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-1ynyl](2,4,6-tri-*t*-butylphenyl)phosphine with butyllithium and 1,2dibromoethane 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 2,4,6tri-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-tbutylphenyl)phosphinidene]cyclobutenes.



In a typical preparative method of the ligand 2, alkynylphosphines 3 were used as starting materials. Thus, we prepared [6-(4methylphenyl)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)-4methylbenzene $(4a)^6$ (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)Cl⁸ (prepared from Mes*PH₂) to form the phosphine **3a**: ³¹P NMR (81 MHz, C_6D_6) $\delta_P = -101.4$ (d, ¹ $J_{PH} = 244.5$ 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**: ³¹P NMR (CDCl₃) $\delta_{\rm P} = -100.9$ (d, ${}^{1}J_{\rm PH} = 220.8$ 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 (CDCl₃) = 149.7] (ca. 40% yield) and a trace amount of (E,Z)-2a [δ_P (CDCl₃) = 154.0 and 170.8, AB, ${}^{3}J_{PP} = 9.7$ 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 PdCl₂(MeCN)₂ in THF to give the corresponding dichloropalladium complex 1a in pure form (36% yield based on Mes*PH₂): Red prisms, mp 162–164 °C; δ_P (CDCl₃) = 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 Xray crystallography.¹⁰ Figure 1 is an ORTEP¹¹ 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).

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The phosphine **3b** was converted to (E,E)-**2b** [$\delta_{\rm p}$ (CDCl₃) = 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 products¹³ 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; $\delta_{\rm p}$ (CDCl₃) = 149.6 and 149.9 (1:1); $M_{\rm n}$ = 2900, $M_{\rm w}/M_{\rm n}$ = 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 ³¹P NMR spectrum of the polymer showed a relatively broad signal at δ_P (CDCl₃) = 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

- # Fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists.
- N. K. Terrett, "Combinatorial Chemistry," Oxford University Press, Inc., New York (1998).
- 2 E. Tsuchida and H. Nishide, Adv. Polym. Sci., 24, 1 (1977).
- 3 "Multiple Bonds and Low Coordination in Phosphorus Chemistry," ed. by M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart (1990); K. B. Dillon, F. Mathey, and J. F. Nixon, "Phosphorus: The Carbon Copy," John Wiley & Sons, Chichester (1998).
- 4 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982); M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, *Tetrahedron Lett.*, 25, 1809 (1984); M. Yoshifuji, K. Toyota, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1984, 689.
- K. Toyota, K. Tashiro, and M. Yoshifuji, Chem. Lett., 1991, 2079;
 K. Toyota, K. Tashiro, M. Yoshifuji, I. Miyahara, A. Hayashi, and K. Hirotsu, J. Organomet. Chem., 431, C35 (1992);
 K. Toyota, K. Masaki, T. Abe, and M. Yoshifuji, Chem. Lett., 1995, 221;
 M. Yoshifuji, Y. Ichikawa, K. Toyota, E. Kasashima, and Y. Okamoto, Chem. Lett., 1997, 87;
 M. Yoshifuji, Y. Ichikawa, N. Yamada, and K. Toyota, Chem. Commun., 1998, 27.
- 6 E. Bosies, A. Eswein, F. Grams, and H.-w. Krell, Ger. Offen. DE, 19548624 (1997); *Chem. Abstr.*, **127**: 121746 (1997).
- 7 **5a**: 28% yield; colorless oil; ¹H NMR (200 MHz, CDCl₃) δ = 1.76–2.00 (4H, m, CH₂), 2.44 (3H, s, Me), 2.70 (2H, t, ³J = 7.3

Hz, CH₂), 3.28 (2H, t, ³*J* = 6.7 Hz, CH₂), and 7.20 (4H, br. t, arom.); ¹³C{¹H} NMR (50 MHz, CDCl₃) δ = 7.0 (CH₂), 21.2 (Me), 32.4 (CH₂), 33.0 (CH₂), 34.4 (CH₂), 128.3 (arom.), 129.1 (arom.), 135.3 (arom.), and 138.7 (arom.). Found: *m*/*z* 274.0216 (M⁺). Calcd for C₁₁H₁₅I, 274.0178. **5b**: 68% yield; colorless oil; ¹H NMR δ = 1.76–2.03 (4H, m, CH₂), 2.71 (2H, t, ³*J* = 7.3 Hz, CH₂), 3.26 (2H, t, ³*J* = 6.7 Hz, CH₂), 5.32 (1H, dd, ³*J* = 11.7 Hz, ²*J* = 0.9 Hz, CH=*CH*H'), 5.83 (1H, dd, ³*J* = 17.6 Hz, ²*J* = 0.9 Hz, CH=*CH*H'), 5.83 (1H, dd, ³*J* = 17.6 Hz, ²*J* = 0.9 Hz, CH=*CH*H'), 5.83 (1H, dd, ³*J* = 17.6 Hz, ²*J* = 0.9 Hz, CH=*CH*H'), 5.83 (1H, dd, ³*J* = 17.6 Hz, ²*J* = 0.9 Hz, CH=*C*HH'), 5.83 (1H, dd, ³*J* = 17.6 Hz, CH=*C*H₂), 7.20 (2H, d, ³*J* = 8.1 Hz, arom.), and 7.41 (2H, d, ³*J* = 8.1 Hz, arom.); ¹³C{¹H} NMR δ = 7.0 (CH₂), 32.2 (CH₂), 33.0 (CH₂), 34.5 (CH₂), 113.1 (CH=*C*H₂), and 141.5 (arom.). Found: *m*/*z* 286.0222 (M⁺). Calcd for C₁₂H₁₅I, 286.0178. **6a**: 78% yield either from **4a** or **5a**; colorless oil; ¹H NMR δ

