JOC Article

Formation and Electrochemical Properties of a 1,4-Diphosphafulvene Including Formal Dimerization of Phosphaallene

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Received February 13, 2004

Reactions of sterically protected 2-bromo-3-phenyl-1-phosphapropenes with bases such as *tert*-butyllithium and potassium *tert*-butoxide successfully afforded a bulky 1,4-diphosphafulvene (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) through a novel and formal dimerization pathway of 1-phosphaallene, together with small amounts of 3-phenyl-1-phosphaallene and 3,4-diphosphanylidenecyclobutene. The structure of the 1,4-diphosphafulvene was confirmed by X-ray crystallography indicating somewhat flattened phosphorus atoms due to the bulky Mes* groups. The electrochemical properties of the 1,4-diphosphafulvene were investigated to show promising suitability as an electron donor, and indeed, it afforded a charge-transfer complex with TCNQ. Preparation and structural elucidation of an alkoxy-functionalized 1-phosphaallene was also performed, and the effect of the alkoxy group on the 1-phosphaallene moiety was characterized.

Introduction

Phosphaallene [−P═C═C<] is a phosphorus congener of allene[1] and is expected to be a good starting material for novel organophosphorus compounds as the utility of the cumulene skeletons has been well established in organic synthesis.[2] Recently, we have reported a synthetic procedure for stable phosphaallenes[3] by utilizing a bulky 1-bromo-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyllithium (a phosphanylidene carbenoid) **1**,[4] together with two examples of topochemical dimerization reactions of kinetically stabilized phosphaallenes affording 1,3-bis(phosphanylidene)cyclobutane and 2,4-dimethylene-1,3-diphosphacyclobutane upon heating in the solid state.[5] These results suggest the utility of low-coordinated phosphorus compounds[1] as synthetic materials for unique organic compounds, leading to further progress in the well-controlled chemical reactions.

We have been studying the preparation and properties of several alkoxy-functionalized phosphaallenes utilizing **1** to clarify the effects of heteroatoms on the phosphaallenes and, furthermore, exploring a simple and straightforward synthetic procedure for phosphaallenes. In the course of our study on phosphaallenes, we have found the formation of a bulky 1,4-diphosphafulvene (benzylidene-2,3-dihydro-1*H*-[1,3]diphosphole) **3** as a formal dimerization product of the 1-phosphaallene derivatives. Fulvenes containing heteroatoms have played an important role in chemistry and material science, as indicated by the research on tetrathiafulvalene (TTF).[6] We report here the formation of 1,4-diphosphafulvene **3** from the precursors of 3-phenyl-1-phosphaallenes and bases. The structural elucidation and electrochemical properties of **3** together with formation of a charge-transfer complex are described. Additionally, the preparation and characterization of 3-methoxy-1-phosphaallene are also mentioned.

Results and Discussion

2,2-Dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [Mes*P═CBr$_2$][7] was lithiated to generate the corresponding 1-bromo-2-phosphaethenyllithium **1**,[4] and the reaction mixture was treated with benzaldehyde followed by quenching with iodomethane. After the usual workup procedure, the corresponding 2-bromo-3-methoxy-3-phenyl-1-phosphapropene **2a** was obtained and characterized. Subsequently, the reaction of **2a** with an equivalent amount of *tert*-butyllithium afforded **3** (31% isolated yield) as yellow crystals, together with 1-phosphaallene **4**[8] in a low yield (2%) and 3,4-diphosphanylidenecyclobutene **5** (6%).[9] In the ^{31}P NMR spectrum of **3**, two nonequivalent signals were observed as an AB

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10.1021/jo0497407 CCC: $27.50
Published on Web 05/11/2004

