Preparation of Sterically Protected 3,4-Bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]-1,2-bis[4-(4-vinylphenyl)butyl]cyclobutene and Its Polymers

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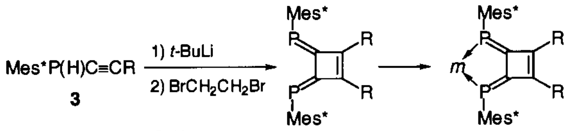
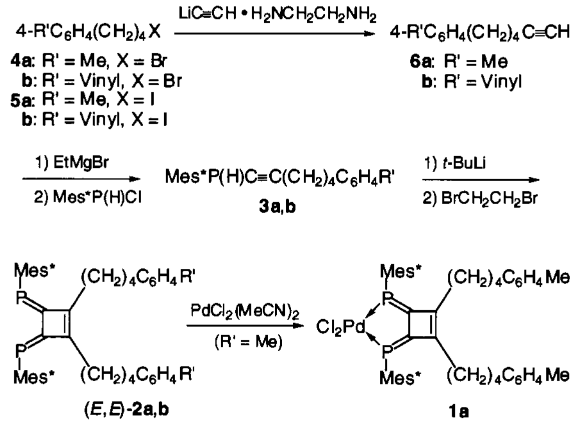
Two new sterically protected 3,4-diphosphinidenecyclobutenes, i.e., 1,2-bis[4-(4-methylphenyl)butyl]-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene, and 3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]-1,2-bis[4-(4-vinylphenyl)butyl]cyclobutene, were prepared. Copolymerization of the latter with styrene was studied. Treatment of [6-(4-vinylphenyl)hex-1-ynyl](2,4,6-tri-*t*-butylphenyl)phosphine with butyllithium and 1,2-dibromoethane afforded a polymer of the latter cyclobutene.

In solid phase synthesis and more recently combinatorial chemistry, polystyrene and the related polymers have been attractive to the synthetic organic chemists.[1] Polymers having special functionalities, such as polymer–metal complexes, have also been of interest in materials science.[2] However, to the best of our knowledge, there have been no studies on polymers containing phosphorus atom(s) in low coordination states.[3,4] We have reported syntheses of sterically protected 3,4-diphosphinidenecyclobutene–metal complexes **1**, utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl substituent (abbreviated to the Mes* group) as sterically protecting auxiliary.[5] Introduction of the diphosphinidenecyclobutene moieties into polymeric structures is interesting from the viewpoint of synthetic chemistry as well as materials chemistry. We report here the preparation of polymers containing the 3,4-diphosphinidenecyclobutene moieties, as well as preparations of 1,2-bis(4-arylbutyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes.



In a typical preparative method of the ligand **2**, alkynylphosphines **3** were used as starting materials. Thus, we prepared [6-(4-methylphenyl)hex-1-ynyl](2,4,6-tri-*t*-butylphenyl)phosphine (**3a**) and (2,4,6-tri-*t*-butylphenyl)[6-(4-vinylphenyl)hex-1-ynyl]phosphine (**3b**) as follows. 4-Bromotoluene was treated in THF with butyllithium and 1,4-dibromobutane to give 1-(4-bromobutyl)-4-methylbenzene (**4a**)[6] (76% yield). When 1,4-diiodobutane was used instead of 1,4-dibromobutane, the corresponding iodide **5a** was obtained.[7] Reaction of **4a** (or **5a**) with lithium acetylide–ethylenediamine complex afforded 6-(4-methylphenyl)hex-1-yne (**6a**).[7] Then the alkyne **6a** was metallated in THF using EtMgBr and the resulting acetylide was allowed to react with Mes*P(H)Cl[8] (prepared from Mes*PH$_2$) to form the phosphine **3a**: ^{31}P NMR (81 MHz, C$_6$D$_6$) $\delta_P = -101.4$ (d, $^1J_{PH} = 244.5$ Hz). The phosphine **3b** was also prepared by a method similar to that for **3a**, starting from 4-bromostyrene, via **5b** and **6b**.[7] **3b**: ^{31}P NMR (CDCl$_3$) $\delta_P = -100.9$ (d, $^1J_{PH} = 220.8$ Hz). It should be noted that reaction of **4b**[9] and lithium acetylide–ethylenediamine complex resulted in the formation of a trace amount of **6b**.



