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Preparation of Sterically Protected 3,4-Bis[(2,4,6-tri-*tert*-butylphenyl)-phosphinidene]cyclobutene Derivatives Having Ring-Fused Structures

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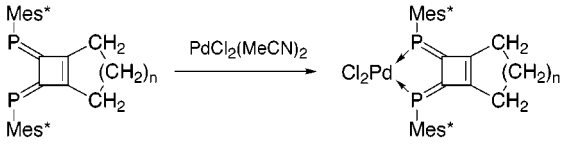
ABSTRACT



Sterically protected 3,4-diphosphinidenecyclobutenes, having ring-fused structures, were prepared. Structures of 8,9-bis[(2,4,6-tri-*tert*-butylphenyl)-phosphinidene]bicyclo[5.2.0]non-1(7)-ene and its dichloropalladium(II) complex were analyzed by X-ray crystallography. A geometrical change induced by the complex formation was exhibited by X-ray crystallographic analysis. The geometrical change in solution was also suggested by ^{1}H NMR spectroscopy in $CDCl_3$.

Multiple bonds containing the heavier main-group elements have been of interest for the past two decades.[1] By utilizing an extremely bulky 2,4,6-tri-*tert*-butylphenyl group (hereafter abbreviated to the Mes* group) as a sterically protecting auxiliary, we and others have prepared several double-bonded phosphorus compounds such as diphosphenes,[1a] phosphacumulenes,[2] and phospharadialenes.[3] We have also reported syntheses of sterically protected 3,4-diphosphinidenecyclobutenes **1**[4] and its application as a ligand with conformationally rigid coordination sites.[5] Moreover, palladium or platinum complexes having the 3,4-diphosphinidenecyclobutene ligand showed catalytic activities.[5c,f−h] Thus,

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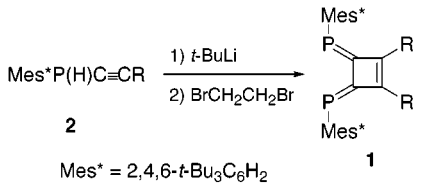
expansion of the structure at the 1- and/or 2-position of the cyclobutene ring and evaluation of the steric and/or electronic effects of the expansion are of interest from the viewpoints of coordination chemistry as well as synthetic organic chemistry. We report here the preparations of 3,4-diphosphinidenecyclobutene derivatives having ring-fused structures.

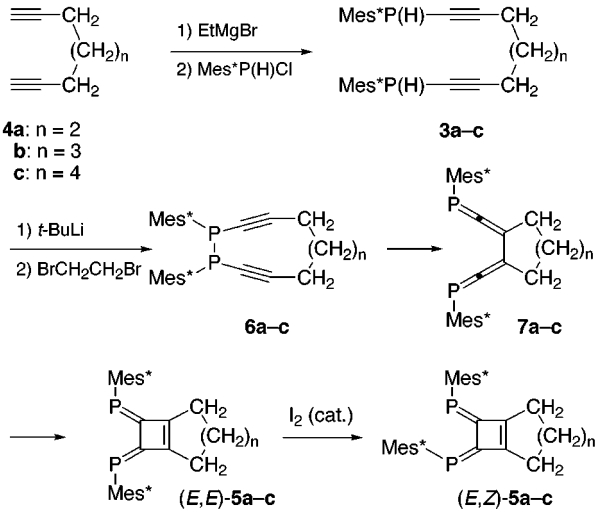
In a typical preparative method of **1**, alkynylphosphines **2** were used as starting material (Scheme 1). Thus, we

Scheme 1



prepared α,ω-bis[(2,4,6-tri-*tert*-butylphenyl)phosphino]diynes **3a**−**c** by reactions of chloro(2,4,6-tri-*tert*-butylphenyl)-phosphine[2f,6] with BrMgC≡CCH$_2$(CH$_2$)$_n$CH$_2$C≡CMgBr [prepared from the corresponding diynes **4a**−**c**; Scheme 2]. **3a**:

