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Coordination Complexes of the Dimethylthiophosphonium Cation and Ligand Exchange

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The quantitative exchange of a 4-(dimethylamino)pyridine ligand on the dimethylthiophosphonium cation by Me_3P demonstrates the coordinative nature of the N–P and P–P bond and diversifies a fundamentally important new direction in the coordination chemistry of phosphorus as an acceptor.

A diverse coordination chemistry as an acceptor site is developing for coordinatively unsaturated phosphorus centers in cationic species.¹ Complexes of the acceptor unit **1** have been reported for the methylenediylphosphenium cation (in [**4a**]AlCl₄)² or phosphadiazonium (e.g., in [**4b**]Otf³ and [**4c**]-Otf⁴) cations (OTf = trifluoromethanesulfonate), and the phosphenium unit **2** is envisaged as the acceptor in the cations of [**5a**]Cl⁵ (DBU = 1,8-diazabicyclo[5.4.0]undec-7ene), [**5c**]OTf³ [DMAP = 4-(dimethylamino)pyridine], and [**5d**]OTf.⁶ Although salts of tricoordinate phosphonium **3** cations,⁷ as well as complexes of dicoordinate⁸ and tetracoordinate⁹ phosphonium centers, are well-known, the first

- [‡] University of New Brunswick.
- (1) Burford, N.; Ragogna, P. J. *Dalton Trans.* **2002**, 4307–4315.
- (2) David, G.; Niecke, E.; Nieger, M.; Radseck, J.; Schoeller, W. W. J. Am. Chem. Soc. **1994**, 116, 2191–2192.
- (3) Burford, N.; Losier, P.; Phillips, A. D.; Ragogna, P. J.; Cameron, T. S. *Inorg. Chem.* **2003**, *42*, 1087–1091.
- (4) Burford, N.; Cameron, T. S.; Clyburne, J. A. C.; Eichele, K.; Robertson, K. N.; Sereda, S.; Wasylishen, R. E.; Whitla, W. A. *Inorg. Chem.* **1996**, *35*, 5460–5467.
- (5) Bouhadir, G.; Reed, R. W.; Réau, R.; Bertrand, G. Heteroat. Chem. 1995, 6, 371–375.
- (6) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. Am. Chem. Soc. 2003, 125, 14404–14410.
- (7) (a) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. J. Am. Chem. Soc. 1989, 111, 6853-6854. (b) Grützmacher, H.; Pritzkow, H. Angew. Chem., Int. Ed. Engl. 1991, 30, 709-710. (c) Loss, S.; Widauer, C.; Grützmacher, H. Angew. Chem., Int. Ed. 1999, 38, 3329-3331.
- (8) (a) Meisel, M.; Lönnecke, P.; Wulff-Molder, D. Angew. Chem., Int. Ed. 1997, 36, 1869–1870. (b) Blättner, M.; Nieger, M.; Rubn, A.; Schoeller, W. W.; Niecke, E. Angew. Chem., Int. Ed. 2000, 39, 2768– 2771. (c) Rovnanik, P.; Kapicka, L.; Taraba, J.; Cernik, M. Inorg. Chem. 2004, 43, 2435–2442.
- (9) Kaukorat, T.; Ernst, L.; Schmutzler, R. Polyhedron 1990, 9, 1463– 1467.

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complexes ($6a^{10}$ and $6b^{11}$) involving the acceptor unit 3 were only recently reported.

$$1 + P = L \rightarrow P +$$

$$4a: L = Ph_3P, R = C(SiMe_3)$$

$$4b: L = pyr, R = NMes^*$$

$$4c: L = Ph_3P, R = NMes^*$$

$$4c: L = Ph_3P, R = NMes^*$$

$$4c: L = Ph_3P, R = NMes^*$$

$$4c: L = DBU, R = N(^{i}Pr)_2$$

$$5b: L = DMAP, R = Me$$

$$5c: L = DMAP, R = Ph$$

$$5d: L = Ph_3P, R = Ph$$

$$5d: L = DMAP, R = CI$$

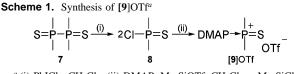
$$6a: L = DMAP, R = CI$$

$$6b: L = Me_3P, R = Me$$

This fundamentally important development of nonmetal Lewis acceptor centers in the chemistry of phosphorus has now been diversified with the discovery of complexes involving the thiophosphonium cation. In addition, the coordinative nature of the ligand-thiophosphonium interaction is confirmed by a ligand-exchange reaction.

