A Novel and Convenient Synthetic Route to a 9-Phosphatriptycene and Systematic Comparisons of 9-Phosphatriptycene Derivatives

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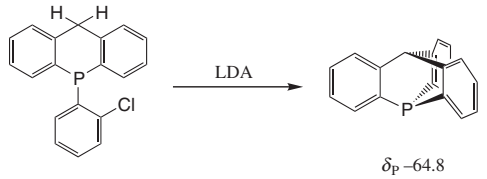
A novel synthetic route to a 9-phosphatriptycene was developed by utilizing *ortho*-lithiation of a triarylphosphine oxide as a key step. Systematic comparisons of the NMR spectra of 9-phosphatriptycene derivatives indicated the large s character of the lone pair orbital or the phosphorus–chalcogen bonds of the 9-phosphatriptycene derivatives.

9-Phosphatriptycene was first synthesized in 1974 by Bickelhaupt[1] and its unique structure and spectroscopic properties have attracted the wide varieties of interest of organic chemists. For example, unusually narrow C–P–C angles compared to those of Ph_3P,[2] which were revealed by X-ray crystallographic analysis of 2-*tert*-butyl-9-phosphatriptycene,[3] and extremely up-field shifts, which were observed in ^{31}P NMR spectra of 9-phosphatriptycene and 9,10-diphosphatriptycene.[4]

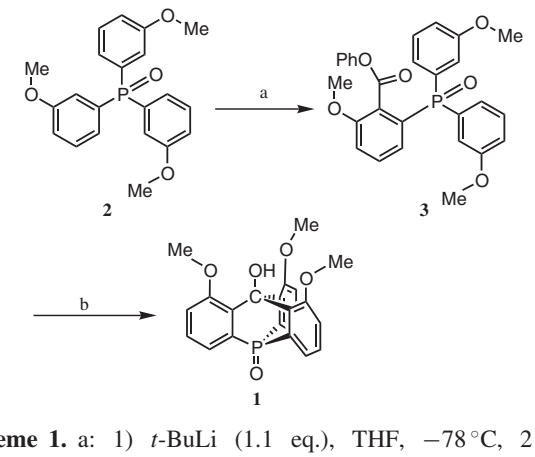


δ_P –64.8

Among three synthetic routes to 9-phosphatriptycene reported by Bickelhaupt, ring closure of 9-(2-chlorophenyl)-9,10-dihydro-9-phosphaanthracene with an excess of lithium diisopropylamide gave the best result. This synthetic route is, however, not suitable for a multi-substituted 9-phosphatriptycene because this reaction proceeded via a benzyne as a reaction intermediate. Here we report a novel synthetic route to 9-phosphatriptycene by utilizing *ortho*-lithiation of tris(3-methoxyphenyl)phosphine oxide **2**, which is potentially suitable for symmetrically multi-substituted 9-phosphatriptycene oxides.

As shown in Scheme 1, a phenoxycarbonyl group was introduced at the ortho-position of tris(3-methoxyphenyl)phosphine oxide **2** by the reaction of **2** with *t*-BuLi and subsequent addition of phenyl chloroformate in 60% yield. 9-Phosphatriptycene oxide **1** was synthesized by treatment of **3** with 2 equivalents of lithium diisopropylamide (LDA) in 51% yield.[5] ^1H NMR of **1** showed the signal due to the hydroxy proton at δ 6.18, indicating that the hydroxy group is hydrogen bonded to the methoxy group intramolecularly, because its chemical shift is significantly down-field shifted compared with that (δ 5.44) of tris(2-methoxyphenyl)methanol. The reactivity of the hydroxy group of **1** also supported the intramolecular hydrogen bonding, that is, H–D exchange of this hydroxy group only with D_2O did not proceed, but the hydroxy proton was readily exchanged by the addition of DCl.

Single crystals of 9-phosphatriptycene oxide **1** were obtained by recrystallization from CH_2Cl_2/MeOH. X-ray crystallographic analysis has definitively confirmed the structure of **1** and ORTEP drawing is shown in Figure 1.[6] This is the first example of the crystal structure of a 9-phosphatriptycene oxide. Triptycene framework has almost C_{3v} symmetry. The P–C bond lengths (1.774(2), 1.786(7), and 1.795(5) Å) are almost same as those of triphenylphosphine oxide, but the C–P–C bond angles (98.5(3), 99.30(11), and 99.5(3)°) of **1** are narrowed compared to those (105.82(12), 106.34(13), and 106.43(12)°) of triphenylphosphine oxide[7] due to steric restriction of triptycene framework as observed in 9-phosphatriptycene and its analogs (9,10-



Scheme 1. a: 1) *t*-BuLi (1.1 eq.), THF, −78 °C, 2 h, 2) $ClCO_2Ph$ (1.1 eq.), −78 °C to rt for overnight; b: LDA (2 eq.), THF, −78 °C, 5 h.