Scheme 2

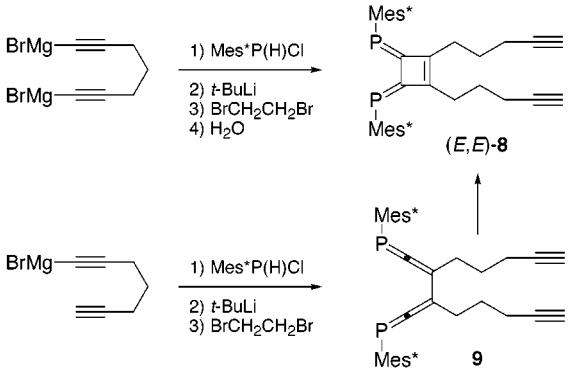


^{31}P NMR (81 MHz, C_6D_6) δ_P = −101.0 (d, $^1J_{PH}$ = 246.7 Hz). **3b**: δ_P = −101.0 (d, $^1J_{PH}$ = 246.5 Hz). **3c**: δ_P = −101.5 (d, $^1J_{PH}$ = 244.6 Hz).

When the phosphines **3a**−**c** were treated successively with *tert*-butyllithium (2 molar equiv) and 1,2-dibromoethane (1 molar equiv), the ring-fused diphosphinidenecyclobutene derivatives (*E*,*E*)-**5a**−**c** were obtained. (*E*,*E*)-**5a**: 25% yield [based on Mes*PH$_2$ used in the preparation of Mes*P(H)-Cl]; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ_P = 148.8. (*E*,*E*)-**5b**: 20% yield; δ_P =147.9. (*E*,*E*)-**5c**: 11% yield; δ_P =147.2. Intermediates **6c** as well as **7a**−**c** were observed by ^{31}P NMR spectroscopic monitoring during the reaction. On the other hand, plausible intermediates **6a**,**b** were not detected by ^{31}P NMR spectroscopic monitoring, probably because the rearrangement reaction is faster due to the larger ring strain, compared to the case of **6c**. **6c**: ^{31}P{^{1}H} NMR (81 MHz, THF−C_6D_6) δ_P = −34.8. **7a**: δ_P = 63.6. **7b**: δ_P = 63.3. **7c**: δ_P = 63.4. The diphosphinidenecyclobutenes (*E*,*E*)-**5a**−**c** thus obtained were converted to the (*E*,*Z*)-isomers by addition of catalytic amounts of iodine in benzene.[7]

It should be noted that the reaction of BrMgC≡C(CH$_2$)$_3$C≡CMgBr with Mes*P(H)Cl (2 molar equiv) followed by reactions with *tert*-butyllithium and 1,2-dibromoethane resulted in the formation of 1,2-dipent-4-ynyl-3,4-diphosphinidenecyclobutene (*E*,*E*)-**8** [δ_P ($CDCl_3$) = 153.6, 6% isolated yield after silica gel column chromatographic and recycling gel permeation column chromatographic treatments] (Scheme 3).

Scheme 3



Thus, the diphosphinidenecyclobutene fused with a five-membered ring was not obtained by the present method. When the reaction of BrMgC≡C(CH$_2$)$_3$C≡CMgBr with Mes*P(H)Cl (2 molar equiv) was quenched with water, monophosphine Mes*P(H)C≡C(CH$_2$)$_3$C≡CH [δ_P($CDCl_3$) = −101.3 (d, $^1J_{PH}$ = 244.5 Hz)] and Mes*P(O)H$_2$ [a hydrolyzed product of unreacted Mes*P(H)Cl] were obtained after gel permeation column chromatography. We could not find either the corresponding diphosphine or its derivatives in this reaction.