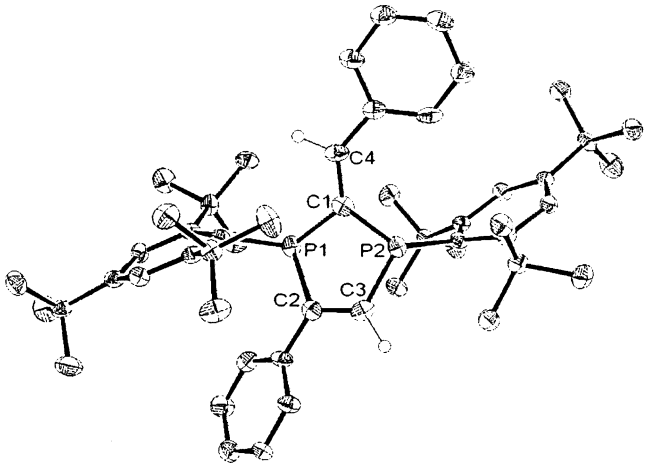
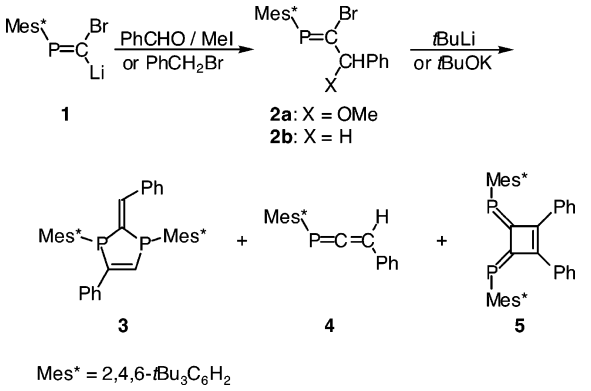


FIGURE 1. ORTEP drawing for the molecular structure of **3**.

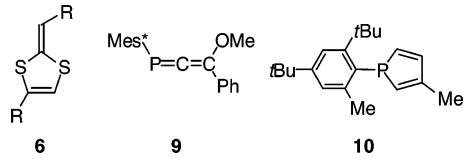
SCHEME 1



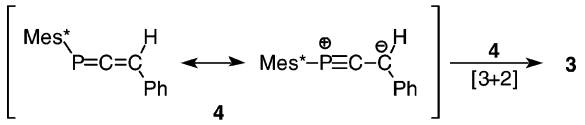
pattern, indicating a coupling of the 1-phosphapropene units and saturation of the P=C bond. In the ^{1}H NMR spectrum of **3**, two olefinic protons accompanying coupling with the ^{31}P nucleus were observed in a low field, which is close to the ^{1}H shifts of the aromatic protons. Alternatively, 2-bromo-2-benzyl-1-phosphaethene **2b**, prepared from **1** and benzyl bromide, was allowed to react with a 2 equiv of potassium *tert*-butoxide to afford **3** (37%) together with **4** (5%) and a trace amount of **5**.

The structure of **3** was confirmed by X-ray crystallography to reveal the 1,4-diphosphafulvene skeleton as shown in Figure 1. The P1-C1-P2-C3 plane is nearly planar [Θ = 6.4(3)°] and the C2 and C4 atoms are displaced by 0.297 and 0.346 Å, respectively. Apparently, the two phenyl rings are conjugated with the 1,4-diphosphafulvene system [Θ(P1-C2-*ipso*-*meta*) = 20.4(6)° and 161.4(4)°; Θ(C1-C4-*ipso*-*meta*) = 16.7(8)° and 163.7(5)°]. The P−C lengths in the ring are comparable with those of unambiguously analyzed 4,5,4′,5′-tetraethyl-1,3,1′,3′-tetraphenyl-2,2′-bis(1,3-diphospholylidene)-1,3,1′,3′-tetrasulfide.[10] The two phosphorus atoms are flattened [Σ(C-P-C) = 325.5° (P1), 321.6° (P2)] compared with 1-benzylphosphole [Σ(C-P-C) = 302.7°],[11] indicating an effect of the bulky substituents.[12] 1,4-Diphosphafulvene **3** is soluble in THF, dichloromethane, chloroform, and toluene but sparingly soluble in hexane. Compound **3** was unstable in silica gel and decomposed during the chromatographic treatment.

