ELSEVIER

Coordination Chemistry Reviews 224 (2002) 151–170

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Reactions of bis(thiophosphoryl)disulfanes and bis(thiophosphinyl)disulfanes with metal species: an alternative, convenient route to metal complex and organometallic dithiophosphates and dithiophosphinates

Ionel Haiduc [a,b,*], Lai Yoong Goh [c]

[a] *Facultatea de Chimie, Universitatea 'Babes-Bolyai', RO-3400 Cluj-Napoca, Romania*
[b] *Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968-0513, USA*
[c] *Department of Chemistry, National University of Singapore, Kent Ridge, Singapore, Singapore 119260*

Received 23 April 2001; accepted 19 June 2001

Contents

---

* Corresponding author. Fax: +40-64-19-0818.
E-mail address: ihaiduc@chem.ubbcluj.ro (I. Haiduc).

PII: S0010-8545(01)00402-7

Abstract

The reactions of bis(thiophosphoryl)disulfanes, and bis(thiophosphinyl)disulfanes, $X_2P(S)SSP(S)X_2$ (X = R, OR; R = alkyl, aryl) with metals and low valent state metal compounds are reviewed. Four types of reactions of the disulfanes are possible: (a) *adduct formation* with ring closure through *chelation* (rare); (b) *metal insertion*, involving homolytic clevage of the S–S bond and oxidative addition of the metal species (typical for active metals and low valent metal species); (c) *redistribution* between M–M and S–S bonds, involving homolytic cleavage of both S–S and M–M bonds and oxidation of the metal with the formation of M–S bonds; (d) *addition* of the (S)PS–SP(S) moieties to metal–metal multiple bonds.

Keywords: Bis(thiophosphoryl)disulfanes; Bis(thiophosphinyl)disulfanes; Dithiophosphates; Dithiophosphinates

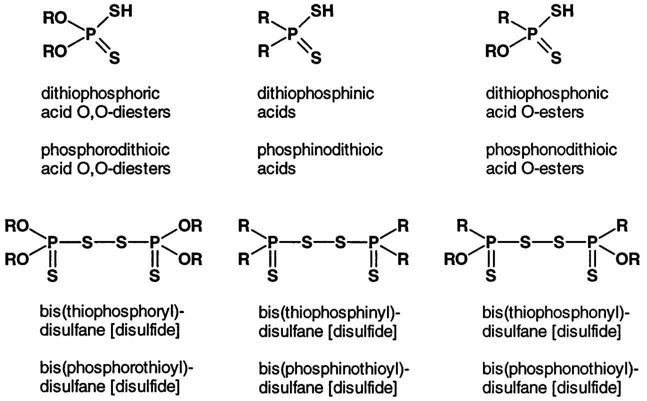
---

1. Introduction

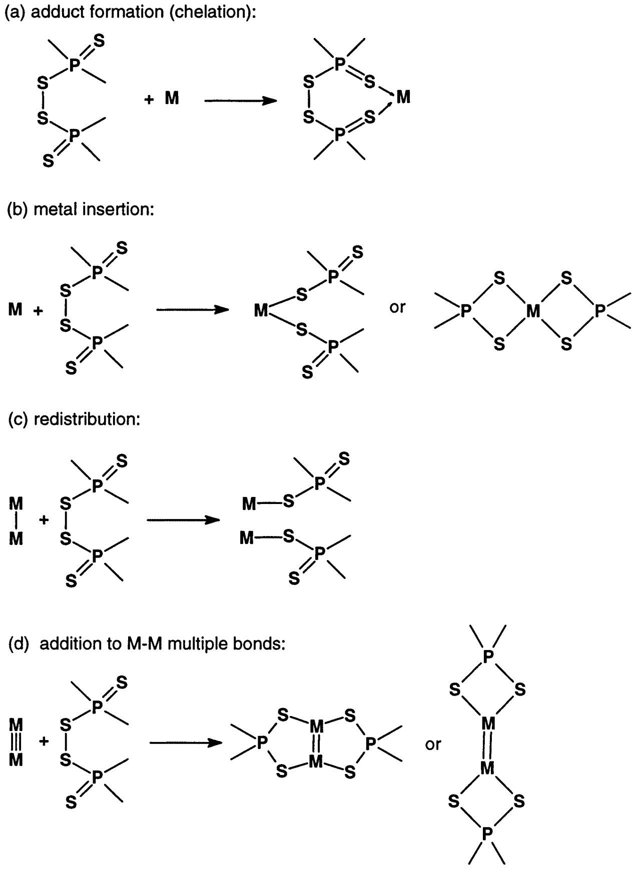
This review deals with compounds containing the $>P(S)–S–S–P(S)<$ skeleton, with alkyl, aryl, alkoxy and aroxy substituents at phosphorus. These reagents are oxidation products of the corresponding dithiophosphorus acids. The nomenclature of the acids uses two alternatives, and their derivatives containing sulfur–sulfur bonds are called either disulfides or disulfanes. As a result, the compounds can be found in the literature under various names (Scheme 1). It should be noted that negligent use of these names sometimes added to the confusion. In this review, we will use the disulfane nomenclature and, accordingly, the compounds will be called bis(thiophosph[or/in/on]yl) disulfanes.