Quantitative chlorination of tetramethyldiphosphine disulfide (7; $\delta_P = 35.5$ ppm, CH₂Cl₂) to dimethylthiophosphoryl chloride (8; $\delta_P = 86.2$ ppm, CH₂Cl₂) is effected with 1 equiv of PhICl₂.

Subsequent in situ reaction of **8** with 1 equiv of DMAP and Me_3SiOTf gives [**9**]OTf (97%; Scheme 1). The crystal structure of [**9**]OTf contains two essentially identical formula



^a (i) PhICl₂, CH₂Cl₂; (ii) DMAP, Me₃SiOTf, CH₂Cl₂, -Me₃SiCl.

units in the triclinic unit cell, and the cation (Figure 1) has approximate C_s symmetry with the pyridine ring, P1 and S1 in the plane, and the NMe₂ group slightly twisted [C7–C6–N9–C11 5.3(4)°] about the N9–C6 bond.

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Dalhousie University.

⁽¹⁰⁾ Rivard, E.; Huynh, K.; Lough, A. J.; Manners, I. J. Am. Chem. Soc. 2004, 126, 2286–2287.

⁽¹¹⁾ Huynh, K.; Lough, A. J.; Manners, I. J. Am. Chem. Soc. 2006, 128, 14002–14003.

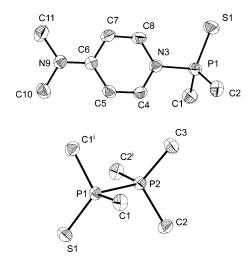


Figure 1. ORTEP view of the cations in [9]OTf (upper; only one of the two independent cations shown) and [10]OTf (lower; crystallographically imposed mirror symmetry) with thermal ellipsoids at the 50% probability level (hydrogen atoms omitted; symmetry code i, x, -y + 0.5, z).

Cation 9 can be described as a DMAP-stabilized thiophosphonium cation. While ${}^{31}P{}^{1}H{}$ NMR spectra of mixtures containing [9]OTf with Ph₃P, ("Pr)₃P, or (MeO)₃P show no evidence of the reaction, the more Lewis basic Me₃P reacts rapidly and quantitatively (as shown by ${}^{31}P{}^{1}H{}$ NMR) with [9]OTf to give a white precipitate (66%), which has been characterized as [10]OTf.¹² The solid-state structure of cation 10 is shown in Figure 1 and can be described as the Me₃P complex of a thiophosphonium cation.¹³ Therefore, formation of 10 is understood in terms of a ligand exchange

Scheme 2. Formation of 10^{*a*}

$$DMAP \rightarrow P = S \xrightarrow{(i)} Me_3P \rightarrow P = S$$

^{*a*} (i) 1 M PMe₃ in toluene, CH₂Cl₂.

Scheme 3. Formation of 11^{*a*}

a (i) Me₂PPMe₂, CH₂Cl₂.

Table 1. E–P (E = N or P) Bond Lengths (Å) and ³¹P NMR δ_P for Derivatives of **4–6**, **9**, and **10**

	L	E-P, Å ($E = N$ or P)	$\delta_{ m P},{ m ppm}~[J,{ m Hz}]$	ref
[4b]OTf	pyr	N, 1.958(8)	71 ^a	3
[5 a]Cl	DBU	N, 1.796(3)	109 ^b	5
[5c]OTf	DMAP	N, 1.789(1)	88^{b}	3
[6a]OTf	DMAP	N, 1.713(2)	-40	10
[9]OTf	DMAP	N, 1.774(2)	88^b	d
$[4a]AlCl_4$	Ph ₃ P	P, 2.267(2)	317, 20 [455]	2
[4c]OTf	Ph ₃ P	P, 2.625(2)	71 [404] ^e	4
[5d]OTf	Ph_3P	P, 2.230(1)	15, -10 [350]	6
[6b]OTf	Me ₃ P	P, 2.223(1)	$3, -1 [13]^b$	11
[10]OTf	Me ₃ P	P, 2.206(1)	38, 16 [46] ^{<i>c</i>}	d

^a In CD₂Cl₂. ^b In CDCl₃. ^c In CD₃CN. ^d This work. ^e Solid state.

