Supporting Information

Syntheses, Structures, Dynamic Behaviour, and Stabilities of Perfectly "Anti-apicophilic" Phosphorane and Its Tautomer under Equilibrium

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Experimental procedure

General. Solvents were purified by MBRAUN MB-SPS. All manipulations were carried out under an argon atmosphere. Dry column chromatography (DCC) and wet column chromatography (WCC) were performed with ICN silica DCC 60A and Wako gel C-200, respectively. NMR spectra were measured with a JEOL ECX400 spectrometer and a Bruker DRX-500 spectrometer. Chemical shifts are reported in δ using tetramethylsilane as an internal standard for ^{1}H, and ^{13}C NMR, or CF_3CO_2H as an external standard for ^{19}F NMR, and 85% H_3PO_4 for ^{31}P NMR spectra. Mass spectra were recorded on a JEOL JMX-SX 102 mass spectrometer using NBA as a matrix solvent. Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of the Department of Chemistry, Graduate School of Science, The University of Tokyo.
5-*t*-butyl-2-methoxymethylbromobenzene was synthesized according to the literature (Yamato, T.; Sakaue, N.; Tanaka, K.; Tsuzuki, H. *New J. Chem.* **2001**, *25*, 434-439).

Synthesis of tris(5-*t*-butyl-2-methoxymethylphenyl)methanol (14). To Mg turnings (0.40 g, 16 mmol) was added a solution of 5-*t*-butyl-2-methoxymethylbromobenzene (2.10 g, 8.17 mmol) in THF (5.8 mL) and the mixture was refluxed for 12 h. To the mixture was added a solution of diethylcarbonate (0.33 mL, 2.7 mmol) in THF (0.5 mL) and the mixture was refluxed for 24 h. The mixture was treated with aq. NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to dry column chromatography (DCC) (SiO_2, hexane-CH_2Cl_2 (1:2)) and washed with hexane to give **14** (0.94 g, 62% yield). **14**: white solid; mp 103-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 1.05 (s, 27H), 3.12 (s, 9H), 4.26 (d, 3H, *J* = 13.0 Hz), 4.54 (d, 3H, *J* = 13.0 Hz), 6.13 (s, 1H), 6.63 (br s, 3H), 7.28 (dd, 3H, *J* = 8.0, 2.0 Hz), 7.46 (d, 3H, *J* = 8.0 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 31.0 (s), 34.3 (s), 57.7 (s), 73.5 (s), 86.1 (s), 123.8 (s), 126.7 (s), 129.1 (s), 134.8 (s), 144.3 (s), 149.1 (s); Anal. Calcd for $C_{37}H_{52}O_4$: C, 79.24; H, 9.35. Found: C, 79.11; H, 9.30.

Synthesis of tris(5-*t*-butyl-2-methoxymethylphenyl)methyl methyl ether (4). A solution of triarylmethanol **14** (400 mg, 0.713 mmol) in THF (2 mL) was added to a suspension of NaH (85 mg, 2.1 mmol) in THF (0.5 mL) at room temperature and the mixture was stirred at room temperature for 1h. To the mixture was added CH_3I (0.45 mL, 21 mmol) and the mixture was stirred at room temperature overnight. The mixture was quenched with EtOH and H_2O and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from hexane to give **4** (276 mg, 69% yield). **4**: white solid; mp 123-124 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 1.23 (s, 27H), 3.07 (s, 9H), 3.14 (s, 3H), 3.89 (br s, 3H), 4.39 (br s, 3H),

7.30-7.32 (m, 6H), 7.52-7.53 (m, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 31.1 (s), 34.4 (s), 54.5 (s), 58.2 (s), 72.1 (s), 91.0 (s), 124.4 (s), 126.5 (s), 127.8 (s), 136.1 (s), 137.7 (s), 148.1 (s); Anal. Calcd for $C_{38}H_{54}O_4$: C, 79.40; H, 9.47. Found: C, 79.20; H, 9.33.