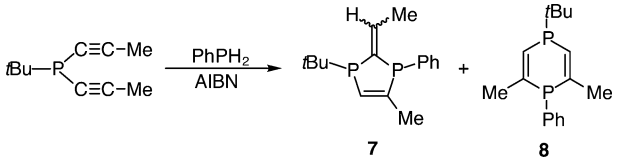
CHART 1



SCHEME 2



SCHEME 3



1,4-Dithiafulvenes **6** (Chart 1), a sulfur congener of **3**, are prepared by formal dimerization of the corresponding thioketenes [R(H)C=C=S] in the presence of bases.[13] In fact, 1,4-diphosphafulvene **3** can be regarded as a formal dimer of **4**. As described in Scheme 2, the 1,4-diphosphafulvene skeleton might be formed through a [1,3]-dipolar cycloaddition of the intermediarily generated phosphaallene due to the polarization together with a [1,2]-migration of the hydrogen under the basic conditions. In the reaction of **4** with *tert*-butyllithium, **3** was observed only in a trace amount,[14] which might indicate an effect of the methoxy group. Märkl et al. mentioned the formation of 1,4-diphosphafulvene (2-ethylidene-2,3-dihydro-1*H*-1,3-diphosphole) **7** from the reaction of *tert*-butyldi(1-propynyl)phosphine with phenylphosphine in the presence of 2,2′-azobisisobutyronitrile (AIBN) together with the formation of 1,4-dihydro-1,4-diphosphinine **8**.[15] The radical-promoted 1,2-addition of phenylphosphine on the acetylene parts might occur in the *endo*- and the *exo*-modes, which indicates a rational pathway for giving 1,4-diphosphafulvenes (Scheme 3).

In contrast to Scheme 1, reaction of **2a** with lithium diisopropylamide (LDA) afforded 3-methoxy-3-phenyl-1-

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(14) In the reaction of **4** with *tert*-butyllithium in THF, the ^{31}P NMR signal of δ_P = −99.7 was observed in the reaction mixture, probably indicating the formation of Mes*P(Li)C≡CPh. After concentration, **4** and **5** were observed in a 1:1 ratio together with a trace amount of **3**.

(15) Märkl, G.; Weber, W.; Weiss, W. *Chem. Ber.* **1985**, *118*, 2365.

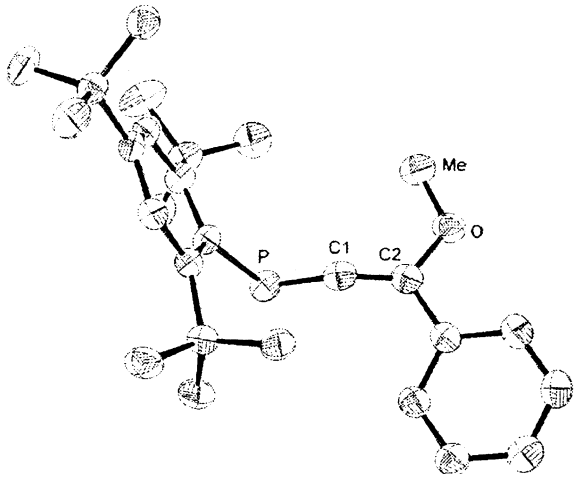

FIGURE 2. ORTEP drawing for the molecular structure of **9**.