of DMAP in **9** by Me₃P (Scheme 2). The analogous reaction of [**9**]OTf with Me₂PPMe₂ gives [**5b**]OTf ($\delta_p = 91.3$ ppm; cf. [**5c**]OTf, $\delta_p = 88$ ppm)³ and Me₂P(S)PMe₂ **11** ($\delta_p = 38.6$ and -55.3 ppm, doublets, ¹*J*_{PP} = 220 Hz)¹⁴ (Scheme 3). While the formation of **5b** and **11** can be described as a PMe₂ metathesis, we envisage a redox reaction or sulfide exchange from thiophosphonium to tetramethyldiphosphine.

The ortho ¹H NMR signals of the DMAP component in **9** ($\delta = 8.6$ ppm; cf. free DMAP, $\delta = 8.1$ ppm) and the ³¹P NMR signal both occur at relatively low field. The ³¹P{¹H} NMR spectrum of [**10**]OTf in CD₃CN shows two doublets ($\delta_p = 38.2$ and 16.4 ppm) with ¹*J*_{PP} = 46 Hz. This value for ¹*J*_{PP} is small compared with values for complexes in which the acceptor phosphorus center bears a lone pair ([**4a**]AlCl₄, ¹*J*_{PP} = 455 Hz;² [**4c**]OTf, ¹*J*_{PP} = 404 Hz;⁴ [**5d**]OTf, ¹*J*_{PP} = 350 Hz⁶).¹⁵

Table 1 compares E–P (E = N or P) bond lengths and ³¹P NMR chemical shifts for the cations in [9]OTf and [10]-OTf with values for related complexes of the types 4–6. The N–P bond lengths in 6a¹⁰ and 9 are similar to those in complexes of phosphenium (2) acceptors and are dramatically shorter than those in complexes of methylenediylphosphenium and phosphadiazonium (1) acceptors. We tentatively interpret these trends in terms of the availability of a discrete vacant acceptor orbital in the acceptors of types 2 and 3, while interaction with ligands disrupts the N–P π bonding in the acceptor 1. Interestingly, the P–P bonds in 6b¹¹ and 10 are substantially shorter than those in 4a, 4c, and 5d, but the ¹J_{PP} values exhibit an opposite trend.

Cations $6b^{11}$ and 10 represent new examples of the rare but developing series of homoatomic coordination com-

⁽¹²⁾ Synthesis of [Me₂P(S)PMe₃]OTf ([10]OTf). The addition of a PMe₃ solution in toluene (1.0 mL, 1 M, 1 mmol) to a solution of [9]OTf (182 mg, 0.5 mmol) in 2 mL of CH₂Cl₂ resulted in the immediate formation of a white precipitate. The solvent was carefully decanted, and the solid was washed with CH₂Cl₂ (2 × 1 mL), Et₂O (4 × 2 mL, and pentane (3 × 2 mL). Residual solvent was removed in vacuo to give the analytically pure product: 106 mg (66%); mp 168–172 °C; Raman (250 mW, 25 °C, cm⁻¹) 2995 (57), 2978 (47), 2917 (87), 2907 (100), 1402 (22), 1228 (10), 1031 (40), 769 (14), 761 (20), 672 (27), 591 (28), 576 (13), 442 (30), 349 (16), 314 (14), 292 (19), 279 (16), 239 (15), 207 (28), 122 (10), 84 (74); ¹H NMR (500.13 MHz, MeCN-*d*₃, 300 K, [ppm]) δ 2.06 [dd, 9H, (*Me*₃P_XP_XSMe₂)⁺, ³J(H₈P_X) = 13.5 Hz, ²J(H₈P_X) = 14.1 Hz]; ¹³C NMR (125.76 MHz, MeCN-*d*₃, [ppm]) δ 4.7 [dd, 3C, (*Me*₃P_XP_YSMe₂)⁺, ¹J(C₈P_X) = 43.5 Hz, ²J(C₈P_X) = 12.9 Hz], 121.2 [q, ¹J(CF) = 321.0 Hz, OTf]; ³¹P NMR (202.46 MHz, MeCN-*d*₃, 300 K, [ppm]) δ 1.64 (P_Y, d), 38.2 [P_X, d, ¹J(P_XP_Y) = 45.8 Hz]; ¹⁹F NMR (235.36 MHz, MeCN-*d*₃, 300 K, [ppm]) δ -79.5 ($-CF_3$, 8). Elem anal. Calcd for C₆H₁₅F₃O₃P₂S₂ (318.24): C, 22.64; H, 4.75. Found: C, 22.59; H, 4.66.