= 1.60–1.86 (4H, m, CH₂), 2.03 (1H, t, ${}^{4}J$ = 2.7 Hz, C=CH), 2.30 (2H, dt, ${}^{3}J = 6.9$ Hz, ${}^{4}J = 2.7$ Hz, CH₂), 2.42 (3H, s, Me), 2.69 (2H, t, ${}^{3}J = 7.5$ Hz, CH₂), and 7.18 (4H, br. s, arom.); ${}^{13}C{}^{1}H{}$ NMR $\delta = 18.4$ (CH₂), 21.1 (Me), 28.1 (CH₂), 30.6 (CH₂), 35.0 (CH₂), 68.5 (C≡CH), 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 $\delta = 1.53 - 1.84$ (4H, m, CH₂), 1.97 (1H, t, ⁴J = 2.6 Hz, C=CH), 2.23 (2H, dt, ${}^{3}J = 6.9$ Hz, ${}^{4}J = 2.6$ Hz, CH₂), 2.64 (2H, t, ${}^{3}J = 7.5$ Hz, CH₂), 5.21 (1H, dd, ${}^{3}J = 10.9$ Hz, ${}^{2}J = 1.0$ Hz, CH=CHH'), 5.73 (1H, dd, ${}^{3}J = 17.6$ Hz, ${}^{2}J = 1.0$ Hz, CH=CHH'), 6.72 (1H, dd, ${}^{3}J = 10.9$ Hz, ${}^{3}J = 17.6$ Hz, CH=CH₂), 7.16 (2H, d, ${}^{3}J = 8.1$ Hz, arom.), and 7.35 (2H, d, ${}^{3}J = 8.1$ Hz, arom.); ${}^{13}C{}^{1}H{}$ NMR $\delta = 18.4$ (CH₂), 28.1 (CH₂), 30.5 (CH₂), 35.2 (CH₂), 68.7 (C=CH), 84.4 (C=CH), 113.0 (CH=CH₂), 126.3 (arom.), 128.7 (arom.), 135.3 (arom.), 136.8 (CH=CH₂), and 142.0 (arom.). Found: m/z 184.1256 (M⁺). Calcd for $\overline{C}_{14}H_{16}$, 184.1252.

- 8 G. Märkl and P. Kreitmeier, *Angew. Chem.*, *Int. Ed. Engl.*, 27, 1360 (1988).
- 9 T. Onozuka, M. Shindo, H. Kiba, and Y. Aosaki, Japan. Kokai Tokkyo Koho JP, 07108179 (1995); *Chem. Abstr.*, **123**: 179001 (1995).
- 10 Recrystallized from CH₂Cl₂. 1/2[C₆₂H₈₈Cl₂P₂Pd]·CH₂Cl₂, $M_r = 621.25$. Monoclinic, space group C2/c (#15), a = 23.821(1), b = 11.2078(4), c = 26.4565(5) Å, $\beta = 108.450(1)^{\circ}$, V = 6700.2(4) Å³, Z = 8, $D_{calc} = 1.232$ gcm⁻³, μ (Mo K α) = 5.99 cm⁻¹. 7342 Unique reflections with $2\theta \le 55.0^{\circ}$. 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).
- 11 C. K. Johnson, ORTEP-II, Oak Ridge National Laboratory Report, ORNL-TM-5138, Oak Ridge, TN, 1976.
- 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, CDCl₃) $\delta = 0.88$ (4H, br. t, ³J = 7.5 Hz, CH₂), 1.03 (4H, t, ³J = 7.6 Hz, CH₂), 1.11 (4H, tt, ³J = 7.8 Hz, CH₂), 1.31 (18H, s, *p*-*t*-Bu), 1.52 (36H, s, *o*-*t*-Bu), 2.35 (4H, t, ³J = 7.4 Hz, CH₂), 5.19 (2H, d, ³J = 10.9 Hz, =CHH'), 5.69 (2H, d, ³J = 17.7 Hz, =CHH'), 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 $[2\times(E,E)-2\mathbf{b}+n(t-B\mathbf{u})+n\mathbf{H}; n = 1-5]$, 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).