phosphaallene **9** in a moderate yield. In this reaction, elimination of hydrogen bromide predominantly occurred to form the P═C═C skeleton. The structure of **9** was characterized by the spectroscopic data and was confirmed by X-ray crystallography (Figure 2). The structural parameters are comparable to those of 3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaallene.[16] The C1-C2-O-Me skeleton displays an *s-cis* type conformation [Θ = 2.2(3)°], and no O···H interaction is observed, whereas the intermolecular C-H π-type interaction is observed between the OCH_3 group and the phenyl ring (C···H 2.81 Å). The ^{31}P NMR signal of **9** was observed in a field lower than that of **4** [δ_P 78.6]. In the ^{13}C NMR spectrum of **9**, the peak due to the central sp carbon was observed in a higher field compared to **4** [δ_C = 240.5], whereas the chemical shift of the terminal sp^2 carbon was lower than that of **4** [δ_C = 113.4]. These NMR tendencies of **4** and **9** are consistent with a similar comparison between phenylallene and 1-methoxy-3-phenylallene.[17]

The electrochemical properties of **3** were investigated by the cyclic voltammetry method. As shown in Figure 3, **3** displayed a reversible oxidation potential at +0.53 V vs Ag/AgCl, as well as two irreversible oxidations at +1.10 V and +1.40 V (sh). The lowest oxidation potential indicates electron-donating ability, which is comparable with the low ionic potential of a bulky phosphole **10**.[12] Moreover, it indicates that **3** can give charge-transfer (CT) complexes, and thus, we performed a reaction of **3** with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an electron-acceptor. Indeed, upon mixing a solution of **3** and TCNQ in THF for 5 h, the color of the reaction mixture turned from yellow to deep green. The IR spectrum of the product in a KBr disk displayed the CN stretchings at 2185 and 2121 cm^{-1} and suggested the formation of a CT complex of **3** with TCNQ by comparing the CN stretching of neutral TCNQ (2225 cm^{-1}). In the UV−vis spectrum of the product, typical absorptions of a radical anion of TCNQ were observed at 853, 830, 770, and 750 nm.[18] Detailed analyses of the CT complex of **3** and

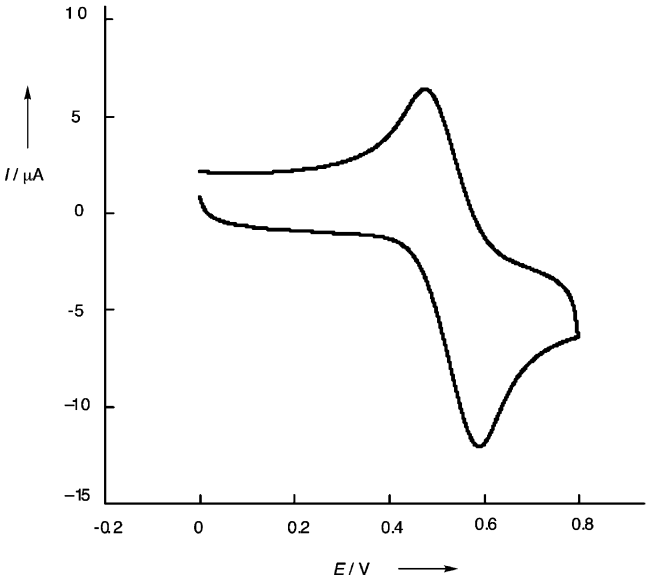

FIGURE 3. Cyclic volammogram of **3**; E = potential, I = current.

electron acceptors, as well as a cationic species generated from **3**, are in progress. Furthermore, the reported perphenyltetraphosphafulvalene[10] was reduced with alkali metals to cleave the P−Ph bond and the generated tetraphosphafulvalene dianions were characterized,[19] and thus, reduction of **3** could afford the corresponding anionic species.[20]

In conclusion, we have described a novel dimerization pathway of 1-phosphaallene equivalents by using **2** and bases to provide a phosphorus-containing heterocyclic system, 1,4-diphosphafulvene **3**. The crystallographic analysis, spectroscopic data, and electrochemical data of **3** revealed several properties of 1,4-diphosphafulvene derivatives. We have reported a preliminary experiment for the CT complex of **3** with TCNQ, suggesting the utility of **3** as an electron-donating compound. Additionally, generation of 3,4-diphosphanylidenecyclobutene **5**, which has been paid considerable attention as ligands of synthetic catalysts,[9] was described, and a 3-methoxy-1-phosphaallene **9** was prepared to indicate the effects of an alkoxy group on the 1-phosphaallene systems. 1-Phosphaallene derivatives including their precursors are expected as useful synthons for unique organophosphorus compounds that appear to be applicable for synthesis of useful materials.

