactions provide versatile and highly useful routes to polycyclic heterocycles.[7] From another standpoint, it is also known from the work of Nelson[8] and Leung[9] that placing a phosphole and a dienophile in the same coordination sphere of a transition metal facilitates the Diels−Alder cycloaddition. Phosphole IMDA is thus a very promising field of study.

In our previous work,[3,6] we showed that 1-alkoxy substituents dramatically enhance the Diels−Alder reactivity of phospholes. As a logical first choice, we thus decided to synthesize 1-allyloxy-3,4-dimethylphosphole (**1**). Mixing allyl-OLi with 1-cyano-3,4-dimethylphosphole[10] and warming the reaction mixture to room temperature leads to **1**, which shows a resonance at 102.4 ppm, together with the corresponding tricyclic product (**2**) at 113.3 ppm. The intramolecular Diels−Alder cycloaddition is complete after ca. 10 min at room temperature (eq 1), the ^{31}P spectrum showing no other resonance than (**2**).[11]



It is immediately obvious that the cyclization has taken place in **2** from inspection of the ^1H NMR spectrum, showing no vinylic protons. The dissymmetry of the structure is shown by the two inequivalent methyl groups and the two bridgehead carbons at 53.57 ppm, J_{CP} = 7.1 Hz (C6) and 54.5 ppm, J_{CP} = 24.0 Hz (C1). The huge difference between the two coupling constants reflects the fact that the P-lone pair points toward C1. The structure was definitively established by X-ray analysis of the P-sulfide **2(PS)** (see the Supporting Information). The 7-phosphanorbornene subunit is apparently somewhat strained with a CPC intracyclic angle of 82.7(1)°. If we transpose the structural data of this P-sulfide to the trivalent species, it becomes quite clear that **2** is a very pyramidal dialkylphosphinite: The sum of the intracyclic angles at P is 289.3°, which means a high coordinating ability for transition metals.

The phosphorus atom in these tricyclic structures is intrinsically chiral. It was thus tempting to check whether

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(11) A similar experiment was performed, mixing 1-isopropoxy-3,4-dimethylphosphole (see ref 3) with allyl alcohol, to test whether intermolecular cycloaddition could occur. No trace of cyclized product could be detected, even under heating.

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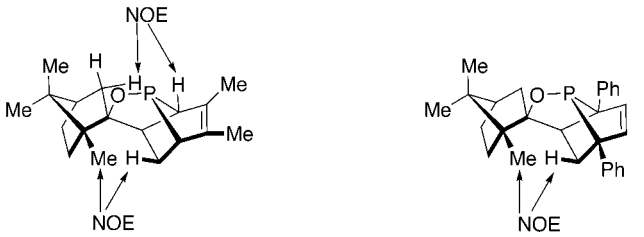
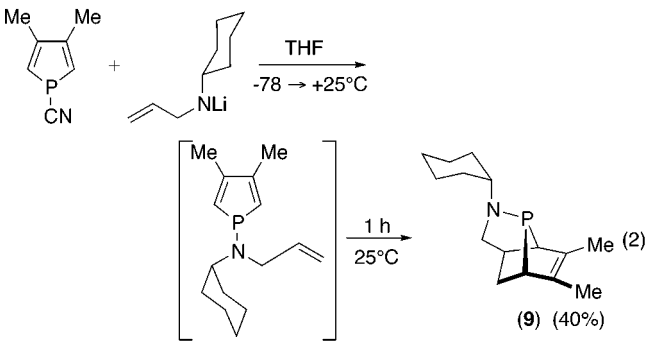


FIGURE 1. Absolute configurations of the major diastereoisomers of **4** and **8**.

it was possible to adapt this process for the synthesis of optically pure species. the enantiopure *endo*-2-vinylborneol was easily prepared by *endo*-vinylation of (+) camphor with vinylmagnesium bromide in the presence of $CeCl_3$ as a catalyst.[12] The intermediate 1-alkoxyphosphole **3** cyclized very rapidly to give **4,** so that it could not be detected by ^{31}P monitoring of the reaction mixture. The tricyclic phosphinite **4** was obtained as a 98:2 mixture of two enantiopure diastereoisomers whose separation is difficult. The stereochemistry of the major diastereoisomer was established using an NOE experiment. Knowing the absolute configuration of (+)-camphor allowed us to establish that the phosphorus center of **4** has the *S* configuration.

We then decided to check whether this intramolecular Diels−Alder cycloaddition was restricted to the rather unhindered dienic systems of 3,4-dimethylphospholes. In fact, the transposition was easily achieved with 2,5-diphenylphospholes as shown in eq 1. The reaction is slower but nevertheless proceeds to completion in 12 h at room temperature. The absolute configuration of the phosphorus center in **8** is *S* as in **4** (Figure 1). No signal corresponding to the isomer having the *R* configuration could be detected.