Lithiation of the phosphine **3a** (6.86 mmol) with *t*-butyllithium (6.88 mmol) in THF followed by treatment with 1,2-dibromoethane (3.47 mmol) afforded (*E*,*E*)-**2a** [δ_P (CDCl$_3$) = 149.7] (ca. 40% yield) and a trace amount of (*E*,*Z*)-**2a** [δ_P (CDCl$_3$) = 154.0 and 170.8, AB, $^3J_{PP} = 9.7$ Hz]. An attempted purification of (*E*,*E*)-**2a** using silica-gel column chromatography and recycling gel-permeation column chromatography (GPC) failed. Thus, the crude diphosphinidenecyclobutene (*E*,*E*)-**2a** was allowed to react with PdCl$_2$(MeCN)$_2$ in THF to give the corresponding dichloropalladium complex **1a** in pure form (36% yield based on Mes*PH$_2$): Red prisms, mp 162–164 °C; δ_P (CDCl$_3$) = 143.9; FAB-MS *m*/*z* 1000 (M$^+$–2Cl–1) and 893 (M$^+$–Pd–2Cl–2). Although the FAB-MS spectrum of **1a** did not give the molecular ion peak, the structure of **1a** was unambiguously confirmed by X-ray crystallography.[10] Figure 1 is an ORTEP[11] drawing of the molecular structure of **1a**.

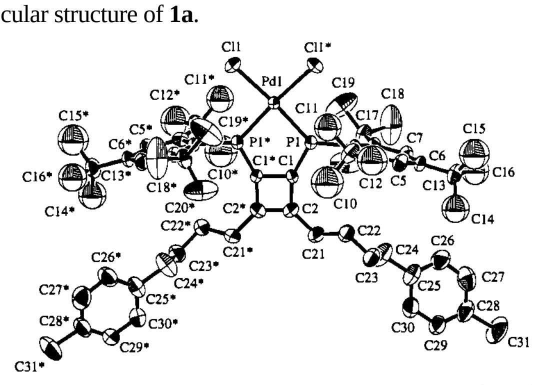
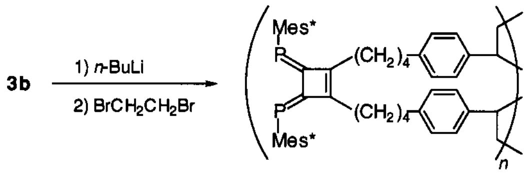


Figure 1. Molecular structure of **1a** showing the atomic labeling scheme with thermal ellipsoids (50% probability). The incorporated solvent molecule and hydrogen atoms were omitted for clarity. Some important bond lengths(Å) and angles(°): Pd–P(1), 2.260(2); Pd–Cl(1), 2.340(2); P(1)–C(1), 1.657(7); C(1)–C(2), 1.46(1); C(1)–C(1*), 1.47(1); C(2)–C(2*), 1.35(1); P(1)–Pd–P(1*), 84.4(1); P(1)–Pd–Cl(1*), 91.43(7); Cl(1)–Pd–Cl(1*), 92.7(1); P(1)–C(1)–C(1*), 118.2(2); P(1)–C(1)–C(2), 154.2(6); C(1*)–C(1)–C(2), 87.6(4); C(1)–C(2)–C(2*), 92.3(4).

The phosphine **3b** was converted to (*E*,*E*)-**2b** [δ_P ($CDCl_3$) = 150.2], by the reaction of **3b** with *t*-butyllithium and 1,2-dibromoethane, in 4% isolated yield (based on **3b**) after treatment with GPC (JAIGEL H1+H2 column).[12] Then preparation of a polymer of **2b** was attempted. Treatment of (*E*,*E*)-**2b** with *t*-butyllithium (12 mol%) afforded not a polymer but dimeric products[13] in a trace amount, however, treatment of a mixture of (*E*,*E*)-**2b** (254 mg, 0.276 mmol) and styrene (273 mg, 2.62 mmol) with *t*-butyllithium (0.014 mmol) in THF at –78 °C afforded a copolymer (90.0 mg after GPC; δ_P ($CDCl_3$) = 149.6 and 149.9 (1:1); M_n = 2900, M_w/M_n = 1.3, determined by GPC using polystyrenes as standard).

