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A GENERAL AND CONVENIENT ROUTE TO DITHIOPHOSPHONATE SALT DERIVATIVES*

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2,4-Diaryl and 2,4-diferrocenyl-1,3-dithiadiphosphetane disulfide dimers, $(\text{R}(\text{S})\text{S})_2$, where $\text{R} = \text{Ph}$ (**1a**), 4- $\text{C}_6\text{H}_4\text{OMe}$ (**1b**) or ferrocenyl (Fc) (**1c**) react with a variety of alcohols, silanols, or trialkylsilyl alcohols to form dithiophosphonic acids in a one-flask procedure. The generated acids have a relatively strong acidity which, upon deprotonation, facilitates the facile high yield conversion to monoanionic salts of the type $[\text{S}_2\text{PR}(\text{OR}')^-]$. The present study reports the systematic preparation of these salts with variation in both R and especially R' groups. Compounds were characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis. High quality single crystals of (**1a**) were obtained from the slow cooling of a viscous melt which allowed for the X-ray crystal structure to be determined. Qualitative solubility data have been obtained for several of the isolated salts to provide valuable information for synthesis design, especially with regard to metal complexation. The title salts are effective precursors to obtain a series of new transition-metal complexes both in aqueous and non-aqueous solvents.

Keywords: dithiophosphonate salts; solubility data; crystal structure; NMR data; ferrocenyl; metal complexes

INTRODUCTION

The phosphor-1,1-dithiolato class of compounds (dithiophosphates, dithiophosphonates, dithiophosphinates, etc.) have found widespread use in diverse technological areas ranging from antioxidant additives in the oil and petroleum industry,¹ agricultural insecticide derivatives,² and metal

* Dedicated to Sheldon Shore on the occasion of his 70th birthday.

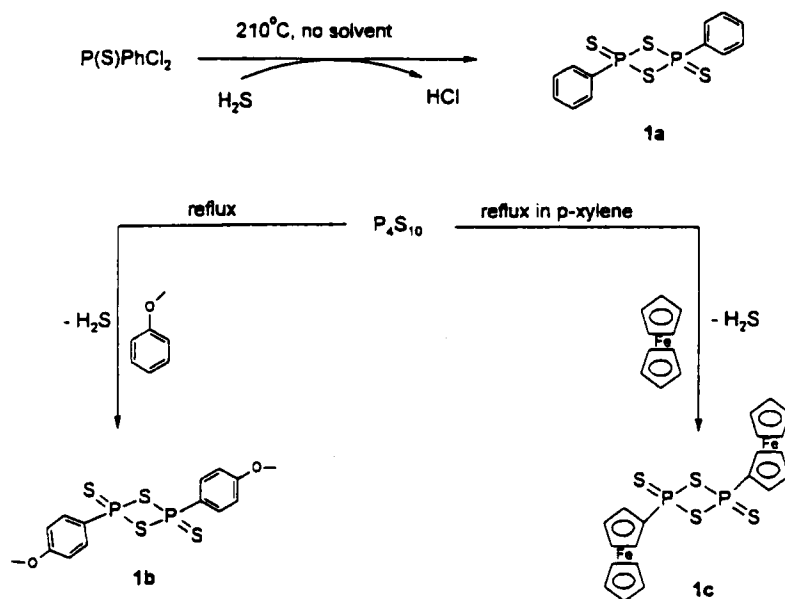
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ore extraction reagents.³ Among this generic class of compounds that have tremendous ligation potential, the dithiophosphates, $[S_2P(OR)_2]^-$, have been the most intensely studied.⁴ Structural investigations have revealed a plethora of coordination patterns resulting from complexation of this ligand to virtually all transition-metals, as well as a large number of main group elements. The organophosphorus analogues, which include the dithiophosphinates, $[S_2PR_2]^-$, and the dithiophosphonates, $[S_2PR(OR')]^-$, have received far less attention.⁵ In particular, although research endeavors to facilitate the formation of stable dithiophosphonic acids have been described,⁶ rational studies on subsequent salt- or metal-complex formation and especially spectroscopic investigations of either have not been reported to date. This observation is further exemplified by the paucity of structurally characterized transition metal complexes where the dithiophosphonates have been utilized as potential bidentate ligands. The aim of the present study is to show the relative ease to form a series of new dithiophosphonates and once isolated, how they can be systematically used as excellent complexing agents for a variety of metal centers such as gold(I), nickel(II) or iron(III).⁷ In the course of these studies, an unusual but effective method was found to grow single crystals of type (**1a**) dimers. Similar attempts in the past proved difficult and resulted in twinned crystals.