To discriminate between the activating effect of the oxygen atom of the alkoxy group and the favorable entropic affect associated with IMDA, we then tried to replace oxygen by other heteroatoms. In our previous work on intermolecular Diels−Alder reactions, we were unable to use nitrogen substituents, and the electron-poor alkenes that were employed preferentially reacted at the phosphorus lone pair of 1-aminophospholes to give ylidic products.[3] Since IMDA does not require electron-poor alkenes, this constraint is removed. We indeed found that it is possible to perform IMDA with the *N*,*N*-(allyl)-(cyclohexyl)amino substituent as shown in eq 2.



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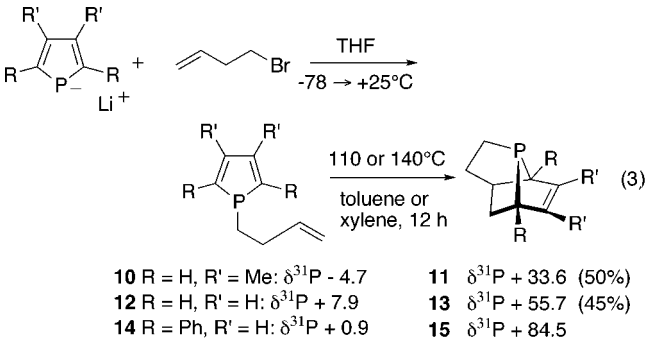
The IMDA goes to completion in 1 h at room temperature. Thus, it is clear that amino groups also confer some activating effect upon the phospholes as do alkoxy substituents. From another standpoint, **9** can be viewed as a convenient source for a variety of P,N-chelating ligands through the easy cleavage of the P−N bond.[13]

The final logical step was to remove the activating heteroatom. We prepared a series of 3-buten-1-ylphospholes (**10**, **12**, and **14**) and studied their evolution under heating (eq 3).



10 R = H, R' = Me: $\delta^{31}P$ - 4.7
12 R = H, R' = H: $\delta^{31}P$ + 7.9
14 R = Ph, R' = H: $\delta^{31}P$ + 0.9

11 $\delta^{31}P$ + 33.6 (50%)
13 $\delta^{31}P$ + 55.7 (45%)
15 $\delta^{31}P$ + 84.5

The IMDA only takes place under rather drastic conditions, 110−140 °C for 10−12 h, and gives the expected tricyclic phosphines in acceptable yields. The size of the downfield shifts of the ^{31}P resonances observed upon cyclization reflects the syn disposition of the lone pair with respect to the double bonds in **11**, **13**, and **15**.[14] Compound **11** was characterized by X-ray crystal structure analysis as its P-sulfide **11(PS)** (see the Supporting Information). The structure is very similar to that of **2(PS)**. However, the P═S bond is longer in **11(PS)** at 1.948(1) vs 1.918(1) Å in **2(PS)**. The P═S bond probably is more polarized in the first case, suggesting a better σ-donor ability for **11** than for **2**, in line with the differences observed between phosphines and phosphinites. At 286 °C, the sum of intracyclic angles is smaller for **11(PS)** than for **2(PS)**.

The drastic reaction conditions used in these all-carbon cases must be compared to the extremely mild conditions used for the IMDA of the alkoxy and amino derivatives. As in our previous work, electronegative heteroatomic P-substituents dramatically activate the phosphole dienic system. It is noteworthy that another way to activate the dienic system of phosphole employs complexation at phosphorus. The P−$W(CO)_5$ complex derived from **10** quantitatively cyclizes in 5 h at 85 °C.[15] At these temperatures, a trivalent phosphole inverts rapidly through a planar aromatic transition state, and this has an adverse effect on the cyclization. Blocking the phosphole in the pyramidal state by complexation is thus obviously favorable. Still, the IMDA of the free phospholes is cheaper and simpler.

The IMDA of phospholes, in addition to the fine-tuning of their reactivity through the variation of their P-substituent, provides a general and useful route to

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tricyclic phosphines, phosphinites, and aminophosphines on the basis of the 7-phosphanorbornene framework. The coordination chemistry and the application to homogeneous catalysis of these new ligands are currently under examination.

