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Syntheses and Reactions of 4- and 8-Phosphathiophenetriptycenes[1]

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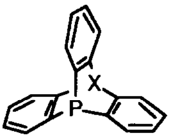
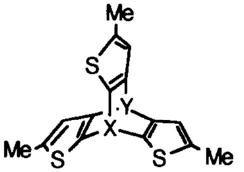
Abstract: 8- and 4-Phosphathiophenetriptycenes **2d** and **2e** were synthesized by reactions of the corresponding trilithium salts with $P(OPh)_3$ in 18% and 17% yields, respectively. The decreased reactivity of **2d** compared to **2e** was shown by competitive oxidation, sulfuration, and selenation reactions. Complexation of **2d** with $M(CO)_5(THF)$ (M=W, Mo) gave the corresponding 1:1 complexes (**12a** and **12b**).

The chemistry of triptycenes, one or two bridgehead carbons of which are replaced by other atoms, is interesting in pursuing the properties of bridgehead atoms fixed in the rigid skeleton. As such triptycenes having one or two phosphorus atoms at their bridgehead, phospha- (**1a**),[2] azaphospha- (**1b**),[3] diphospha- (**1c**),[2b,4] arsaphospha- (**1d**),[5] and phosphastiba- (**1e**)[5] triptycenes have been reported. Recently we reported the first synthesis of thiophenetriptycene **2a** in which three 2,3-thiophene rings are characteristically oriented to the same direction.[6,7] We have also reported the preparation and some reactions of 4-sila- and 4-sila-8-phosphathiophenetriptycenes, **2b** and **2c**.[8] The chemistry of thiophenetriptycenes having heteroatoms at their bridgeheads is interesting because surroundings around the two bridgeheads are not equal to each other. In this communication we report the syntheses of 8-phosphathiophenetriptycene **2d** and its isomer **2e**, their relative reactivities of these compounds, and the potential of **2d** as a phosphine ligand.



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

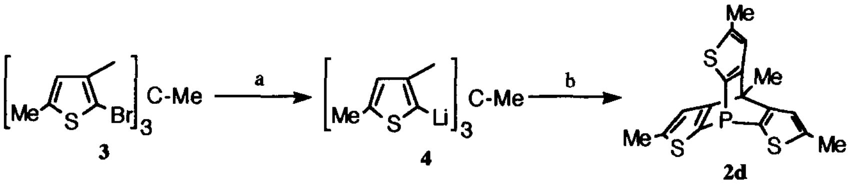


2a: X=C-OH, Y=C-CH_3
b: X=C-OH, Y=Si-Me
c: X=P, Y=Si-Me
d: X=P, Y=C-CH_3
e: X=C-CH_3, Y=P

1,1,1-Tris(2-bromo-5-methyl-3-thienyl)ethane (**3**)[6] was treated with *t*-BuLi (6 molar amounts) in Et_2O at -50~-40 °C and the resulting trilithium salt **4** was allowed to react with an excess amount of $P(OPh)_3$ (2 equiv) to yield the desired 8-phosphathiophenetriptycene **2d** in 18% yield (Scheme 1). Compound **2d** is colorless crystals (mp 280-282 °C) and its spectroscopic data are as follows:[9] ^1H NMR ($CDCl_3$) δ 2.28 (s, 3H), 2.37 (s, 9H), 6.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 15.4 (Me), 17.8 (Me), 50.6 (C), 122.2 (CH), 141.1 (C, d, $J_{C\text{-}P}$=1.8 Hz), 142.7 (C, d, $J_{C\text{-}P}$=17.1 Hz), 163.8 (C, d, $J_{C\text{-}P}$=2.5 Hz); ^{31}P NMR ($CDCl_3$) δ -98.0; UV-Vis (MeCN) λ_{max} (log ε) 310 nm (3.78), 281 (sh, 3.28), 261 (4.10), 223 (4.28).