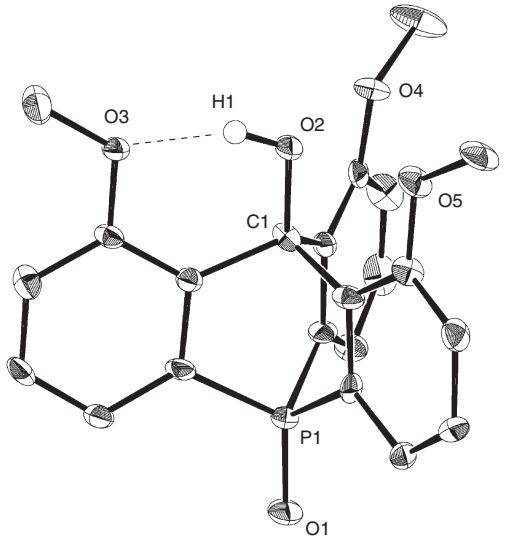
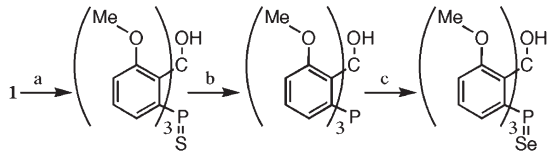


Figure 1. ORTEP drawing of 9-phosphatriptycene oxide **1** (50% probability).

azaphosphatriptycene[8] and 9,10-diphosphatriptycenes[4]). Interatomic distance of H1···O3 is 1.78(3) Å, and the bond angle of O2–H1···O3 is 149.8(3.3)°, suggesting the existence of intramolecular hydrogen bonding of the hydroxy group with oxygen atom of the methoxy group in the crystal structure of **1**.

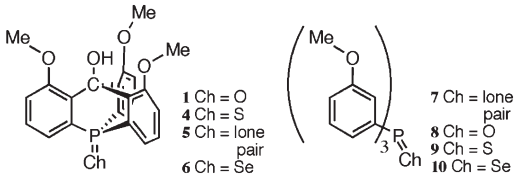


Scheme 2. a: LR (5 eq.), toluene, reflux, 18.5 h; b: *n*-Bu_3P (5 eq.), toluene-d_8, 130 °C, 110.5 h; c: Se (12 eq.), $CDCl_3$, 75 °C, 5h.

The reaction of **1** with Lawesson's reagent (LR) afforded 9-phosphatriptycene sulfide **4** quantitatively, and subsequent reduction of **4** with tributylphosphine gave 9-phosphatriptycene **5** in 71% yield.[9] 9-Phosphatriptycene selenide **6** was quantitatively obtained by treatment of **5** with elemental selenium. ^{31}P NMR signals of **1**, **4**, **5**, and **6** are up-field shifted compared to those of the corresponding tris(3-methoxyphenyl)phosphine **7**, its oxide **2**, sulfide **8**, and selenide **9**, respectively. As revealed by X-ray crystallographic analysis, the C–P–C bond angles of 9-phosphatriptycene derivatives are close to 90° compared to those of the triarylphosphine derivatives. Therefore, the central phosphorus atoms are hard to take sp^3 hybrid state and results in increase of p character of the P–C bond. Indeed, the $^1J_{PC}$ values of 9-phosphatriptycene chalcogenides **1**, **4**, and **6** are smaller than those of the corresponding triarylphosphine chalcogenides **2**, **8** and **9**. On the other hand, the molecular orbital of the lone pair of 9-phosphatriptycenes and phosphorus–chalcogen bonds of 9-phosphatriptycene chalcogenides have larger s character than those of triarylphosphine **7** and its chalcogenides **2**, **8** and **9**, respectively. Such large s character of the lone pair orbital and the phosphorus–chalcogen bonds set the central phosphorus nuclei in the magnetically shielded environments, which causes the up-field shift of ^{31}P NMR. Moreover, the $^1J_{PSe}$ value of 9-phosphatriptycene selenide **6** is larger than that of tris(3-methoxyphenyl)phosphine selenide.