Experimental Section

All reactions were performed under argon. The solvents were purified, dried, and degassed by standard techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 300.13, 75.47, and 121.50 MHz, respectively, and analyzed using Bruker's XWINNMR 3.0 software, as well as SwaN-MR 3.6.1.[16] Numerical simulation of the phosphole part of **12** was performed with SwaN-MR. Elemental analyses were performed by the Service de Microanalyze, ICSN, CNRS, Gif sur Yvette. High-resolution mass spectra were recorded by the Service de Spectrométrie de Masse, École Normale Supérieure, Département de Chimie, Paris. All commercial reagents were used without further purification, except for chloroalkanes, which were passed through a short column of silica, and *N*,*N*-(allyl)(cyclohexyl)amine, which was distilled before use.

1-Allyloxy-3,4-dimethyl-*1H*-phosphole 1: ^{31}P NMR ($CDCl_3$) δ 102.4.

Typical Procedure for the Preparation of Tricyclic Phosphinites and Aminophosphines. 7,8-Dimethyl-3-oxa-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene 2. To a solution of 2 mmol (116 mg, 0.136 mL) of propen-2-ol in 15 mL of dry THF at 0 °C was added slowly 1.25 mL of butyllithium (2 mmol, c = 1.6 M in hexane). The solution was then cooled to −78 °C, and solid 1-cyano-3,4-dimethylphosphole (274 mg, 2 mmol) was added in one portion. The resulting mixture was allowed to warm to room temperature and stirred for 1 h. After solvent evaporation, the crude oil was rapidly filtered over a short column of silica, using degassed dichloromethane as eluent. The solvent was then removed under vacuum to give a colorless oil (290 mg) in 85% yield: ^{1}H NMR ($CDCl_3$) δ 4.39−4.33 (td, 1H), 4.03−3.98 (md, 1H), 2.64−2.57 (d, 1H), 2.56−2.47 (md, 1H), 2.47−2.38 (md, 1H), 1.71 (m, 3H), 1.62 (m, 3H), 1.65−1.58 (m, 1H), 1.44−1.35 (m, 1H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 131.3 (d, J_{PC} = 15.9 Hz), 126.1 (d, J_{PC} = 14.9 Hz), 84.2 (d, J_{PC} = 7.4 Hz), 54.5 (d, J_{PC} = 24.0 Hz), 53.6 (d, J_{PC} = 7.1 Hz) 38.5 (d, J_{PC} = 2.1 Hz), 32.3, 15.3, 13.9; 111.15; MS (CI NH_3) m/z 168 (M^+, 34), 119 (M − POH_2 100), 88 ($POCH_2CHCH_2$, 85).

7,8-Dimethyl-3-oxa-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene *P*-Sulfide 2(PS). To a solution of **2** (168 mg, 1 mmol) in dichloromethane was added 40 mg (0.156 mmol, 1.25 equiv) of S_8 and a catalytic amount of dry *N*-methylimidazole. The solution was stirred for 2 h at room temperature, and the disappearance of the starting material was checked by ^{31}P NMR. The product was then purified by chromatography on silica gel, using petroleum ether/ethyl acetate (85:15) as eluent: yield 86% (172 mg); ^{1}H NMR ($CDCl_3$) δ 4.45 (dd, 1H, J_{HH} = 8.3 Hz, J_{PH} = 12.4 Hz, H4endo), 4.29 (ddd, 1H, J_{HH} = 8.3, 1.7, 1.5 Hz, H4exo), 2.82 (ddd, 1H, J_{PH} = 9.8 Hz, J_{HH} = 2.4, 1.8 Hz, H6), 2.73 (ddd, 1H, J_{PH} = 7.5 Hz, J_{HH} = 4.2, 1.8 Hz, H1), 2.50 (mdd, 1H, J_{PH} = 33.3 Hz, J_{HH} = 8.3 Hz, H5), 2.19 (dd, 1H, J_{HH} = 11.7, 4.2 Hz, H9exo), 1.80 (m, 3H, Me), 1.78 (m, 3H, Me), 1.47 (dddd, 1H, J_{PH} = 21.0 Hz, J_{HH} = 11.7, 8.3, 1.7 Hz, H9endo); {^{1}H}^{13}C NMR ($CDCl_3$) δ 134.4 (d, J_{PC} = 12.0 Hz), 126.4 (d, J_{PC} = 10.1 Hz), 80.7 (d, J_{PC} = 1.4 Hz, *C4*), 53.1 (d, J_{PC} = 60.1 Hz, *C1*), 50.4 (d, J_{PC} = 59.2 Hz, *C6*), 35.3 (d, J_{PC} = 35.8 Hz, *C5*), 34.7 (d, J_{PC} = 10.9 Hz, *C9*), 15.5 (d, J_{PC} = 5.4 Hz), 14.2 (d, J_{PC} = 6.3 Hz); ^{31}P NMR ($CDCl_3$) δ 135.9; MS (CI NH_3) m/z 200 (16, M^+), 118 (99, (M − S=PH_2OH)$^+$), 106 (100, *o*-xylene$^+$).