RESULTS AND DISCUSSION

The reactions of $(RP(S)S)_2$ type dimers have been reported in abundance.⁸ This class of compounds was reviewed in 1965⁹ and again in 1980.¹⁰ The preparation and characterization of dimer (**1a**) in satisfactory yield was first described in 1962.⁶ The procedure is not facile and is based upon the reaction between $P(S)PhCl_2$ (liquid) and anhydrous H_2S (gas) introduced subsurface at elevated temperatures ($>210^\circ C$) with the release of copious quantities of corrosive HCl as a by-product. A significant improvement to the former synthesis was the formation of the closely related dimer (**1b**) reported in 1978 by Lawesson and co-workers.¹¹ Dimer (**1b**) became commonly referred to as Lawesson's reagent and is also commercially available. The main use of (**1b**) derives from the quantitative conversion of ketones to thiones in organic chemistry. The general chemistry of Lawesson's reagent was summarized¹² in 1985 and again in 1993.¹³ The main thermodynamic driving force for the success of (**1b**) as a thionation rea-

gent is (akin to the Wittig reaction) the oxophilic nature of the phosphorus center. Reaction of Lawesson's reagent with carboxylic acid chlorides,¹⁴ esters, acetals, epoxides, sodium alkoxide, and thiols have been described.¹⁵ Formation of (1b) is obtained directly from the reaction between the electron-rich aromatic compound anisole and P_4S_{10} at reflux temperature. Woollins and co-workers¹⁶ have demonstrated that ferrocene, as an electron-rich organometallic with aromatic character, is a viable substitute for anisole and leads to the preparation of dimer (1c) under similar reaction conditions as employed for (1b). These reactions are summarized in scheme 1.



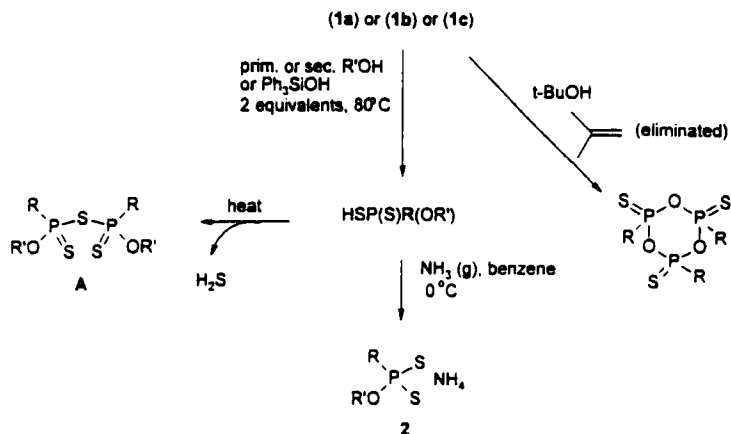
SCHEME 1

It has been well established that reaction of the dimers (1a) or (1b) with 2 stoichiometric equivalents of alcohol forms dithiophosphonic acid derivatives. Acid formation is, however, only possible if the starting alcohol is either primary or secondary. Reaction with a tertiary alcohol leads to elimination reactions. For example, tertiary butanol readily eliminates isobutene. The present study found that the use of silanols such as R_3SiOH