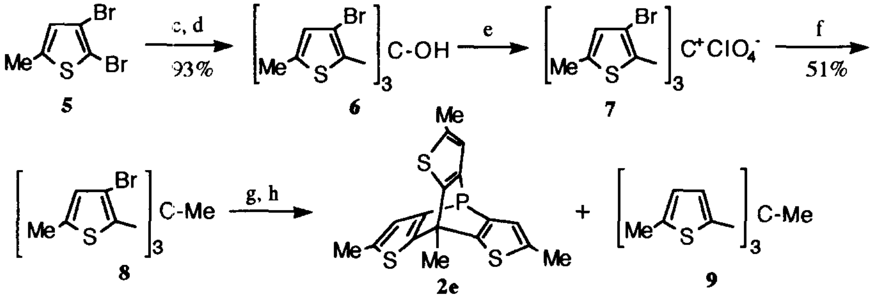
On the other hand, 4-phosphathiophenetriptycene **2e** was synthesized as shown in Scheme 2. Lithiation of 2,3-dibromo-5-methylthiophene (**5**) with *sec*-BuLi followed by treatment with $(EtO)_2C{=}O$ gave **6** in 93% yield. The alcohol **6** was converted to the perchlorate **7** which was treated with MeMgI (excess) in ether leading **8** in 51% yield.[10] Trilithiation of **8** with *t*-BuLi (6 molar amounts) in Et_2O followed by treatment with $P(OPh)_3$ yielded the desired **2e** contaminated with **9**. Recrystallization of the mixture from hexane gave **2e** in 17% yield. Analytically pure **2e** was obtained by repeated recrystalization (at least 3 times) from hexane (mp 274-277 °C): ^1H NMR ($CDCl_3$) δ 2.26 (s, 3H), 2.34 (s, 9H), 6.85 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 15.1 (Me), 18.6 (Me), 50.2 (C, d, $J_{C\text{-}P}$=3.1 Hz), 127.5 (CH, d, $J_{C\text{-}P}$=32.1 Hz), 134.8 (C, d, $J_{C\text{-}P}$=7.6 Hz), 147.7 (C, d, $J_{C\text{-}P}$=13.7 Hz), 161.4 (C, d, $J_{C\text{-}P}$=6.1 Hz); ^{31}P NMR ($CDCl_3$) δ -90.7; UV-Vis (MeCN) λ_{max} (log ε) 310 nm (3.78), 281 (sh, 3.28), 261 (4.10), 223 (4.28).

In the ^{31}P NMR spectra, the phosphorus atom in **2d** resonates at higher field (δ -98.0) than that in **2e** (δ -90.7) (cf. **1a**:δ -65; **1b**:δ -80; **1c**: δ -43), indicating the greater s character of the lone pair electrons of the phosphorus atom in **2d** compared with that in **2e**.[2a-b,4c,11]



a: *t*-BuLi (6 molar amounts)/Et_2O/-50~-40 °C, 1 h; b: $P(OPh)_3$ (2 equiv).

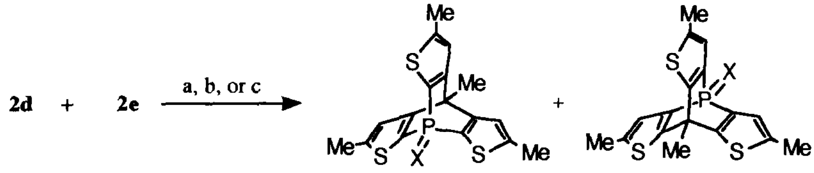
Scheme 1



c: *sec*-BuLi/Et_2O/-50~-40 °C/1 h; d: $(EtO)_2C=O$ (0.3 equiv); e: $HClO_4/Ac_2O$/-40~-30 °C; f: MeMgI/Et_2O/0 °C and then r.t.; g: *n*-BuLi (6 molar amounts)/Et_2O/-78 °C, 1 h; h: $P(OPh)_3$ (equimol)/-78 °C and then r.t.