Interestingly, when **3b** (778 mg, 1.69 mmol) was treated with *n*-butyllithium (1.69 mmol) and 1,2-dibromoethane (0.85 mmol) in THF at –78 °C, a polymer of **2b** was obtained in ca. 70% yield based on **3b** (M_n = 12000, M_w/M_n = 72).[14] ^{31}P NMR spectrum of the polymer showed a relatively broad signal at δ_P ($CDCl_3$) = 151.0, indicating (*E*,*E*)-configuration about the phosphorus–carbon double bond. The polymer was soluble in several solvents such as chloroform and THF.



When the polymer was treated with $PdCl_2(MeCN)_2$ in THF, a brown solid was precipitated. The solid was insoluble in common solvents. Further studies on the properties of the polymer of **2b** and their derivatives are in progress.

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References and Notes

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7 **5a**: 28% yield; colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ = 1.76–2.00 (4H, m, CH_2), 2.44 (3H, s, Me), 2.70 (2H, t, ^3J = 7.3 Hz, CH_2), 3.28 (2H, t, ^3J = 6.7 Hz, CH_2), and 7.20 (4H, br. t, arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 7.0 (CH_2), 21.2 (Me), 32.4 (CH_2), 33.0 (CH_2), 34.4 (CH_2), 128.3 (arom.), 129.1 (arom.), 135.3 (arom.), and 138.7 (arom.). Found: *m*/*z* 274.0216 (M^+). Calcd for $C_{11}H_{15}I$, 274.0178. **5b**: 68% yield; colorless oil; ^1H NMR δ = 1.76–2.03 (4H, m, CH_2), 2.71 (2H, t, ^3J = 7.3 Hz, CH_2), 3.26 (2H, t, ^3J = 6.7 Hz, CH_2), 5.32 (1H, dd, ^3J = 11.7 Hz, ^2J = 0.9 Hz, CH=C*H*H'), 5.83 (1H, dd, ^3J = 17.6 Hz, ^2J = 0.9 Hz, CH=CH*H*'), 6.86 (1H, dd, ^3J = 10.9 Hz, ^3J =17.6 Hz, C*H*=CH_2), 7.20 (2H, d, ^3J = 8.1 Hz, arom.), and 7.41 (2H, d, ^3J = 8.1 Hz, arom.); $^{13}C\{^1H\}$ NMR δ = 7.0 (CH_2), 32.2 (CH_2), 33.0 (CH_2), 34.5 (CH_2), 113.1 (CH=*C*H_2), 126.3 (arom.), 128.6 (arom.), 135.4 (arom.), 136.7 (*C*H=CH_2), and 141.5 (arom.). Found: *m*/*z* 286.0222 (M^+). Calcd for $C_{12}H_{15}I$, 286.0178.
6a: 78% yield either from **4a** or **5a**; colorless oil; ^1H NMR δ = 1.60–1.86 (4H, m, CH_2), 2.03 (1H, t, ^4J = 2.7 Hz, C≡CH), 2.30 (2H, dt, ^3J = 6.9 Hz, ^4J = 2.7 Hz, CH_2), 2.42 (3H, s, Me), 2.69 (2H, t, ^3J = 7.5 Hz, CH_2), and 7.18 (4H, br. s, arom.); $^{13}C\{^1H\}$ NMR δ = 18.4 (CH_2), 21.1 (Me), 28.1 (CH_2), 30.6 (CH_2), 35.0 (CH_2), 68.5 (C≡*C*H), 84.4 (*C*≡CH), 128.3 (arom.), 129.1 (arom.), 135.2 (arom.), and 139.2 (arom.). Found: *m*/*z* 172.1251 (M^+). Calcd for $C_{13}H_{16}$, 172.1252. **6b**: 41% yield; colorless oil; ^1H NMR δ = 1.53–1.84 (4H, m, CH_2), 1.97 (1H, t, ^4J = 2.6 Hz, C≡CH), 2.23 (2H, dt, ^3J = 6.9 Hz, ^4J = 2.6 Hz, CH_2), 2.64 (2H, t, ^3J = 7.5 Hz, CH_2), 5.21 (1H, dd, ^3J = 10.9 Hz, ^2J = 1.0 Hz, CH=C*H*H'), 5.73 (1H, dd, ^3J = 17.6 Hz, ^2J = 1.0 Hz, CH=CH*H*'), 6.72 (1H, dd, ^3J = 10.9 Hz, ^3J =17.6 Hz, C*H*=CH_2), 7.16 (2H, d, ^3J = 8.1 Hz, arom.), and 7.35 (2H, d, ^3J = 8.1 Hz, arom.); $^{13}C\{^1H\}$ NMR δ = 18.4 (CH_2), 28.1 (CH_2), 30.5 (CH_2), 35.2 (CH_2), 68.7 (C≡*C*H), 84.4 (*C*≡CH), 113.0 (CH=*C*H_2), 126.3 (arom.), 128.7 (arom.), 135.3 (arom.), 136.8 (*C*H=CH_2), and 142.0 (arom.). Found: *m*/*z* 184.1256 (M^+). Calcd for $C_{14}H_{16}$, 184.1252.

