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4,8-Diphosphathiophenetriptycenes[1]

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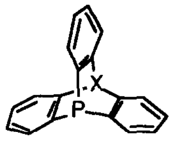
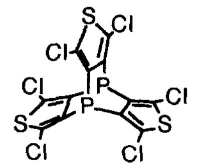
Abstract: **Unsubstituted and trimethyl-4,8-diphosphathiophenetriptycenes (4 and 3d) were synthesized by reduction of the corresponding phosphine oxides (8a and 8b) with trichlorosilane which were prepared by the reaction of trilithium salts, derived from tri-3-thienylphosphine oxides (7a and 7b), with $P(OPh)_3$. The reaction of 3d with $W(CO)_5(THF)$ gave a 1:2 complex 12 in high yield.**

Triptycene derivatives having phosphorus atoms at their bridgeheads have been synthesized from the interest in the chemical and physical properties of the phosphorus atoms fixed in a rigid ring system.[2-6] Phospha- (**1a**),[2] azaphospha- (**1b**),[3] diphospha- (**1c**),[2b,4] arsaphospha- (**1d**),[5] and phosphastiba- (**1e**)[5] triptycenes and, in addition, a thiophene analog of **2**[6] were reported as such compounds. We recently reported the syntheses and reactivities of 4-sila-8-phosphathiophenetriptycene (**3a**)[7] and 4- and 8-phosphathiophenetriptycenes (**3b** and **3c**).[8] 4,8-Diphosphathiophenetriptycenes, **3d** and the parent compound **4**, are our next target molecules where two phosphorus atoms are fixed in different environments in contrast with **1c** and **2**. We report here the syntheses and properties of 4,8-diphosphathiophenetriptycenes, **3d** and **4**.



1a: X=CH
b: X=NH
c: X=P
d: X=As
e: X=Sb



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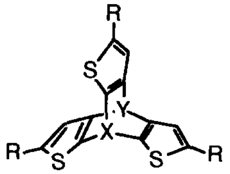
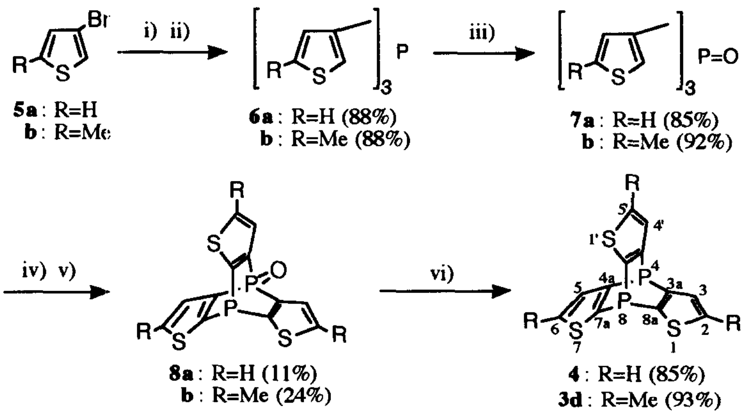
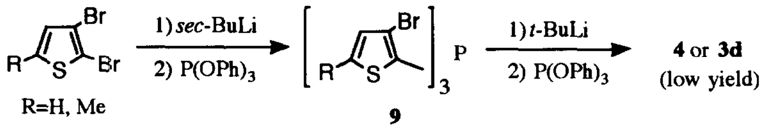


R=Me
3a: X=P, Y=Si-Me
b: X=C-Me, Y=P
c: X=P, Y=C-Me
d: X=Y=P
R=H
4: X=Y=P

Tri-3-thienylphosphine oxide (**7a**)[9] was prepared by oxidation of tri-3-thienylphosphine (**6a**)[10] with H_2O_2 in acetone at 0 °C in 85% yield. The 2-positions of thiophene rings in **7a** were lithiated with *n*-BuLi in Et_2O at room temperature[11] and the resulting trilithium salt was treated with a large excess amount of $P(OPh)_3$ (15 equiv) at -78 °C to provide 4,8-diphosphathiophenetriptycene 4-oxide (**8a**) in 11% yield. Reduction of **8a** with an excess amount of trichlorosilane in refluxing benzene[12] gave the desired 4,8-diphosphathiophenetriptycene **4** in 85% yield. Similarly, the phosphine oxide **8b** was obtained by the reaction of the trilithium salt, derived from **7b**, with $P(OPh)_3$ (15 equiv) in 24% yield. The reactions using 1.5-2 equiv of $P(OPh)_3$ yielded **8b** only in less than 10% yield. Reduction of **8b** with trichlorosilane yielded 2,5',6-trimethyl-4,8-diphosphathiophenetriptycene **3d** in 93% yield. On the other hand, attempts to obtain **4** or **3d** by direct cyclization of trilithium salts, prepared from tris(3-bromo-2-thienyl)phosphines **9**, with $P(OPh)_3$ resulted in the formation of **4** or **3d** in very low yields.



i) *sec*-BuLi/Et_2O/-78 °C/1 h; ii) $P(OPh)_3$ (0.3 equiv); iii) H_2O_2/Acetone/0 °C; iv) *n*-BuLi (3.1 equiv)/Et_2O/r.t.; v) $P(OPh)_3$ (15 equiv)/-78°C and then r.t.; vi) $HSiCl_3$ (16-18 equiv)/PhH/refl., 2 h.