In summary, we have reported the novel synthetic route to the symmetrically tri-substituted 9-phosphatriptycene oxide. The feature of this way is easy access to 9-phosphatriptycene from the phosphine oxide only by two steps. Systematic comparisons of NMR spectral data between the 9-phosphatriptycene derivatives and the corresponding triarylphosphine derivatives suggested that the lone pair orbital or the phosphorus–chalcogen bonds of the 9-phosphatriptycene derivatives have large s character.

Table 1. Spectroscopic comparisons between 9-phosphatriptycene and triarylphosphine derivatives.



	δ_P	$^1J_{PC}$/Hz	$^1J_{PSe}$/Hz		δ_P	$^1J_{PC}$/Hz	$^1J_{PSe}$/Hz
5	−68.7	12.0	—	**7**	−2.6	10.9	—
1	2.0	93.0	—	**2**	30.3	103.1	—
4	10.0	75.9	—	**8**	44.6	84.3	—
6	3.9	67.8	827	**9**	38.1	76.0	732

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References and Notes

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5 **1**: ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 9H), 6.18 (s, 1H), 6.95 (d, J = 8.3 Hz, 3H), 7.20 (td, J = 7.7 and 3.4 Hz, 3H), and 7.62 (dd, J = 12.3 and 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.66 (s), 83.69 (d, J = 23.1 Hz), 117.11 (d, J = 1.9 Hz), 120.62 (d, J = 5.0 Hz), 127.69 (d, J = 14.1 Hz), 134.76 (d, J = 93.0 Hz), 137.75 (d, J = 7.3 Hz), and 157.16 (d, J = 13.5 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ 2.0; HRMS (FAB$^+$): m/z calcd for $C_{22}H_{20}O_5P$ 395.1048; found 395.1031 ([M+H]$^+$).
6 Crystallographic data of **1**: at −153 °C, orthorhombic, space group $Pna2_1$, a = 16.119(10), b = 8.122(5), c = 13.408(8) Å, V = 1755.5(18) Å^3, Z = 4, R_1 ($I > 2.00\ \sigma\ (I)$) = 0.0583, wR_2 (all data) = 0.1463 GOF = 1.105. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-221540. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Instruction for depositing the crystallographic data is available on the Web at http://www.ccdc.cam.ac.uk/conts/depositing.html.
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9 **4**: ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 9H), 6.26 (s, 1H), 6.97 (d, J = 8.5 Hz, 3H), 7.21 (td, J = 8.3 and 3.7 Hz, 3H), and 7.69 (dd, J = 14.8 and 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.69 (s), 116.98 (s), 121.27 (d, J = 8.8 Hz), 127.43 (d, J = 13.1 Hz), 134.68 (d, J = 75.9 Hz), 136.58 (d, J = 4.3 Hz), and 157.00 (d, J = 12.0 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ 10.0; HRMS (FAB$^+$): m/z calcd for $C_{22}H_{20}O_4P$ 379.1099; found 379.1979 ([M+H]$^+$). **5**: ^1H NMR (500 MHz, $CDCl_3$) δ 3.89 (s, 9H), 6.33 (s, 1H), 6.86 (d, J = 8.2 Hz, 3H), 7.03 (td, J = 7.7 and 2.3 Hz, 3H), and 7.39 (dd, J = 10.9 and 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.88 (s), 88.65 (s), 116.26 (s), 125.73 (d, J = 38.8 Hz), 126.81 (d, J = 14.6 Hz), 128.49 (d, J = 12.0 Hz), 132.09 (d, J = 9.9 Hz), and 157.43 (s); ^{31}P NMR (109 MHz, $CDCl_3$) δ −68.7; LRMS (EI): m/z 378 (M$^+$); HRMS (FAB$^+$): m/z calcd for $C_{22}H_{20}O_4PS$ 411.0820; found 411.0808 (M$^+$). **6**: ^1H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 9H), 6.30 (s, 1H), 6.98 (d, J = 8.0 Hz, 3H), 7.21 (tdd, J = 7.8, 4.0, 1.0 Hz, 3H), 7.71 (ddd, J = 15.6, 7.2, 1.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.76 (s), 117.14 (s), 122,50 (d, J = 10.4 Hz), 127.37 (d, J = 16.1 Hz), 133.55 (d, J = 67.8 Hz), 136.31 (d, J = 2.9 Hz), 156.91 (d, J = 11.3 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ 3.9, $^{77}Se\{^1H\}$ NMR (95 MHz, $CDCl_3$) δ 601.3 (d, J = 827 Hz).; The signals of the bridgehead carbons of **4** and **6** were not observed.

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