(the silicon analogue of a tertiary alcohol, $R \neq H$) is an interesting alternative since it circumvents the above elimination reaction. Indeed, the reaction between (1b) and Ph_3SiOH (molar ratio 1:2) yields the acid $\text{HSP(S)(4-C}_6\text{H}_4\text{OMe)(OSiPh}_3\text{)}$ without an unwanted elimination reaction. The acid was also readily converted to the corresponding salt (2s) in satisfactory yield. The use of trialkylsilyl alcohols was also effectively utilized which led to new S-P-O-C-Si moieties as in the salt (2c). We also report the use of the dimer (1c) to form new dithiophosphonic salts. This ligand type is of interest due to the organometallic moiety directly attached to the phosphorus center. From dimers (1a) and (1b) dithiophosphonate acids were generated in a "one-flask" procedure by addition of 2 equivalents of alcohol, silanol or trialkylsilyl alcohols. A wide variety of alcohols could be utilized in this respect, including unsaturated (allyl), sterically demanding (adamantyl, SiPh_3), and quasi-strained (cyclopentyl). Tremendous flexibility with respect to solubility and functionality could thus be obtained from the appropriate choice of alcohol. In cases where the alcohols were solids, they were dissolved in a small amount of benzene. The mixture was heated at $\sim 80^\circ\text{C}$ for approximately 30 minutes which resulted in clear, viscous, and volatile acids. The elimination of H_2S at elevated temperatures ($>100^\circ\text{C}$) is well established also for the acid form of the dithiophosphonates which lead to compounds of the type A. Once the acid formed, it was dissolved in a small amount of benzene followed by slow addition of anhydrous ammonia which is bubbled through the solution with vigorous agitation at 0°C . These reactions are summarized in scheme 2. The appropriate key is based on the generic structure labeled 2.

Woollins and co-workers¹⁶ have previously reported that treatment of (1c) with catechol (molar ratio 1:2) "gives a mixture of products". Based on the present study it is certain that one such product is compound B which then converts to compound C "if the reaction is performed in boiling toluene" leading to the elimination of H_2S (g). Obviously, since compounds of type C are not Lowry-Brønsted acids, it is a synthetic "dead-end" insofar as salt formation is concerned. Salts derived from dimer (1c) were obtained in a slightly modified manner (see experimental section). These reactions are summarized in scheme 3.

The isolated salts were also readily oxidized by mild oxidizing agents such as iodine. For example, the salt (2r) was dissolved in methanol and 0.5 equivalent I_2 was added which resulted in the immediate precipitation of the new compound (3) as shown in scheme 4. The dimer (1c) has been

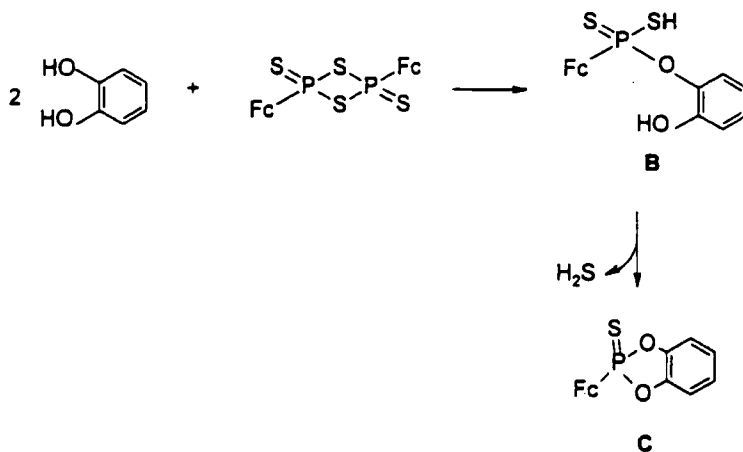


For R = Ph and R' = allyl (**2a**), Et (**2b**), adamantyl (**2l**), C₃H₉ (**2m**), C₆H₁₁ (**2n**)

For R = 4-C₆H₄OMe and R' = CH₂SiMe₃ (**2c**), Et (**2d**), 1-Bu (**2e**), CH₂CH(CH₂)₂ (**2f**),
 CH₂CH₂CH(CH₂)₂ (**2g**), (CH₂)₂O(CH₂)₂OCH₃ (**2h**), 1-octyl (**2i**), C₅H₉ (**2o**),
 (1*R*,2*S*,5*R*)-(-)-menthyl (**2p**), CH(CH₂CH₂)₂ (**2q**), SiPh₃ (**2s**)

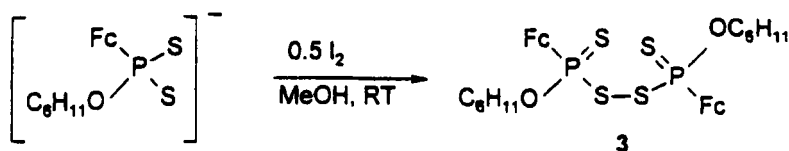
For R = Fc and R' = (CH₂)₂O(CH₂)₂OCH₃ (**2j**), 1-octyl (**2k**), C₆H₁₁ (**2r**),
 SiPh₃ (**2t**)