The compound (*E*,*E*)-**8** was alternatively obtained in 30% yield in the reaction of Mes*P(H)Cl with BrMgC≡C(CH$_2$)$_3$C≡CH followed by addition of *tert*-butyllithium and 1,2-dibromoethane. In the latter reaction, intermediate bis(phosphaallene) **9** was observed [δ_P(THF−C_6D_6) = 75.5] by ^{31}P NMR spectroscopic monitoring of the reaction. As shown in Scheme 4, (*E*,*E*)-**8** was also formed by desilylation reaction of (*E*,*E*)-1,2-bis[5-(trimethylsilyl)pent-4-ynyl]-3,4-

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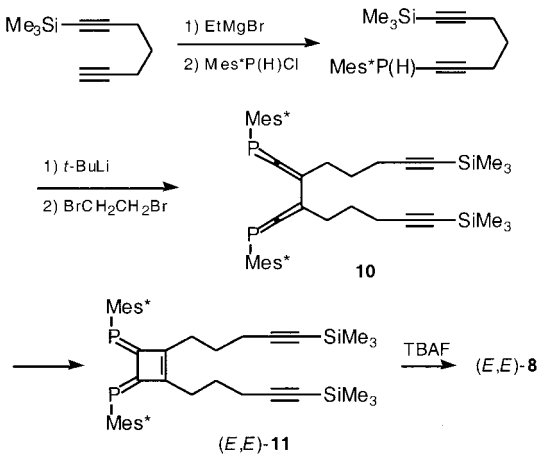
Scheme 4



diphosphinidenecyclobutene **11** [$\delta_P(CDCl_3) = 153.9$][8] with tetrabutylammonium fluoride.

The structure of (*E*,*E*)-**5b** was confirmed by X-ray crystallography.[9,10] Figure 1 shows a molecular structure of

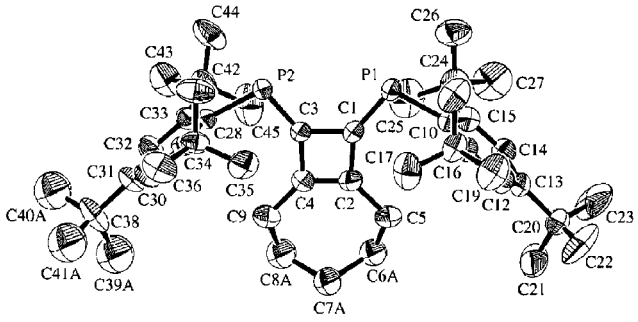
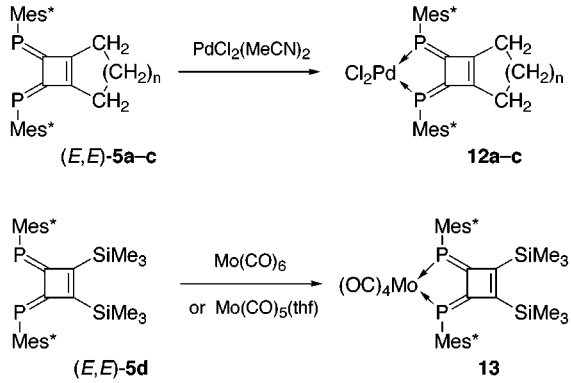


Figure 1. Molecular structure of (*E*,*E*)-**5b** showing the atomic labeling scheme with thermal ellipsoids (30% probability).

(*E*,*E*)-**5b**.[11,12] The methyl groups C(39)−C(41) of a *p*-*tert*-butyl group and the methylenes C(6)−C(8) of the seven-membered ring were disordered. The atoms C(1)−C(5), C(9), P(1), and P(2) were on the same plane within 0.012(8) Å. The two Mes* groups were nearly perpendicular to this plane [interplanar angles between the diphosphinidenecyclobutene plane and the aromatic rings C(10)−C(15) and C(28)−C(33) are 87.5(3)° and 87.5(2)°, respectively].