(*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2-spiro-4′-(*R*′)-7′,8′-dimethyl-3′-oxa-2′-phosphatricyclo[3.3.1.0^{2,6}]non-7′-ene 4. After solvent evaporation, the crude oil was rapidly filtered over a short column of silica, using degassed dichloromethane/petroleum ether (30:70) as eluent. The solvent was then removed under vacuum to give a colorless oil (1.43 g) in 55% yield: [α] −42 (c = 15 mg/mL, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 2.79 (dm, 1H, J_{PC} = 11.5 Hz), 2.4−2.35 (m, 2H), 2.25 (dd, 1H, J = 4.6, 11.7 Hz), 2.09 (m, 1H), 1.71 (m, 3H), 1.64 (m, 3H), 1.6−1.5 (m, 3H), 1.34 (d, 1H, J = 13.2 Hz), 1.07 (s, 3H), 1.07−0.99 (m, 1H), 0.94 (s, 3H), 0.87−0.85 (m, 2H), 0.80 (s, 3H); {^{1}H} ^{13}C NMR ($CDCl_3$) δ 133.9 (d, J_{PC} = 16.3 Hz), 125.6 (d, J_{PC} = 14.6 Hz), 104.1 (d, J_{PC} = 7.5 Hz), 54.2 (d, J_{PC} = 3.9 Hz), 52.8 (d, J_{PC} = 24.8 Hz), 52.1 (d, J_{PC} = 1.1 Hz), 49.3, 48.9 (d, J_{PC} = 3.4 Hz), 44.6, 32.3, 27.8, 27.6, 22.8, 20.9, 20.7, 15.4, 14.0, 13.8 (d, J_{PC} = 1.7 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 115.8. Anal. Calcd for **4(PS)**: C, 67.05; H, 8.44. Found: C, 66.91; H, 8.44.

1,6-Diphenyl-3-oxa-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene 6. The resulting mixture was allowed to warm to room temperature and stirred for an additional 12 h. The product was purified by chromatography on silica, using degassed petroleum ether/dichloromethane (60:40) as eluent: yield 65% (of a pale yellow solid); ^{1}H NMR ($CDCl_3$) δ 7.57−7.49 (m, 4H, H_{ortho}), 7.4−7.38 (m, 4H, H_{meta}), 7.37−7.28 (m, 2H, H_{para}), 6.31 (dd, 1H, J_{HH} = 6.5 Hz, J_{HP} = 1.7 Hz, H7/8), 6.07 (dd, 1H, J_{HH} = 6.5 Hz, J_{HP} = 2.0 Hz, H7/8), 4.60 (d, 1H, J_{HH} = 8.4 Hz, $H4_{exo}$), 4.25 (md, 1H, J_{HH} = 8.5 Hz, $H4_{endo}$), 2.84 (ddd, 1H, J_{HH} = 1.6, 7.0 Hz, J_{HP} = 9.3 Hz, H5), 2.40 (d, 1H, J_{HH} = 11.6 Hz, $H9_{endo}$), 2.20 (dddd, 1H, J_{HH} = 11.6, 7.1, 2.2 Hz, J_{HP} = 2.2 Hz, $H9_{exo}$); {^{1}H} ^{13}C NMR ($CDCl_3$) δ 141.4 (d, J_{PC} = 8.2 Hz, C_{ipso}), 140.2 (d, J_{PC} = 6.1 Hz, C_{ipso}), 134.2 (d, J_{PC} = 18.6 Hz, C7/8), 130.8 (d, J_{PC} = 16.8 Hz, C7/8), 128.8, 128.7, 128.3 (d, J_{PC} = 10.6 Hz), 127.1, 129.9 (d, J_{PC} = 6.7 Hz), 126.5 (d, J_{PC} = 1.3 Hz), 83.8 (d, J_{PC} = 6.8 Hz, C4), 66.0 (d, J_{PC} = 24.9 Hz, C1), 66.0 (d, J_{PC} = 8.4 Hz, C6), 44.4 (C5), 41.2 (C9); {^{1}H}^{31}P NMR ($CDCl_3$) δ 148.6; MS m/z 292 (M^+, 100), 262 (M^+ − OCH_2, 28), 261 (M+ − POH_2, 48), 167 (*o*-methylenebiphenyl$^+$, 32) Anal. Calcd for **6**: C, 78.07; H, 5.86. Found: C, 77.67; H, 5.94.