SCHEME 2



SCHEME 3

used to form novel 1,2-thiaphosphetanes,¹⁷ P-S-N-type heterocycles,¹⁸ and most recently cycloaddition reactions with dienes, alkenes and thioaldehydes.¹⁹



SCHEME 4

X-ray crystal structure of (1a)

Sheldrick and co-workers previously reported the X-ray crystal structure of (1a).²⁰ They obtained the compound from an unusual synthetic route, and their structural analysis was based on data obtained from a twinned crystal. Indeed, several attempts to produce single crystals of compound (1a) proved elusive.²¹ The structure of (1a) was re-examined in the present study from a *single* crystal. The structure is shown in Figure 1 and the bond lengths and angles are shown in Table I.

TABLE I Selected bond lengths (Å) and angles (°) for (PhP(S)S)₂ (1a)

S(1)-P(1)	2.1112(11)		
S(1)-P(1)#1	2.1330(11)	S(2)-P(1)-S(1)	116.09(5)
P(1)-C(11)	1.810(3)	C(11)-P(1)-S(1)#1	105.55(10)
P(1)-S(2)	1.9310(11)	S(2)-P(1)-S(1)#1	116.27(5)
P(1)-S(1)#1	2.1330(11)	S(1)-P(1)-S(1)#1	93.42(5)
C(12)-C(13)	1.383(5)	C(13)-C(12)-C(11)	120.6(3)
C(12)-C(11)	1.382(4)	C(15)-C(16)-C(11)	120.0(3)
C(16)-C(15)	1.380(5)	C(15)-C(14)-C(13)	119.9(3)
C(16)-C(11)	1.392(4)	C(12)-C(11)-C(16)	119.1(3)
C(14)-C(15)	1.378(5)	C(12)-C(11)-P(1)	119.0(2)
C(14)-C(13)	1.381(5)	C(16)-C(11)-P(1)	121.8(2)
P(1)-S(1)-P(1)#1	86.58(5)	C(14)-C(15)-C(16)	120.4(3)
C(11)-P(1)-S(2)	115.23(11)	C(14)-C(13)-C(12)	119.8(3)
C(11)-P(1)-S(1)	107.77(11)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1.-y+1.-z

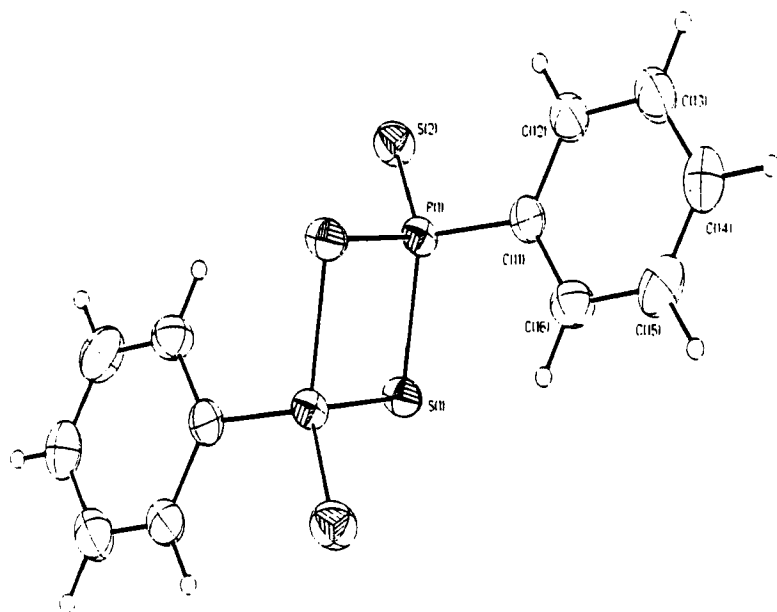


FIGURE 1 Perspective view of the molecular structure of $(\text{PhP}(\text{S})\text{S})_2$ (**1a**) showing the atom labeling scheme for the asymmetric unit. Thermal ellipsoids are drawn at 50% probability level

The structural study here demonstrates how single crystals of these and related compounds may be obtained. It is clear from Table II, however, that most of the crystallographic data (including space group and unit cell dimensions) obtained in the present study are consistent with the previous data. Nevertheless, our structure leads to better refinement as evidenced by evaluating the relevant crystal data parameters, the result of which we ascribe to the fact that the structure was solved from a single, and not a twinned crystal.