Scheme 2

In order to investigate the difference in the nucleophilicity of phosphorus atoms in **2d** and **2e**, competitive chalcogenation reactions were examined. A 1:1 mixture of **2d** and **2e** was treated with an equimolar amount of *m*-CPBA in CH_2Cl_2 at 0 °C to afford the corresponding phosphine oxides **10a** and **11a** in 34.2% and 72.2% yields, respectively, with recovery of **2d** (61.3%) and **2e** (22.7%), thus giving the relative rate ratio ($k_{rel}=k_{2e}/k_{2d}=\{\log(1\text{-}0.722)\}/\log(1\text{-}0.342)\}$) of 3.06. On the other hand, sulfuration of an equimolar mixture of **2d** and **2e** with elemental sulfur and selenation of the mixture with elemental selenium gave **10b** and **11b**, and **10c** and **11c**, respectively, in the presence of DBU, and the k_{rel} values of sulfuration (1.37) and selenation (10.7) were obtained. In the all cases **2d** was less reactive than **2e**. In addition, k_{rel} values of **2c** and **2f** (X=P, Y=P=O)[12] to **2d** for *m*-CPBA oxidation were determined to obtain the relationship between the k_{rel} values and the ^{31}P NMR chemical shifts (δ_P).[13] The results are summarized in Table 1. Interestingly, a good correlation (r=0.999) was observed between log k_{rel} and δ_P values of 8-phosphathiophenetriptycenes, **2c** (δ_P -92.2), **2d**, and **2f** (δ_P -104.6) (Fig.1). It was reported that the nucleophilicity of phosphines correlated with not their own δ_P values but the δ_P values of the corresponding phosphine oxides.[14] Although it has been shown that the nucleophilicity of phosphines generally correlates with inductive effect of their substituents, in some phosphines steric hindrance by the substituents dominates the inductive effect.[15-17] Therefore, the significant deviation of 4-phosphathiophenetriptycene **2e** from the correlation line in Fig.1 would be ascribed to steric effect. In other words, the lower reactivity of **2d** than **2e** can be interpreted by considering larger steric hindrance by the three sulfur atoms in addition to the decreased nucleophilicity by higher s character of the lone pair electrons.



10a: X=O (34.2%)
b : X=S (41.3%)
c : X=Se (14.6%)

11a: X=O (72.2%)
b : X=S (51.7%)
c : X=Se (81.4%)

a: m-CPBA/CH_2Cl_2/r.t.; b: S_8/DBU/C_6H_6/r.t./40 min; c: Se/DBU/refl./30 min.

Table 1. Relative reactivity on chalcogenation.

Chalcogenation	Substrate	k_{rel}
Oxidation	**2d**	1.00
	2e	3.06
	2c	1.60
	2f	0.560
Sulfuration	**2d**	1.00
	2e	1.37
Selenation	**2d**	1.00
	2e	10.7

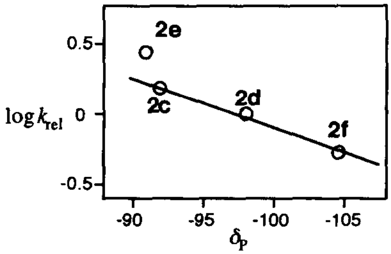
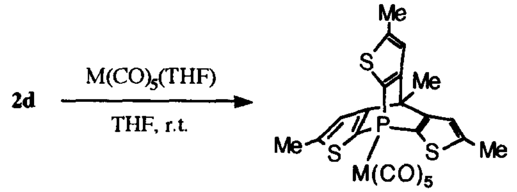


Fig. 1. Plot of log k_{rel} on oxidation *vs.* δ_P.

A few reports have appeared on coordination studies of bicyclic compounds containing phosphorus atoms at the bridgeheads.[18] While the compound **2d** did not react with $W(CO)_6$ in refluxing THF, treatment of **2d** with $W(CO)_5(THF)$ or $Mo(CO)_5(THF)$ in THF at room temperature yielded a 1:1 complex **12a** or **12b** in 93% or 85% yields, respectively. In the ^{31}P NMR of **12a**, the satellite signals due to $^1J_{P\text{-}W}$ (259 Hz) were observed, indicating the formation of a P-W bond.[19]



12a: M=W
δ_P -56.3 ($^1J_{P\text{-}W}$ 259 Hz)
12b: M=Mo
δ_P -34.0.

In summary, 4- and 8-phosphathiophenetriptycenes were synthesized and their relative reactivities were investigated. The relative rate study of a series of phosphathiophenetriptycenes for m-CPBA oxidation showed a good correlation between their k_{rel} and δ_P values and the distinct steric hindrance between 4- and 8-bridgeheads, which would give an insight into the nucleophilicity of phosphines.

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