(*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2-spiro-4′-(*R*′)-(1′,6′)-diphenyl-3′-oxa-2′- phosphatricyclo[3.3.1.0^{2,6}]non-7′-ene 8. The solution was warmed to room temperature and stirred for an additional 45 min. The product was purified by chromatography on silica, using degassed petroleum ether/dichloromethane (95:5) as eluent: yield 30%; [α] −74 (c = 15 mg/mL, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.47−7.24 (m, 10H), 6.21 (dd, 1H, J_{HH} = 6.4 Hz, J_{HP} = 1.7 Hz, H8′), 5.86 (d, 1H, J_{HH} = 6.4 Hz, H7′), 3.13 (d, 1H, J_{HH} = 12.0 Hz, *H9′exo*), 2.91 (dd, 1H, J_{HH} = 6.7 Hz, J_{HH} = 9.4 Hz, H5′), 1.94 (dd, 1H, J_{HH} = 12.0, 6.8 Hz, *H9′endo*), 1.71−1.58 (m, 1H), 1.64 (s, 2H, CH_2), 1.42−1.34 (m, 2H), 1.07 (s, 3H), 0.99−0.87 (m, 1H), 0.87 (s, 3H), 0.78 (s, 3H), 0.77−0.71 (m, 1H); {^{1}H} ^{13}C NMR ($CDCl_3$) δ 143.1 (d, J_{PC} = 6.4 Hz), 142.2 (d, J_{PC} = 8.8 Hz), 137.5 (d, J_{PC} = 19.5 Hz), 132.2 (d, J_{PC} = 15.1 Hz), 129.5 (d, J_{PC} = 21.0 Hz), 128.8, 128.7 (d, J_{PC} = 5.0 Hz), 128.5 (d, J_{PC} = 7.9 Hz), 128.5, 127.6, 126.6, 126.2, 105.1 (d, J_{PC} = 7.9 Hz, C4′), 67.1 (d, J_{PC} = 4.3 Hz, C6′), 63.8 (d, J_{PC} = 26.0 Hz, C1′), 55.5 (d, J_{PC} = 3.9 Hz, C5′), 53.7 (C1/7), 50.0 (C1/7), 49.1 (C3/5), 44.8 (C4), 37.2 (C9′), 31.8 (C6), 27.5 (C3/5), 20.7 (C7-Me), 20.7 (C7-Me), 15.0 (d, J_{PC} = 2.8 Hz, C1-Me); {^{1}H}^{31}P NMR ($CDCl_3$) δ 148.6; MS m/z 414 (M^+, 32), 398 (M^+ − CH_4, 18), 366 (M^+ − POH_2, 17), 299 (M^+ − PhC≡CMe, 32), 262 (M^+ − camphor, 36), 252 (2,5-diphenyl-1*H*-phosphole oxide$^+$, 33), 152 (camphor$^+$, 26), 137 (camphene$^+$, 100).

3-Cyclohexyl-7,8-dimethyl-3-aza-2-phosphatricyclo-[3.3.1.0^{2,6}]non-7-ene 9. The resulting mixture was allowed to warm to room temperature and stirred for 10 h. After solvent evaporation, the crude oil was rapidly filtered over a short column of silica, using degassed dichloromethane as eluent. The solvent was then removed under vacuum to give a colorless oil in 40% yield: ^{1}H NMR ($CDCl_3$) δ 3.21 (md, 1H, $^1J_{HH}$ = 8.1 Hz, H4), 3.11 (md, 1H, $^1J_{HH}$ = 8.1 Hz, H4), 2.60 (m, 1H, NC-H), 2.47 (ddm, 1H, J_{HP} = 18.6 Hz, J_{HH} = 4.1 Hz, H1), 2.44 (m, 1H, H5), 2.37 (md, 1H, J_{HP} = 10.9 Hz, H6), 1.77−1.68 (4H), 1.67 (m, 3H), 1.60 (m, 3H), 1.59−1.52 (m, 1H),1.44 (dd, 1H, J_{HH} = 4.1, 11.0 Hz, H9), 1.35−1.03 (7H); {^{1}H} ^{13}C NMR ($CDCl_3$) δ 132.2 (d, J_{PC} = 17.1 Hz, C7/8), 127.3 (d, J_{PC} = 15.3 Hz, C7/8), 61.8 (d, J_{PC} = 6.3 Hz, C4), 58.0 (d, J_{PC} = 12.8 Hz, N-*C*-H), 56.6 (d, J_{PC} = 18.7 Hz, C1), 52.4 (d, J_{PC} = 3.0 Hz, C6), 40.2 (d, J_{PC} = 2.0 Hz, C5), 34.2 (C9), 33.5 (d, J_{PC} = 2.9 Hz), 33.5 (d, J_{PC} = 4.0 Hz), 26.1, 25.9, 25.8, 15.0 (d, J_{PC} = 1.9 Hz), 14.0 (d, J_{PC} = 1.0 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 73.6; MS m/z 265 (M = O^+, 17). Anal. Calcd for **9(PS)**: C, 64.02; H, 8.60. Found: C, 63.76; H, 8.57.