Reaction of (*E*,*E*)-**5a**−**c** with $PdCl_2(MeCN)_2$ in THF gave dichloropalladium(II) complexes **12a**−**c** (Scheme 5). In ^1H

Scheme 5



NMR spectra of **12a**−**c**, signals due to the methylene protons showed downfield shifts compared with the corresponding signals of the free ligands (*E*,*E*)-**5a**−**c**. For example, methylene signals for **12b** appear at $\delta = 1.46$ (4H, br s), 1.56 (2H, br s), and 1.87 (4H, br s), while those for the free ligand (*E*,*E*)-**5b** appear at $\delta = 0.86$ (4H, br s), 1.05 (4H, pseudo t), and 1.26 (2H, m). Probably the aromatic rings of the Mes* groups in the free ligands [(*E*,*E*)-**5a**−**c**] are close to the methylenes, causing strong shielding effect in the ^1H NMR spectra. This shielding effect might be decreased when the Mes* groups move away from the methylenes upon coordination of the phosphorus atoms to the metal.

This is demonstrated by the crystal structure analysis of the ligand and the complex.[10] Figure 2 shows the molecular structures of **12b** in the crystal.[13,14] The angles C(1)−P(1)−C(10) and C(3)−P(2)−C(28) become larger upon coordination, and both aromatic rings move apart from the methylenes

(8) Crude compound **11** was obtained in ca. 49% yield [via intermediate bis(phosphaallene) **10**; δ_P (THF−C_6D_6) = 75.8] and used without purification. Attempted purification of **11** failed because of partial decomposition during the isolation process.

(9) The structure was solved with SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(10) The complete crystal data are deposited at at the Cambridge Crystallographic Data Centre (Nos. CCDC-173600 for (*E*,*E*)-**5b** and CCDC-173599 for **12b**).

(11) Johnson, C. K.; ORTEP-II, Oak Ridge National Laboratory Report, ORNL-TM-5138, 1976, Oak Ridge, TN.

(12) Hydrogen atoms are omitted for clarity. The atoms [C(6)−C(8) and C(39)−C(41)] were disordered, but only atoms with a dominant occupancy factor are displayed. Some selected bond lengths(Å) and angles (deg): P(1)−C(1), 1.661(6); P(2)−C(3), 1.673(5); C(1)−C(2), 1.472(8); C(3)−C(4), 1.481(7); C(1)−C(3), 1.505(8); C(2)−C(4), 1.351(8); C(2)−C(5), 1.509(9); C(4)−C(9), 1.487(10); P(1)−C(10), 1.859(5); P(2)−C(28), 1.830(5); C(1)−P(1)−C(10), 99.6(2); C(3)−P(2)-C(28), 100.4(2); P(1)−C(1)−C(2), 143.1(4); P(1)−C(1)−C(3), 130.0(4); C(2)−C(1)−C(3), 86.9(5); C(1)−C(2)−C(4), 93.5(4); C(1)−C(2)−C(5), 132.4(6); C(4)−C(2)−C(5), 134.2(6); P(2)−C(3)−C(1), 130.3(4); P(2)−C(3)−C(4), 142.6(5); C(1)−C(3)−C(4), 87.2(4); C(2)−C(4)−C(3), 92.5(5); C(2)−C(4)−C(9), 134.2(6); C(3)−C(4)−C(9), 133.4(6).

(13) The structure was solved with SAPI91: Hai-Fu, F.; Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan, 1991.

(14) Hydrogen atoms and incorporated solvent molecules are omitted for clarity. Some selected bond lengths (Å) and angles (deg): Pd−P(1), 2.267(2); Pd−P(2), 2.256(2); Pd−Cl(1), 2.329(2); Pd−Cl(2), 2.331(2); P(1)−C(1), 1.654(9); P(2)−C(3), 1.652(8); C(1)−C(2), 1.46(1); C(3)−C(4), 1.49(1); C(1)−C(3), 1.47(1); C(2)−C(4), 1.38(1); C(2)−C(5), 1.49(1); C(4)−C(9), 1.47(1); P(1)−C(10), 1.815(8); P(2)−C(28), 1.799(9); P(1)−Pd−P(2), 85.20(8); Cl(1)−Pd−Cl(2), 93.81(8); P(1)−Pd−Cl(1), 91.23(8); P(2)−Pd−Cl(2), 89.76(8); Pd−P(1)−C(1), 108.4(3); Pd−P(1)−C(10), 137.5(3); Pd−P(2)−C(3), 108.9(3); Pd−P(2)−C(28), 132.8(3); C(1)−P(1)−C(10), 114.1(4); C(3)−P(2)−C(28), 118.2(4); P(1)−C(1)−C(2), 152.7(7); P(1)−C(1)−C(3), 118.9(6); C(2)−C(1)−C(3), 88.4(6); C(1)−C(2)−C(4), 92.8(7); C(1)−C(2)−C(5), 134.8(8); C(4)−C(2)−C(5), 132.4(8); P(2)−C(3)−C(1), 118.6(6); P(2)−C(3)−C(4), 153.3(7); C(1)−C(3)−C(4), 88.0(6); C(2)−C(4)−C(3), 90.9(7); C(2)−C(4)−C(9), 134.2(8); C(3)−C(4)−C(9), 134.9(8).