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10 Recrystallized from CH_2Cl_2. $1/2[C_{62}H_{88}Cl_2P_2Pd]\cdot CH_2Cl_2$, M_r = 621.25. Monoclinic, space group *C*2/*c* (#15), a = 23.821(1), b = 11.2078(4), c = 26.4565(5) Å, β = 108.450(1)°, V = 6700.2(4) $Å^3$, Z = 8, D_{calc} = 1.232 gcm^{-3}, μ (Mo Kα) = 5.99 cm^{-1}. 7342 Unique reflections with $2\theta \le 55.0°$. Of these, 4546 with $I > 3.0\sigma(I)$ were used for R_1 calculation. The structure was solved by heavy-atom Patterson methods. Non-hydrogen atoms except for C(10)–C(12) and C(14)–C(16) were refined anisotropically. Hydrogen atoms except for those on C(10)–C(12) and C(14)–C(16) were included but not refined. R_1 = 0.068, R = 0.068, R_w = 0.091. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (no. CCDC-156637).

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12 A side reaction seems to have taken place, in which one of the vinyl groups of (*E*,*E*)-**2b** was attacked by *t*-BuLi. (*E*,*E*)-**2b**: pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ = 0.88 (4H, br. t, ^3J = 7.5 Hz, CH_2), 1.03 (4H, t, ^3J = 7.6 Hz, CH_2), 1.11 (4H, tt, ^3J = 7.8 Hz, CH_2), 1.31 (18H, s, *p*-*t*-Bu), 1.52 (36H, s, *o*-*t*-Bu), 2.35 (4H, t, ^3J = 7.4 Hz, CH_2), 5.19 (2H, d, ^3J = 10.9 Hz, =C*H*H'), 5.69 (2H, d, ^3J = 17.7 Hz, =CH*H*'), 6.68 (2H, dd, ^3J = 17.7 Hz and 10.9 Hz, CH=), 6.98 (4H, d, ^3J = 8.0 Hz, arom.), 7.28 (4H, d, ^3J = 8.0 Hz, arom.), and 7.32 (4H, *m*-Mes*).

13 ^1H NMR spectrum, molecular weight measurement (by GPC), and MALDI-TOF MS indicate formation of a mixture of products, whose molecular weights correspond to [2×(*E*,*E*)-**2b**+*n*(*t*-Bu)+*n*H; *n* = 1–5], however, attempted separation and characterization have been unsuccessful because of the low yield.

14 A MALDI-TOF MS showed only weak signals less than 12000, including those corresponding to dodecamer (Found: *m*/*z* 11030; Calcd: 11024) and undecamer (Found: *m*/*z* 10107; Calcd: 10105).