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1-But-3-enyl-3,4-dimethyl-1*H*-phosphole 10. To a solution of 1-phenyl-3,4-dimethylphosphole[17] (10 mmol, 1.88 mg) in 25 mL of dry THF was added a 10-fold excess of lithium (lithium wire, **10%** Na). The solution was vigorously stirred at room temperature, until the solution did not contain any starting material left, as shown by its ^{31}P NMR spectrum. The remaining lithium was then removed, and 1.2 mL *tert*-butyl chloride (0.93 g, 10 mmol) was added. The solution was heated at 65 °C for 30 min and cooled to −78 °C. A solution of 4-bromo-1-butene (10 mmol, 1.35 g, 1 mL) in 25 mL of THF was then added dropwise. The mixture was allowed to warm to room temperature and quenched with one drop of water. After solvent evaporation, the resulting oil was dissolved in 10 mL of degassed dichloromethane, and extracted with hexane, to give 1.4 g of a clear yellow liquid in 84% yield: ^{1}H NMR ($CDCl_3$) δ 6.36 (d, 2H, J_{PH} = 30.8 Hz), 5.78 (tdd, 1H, J_{HH} = 17.4, 10.1, 6.7 Hz), 4.99 (md, 1H, J_{HH} = 17.4 Hz), 4.94 (md, 1H, J_{HH} = 10.1 Hz), 2.11 (m, 2H), 2.07 (d, 6H, J_{PH} = 2.7 Hz), 1.79 (m, 2H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 148.8 (d, J_{PC} = 7.2 Hz), 139.1 (d, J_{PC} = 8.9 Hz), 128.8 (d, J_{PC} = 3.1 Hz), 114.7, 31.5 (d, J_{PC} = 6.4 Hz), 23.3 (d, J_{PC} = 15.45 Hz), 17.9 (d, J_{PC} = 3.7 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ −4.7; MS 166 (M^+, 40), 125 (M − allyl$^+$, 100); HRMS for **10-H**+ calcd 167.0990, found 167.0991.

Typical Procedure for the Preparation of Tricyclic Phosphines. 7,8-Dimethyl-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene 11. Compound **10** (1.4 g, 8.4 mmol) was heated in 50 mL of refluxing toluene for 10 h. The disappearance of the starting material was checked by a ^{31}P NMR spectrum of the crude reaction mixture. The solvent was removed under vacuum, and the product was passed swiftly over a pad of silica, using dry and degassed dichloromethane as eluent. A yellowish liquid was obtained in 45% yield: ^{1}H NMR ($CDCl_3$) δ 2.36−2.28 (m, 2H), 2.27−2.18 (m, 1H), 2.18−2.10 (m, 1H), 1.85−1.75 (m, 1H), 1.64 (s, 3H), 1.60 (s, 3H), 1.41−1.27 (m, 2H), 1.37−1.22 (m, 1H), 1.20−1.05 (m, 1H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 134.6 (d, J_{PC} = 14.1 Hz, C7/8), 129.8 (d, J_{PC} = 13.8 Hz, C7/8), 54.5 (d, J_{PC} = 3.4 Hz, C6), 48.7 (d, J_{PC} = 11.2 Hz, C1), 39.6 (C5), 37.8 (d, J_{PC} = 2.1 Hz), 32.4 (d, J_{PC} = 2.8 Hz), 20.4 (d, J_{PC} = 21.0 Hz, C3), 15.0 (d, J_{PC} = 1.8 Hz), 13.3 (d, J_{PC} = 1.9 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 33.66; MS *m*/*z* 166 (100, M^+), 165 (65, M − H$^+$), 138 (30, (M − C_2H_4)$^+$), 133 (32, (M − PH_2)$^+$), 125 (63, (M − allyl)$^+$), 119 (52, (M − H_2PCH_2)$^+$), 106 (49, *o*-xylene$^+$), 105 (40, (M − H_2PCH_2-CH_2)$^+$).