Experimental Section

Compound 2a. To a solution of 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene [Mes*P═CBr$_2$] (300 mg, 0.67 mmol) in THF (20 mL) was added butyllithium (0.67 mL, 1.6 M solution in hexane, 1 M = 1 mol dm^{-3}) at −100 °C, and after 15 min of stirring benzaldehyde (0.67 mmol) was added to the reaction mixture. The solution was warmed to room

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(17) Elsevier: C. J.; Meijer, J.; Tadema, G.; Vermer, V.; Runge, W. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1093.

(18) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374. Extra absorptions were observed at 667 and 620 nm, which might indicate the formation of a cation radical of **3**.

(19) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1031.

(20) No obvious reduction peak was observed in the cyclic voltammetry of **3** under the conditions described in Figure 3.

temperature, and iodomethane (1.34 mmol) was added. The mixture was stirred for 3 h, and the solvent was removed in vacuo. The residue was extracted with hexane and subjected to silica gel column chromatography (hexane/AcOEt = 100:1) to afford 270 mg of **2a** (82% yield): pale yellow solids, mp 71−73 °C; ^{31}P NMR (162 MHz, $CDCl_3$) δ 259.9 (d, $^3J_{PH}$ = 13 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4−7.6 (7H, m, arom), 5.33 (1H, d, $^3J_{PH}$ = 13 Hz, CH), 3.52 (3H, s, OMe), 1.61 (9H, s, *o*-*t*Bu), 1.42 (9H, s, *o*-*t*Bu), 1.41 (9H, s, *p*-*t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.2 (d, $^1J_{PC}$ = 64 Hz, P═C), 154.2 (s, *o*-Mes*), 153.9 (s, *o*-Mes*), 151.4 (s, *p*-Mes*), 139.8 (d, $^3J_{PC}$ = 11 Hz, *ipso*-Ph), 137.1 (d, $^1J_{PC}$ = 54 Hz, *ipso*-Mes*), 128.5 (s, *o*-Ph), 128.4 (s, *p*-Ph), 127.8 (s, *m*-Ph), 123.0 (s, *m*-Mes*), 122.6 (s, *m*-Mes*), 89.1 (d, $^2J_{PC}$ = 37 Hz, CH), 57.7 (s, OMe), 38.5 (s, *o*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 33.7 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 33.4 (d, $^4J_{PC}$ = 6 Hz, *o*-C*Me*$_3$), 32.1 (s, *p*-C*Me*$_3$); EI-MS *m*/*z* (rel intensity) 489 (M^+ + 1; 0.6%), 487 (M^+ − 1; 0.6%), 475 (M^+ − Me + 2; 1%), 473 (M^+ − Me; 1%), 459 (M^+ − OMe + 2; 30%), 457 (M^+ − OMe; 30%), 409 (M^+ − Br; 33%), 377 (M^+ − Br − OMe + 1; 57%), 219 (Mes*P$^+$ − *t*Bu; 100%); HRMS calcd for $C_{27}H_{38}{}^{78}BrOP$ − H 487.1760; found 487.1756.