Compounds **4** and **3d** were purified by sublimation and obtained as white powder. They are stable for a long time in a refrigerator. Structure elucidations of thiophenetriptycenes **4** and **3d**, as well as **8a** and **8b**, were done by their spectroscopic data.[13] Their ^{31}P NMR and UV-Vis spectral data are summarized in Table 1.

Table 1. ^{31}P NMR and UV-Vis spectral data of **8a-b**, **4**, and **3d**

Compound	^{31}P NMR δ	UV-Vis λ_{max} /nm (log ε)
8a	-105.7 (d, J_{P-P}=6 Hz, P-8) 10.8 (d, J_{P-P}=6Hz, P-4)	299 (3.51), 272 (4.06)^a
8b	-104.6 (d, J_{P-P}=5 Hz, P-8) 9.6 (d, J_{P-P}=5 Hz, P-4)	315 (3.72), 275 (4.10), 268 (4.11)^a
4	-93.4 (d, J_{P-P}=24 Hz, P-8) -87.1 (d, J_{P-P}=24 Hz, P-4)	310 (3.27), 265 (3.90), 232 (3.94)^b
3d	-92.8 (d, J_{P-P}=23 Hz, P-8) -85.8 (d, J_{P-P}=23 Hz, P-4)	322 (3.52), 269 (3.95), 235 (4.10)^b

a : In CH_3CN. b : In CH_2Cl_2.

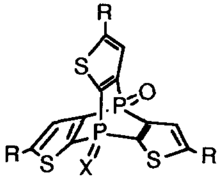
In the ^{31}P NMR of **4** and **3d**, the higher field signals were assigned to the phosphorus atoms at the 8-position by analogy with the δ_P values of **3b** (-90.7) and **3c** (-98.0). The observed values of three-bond ortho ^{31}P-^{31}P coupling constants ($^3J_{P-P}$) of **4** (24 Hz) and **3d** (23 Hz) are very similar to the calculated value of diphosphatriptycene (**1c**, 24.2 Hz).[4d] The δ_P value of **8a** (-105.7) is the highest among a series of phosphathiophenetriptycenes,[7,8] which could be ascribed to the effect of the electron-withdrawing P=O group.

In the UV-Vis spectra, the longest absorption maxima appear around 300 nm, 12-16 nm bathochromic shifts being observed by introduction of three methyl groups.

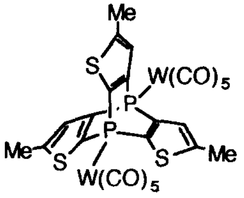
In the ^{13}C NMR of **4**, four thiophene ring carbons appear at δ 127.7 (C-2), 131.7 (C-3), 152.7 (C-8a), and 154.5 (C-3a), where the distinction between two carbons (C-2 and C-3) is based on the characteristic large $^2J_{C\text{-}P}$ value for C-3 (39.6 Hz) in contrast to C-2 ($J_{C\text{-}P}$=9.8, 3.3 Hz).[4d] This tendency is also the case for C-3 of **3d** (38.9 Hz). In the ^{1}H NMR of **4**, two kinds of protons appear at δ 7.13-7.17 (m) and 7.43 (dd). The latter peak was assigned to H-3 from the selectively ^{1}H-decoupled ^{13}C NMR spectrum. This downfield shift of H-3 would be due to the deshielding effect of the lone pair electrons of P-4.

Compounds **4** and **3d** were readily oxidized to the corresponding dioxides **10** and **11a** by heating in refluxing ethanol under air. The spectroscopic data of the dioxide **11a** agreed with those of the authentic sample obtained by oxidation of **8b** (*m*-CPBA/r.t., 98%). Incidentally, reactions of **8b** with elemental sulfur or selenium in benzene in the presence of DBU gave **11b** or **11c** in high yields.[14]

Only a few reports have appeared on coordination studies of bicyclic compounds containing phosphorus atoms at the both bridgeheads in spite of their potentiality of forming one-dimentional polymers where organic substrates and metal moieties are arranged alternatively.[15] Reaction of **3d** with W(CO)$_5$(THF) (2.2 molar amounts) in THF at room temperature gave a 1:2 complex **12** in high yield (72%). The ^{31}P NMR of **12** shows two doublets ($^3J_{P\text{-}P}$=1 Hz) at δ -53.2 and -47.6, each of which accompanies the satellite signals due to one-bond ^{31}P-^{183}W coupling (269 and 256 Hz, respectively).[16] The ^{1}H and ^{13}C NMR of **12** indicate that the P-W bonds rotate freely in the NMR time scale at room temperature.[13]



R=H
10: X=O
R=Me
11a: X=O
b: X=S
c: X=Se



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In summary, 4,8-diphosphathiophenetriptycenes, **4** and **3d**, were synthesized and fully characterized by spectroscopic means. The reaction of **3d** with W(CO)$_5$(THF) gave a 1:2 complex **12** in good yield. The chemical and physical properties of **12** and the coordination chemistry of **4** and **3d** with other metals are under investigation.