The structural chemistry of metal complex and organometallic dithiophosphates, dithiophosphinates and dithiophosphonates has been reviewed [1,2]. The remarkable ability of the dithiophosphorus ligands to display a broad diversity of coordination patterns is worth underscoring.

This article was instigated by the publication of a review on "The reactivity of metal species toward thiuram sulfides: an alternative route to the synthesis of metal dithiocarbamates", by Victoriano [3]. Since both thiuram disulfides, $R_2NC(S)SSC(S)NR_2$ and thiophosphorus disulfides (disulfanes), $R_2P(S)SSP(S)R_2$ contain the reactive –S–S– functional moiety which determines their chemical properties, the two classes of compounds exhibit similar (but sometimes different) chemical behavior toward metal species. The preparative potential, in both cases, has not been fully exploited, although



Scheme 1.



Scheme 2.

some very interesting and promising results have already been reported. Since we were somewhat active in the field [4], we found it useful to review the reactions of phosphorus compounds containing the >P(S)SSP(S)< skeleton and to reveal their synthetic usefulness.

So far only bis(thiophosphoryl) and bis(thiophosphinyl)disulfanes were used in reactions with metal species. The less common, but known, bis(thiophosphonyl)disulfanes [5] have yet to be investigated, but their reactions would be probably similar. The bis(thiophosphinyl)monosulfanes (monosulfides), $R_2P(S)SP(S)R_2$, are expected to form six-membered chelate rings with metals, but they are cleaved to form metal dithiophosphinates, $M(S_2PR_2)_2$ (R = Me, M = Cd, Hg [6]; R = Ph, M = Pd [7]). Their use for the synthesis of metal dithiophosphinates is less efficient, since only half of the phosphorus moieties of the monosulfide are incorporated in the final product, because of sulfur deficiency; the fate of the other half has not been established. Therefore, the disulfanes remain the reagents of choice.

The reagents discussed in this review present not only academic interest. They found various uses and are involved in some important technical processes.

Bis(thiophosphoryl)disulfanes were recommended for practical uses such as stabilizers for polymer compositions [8], vulcanization accelerators [9], are used as antioxidant and antiwear additives in ashless and extreme-pressure engine lubricant oils and are also involved in the mechanism of antioxidant action of metal dithiophosphate lubricant oil additives [10]. Some bis(thiophosphoryl)disulfanes $(RO)_2P(S)SSP(S)(OR)_2$ show fungicidal activity [11].

For the compounds based upon the >P(S)SSP(S)< skeleton at least four types of reactions can be expected (Scheme 2):

a. *adduct formation* resulting in ring closure through *chelation*;
b. *metal insertion*—involving homolytic cleavage of the S–S bond and oxidative addition of the metal species;
c. *redistribution* between M–M and S–S bonds, involving homolytic cleavage of both S–S and M–M bonds and oxidation of the metal;
d. *addition* to metal–metal multiple bonds.

With the exception of (d), all others are more or less well documented.

2. Bis(thiophosphoryl)disulfanes

2.1. Preparation and formation

Numerous methods are available for the synthesis of bis(thiophosphoryl)disulfanes; there are also some other reactions in which these compounds are formed, but which have no or little preparative value. A comprehensive review of all these has been published in 1984 [12].

The most common method used for the preparation of bis(thiophosphoryl)disulfanes is based upon the oxidation of alkali metal salts of dithiophosphoric acids with iodine dissolved in potassium iodide aqueous solution [Eq. (1)] [12,13].