TABLE II X-ray crystallographic results for $(\text{PhP}(\text{S})\text{S})_2$ from the two determinations

<i>R</i> (<i>trans</i>)	<i>P-S</i>	<i>P=S</i>	<i>S-P-S</i>	<i>S-P=S</i>
Ph (ref. 20)	2.108(2)	1.920(2)	93.1(1)	116.1(1)
Ph (this work)	2.111(1)	1.931(1)	93.42(5)	116.09(5)

It was observed that (1a) has remarkable thermal stability, and can be heated beyond its melting point without decomposition leading to a yellow viscous melt. Slow cooling of the melt yielded a crop of large, pale-yellow single crystals.

Solution $^{31}\text{P}\{^1\text{H}\}$ NMR studies

The present study reports the first $^{31}\text{P}\{^1\text{H}\}$ NMR data on the dithiophosphonates. The data are summarized in Table III. All compounds resonate with a singlet peak in the range 90 – 112 ppm. No obvious trend could be observed with respect to change in functionality of the salt and position within the range.

TABLE III Yields, melting points, $^{31}\text{P}\{^1\text{H}\}$ NMR data, and elemental analyses for the salts $[\text{NH}_4][\text{S}_2\text{PR}(\text{OR})]$, 2a – 2t

Compound	Yield(%)	M.p.(°C)	$^{31}\text{P}\{^1\text{H}\}^{\text{a}}$	Analysis(%) ^b	
				H	C
Salts obtained from primary alcohols:					
2a ^c	83	128	107.68	5.58(5.70)	43.61(43.71)
2b	81	152	104.93	5.81(6.00)	40.23(40.83)
2c	92	140	110.14	7.11(6.85)	40.51(40.84)
2d	86	106	102.90	6.15(6.08)	40.15(40.74)
2e	86	153	105.21	6.84(6.87)	44.83(45.03)
2f	93	180	104.65	6.52(6.87)	44.59(45.03)
2g	95	145	107.42	6.94(7.21)	46.79(46.88)
2h	96	150	108.68	6.56(6.53)	42.31(42.46)
2i	79	97	102.88	8.25(8.07)	51.70(51.55)
2j	87	159–160	101.54	5.62(5.80)	42.94(43.17)
2k	91	135–136	96.07	6.65(7.07)	49.67(50.58)
Salts obtained from secondary alcohols:					
2l	94	128–129	90.43	6.88(7.08)	55.98(56.27)
2m	85	n.o.	103.51	n.o. (readily hydrolyze)	
2n	88	174	104.03	6.89(6.96)	49.66(49.80)
2o	76	196	103.23	6.72(6.60)	47.26(47.19)
2p ^d	88	192–193	105.08	7.90(8.05)	54.06(54.37)

Compound	Yield(%)	M.p.(°C)	$^3J_{P/H}^a$	Analysis(%) ^b	
				H	C
2q	94	136	101.97	7.32(7.21)	46.52(46.88)
2r	82	n.o.	106.64	n.o.	
Salts obtained from silanols:					
2s	84	168–172	93.01	5.24(5.29)	59.83(60.58)
2t	89	166–167	90.84	4.86(4.92)	58.34(58.63)

- a. Recorded in $CDCl_3$, values in ppm, all singlet peaks.
 b. Calculated values in parentheses.
 c. For key, see Scheme 2. n.o. = not obtained.
 d. As the $[NHEt_3]^+$ salt.

Qualitative solubility studies

Knowledge about the solubility of compounds, either to make the appropriate choice of solvent for spectroscopic measurements or as an aid in preparative chemistry, is useful. To this end a series of qualitative solubility tests were performed on a number of the salts. A variety of solvents were tested over a wide range of dielectric constants. Good solubility of ligands leads to better stoichiometric control which in turn dramatically improves the overall yield. For example, the salt (**2c**) is extremely soluble in water whereas (**2j**) is not. Thus the reaction between (**2c**) and an aqueous solution of $FeCl_3 \cdot 6H_2O$ (molar ratio 3:1) leads to immediate precipitation of the complex $[Fe\{S_2P(OCH_2SiMe_3)(4-C_6H_4OMe)\}_3]$ in high (>85%) yield. Whereas, the same reaction with (**2j**) as the ligand leads to $[Fe\{S_2P(O-(CH_2)_2O(CH_2)_2OCH_3)(Fc)\}_3]$ in less than 30% yield since unreacted ligand must first be removed by extraction.²² Another benefit of performing such reactions in water is that the NH_4Cl by-product is dissolved and removed in a single filtration step. The results obtained are summarized in Table IV.