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13. All new compounds gave satisfactory analytical and spectral data. Selected spectral data are as follows: **8a**: mp >220 °C dec; ^{1}H NMR δ 7.27 (ddd, $J_{H\text{-}H}$=4.8 Hz, $J_{H\text{-}P}$=5.8, 2.6 Hz, 3H, H-2), 7.71 (dd, $J_{H\text{-}H}$=4.8 Hz, $J_{H\text{-}P}$=3.5 Hz, 3H, H-3); ^{13}C NMR δ 128.97 (dd, $J_{C\text{-}P}$=16.3, 3.4 Hz, C-2), 129.00 (d, $J_{C\text{-}P}$=14.0 Hz, C-3), 149.2 (dd, $J_{C\text{-}P}$=109.8, 1.5 Hz, C-3a), 153.3 (dd, $J_{C\text{-}P}$=20.3, 16.3 Hz, C-8a); MS *m*/*z* 324 (M^{+}, 50), 293 (11), 277 (100); IR (KBr) 1222 cm^{-1} (P=O). **8b**: mp 324.5-328.5 °C dec; ^{1}H NMR δ 2.44 (s, 9H), 7.34 (d, $J_{H\text{-}P}$=2.8 Hz, 3H); ^{13}C NMR δ 15.0 (Me), 127.3 (d, $J_{C\text{-}P}$=13.6 Hz, C-3), 144.0 (dd, $J_{C\text{-}P}$=16.7, 3.0 Hz, C-2), 149.0 (d, $J_{C\text{-}P}$=109.4 Hz, C-3a), 150.8 (dd, $J_{C\text{-}P}$=19.8, 15.2 Hz, C-8a); MS *m*/*z* 366 (M^{+}, 58), 319 (100); IR (KBr) 1236 cm^{-1} (P=O). **4**: mp 286-289 °C dec; ^{1}H NMR δ 7.13-7.17 (m, 3H, H-2), 7.43 (dd, $J_{H\text{-}H}$=4.5 Hz, $J_{H\text{-}P}$=1.5 Hz, 3H, H-3); ^{13}C NMR δ 127.7 (dd, $J_{C\text{-}P}$=9.8, 3.3 Hz, C-2), 131.7 (d, $J_{C\text{-}P}$=39.6 Hz, C-3), 152.7 (dd, $J_{C\text{-}P}$=13.7, 6.1 Hz, C-8a), 154.5 (dd, $J_{C\text{-}P}$=11.8, 2.7 Hz, C-3a); MS *m*/*z* 308 (M^{+}, 100), 277 (20), 263 (23), 245 (89). **3d**: mp 284 °C dec; ^{1}H NMR δ 2.40 (s, 9H), 7.08 (s, 3H); ^{13}C NMR δ 15.1 (Me), 130.6 (d, $J_{C\text{-}P}$=38.9 Hz, C-3), 142.5 (dd, $J_{C\text{-}P}$=9.9, 3.2 Hz, C-2), 150.2 (dd, $J_{C\text{-}P}$=12.7, 5.9 Hz, C-8a), 150.3 (dd, $J_{C\text{-}P}$=11.4, 2.5 Hz, C-3a); MS *m*/*z* 350 (M^{+}, 100), 319 (29), 287 (67). **12**: ^{1}H NMR δ 2.49 (s, 9H), 7.45 (d, J=2.9 Hz, 3H); ^{13}C NMR δ 15.4 (Me), 131.6 (dd, $J_{C\text{-}P}$=25.3, 5.3 Hz, C-3), 144.0 (dd, $J_{C\text{-}P}$=14.2, 4.8 Hz, C-2), 149.8 (dd, $J_{C\text{-}P}$=48.2, 1.3 Hz), 150.9 (d, $J_{C\text{-}P}$=40.5 Hz), 194.8 (d, $J_{C\text{-}P}$=6.8 Hz, $J_{C\text{-}W}$=124.4 Hz), 195.4 (d, $J_{C\text{-}P}$=25.9 Hz), 196.0 (d, $J_{C\text{-}P}$=6.9 Hz, $J_{C\text{-}W}$= 124.4 Hz), 196.3 (d, $J_{C\text{-}P}$=24.9 Hz).
14. ^{31}P NMR chemical shifts (δ) of **10** and **11a-c** are as follows (values in parentheses describe $^{3}J_{P\text{-}P}$ values in Hz otherwise noted): **10**: -0.42 (37), -1.6 (37); **11a**: -2.6 (42), -1.2 (42); **11b**: -6.6 (38), 0.94 (38); **11c**: -28.7 (36, $^{1}J_{P\text{-}Se}$=847 Hz), 0.54 (36).
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