$$2MS_2P(OR)_2 + I_2 \rightarrow (RO)_2P(S)SSP(S)(OR)_2 + 2MI \quad (1)$$

The method is rather general and was used for all common alkyl derivatives. Thus, $(RO)_2P(S)SSP(S)(OR)_2$ with R = Me, Et, Pr, ^{i}Pr, Bu, ^{s}Bu, pentyl, cyclohexyl, octyl, Ph, $PhCH_2$, thymyl and similar mixed disulfanes were prepared in 61–81% yields from $KS_2P(OR)_2$ and iodine [14]. Solutions of iodine in CH_2Cl_2 can also be used (e.g. with R = ^{i}Pr) [15] and this can be the method of choice if the presence of water is to be avoided. Similarly prepared were some heterocyclic bis(thiophosphoryl)disulfanes. Thus, the treatment of the potassium salt of 4,7-dimethyl-2-mercapto-2-thiono-1,3,2-dioxaphosphorinane with iodine in aqueous KI gave the corresponding disulfane [16]. Care should be exercised in the use of this method, since oxidation by iodine in alkaline media can proceed further, with formation of anions of dialkylphosphoric acid esters, $(RO)_2PO_2^-$ [17,18].

Oxidation with nitrite has also been reported. Bis(diarylthiophosphoryl)disulfanes were prepared by oxidation of potassium dithiophosphate salts with potassium nitrite in sulfuric acid medium. Thus, $KS_2P(OC_6H_4Me\text{-}p)_2$ in H_2O treated with KNO_2, followed by concentrated H_2SO_4 gave a 82.7% yield of $(RO)_2P(S)SSP(S)(OR)_2$, $R = p\text{-}MeC_6H_4$; the *meta* isomer was prepared similarly [19].

Oxidation of bis(2-ethylhexyl) hydrogen dithiophosphate, $(BuCHEtCH_2O)_2P(S)SH$ with nitric acid at 22 °C, for 1 h, gave $(RO)_2P(S)SSP(S)(OR)_2$, $R = BuCHEtCH_2$, as the major product. The method can be used as an alternative to the iodine oxidation [20].

A synthesis of bis[di(2-ethylhexyl)thiophosphoryl]-disulfane by reaction of *O,O*-di(2-ethylhexyl)dithiophosphate with copper(II) sulfate, followed by oxidation with HNO_3 has also been described [21].

The oxidation with NaOCl was used for the preparation of $({}^iPrO)_2P(S)SSP(S)(O{}^iPr)_2$ in 91–100% yield by the reaction of $MS_2P(O{}^iPr)_2$ (M = alkali metal) with NaOCl at pH 6–10 [22].

Although not used for preparative purposes, oxidation with Cr(VI) was reported for *O,O′*-dibutyldithiophosphato ion, leading to formation of tris(dibutyldithiophosphato) chromium(III), $Cr\{S_2P(OBu)_2\}_3$, and bis(dibutylthiophosphoryl)disulfane, $(BuO)_2P(S)SSP(S)(OBu)_2$, in an acidic solution (pH 1.2–1.7). The reaction can be analytically useful [23].

Oxidation with hydrogen peroxide can be another method of choice for the preparation of bis(thiophosphoryl)disulfanes, e.g. for $[({}^iPrO)_2P(S)SSP(S)(O{}^iPr)_2$ (96.5% yield) [9c].

The reactions of dithiophosphoric acids with cumene hydroperoxide or other organic peroxides, much investigated in relation with the study of the mechanisms of antioxidant action of dithiophosphates in lubricating oils, also involve the formation of bis(thiophosphoryl)disulfanes [24].

The oxidation of $(RO)_2P(S)SH$ with sulfoxides (e.g. DMSO) appears as another excellent method for preparing bis(thiophosphoryl)disulfanes in high yields (R = Me, 57%; $R = {}^iPr$, 81%; R = Ph, 80%). The reaction can be carried out at room temperature, in benzene solution [25]. It follows that the use of DMSO as solvent should be avoided in the chemistry of dithiophosphates.

Electrochemical oxidation, at -0.302 V, of $(MeO)_2P(S)SH$ to $(MeO)_2P(S)SSP(S)(OMe)_2$, has been reported [26]. Similarly, the electrochemical oxidation of zinc bis(*O,O*-dialkyl dithiophosphates), mediated by 1,1′-bis(methoxycarbonyl)ferrocene, in CH_3CN on a glassy carbon electrode produced the disulfanes $(RO)_2P(S)SSP(S)(OR)_2$ in nearly quantitative yields, at $+0.90$ V (85–90%) [27].

The oxidation potentials for the redox system [Eq. (2)]:

$$2(RO)_2PS_2^- - 2e^- \rightleftarrows (RO)_2P(S)SSP(S)(OR)_2 \qquad (2)$$

have been measured and were found to decrease with increasing the length of the alkyl chain [28].

