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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 Me₃P 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 envisored as the acceptor in the phosphenium unit **2** is envisaged as the acceptor in the cations of $[5a]Cl^5$ (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

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

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; δ_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 Me3SiOTf gives [**9**]OTf (97%; Scheme 1). The crystal structure of [**9**]OTf contains two essentially identical formula

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 $[*C*7–*C*6$ N9-C11 5.3(4) $^{\circ}$] about the N9-C6 bond.

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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 ³¹P{¹H} NMR spectra of mixtures containing [9]OTf with Ph₃P, (^{*n*}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*

$$
DMAP \rightarrow P = S
$$

\n
$$
\downarrow
$$

\n9
\n
$$
Me_3P \rightarrow P = S
$$

\n
$$
\downarrow
$$

\n10

 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	$E-P$, \AA ($E = N$ or P)	δ_{P} , ppm [<i>J</i> , Hz]	ref
$[4b]$ OTf	pyr	N, 1.958(8)	71 ^a	3
[5a]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_3P	P, 2.267(2)	317, 20 [455]	2
$[4c]$ OTf	Ph_3P	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 $[46]$ ^c	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 (δ_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, $^{1}J_{PP} = 220 \text{ Hz}^{14}$ (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** $(\delta = 8.6 \text{ ppm}; \text{ cf. free DMAP}, \delta = 8.1 \text{ ppm})$ and the ³¹P NMR signal both occur at relatively low field. The $^{31}P\{^1H\}$ 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, $^{1}J_{PP} = 455 \text{ Hz};^{2}$ [4c]OTf, $^{1}J_{PP} = 404 \text{ Hz};^{4}$ [5d]OTf, $^{1}J_{PP} = 350 \text{ Hz};^{6}$ 15 350 $Hz⁶$).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 $6a^{10}$ 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 $^{1}J_{\text{PP}}$ values exhibit an opposite trend.

Cations $6b¹¹$ 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 CH_2Cl_2 resulted in the immediate formation of a white precipitate. The solvent was carefully decanted, and the solid was washed with CH_2Cl_2 (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-
d₃, 300 K, [ppm]) δ 2.06 [dd, 9H, (Me₃P_XP_YSMe₂)⁺, ²J(H_AP_X) = 7.0 *d*₃, 300 K, [ppm]) *δ* 2.06 [dd, 9H, (*Me*₃P_XP_YSMe₂)⁺, ²*J*(H_AP_X) = 7.0
Hz, ³*J*(H_AP_V) = 8.4 Hzl, 2.17 [dd, 6H, (Me₃P_VP_VS*Me*₂)⁺, ³*J*(H_PP_V) Hz , $\frac{3J(\text{H}_A\text{P}_Y)}{J(\text{H}_B\text{P}_Y)} = 8.4 \text{ Hz}$], 2.17 [dd, 6H, $(\text{Me}_3\text{P}_X\text{P}_Y\text{S}Me_2)^+$, $\frac{3J(\text{H}_B\text{P}_X)}{J(\text{H}_B\text{P}_Y)} = 14.1 \text{ Hz}^{1.13} \text{C}$ NMR (125.76 MHz MeCN-= 13.5 Hz, ²*J*(H_BP_Y) = 14.1 Hz]; ¹³C NMR (125.76 MHz, MeCN-
d₃ [ppm]) δ 4.7 [dd. 3C, (*Me*₂P_YP_YSMe₂)⁺ ¹*J*(C_AP_Y) = 43.5 Hz *d*₃, [ppm]) *δ* 4.7 [dd, 3C, (*Me*₃P_XP_YS*Me*₂)⁺, ¹*J*(C_AP_X) = 43.5 Hz, 2*J*(C_AP_Y) = 2.9 Hz], 18.3 [dd, 2C, (Me₃P_XP_YS*Me*₂)⁺, ¹*J*(C_BP_Y) = 48.9
Hz ²*J*(C_PP_Y) = 12.9 Hz] 121.2 [α Hz, ²*J*(C_BP_X) = 12.9 Hz], 121.2 [q, ¹*J*(CF) = 321.0 Hz, OTf]; ³¹P
NMR (202.46 MHz, MeCN-*d*₃, 300 K, [ppm]) *δ* 16.4 (P_Y, d), 38.2 $[P_X, d, \frac{1}{J}(P_XP_Y) = 45.8 \text{ Hz}]$; ¹⁹F NMR (235.36 MHz, MeCN- d_3 , 300 K, [ppm]) δ -79.5 (-CF₃, s). 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 N_2 gas stream of a Bruker AXS P4 diffractometer with a sealed-tube generator and a SMART 1000 CCD detector (graphite-
monochromated Mo K α radiation with $\lambda = 0.71073$ Å). Crystal data monochromated Mo Kα radiation with $\lambda = 0.71073$ Å). Crystal data
for 1910 Tf: CuoH₁₆F₃N₂O₃PS₂ fw = 364.34, triclinic, space group for [**9**]OTf: $C_{10}H_{16}F_3N_2O_3PS_2$, fw = 364.34, triclinic, space group $P\overline{1}$, $Z = 4$, $q = 9.297(3)$, $\overline{1}$, $\overline{1}$, $\overline{2}$, $\overline{1}$, $\overline{3}$, $\overline{4}$, $\overline{5}$, $\overline{4}$, $\overline{5}$, $\overline{4}$, $\overline{5}$, *P*1, *Z* = 4, *a* = 9.297(3) Å, *b* = 11.347(4) Å, *c* = 15.335(5) Å, α = 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 collect $= 752$, $T = 198(1)$ K, $\mu = 0.477$ mm⁻¹, 6924 reflections collected, 6924 unique reflections 4678 reflections observed $[F \ge 2\sigma(F)]$ The 6924 unique reflections, 4678 reflections observed $[F \geq 2\sigma(F)]$. The final was $R1 = 0.0431$ and wR2 = 0.1221 (all data). Crystal data for [**10**]OTf: C₆H₁₅F₃O₃P₂S₂, 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 *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 $(R_{i\alpha} = 0.0330)$ 8791 reflections collected, 1604 unique reflections ($R_{\text{int}} = 0.0330$), 1480 reflections observed $[F \geq 2\sigma(\bar{F})]$. The final was R1 = 0.0294 and $wR2 = 0.0819$ (all data).

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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-

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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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