Compound 2b. To a solution of Mes*P═CBr_2 (230 mg, 0.51 mmol) in THF (15 mL) was added butyllithium (0.51 mmol) at −78 °C, and the mixture was stirred for 15 min. The reaction mixture was treated with benzyl bromide (0.51 mmol) and warmed to room temperature. The solvent was removed in vacuo, and the residue was extracted with hexane. The solution was subjected to silica gel column chromatography (hexane) to afford 150 mg of **2b** (64% yield): pale yellow needles (EtOH), mp 117−119 °C; ^{31}P NMR (162 MHz, $CDCl_3$) δ 248.2 (t, $^3J_{PH}$ = 21 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3−7.6 (7H, m, arom), 4.15 (2H, d, $^3J_{PH}$ = 21 Hz, CH_2), 1.48 (18H, s, *o*-*t*Bu), 1.34 (9H, s, *p*-*t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2 (d, $^1J_{PC}$ = 61 Hz, P═C), 153.8 (d, $^2J_{PC}$ = 2 Hz, *o*-Mes*), 151.3 (s, *p*-Mes*), 138.7 (d, $^3J_{PC}$ = 13 Hz, *ipso*-Ph), 138.7 (d, $^1J_{PC}$ = 53 Hz, *ipso*-Mes*), 130.0 (s, *o*-Ph), 128.8 (s, *m*-Ph), 127.4 (s, *p*-Ph), 122.7 (s, *m*-Mes*), 50.7 (d, $^2J_{PC}$ = 33 Hz, CH_2), 38.5 (s, *o*-*C*Me$_3$), 35.7 (s, *p*-*C*Me$_3$), 33.4 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 32.1 (s, *p*-C*Me*$_3$). Anal. Calcd for $C_{26}H_{36}BrP$: C 67.96, H 7.91, Br 17.39. Found: C 68.14, H 7.83, Br 17.37.

Preparation of 3. From 2a. To a solution of **2a** (170 mg, 0.35 mmol) in THF (15 mL) was added *tert*-butyllithium (0.36 mmol, 1.5 M solution in pentane) at −100 °C, and the mixture was stirred for 15 min. The mixture was warmed to room temperature, and the solvent was removed in vacuo. The residue was extracted in hexane, and the solution was concentrated. The residual solids were recrystallized from hexane to afford 41 mg of **3** (31% yield). The filtrate was subjected to silica gel column chromatography (hexane) to afford 3 mg of **4** (2% yield) and 9 mg of **5** (6% yield). **From 2b.** To a solution of **2b** (303 mg, 0.66 mmol) in THF (20 mL) was added potassium *tert*-butoxide (1.32 mmol, dissolved in 10 mL of THF) at 0 °C, and the mixture was stirred for 15 min. The mixture was warmed to room temperature, and the solvent was removed in vacuo. The residue was extracted in hexane, and after concentration the residual solid was recrystallized from hexane to afford 93 mg of **3** (37% yield). The filtrate was subjected to silica gel column chromatography (hexane) to afford 12 mg of **4** (5% yield) and a trace amount of **5**. **3**: yellow plates (hexane), mp 205−206 °C; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 54.5 (d, $^2J_{PP}$ = 25 Hz, P1), 23.5 (d, $^2J_{PP}$ = 25 Hz, P2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, m, *m*-Mes*), 7.49 (2H, m, *m*-Mes*), 7.15 (5H, m, Ph), 6.90 (3H, m, Ph),); 6.81 (1H, dd, $^3J_{PH}$ = 38 Hz, $^3J_{PH}$ = 13 Hz, C(H)Ph), 6.48 (1H, dd, $^2J_{PH}$ = 17 Hz, $^3J_{PH}$ = 6 Hz, ═CH), 6.36 (2H, m, Ph), 1.65 (36H, s, *o*-*t*Bu), 1.36 (18H, s, *p*-*t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.5 (dd, $^2J_{PC}$ = 19 Hz, $^3J_{PC}$ = 3 Hz, *ipso*-Ph), 138.4 (dd, $^3J_{PC}$ = 9 Hz, $^3J_{PC}$ = 3 Hz, *ipso*-Ph), 135.0 (dd, $^1J_{PC}$ = 28 Hz, $^2J_{PC}$ = 23 Hz, P*C*Ph), 134.8 (dd, $^1J_{PC}$ = 42 Hz, $^1J_{PC}$ = 35 Hz, P*C*P), 129.3 (dd, $^1J_{PC}$ = 61 Hz, $^3J_{PC}$ = 3 Hz, *ipso*-Mes*), 128.8 (dd, $^1J_{PC}$ = 60 Hz, $^3J_{PC}$ = 1 Hz, *ipso*-Mes*), 128.2 (s, *o*-Ph), 128.0 (s, *o*-Ph), 127.9 (dd, $^2J_{PC}$ = 6 Hz, $^2J_{PC}$ = 4 Hz, CHPh), 127.3 (dd, $^1J_{PC}$ = 23 Hz, $^2J_{PC}$ = 10 Hz, ═CH), 127.2 (s, *m*-Ph), 127.2 (s, *p*-Ph), 31.6 (s, *p*-C*Me*$_3$), 125.8 (s, *m*-Mes*), 40.2 (d, $^3J_{PC}$ = 4 Hz, *o*-*C*Me$_3$), 40.0 (d, $^3J_{PC}$ = 4 Hz, *o*-*C*Me$_3$), 35.3 (s, *p*-*C*Me$_3$), 35.2 (s, *p*-*C*Me$_3$), 34.4 (d, $^4J_{PC}$ = 6 Hz, *o*-C*Me*$_3$), 33.9 (d, $^4J_{PC}$ = 3 Hz, *o*-C*Me*$_3$), 31.7 (s, *p*-C*Me*$_3$); UV (CH_2Cl_2) λ_{max}/nm (log ϵ) 256 (4.61), 417 (3.97). Anal. Calcd for $C_{52}H_{70}P_2$: C 82.50, H 9.32. Found: C 82.32, H 9.28.