TABLE IV Solubility data for selected ligands^a

Compound	Acetone	CH_3CN	EtOH	Hexane	Ether	CH_2Cl_2	Water	THF
2a	VS	S	VS	I	I	I-PS	S	S
2b	S	VS	VS	PS	PS	I	VS-S	PS
2c	S	PS	S	I	PS	S	VS	S

<i>Compound</i>	<i>Acetone</i>	<i>CH₃CN</i>	<i>EtOH</i>	<i>Hexane</i>	<i>Ether</i>	<i>CH₂Cl₂</i>	<i>Water</i>	<i>THF</i>
2f	S	S	VS	I	I	I	VS	S
2j	S	S	S	I	I-PS	VS	I	VS
2l	S	S	S	I	I	PS	PS	VS
2n	S	S	PS	I	I	VS	I	VS
2q	VS	S	VS	I	I	S	VS	S
2r	S	S	S	I	I-PS	VS	I	VS

*Key to symbols: I = insoluble, PS = partly soluble, S = soluble, VS = very soluble. The solubility data is based on the following experimental criteria: 0.02 g of free flowing dry solid was dissolved in 1.0 mL of the appropriate solvent and was hard shaken for 5–10 seconds at 23°C. The symbol I means the material was quantitatively recovered after filtration, PS means a small amount (~ 10%) of the material dissolved, S means a large amount (~ 80%) of the material dissolved (and would fully dissolve in a larger volume), VS means a clear solution emerged immediately.

CONCLUSIONS

This report describes the formation and isolation of new dithiophosphonate salts in satisfactory yield. Starting from readily available dimeric precursors, salts can be obtained with a variety of functionalities and different solubility properties. The ³¹P NMR spectra of these salts all reveal a singlet peak and are found in the range 90–112 ppm. The feasibility of substituting tertiary alcohols with silanols that lead to previously inaccessible products has been demonstrated. The salts are useful precursors to metal-dithiophosphonate complexes.

EXPERIMENTAL

Caution: The organophosphorus compounds are malodorous, volatile (in acid form), and highly toxic. Manipulation of these compounds should be performed in a well-ventilated fume-hood.

General Information

All reactions and manipulations were carried out under an inert atmosphere with a positive nitrogen gas flow using standard Schlenk techniques.²³ All solvents were freshly distilled and used immediately. Diethyl ether, THF, benzene, toluene and hexane were distilled under dinitrogen

over a Na/K alloy with the formation of a benzophenone ketyl indicator. Iodine, tetraphosphorus decasulfide, cyclopentanol, 1-octanol, 1-adamantanol, cyclohexanol, allyl alcohol, (1R,2S,5R)-(-)-menthol, trimethylsilyl alcohol, triphenylsilanol, 2-(2-methoxyethoxy)ethanol, 3-pentanol, 3-methyl-1-butanol, and 2-methyl-1-propanol were obtained from Aldrich. Phenyl dichlorophosphine was obtained from Strem Chemicals. Anisole was obtained from Kodak Chemicals. 1-Butanol was obtained from Fischer Scientific Co. Hydrogen sulfide and ammonia gases were obtained from Matheson Gas Products Co. All chemicals were used as received, except NEt_3 which was distilled prior to use.

Instrumentation

Melting points were measured on a Unimelt (A.H. Thomas Co, Philadelphia PA) capillary melting point apparatus and are uncorrected. Elemental analyses were performed at Desert Analytics Inc., Tucson AZ. Solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on either a Varian XL 200 MHz broadband spectrometer operating at 81 MHz, or a Varian UnityPlus-300 spectrometer operating at 121.4 MHz with chemical shifts reported relative to a 85% H_3PO_4 in D_2O external standard solution.