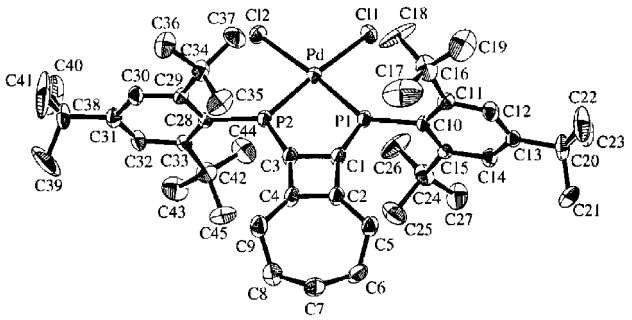


Figure 2. Molecular structure of **12b** showing the atomic labeling scheme with thermal ellipsoids (30% probability).

in **12b**, compared with those in (*E*,*E*)-**5b** [in (*E*,*E*)-**5b** the angle C(1)−P(1)−C(10) is 99.6(2)° and the angle C(3)−P(2)−C(28) is 100.4(2)°, whereas in **12b** the angle C(1)−P(1)−C(10) is 114.1(4)° and the angle C(3)−P(2)−C(28) is 118.2(4)°].

The substantial changes in the angles C(1)−P(1)−C(10) and/or C(3)−P(2)−C(28) may affect the coordination abilities of the ligands: In the reaction of (*E*,*E*)-**5b** with an excess amount of $Mo(CO)_5$(thf), neither a chelate complex nor a monodentate complex was detected by ^{31}P NMR spectroscopic monitoring. Moreover, the reaction of (*E*,*E*)-**5b** with an excess amount of $Mo(CO)_6$ in refluxing 1,4-dioxane led to decomposition, and no formation of the corresponding chelate-type tetracarbonylmolybdenum complex was observed by ^{31}P NMR spectroscopy, in contrast to the previous results using (*E*,*E*)-**5d** as follows: The reactions of (*E*,*E*)-**5d** with an excess amount of $Mo(CO)_5$(thf) or $Mo(CO)_6$ gave only chelate complex **13** as a stable compound,[5a] probably because the Mes*P═C−C═PMes* moiety in (*E*,*E*)-**5d** is preoriented in favor of chelate formation due to steric repulsion between the bulky Mes* group and the trimethylsilyl group. Actually, the angles corresponding to C(1)−P(1)−C(10) and C(3)−P(2)−C(28) in (*E*,*E*)-**5d** largely deviate from those in (*E*,*E*)-**5b** [in (*E*,*E*)-**5d**, the angles are 110.7(3)° and 108.0(3)°] and are very close to those for **13** [109.7(2)° and 108.7(2)°].[5b] This fact suggests that the steric effect of the substituents at the 1- or 2-position plays an important role in coordination and in catalytic abilities[5c,f−h] of the complexes. Further studies on the properties of the ring-fused diphosphinidenecyclobutene derivatives are now in progress.

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Supporting Information Available: Experimental procedures and spectroscopic data for compounds (*E*,*E*)-**5a**−**c**, (*E*,*Z*)-**5a**−**c**, **8**, and **12a**−**c**, including the crystal data of (*E*,*E*)-**5b** and **12b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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