Synthesis of phosphonate 5. Lithium naphthalenide (1.73 M THF solution, 2.0 mL, 3.48 mmol) was added to a solution of methyl ether **4** (1.00 g, 1.74 mmol) in THF (10 mL) at –78 °C and the mixture was stirred at –78 °C for 0.5 h. To the mixture was added PCl_3 (0.61 mL, 6.7 mmol) and the mixture was stirred at –78 °C for 2 h. The reaction mixture was warmed to room temperature, and the solvents were removed under the reduced pressure. The resulting solid was dissolved in THF (10 mL) and the mixture was refluxed overnight. To the mixture was added aq. H_2O_2 (30%, 5 mL) and the mixture was stirred at room temperature for 0.5 h. The mixture was treated with H_2O and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to dry column chromatography (DCC) (SiO_2, Et_2O-$CHCl_3$ (1:3)) to give **5** (442 mg, 45% yield). **5**: white solid; mp 277-280 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 1.02 (s, 9H), 1.06 (s, 9H), 1.25 (s, 9H), 2.99 (s, 3H), 4.05 (d, 1H, *J* = 11.8 Hz), 4.29 (dd, 1H, *J* = 11.8, 1.7 Hz), 5.00 (dd, 1H, *J* = 13.4, 13.4 Hz), 5.29-5.43 (m, 3H), 6.37 (m, 1H), 6.91 (d, 1H, *J* = 1.7 Hz), 7.00 (d, 1H, *J* = 8.1 Hz), 7.07 (d, 1H, *J* = 8.1 Hz), 7.28-7.35 (m, 4H), 7.54 (d, 1H, *J* = 8.1 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 30.9 (s), 30.9 (s), 31.1 (s), 34.1 (s), 34.5 (s), 34.6 (s), 50.0 (d, *J* = 118 Hz), 58.2 (s), 69.4 (d, *J* = 5.1 Hz), 70.2 (d, *J* = 7.1 Hz), 72.9 (s), 123.9 (s), 124.4 (s), 124.4 (s), 124.7 (s), 124.9 (s), 127.3 (d, *J* = 8.4 Hz), 128.3 (d, *J* = 1.6 Hz), 128.4 (s), 128.6 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 12.2 Hz), 130.8 (s), 133.8 (d, *J* = 7.6 Hz), 136.6 (d, *J* = 5.8 Hz), 137.3 (s), 137.3 (d, *J* = 6.6 Hz), 149.2 (s), 150.3 (s), 151.3 (s); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 27 °C) δ 16.8; HRMS (FAB) *m*/*z* calcd for $C_{35}H_{45}O_4P$ 560.3056, found 560.3051. Anal. Calcd for $C_{35}H_{45}O_4P$: C, 74.97; H, 8.09. Found: C, 74.72; H, 8.11.

Synthesis of phosphonium salt 6. Methyl triflate (1.0 mL, 8.8 mmol) was added to a solution of phosphonate **5** (1.00 g, 1.78 mmol) in $CHCl_3$ (10 mL) at room temperature and the mixture was stirred at ambient temperature for 6h. After the removal of the solvent and excess methyl triflate under the reduced pressure, the residue was washed with ether to give **6** (0.95 g, 79% yield). **6**: white solid; mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ 1.16 (s, 27H), 5.32 (dd, 3H, *J* = 13.8, 7.3 Hz), 5.71 (dd, 3H, *J* = 20.2, 13.8 Hz), 6.83 (s, 3H), 7.41 (d, 3H, *J* = 8.0 Hz), 7.54 (d, 3H, *J* = 8.0 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 30.8 (s), 34.9 (s), 41.9 (d, *J* = 98.2 Hz), 74.6 (d, *J* = 5.7 Hz), 119.3 (q, *J* = 316.5 Hz), 127.0 (d, *J* = 8.3 Hz), 127.3 (s), 127.5 (s), 128.5 (d, *J* = 12.6 Hz), 129.2 (d, *J* = 8.3 Hz), 154.1 (s); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 27 °C) δ 39.9; ^{19}F NMR (376 MHz, $CDCl_3$, 27 °C) δ –80.0; HRMS (FAB) *m*/*z* calcd for $C_{34}H_{42}O_3P$ 529.2872, found 529.2864. Anal. Calcd for $C_{35}H_{42}F_3O_6PS$: C, 61.93; H, 6.24. Found: C, 61.84; H, 6.50.