X-ray crystallography

A single crystal of (1a) suitable for X-ray studies, obtained by slow cooling of a sample heated above its melting point of 240°C , was mounted on the tip of a quartz fiber with fast-adhesive glue. Diffraction analyses were carried out using an automated Nicolet R3 four-circle diffractometer utilizing the Wyckoff scanning technique with graphite monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Refined cell parameters were determined from setting angles of 25 reflections with $20^\circ < 2\theta < 30^\circ$. Unit cells were determined using search, center, index, and least squares refinement routines. The Laue classes and lattice dimensions were verified by axial oscillation photography. The intensity data were corrected for absorption, Lorentz and polarization effects. An empirical absorption correction was performed based on ψ scans of five strong reflections spanning a range of 2θ values. All data processing were performed on a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic package (version 5.1) and Siemens SHELXTL PLUS (Micro Vax II).²⁴ The systematic

absences were consistent with the space group assigned. The crystal structure was solved using direct methods to determine the P and S atom positions, while all other atoms were located with difference Fourier maps. Structure refinements were carried out using SHELX-93. The position of the hydrogen atoms were calculated by assuming idealized geometry's, C-H = 0.93 Å.

TABLE V Crystal data and structure refinement for (PhP(S)S)₂ (1a)

Empirical formula	C ₁₂ H ₁₀ P ₂ S ₄
Formula weight	344.38
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 6.6300(10) Å, α = 90° b = 14.459(3) Å, β = 95.30(3)° c = 7.673(2) Å, γ = 90°
Volume, Z	732.4(3) Å ³ , 2
Density (calculated)	1.562 g/cm ³
Absorption coefficient	0.844 mm ⁻¹
F(000)	352
Crystal size	0.3 × 0.3 × 0.1 mm
Theta range for data collection	2.82 to 22.49 deg.
Limiting indices	0 ≤ h ≤ 7, 0 ≤ k ≤ 15, -8 ≤ l ≤ 8
Reflections collected	1049
Independent reflections	956 [R(int) = 0.0153]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	956 / 0 / 83
Goodness-of-fit on F ²	1.137
Final R indices [I > 2σ(I)]	R1 = 0.0330, wR2 = 0.0807
R indices (all data)	R1 = 0.0398, wR2 = 0.0842
Extinction coefficient	0.61(2)
Largest diff. peak and hole	0.257 and -0.317 e.Å ⁻³

Preparation of compounds

(4-C₆H₄OMeP(S)S)₂ (**1b**). A 500-mL three-neck round-bottom flask equipped with a dinitrogen inlet was charged with P₄S₁₀ (44.4 g, 0.1 mol) and anisole (108 g, 1.0 mol). The mixture was refluxed for 6 hours at ~160°C and subsequently cooled to room temperature. The yellow solid was filtered and washed with a benzene/toluene solution, followed by washings with chloroform and ether. The yellow powder was dried in the air, and stored in a vacuum desiccator. Yield: 71.4 g (88%). M.p.: 228°C. The X-ray crystal structure of **1b** has been determined.

(FeC₁₀H₉P(S)S)₂ (**1c**). A 50-mL round-bottom flask was charged with a solution of ferrocene (1.0 g, 5.37 mmol) in *p*-xylene (30 mL) at room temperature which yielded an orange color. The flask was heated to ~100°C and P₄S₁₀ (0.59 g, 1.3 mmol) was added in one portion. The mixture was heated to reflux for 30–40 minutes and then cooled to room temperature. The product was filtered and washed with toluene. The deep orange product was air dried and stored in a vacuum desiccator. Yield: 1.25 g (86%). M.p.: Decompose above 180°C giving a black solid, not melting below 240°C. The material was too insoluble to obtain spectroscopic data and was used without further purification.

A general preparation for the dithiophosphonate ammonium salts is described below using **2a** as a representative example. Using the appropriate dimer that dictates the R group, the procedure is the same for both R = Ph and R = C₆H₄OMe. The physical properties and NMR data for all other isolated and characterized [NH₄][S₂PR(OR')] salts (**2a** – **2t**) are found in Table III.