7,8-Dimethyl-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene *P*-Sulfide 11(PS). To a solution of **11** (166 mg, 1 mmol) in dichloromethane was added 40 mg (0.156 mmol, 1.25 equiv) of S_8 and a catalytic amount of dry *N*-methylimidazole. The solution was stirred for 2 h at room temperature, and the disappearance of the starting material was checked by ^{31}P NMR. The product was then purified by chromatography on silica gel, using petroleum ether/diethyl ether (80:20) as eluent: yield 77% (152 mg); ^{1}H NMR ($CDCl_3$) δ 2.62 (m, 1H), 2.51 (m, 1H), 2.26 (m, 1H), 2.25 (m, 1H), 2.09 (m, 1H), 1.97 (m, 1H), 1.93 (m, 1H), 1.87 (m, 1H), 1.79 (m, 6H), 1.46 (m, 1H); {^{1}H}^{13}C NMR ($CDCl_3$) 134.1 (d, J_{PC} = 6.1 Hz), 127.2 (d, J_{PC} = 6.9 Hz), 54.7 (d, J_{PC} = 50.3 Hz), 50.8 (d, J_{PC} = 50.2 Hz), 34.2 (d, J_{PC} = 41.0 Hz), 33.6 (d, J_{PC} = 12.9 Hz), 32.8, 24.0 (d, J_{PC} = 37.5 Hz), 15.5 (d, J_{PC} = 5.2 Hz), 14.2 (d, J_{PC} = 5.2 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 115.2; MS *m*/*z* 198 (24, M^+), 143 (52, (M − $CH_2CH_2CHCH_2$)$^+$), 132 (100, (M − S=PH_3)$^+$), 106 (43, *o*-xylene$^+$). Anal. Calcd: C, 60.58; H, 7.81. Found: C,60.64; H, 7.67.

1-But-3-enyl-1*H*-phosphole 12. To a solution of 1-phenylphosphole (20 mmol, 3.2 mg) in 75 mL of dry THF was added a 10-fold excess of lithium (lithium wire, **10%** Na). The solution was vigorously stirred at room temperature until the solution did not contain any starting material left, as shown by its ^{31}P NMR spectrum. The remaining lithium was then removed, and 2.2 mL of *tert*-butyl chloride (1.85 g, 20 mmol) was added. The solution was heated at 65 °C for 30 min and cooled to −78 °C. A solution of 4-bromo-1-butene (20 mmol, 2.7 g, 2 mL) in 25 mL of THF was then added dropwise. The mixture was allowed to warm to room temperature and quenched with one drop of water. After solvent evaporation, the resulting oil was dissolved in 10 mL of degassed dichloromethane and extracted with hexane. The solvent was removed under vacuum, and the resulting liquid was further purified by a silica gel chromatography using degassed petroleum ether as eluent, to give 2.35 g of a clear yellow liquid in 85% yield: ^{1}H NMR ($CDCl_3$) δ 7.03 (m, 2H, $^3J_{HH}$ = 2.8, 7.3 Hz, $^4J_{HH}$ = 1.0 Hz, $^3J_{HP}$ = 14.3 Hz), 6.87 (m, 2H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.0, 2.3 Hz, $^2J_{HP}$ = 38.3 Hz), 5.78 (tdd, 1H, J_{HH} = 17.0, 10.3, 6.5 Hz), 5.02 (md, 1H, J_{HH} = 17.0 Hz), 4.97 (md, 1H, J_{HH} = 10.3 Hz), 2.18−2.08 (m, 2H), 1.99−1.92 (m, 2H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 138.6 (d, J_{PC} = 8.5 Hz), 137.0 (d, J_{PC} = 7.3 Hz), 134.3 (d, J_{PC} = 6.1 Hz), 115.1, 31.6 (d, J_{PC} = 5.3 Hz), 22.5 (d, J_{PC} = 14.3 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 7.9; MS *m*/*z* 138 (M^+, 90), 137 (M − H, 100), 110 (M − C_2H_4, 60), 97 (M − allyl, 80), 84 (C_4H_5P, 30); HRMS for **12-H**+ calcd 139.0677, found 139.0674.

2-Phosphatricyclo[3.3.1.0^{2,6}]non-7-ene 13. The product was obtained as a yellowish oil in 40% yield: ^{1}H NMR ($CDCl_3$) δ 6.15 (m, 1H, J_{PH} = 13.1 Hz), 5.97 (m, 1H, J_{PH} = 10.5 Hz), 2.61 (m, 2H), 2.22 (m, 2H), 1.73 (m, 1H), 1.49−1.17 (m, 4H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 135.3 (d, J_{PC} = 15.1 Hz), 129.8 (d, J_{PC} = 15.0 Hz), 49.2 (d, J_{PC} = 4.6 Hz), 43.2 (d, J_{PC} = 12.7 Hz), 38.3, 38.0 (d, J_{PC} = 2.0 Hz), 32.3 (d, J_{PC} = 2.7 Hz), 20.9 (d, J_{PC} = 21.0 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 55.7; MS (CI) *m*/*z* 139 (M + 1, 80). Anal. Calcd for **13(PS)**: C, 56.45; H, 6.51. Found: C, 56.21; H, 6.46.