Synthesis of 6-carbaphosphatrane 2 and its tautomer 3. $LiAl(O\text{-}t\text{-}Bu)_3H$ (1.1 M THF solution, 0.80 mL, 0.88 mmol) was added to a slurry of phosphonium salt **6** (600 mg, 0.884 mmol) in Et_2O (50 mL) at room temperature and the mixture was stirred at room temperature for 2h. The mixture was quenched with degassed H_2O and extracted with Et_2O. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to wet column chromatography (WCC) (SiO_2, Et_2O-hexane (1:1)) and recrystallized from Et_2O-hexane to give **2** and **3** as a white solid (295 mg, 63% yield.) **2**: ^{1}H NMR (500 MHz, C_6D_6, 27 °C) δ 1.09 (s, 27H), 4.73 (dd, 3H, *J* = 28.0, 13.7 Hz), 4.87 (dd, 3H, *J* = 13.7, 5.7 Hz), 6.56 (s, 3H), 6.86 (d, 3H, *J* = 7.8 Hz), 7.13 (d, 1H, *J* = 882 Hz), 7.15 (d, 3H, *J* = 7.8 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 31.0 (s), 34.5 (s), 57.2 (d, *J* = 121 Hz), 69.5 (d, *J* = 19.8 Hz), 123.0 (s), 124.8 (s), 126.1 (s), 134.2 (d, *J* = 13.2 Hz), 139.1 (d, *J* = 6.6 Hz), 150.7 (s); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 27 °C) δ –58.3. **3**: ^{1}H NMR (500 MHz, C_6D_6, 27 °C) δ 1.09 (s, 9H), 1.10 (s, 9H), 1.15 (s, 9H), 1.75-1.79 (m, 1H), 4.38 (dd, 1H, *J* = 13.2, 9.1 Hz), 4.47 (dd, 1H, *J* = 12.8, 7.4 Hz), 4.56 (ddd, 1H, *J* = 13.2, 3.6, 3.6 Hz), 4.64-4.70 (m, 2H), 5.00 (dd, 1H, *J* = 14.9, 5.0 Hz), 6.73-6.79 (m, 3H), 7.04-7.13 (m, 3H), 7.32 (d, 1H, *J* = 8.0 Hz), 7.49 (d, 1H, *J* = 1.7 Hz), 7.89 (d, 1H, *J* = 8.1 Hz); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 27 °C) δ 31.0 (s), 31.0 (s), 31.3 (s), 34.4 (s), 34.5 (s), 34.6 (s), 52.9 (d, *J* = 36.9 Hz), 62.6 (d, *J* = 6.7 Hz), 62.9 (d, *J*

= 22.6 Hz), 69.1 (d, J = 10.4 Hz), 123.1 (s), 123.6 (s), 124.2 (s), 124.4 (s), 125.9 (d, J = 6.0 Hz), 126.2 (s), 128.2 (d, J = 4.2 Hz), 129.4 (s), 131.6 (s), 131.7 (d, J = 5.8 Hz), 132.7 (d, J = 3.2 Hz), 134.8 (s), 136.9 (d, J = 15.9 Hz), 138.1 (d, J = 5.2 Hz), 141.4 (d, J = 6.6 Hz), 150.4 (s), 150.8 (s), 151.2 (s); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 27 °C) δ 121. **2**, **3**: HRMS (FAB) m/z calcd for $C_{34}H_{43}O_3P$ 530.2950, found 530.2950. Anal. Calcd for $C_{34}H_{43}O_3P$: C, 76.95; H, 8.17. Found: C, 76.77; H, 8.17.

Variable-temperature NMR experiments of 2 and 3. A mixture of **2** and **3** (10 mg, 0.019 mmol) was dissolved in benzene-d_6 (0.4 mL), $CDCl_3$ (0.4 mL), and THF-d_8 (0.4 mL), respectively, and ^{1}H NMR spectra were measured over a temperature range of 307-342 K. The ratio of **2** and **3** was determined by integral values of aromatic protons ($CDCl_3$, THF-d_8) and methylene protons (benzene-d_6).