⁽¹³⁾ Recrystallization of [10]OTf ([9]OTf) from MeCN (CH₂Cl₂) by Et₂O diffusion gave single crystals suitable for X-ray analysis. Single crystals of [9]OTf and [10]OTf were mounted in paratone oil and transferred to the cold N2 gas stream of a Bruker AXS P4 diffractometer with a sealed-tube generator and a SMART 1000 CCD detector (graphitemonochromated Mo K α radiation with $\lambda = 0.71073$ Å). Crystal data for [9]OTf: $C_{10}H_{16}F_3N_2O_3PS_2$, fw = 364.34, triclinic, space group P1, Z = 4, a = 9.297(3) Å, b = 11.347(4) Å, c = 15.335(5) Å, $\alpha =$ 98.446(5)°, β = 97.670(5)°, γ = 91.537(5)°, V = 1584.0(9) Å³, F(000) = 752, T = 198(1) K, μ = 0.477 mm⁻¹, 6924 reflections collected, 6924 unique reflections, 4678 reflections observed $[F > 2\sigma(F)]$. The final was R1 = 0.0431 and wR2 = 0.1221 (all data). Crystal data for [10]OTf: $C_6H_{15}F_3O_3P_2S_2$, fw = 318.24, orthorhombic, space group *Pnma*, Z = 4, a = 12.442(4) Å, b = 9.126(3) Å, c = 11.707(4) Å, V= 1329.2(8) Å³, F(000) = 656, T = 173(1) K, $\mu = 0.666$ mm⁻¹, 8791 reflections collected, 1604 unique reflections ($R_{int} = 0.0330$), 1480 reflections observed $[F > 2\sigma(F)]$. The final was R1 = 0.0294 and wR2 = 0.0819 (all data).

⁽¹⁴⁾ Gruber, M.; Schmutzler, R. Chem. Ber. 1990, 123, 1313-1317.

⁽¹⁵⁾ Gil, V. M. S.; Philipsborn, W. V. Magn. Reson. Chem. 1989, 27, 409– 430.

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plexes, which have only been observed for phosphorus^{6,16} and antimony.¹⁷ As such, **6b** and **10** define a new direction in the development of *catena*-phosphorus cations.¹⁸

In summary, dimethylthiophosphoryl chloride reacts with DMAP and Me₃SiOTf to give a cationic adduct **9** represent-

(18) (a) Burford, N.; Dyker, C. A.; Decken, A. Angew. Chem., Int. Ed. 2005, 44, 2364–2367. (b) Burford, N.; Dyker, C. A.; Lumsden, M. D.; Decken, A. Angew. Chem., Int. Ed. 2005, 44, 6196–6199. (c) Weigand, J. J.; Burford, N.; Lumsden, M. D.; Decken, A. Angew. Chem., Int. Ed. 2006, 45, 6733–6737. (d) Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. J. Am. Chem. Soc. 2006, 128, 9632–9633. (e) Weigand, J. J.; Riegel, S. D.; Burford, N.; Decken, A. J. Am. Chem. Soc. 2007, 129, 7969–7976.

ing a complex of the dimethylthiophosphonium cation. The quantitative ligand exchange of DMAP for Me₃P gives **10**, demonstrating the coordinative nature of the N–P and P–P bonds. In the analogous exchange reaction with Me₂PPMe₂, a redox reaction is observed rather than the formation of a diphosphine—thiophosphonium complex.

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Supporting Information Available: X-ray crystallographic files in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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^{(16) (}a) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *Chem. Commun.* 2003, 2066–2067. (b) Burford, N.; Herbert, D. E.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* 2004, *126*, 17067–17073. (c) Burford, N.; Phillips, A. D.; Spinney, H. A.; Lumsden, M. D.; Werner-Zwanziger, U.; Ferguson, M. J.; McDonald, R. *J. Am. Chem. Soc.* 2005, *127*, 3921–3927.

⁽¹⁷⁾ Althaus, H.; Breunig, H. J.; Lork, E. Chem. Commun. 1999, 1971–1972.