Compound 9. To a solution of **2a** (322 mg, 0.66 mmol) in THF (20 mL) was added LDA (ca. 0.66 mmol, prepared from diisopropylamine and butyllithium at 0 °C in THF) at −78 °C, and the mixture was stirred for 15 min. The mixture was warmed to 0 °C and stirred for 1 h. After warming up to room temperature, the solvent was removed in vacuo, and the residue was extracted with hexane. The solution was concentrated and the residual solid was recrystallized from ethanol to afford 69 mg of **9** (26% yield): pale yellow crystals, mp 139−142 °C; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 144.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3−7.6 (7H, m, arom), 3.66 (3H, s, OMe), 1.60 (18H, s, *o*-*t*Bu), 1.35 (9H, s, *p*-*t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 229.2 (d, $^1J_{PC}$ = 19 Hz, P═*C*═C), 154.1 (d, $^2J_{PC}$ = 4 Hz, *o*-Mes*), 151.9 (d, $^3J_{PC}$ = 3 Hz, *ipso*-Ph), 150.1 (s, *p*-Mes*), 136.1 (d, $^1J_{PC}$ = 74.8 Hz, *ipso*-Mes*), 133.8 (d, $^2J_{PC}$ = 7 Hz, P═C═*C*), 129.1 (s, *p*-Ph), 128.4 (s, *m*-Ph), 127.8 (s, *o*-Ph), 122.6 (s, *m*-Mes*), 58.1 (s, OMe), 38.6 (s, *o*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 34.2 (d, $^4J_{PC}$ = 7 Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$). Anal. Calcd for $C_{27}H_{37}OP$: C 79.35, H 9.15. Found: C 79.37, H 8.92.

X-ray Crystallography. Single crystals were obtained by recrystallization from a mixture of hexane and dichloromethane at 0 °C (for **3**) or from ethanol at room temperature (for **9**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-230188 (**3**) and -230189 (**9**).

Acknowledgment. This work was supported in part by Grants-in-Aid for Scientific Research (13304049 and 14044012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Comments in Figures 1−3 and CIF files for **3** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0497407