1-But-3-enyl-2,5-diphenyl-1*H*-phosphole 14. To a solution of 3 mmol (936 mg) of 1,2,5-triphenyl-1*H*-phosphole in 30 mL of dry THF was added 6 mmol (138 mg) of sodium. The solution was stirred vigorously for 10 h and then cooled to −78 °C, and a solution of 4 mmol (540 mg, 0.4 mL) of 3-bromobut-1-ene in 10 mL of THF was added dropwise. The product was purified by chromatography on a short column of silica, using degassed petroleum ether as eluent: yield 52%; ^{1}H NMR ($CDCl_3$) δ 7.64−7.59 (m, 4H), 7.45−7.38 (m, 4H), 7.34−7.27 (m, 2H), 7.28 (d, 2H, J_{PH} = 9.7 Hz), 5.60 (m, 1H), 4.84 (s, 1H), 4.81−4.77 (m, 1H), 2.01 (m, 1H), 1.98 (m, 1H), 1.87−1.76 (m, 2H); {^{1}H}^{13}C NMR ($CDCl_3$) δ 151.1 (d, J_{PC} = 2.1 Hz), 138.5 (d, J_{PC} = 7.1 Hz), 137.2 (d, J_{PC} = 16.8 Hz), 132.3 (d, J_{PC} = 8.2 Hz), 129.2, 129.1, 129.0, 127.3, 126.5 (d, J_{PC} = 9.6 Hz), 114.8, 29.2, 23.6 (d, J_{PC} = 16.3 Hz); {^{1}H}^{31}P NMR ($CDCl_3$) δ 0.88; MS *m*/*z* 290 (M^+, 100), 248 (M^+ − allyl, 76), 234 (M^+ − butenyl, 29), 230 (terphenyl$^+$, 32); HRMS for **14** calcd 291.1303, found 291.1298.

1,6-Diphenyl-2-phosphatricyclo[3.3.1.0^{2,6}]non-7-ene 15. After **14** was heated in refluxing chlorobenzene for 12 h, the product was passed through a short column of silica, using degassed dichloromethane/petroleum ether (3:7) as eluent: yield 31%; ^{1}H NMR (C_6D_6) δ 7.44 (m, 2H, C1-Ph, H_{ortho}), 7.37 (m, 2H, C6-PH, H_{ortho}), 7.19−7.11 (m, 4H, H_{meta}), 7.05 (m, 2H, H_{para}), 6.06 (dd, 1H, J_{HH} = 6.2 Hz, J_{HP} = 2.9 Hz, H7), 5.87 (dd, 1H, J_{HH} = 6.2 Hz, J_{HP} = 2.5 Hz, H8), 2.40 (m, 1H, H5), 1.92 (m, 2H, H9), 1.86 (md, 1H, J_{HH} = 10.3 Hz, H4), 1.68 (d, 1H, J_{HH} = 6.2 Hz, H4), 1.28 (dd, 1H, J_{HH} = 15.2 Hz, J_{HH} = 9.5 Hz, H3), 1.15 (md, 1H, J_{HH} = 15.2 Hz (d), H3); {^{1}H}^{13}C NMR (C_6D_6) δ 142.7 (d, J_{PC} = 6.4 Hz, C_{ipso}), 142.5 (d, J_{PC} = 7.8 Hz, C_{ipso}), 138.8 (d, J_{PC} = 16.8 Hz, C8), 134.6 (d, J_{PC} = 15.5 Hz, C7), 128.79 (C_{meta}), 128.76 (C_{meta}), 128.5 (d, J_{PC} = 11.6 Hz, C_{ortho}), 127.8 (d, J_{PC} = 7.8 Hz, C_{ortho}), 126.7 (C_{para}), 126.5 (d, J_{PC} = 1.7 Hz, C_{para}), 67.2 (d, J_{PC} = 4.1 Hz, C6), 61.0 (d, J_{PC} = 11.7 Hz, C1), 46.1 (C5), 40.5 (d, J_{PC} = 2.2 Hz, C9), 36.3 (d, J_{PC} = 1.8 Hz, C4), 20.0 (d, J_{PC} = 24.8 Hz, C3); {^{1}H}^{31}P NMR (C_6D_6) δ 98.5; {^{1}H}^{31}P NMR ($CDCl_3$) δ 84.5; MS *m*/*z* 290 (M^+, 100), 249 (M^+ − CH_2CH_2CH, 23), 230 (terphenyl$^+$, 65).

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Supporting Information Available: ORTEP files, tables, and CIF file for compounds **2(PS)** and **11(PS)**; NMR spectra for compounds **2(PS)**, **10**, **12**, **14**, and **15**; ^{1}H NMR simulation of the phosphole ring of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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