[NH₄][S₂PPh(OCH₂CH=CH₂)] (**2a**). A 25-mL Schlenk tube was charged with **1a** (2.08 g, 6.01 mmol) and placed under vacuum for 30 minutes. The solid was then heated to ~70°C and an equivalent amount of allyl alcohol (0.69 g, 12.02 mmol) was added over 30 seconds. Note: in cases where the alcohol is a solid, it was added as a concentrated benzene solution; a slight excess of alcohol and a higher temperature (ca. 85°C) did not have an adverse affect on the product formation or yield. The temperature was maintained at 70–75°C until dissolution of all the solids were observed, and then stirred for an additional 20 minutes. Typically, the acids formed were pale green or orange/yellow colored (depending on the alcohol type) viscous oils. No attempt was made to isolate any of these acids. A concentrated benzene solution of the acid was prepared. The solu-

tion was stirred in an ice bath for 10 minutes, and then anhydrous gaseous NH_3 was slowly bubbled through the solution with vigorous agitation. In all cases a colorless precipitate with a sticky consistency was formed immediately. The material was dried and consolidated with hexane additions, filtered on a frit, and washed with hexane. The isolated air dried salts can be stored under dinitrogen as free flowing colorless powders.

A small scale (ca. 1 g) general procedure for the preparation and isolation of the $[\text{NH}_4][\text{S}_2\text{PFc}(\text{OR}')]$ salts is described below. The reaction can be scaled-up ten-fold. Special preparative precautions should, however, be taken into account due to large amounts of H_2S gas that evolves. The preparation of the ferrocenyl derivatives are somewhat different than for the other dithiophosphonate ammonium salts described above. A general procedure that applies to all the ferrocenyl derivatives therefore is given below.

$[\text{NH}_4][\text{S}_2\text{PFc}(\text{OR}')]$ A Schlenk tube was charged with **1c** (1 equiv.) as a finely divided orange-brown powder and dried under vacuum for 15 minutes at 75°C . The temperature should not exceed 80°C . A high boiling point ($> 100^\circ\text{C}$) alcohol (2.5 – 3.0 equiv.) was added to 1 mL benzene and the resulting solution was added drop-wise to the dimer with stirring. Note: in cases where the alcohol is a solid, exactly 2.0 equivalents was used; and the alcohol was added as a saturated benzene solution. The mixture was stirred at $75\text{--}80^\circ\text{C}$ until complete dissolution of all solids were observed, which typically led to a very dark colored solution at this concentration after ca. 45–60 minutes. The ensuing solution was used to rinse unreacted solid particles off the sides of the flask and allowed to react further. The reaction vessel was then placed in an ice bath, and the mixture stirred for 10 minutes at 0°C . Anhydrous gaseous NH_3 was slowly bubbled through the cold solution *via* a glass needle which yielded an immediate precipitate. In some cases it was necessary to partially remove the solvent under reduced pressure to induce precipitation. The material was filtered on a frit, and the excess alcohol washed away with 3 portions of cold benzene. The ammonium salt was then dissolved in THF (10 mL), and filtered through anhydrous $\text{MgSO}_4/\text{Celite}$ which led to orange colored filtrates after washing with THF. The volume of the filtrate was reduced *in vacuo*. Ether was added to precipitate the product once the solution became concentrated. The product was filtered and washed with ether (some salts are partially soluble in ether), and air dried.

$\text{Fc}(\text{C}_6\text{H}_{11}\text{O})\text{P}(\text{S})\text{-S-S-P}(\text{S})(\text{OC}_6\text{H}_{11})\text{Fc}$ (3) A 25-mL Schlenk tube was charged with $[\text{NH}_4][\text{S}_2\text{PFc}(\text{OC}_6\text{H}_{11})]$ (4.0 mmol) in a 15 mL MeOH solution at room temperature. Sublimed iodine (2.01 mmol) was dissolved in MeOH (5 mL) and slowly added to the solution. An orange colored precipitate formed. The mixture was stirred for 20 minutes, filtered in the air, and the product dried under vacuum for 2 hours. Yield: 78%. M.p.: 160°C (dec. to red color). Anal. Calcd for $\text{C}_{32}\text{H}_{48}\text{O}_2\text{P}_2\text{S}_4\text{Fe}_2$: C, 50.67; H, 5.31. Found: C, 50.80; H, 5.08. $^3\text{1P}\{^1\text{H}\}$ NMR (chloroform- d_1 , 200 MHz, 19°C, δ): 93.34 (s).

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