A rare synthesis of bis(dialkyl- or -arylthiophosphoryl)disulfanes involves the reaction of $(RO)_2P(S)SH$ with $(R'O)_2P(S)SZ$ (Z = morpholino) (R, R′ = alkyl) to give $(RO)_2P(S)SSP(S)(OR')_2$. When R and R_1 were dissimilar, mixtures of two symmetrically substituted disulfides were formed, except for R = Et or Pr and R′ = Ph, when unsymmetrical $(RO)_2P(S)SSP(S)(OPh)_2$ was obtained [29]. Since unsymmetrical bis(dithiophosphoryl)disulfanes are rarely seen, this method can be useful for their preparation. Similar reactions of $(RO)_2P(S)SH$ with $(R'O)_2P(S)Cl$ also gave the corresponding disulfanes [30].

Among the uncommon preparations of bis(dithiophosphoryl)disulfanes the reactions of silyl dithiophosphates with thionylamines can be cited. The reaction of trimethylsilyl dithiophosphates, e.g. $({}^iPrO)_2P(S)SSiMe_3$, with thionylamines RN:SO [R = Me, Ph, Ac, $(MeO)_2P(O)$] does not depend on the nature of R and proceeds with initial addition to the S=O bond, to give bis(thiophosphoryl)disulfanes and -trisulfanes, $Me_3SiOSiMe_3$ and the corresponding disilylamines. Thus, from $({}^iPrO)_2P(S)SSiMe_3$ with PhN:SO the products were $({}^iPrO)_2P(S)XP(S)(O{}^iPr)_2$ (X = SS, SSS), $Me_3SiOSiMe_3$ and $PhN(SiMe_3)_2$ [31]. The reaction cannot have preparative usefulness, since the starting materials are not common chemicals.

Disproportionation reactions of metal dithiophosphates also leads to the formation of bis(thiophosphoryl)disulfanes. In such reactions, a metal in a higher oxidation state is reduced to a lower oxidation state, while the dithiophosphate anion is oxidized to the disulfane [Eq. (3)].

$$3(RO)_2PS_2^- + M^{n+} \rightarrow (RO)_2P(S)SSP(S)(OR)_2 + MS_2P(OR)_2 \qquad (3)$$

The process was observed in reactions of alkali metal or ammonium salts of dithiophosphoric acids with copper(II) salts. In this case there is a solvent dependent equilibrium [Eq. (4)], involving copper(I) and copper(II) species [32].

$$2Cu[S_2P(OR)_2]_2 \rightleftarrows 2CuS_2P(OR)_2 + (RO)_2P(S)SSP(S)(OR)_2 \qquad (4)$$

Disproportionation has also been observed in the attempts to prepare thallium(III) dithiophosphates [33], during handling of the labile cobalt(III) dithiophosphates [34], and in redox reactions of antimony(III) dithiophosphates with ferric chloride. The reaction of antimony(III) tris(*O,O*-diethyldithiophosphate), $Sb\{S_2P(OEt)_2\}_3$, with three equivalents of $FeCl_3$ in ether gave bis(diethylthiophosphoryl)disulfane, $(EtO)_2P(S)$-

SSP(S)(OEt)$_2$, and dichloroantimony *O,O*-diethyldithiophosphate, $Cl_2SbS_2P(OEt)_2$ as the major products, presumably via disproportionation of an iron(III) intermediate, $Fe\{S_2P(OEt)_2\}_3$, which cannot be isolated. Several other antimony(III) tris(*O,O*-disubstituted dithiophosphates) were prepared, and the major organic product obtained by reaction of each of these compounds with three equivalents of $FeCl_3$ was the corresponding bis(thiophosphoryl) disulfane [35].

The tellurium(IV) derivative $Ph_2Te\{S_2P(OEt)_2\}_2$, could be prepared from Ph_2TeCl_2 with excess of $KS_2P(OEt)_2$ in dichloromethane in only 15% yield, because of instability in this solvent and disproportionation into $TePh_2$ and $(EtO)_2P(S)SSP(S)(OEt)_2$ [36].

2.2. Molecular structure by single-crystal X-ray diffraction

The crystal and molecular structures of several bis(thiophosphoryl)disulfanes have been determined by X-ray diffraction. These include: bis(*O,O′*diethylthiophosphoryl)disulfane, $[(EtO)_2P(S)S]_2$ [37], bis(dimethylthiophosphoryl)disulfane $(MeO)_2P(S)S]_2$ [38], bis(dineopentylthiophosphoryl)disulfane, $[(^tBuCH_2O)_2P(S)S]_2$ [38], bis(*O,O′*-diisopropylthiophosphoryl)disulfane, $[(^iPrO)_2P(S)S]_2$ [39] [40], bis(diphenylthiophosphoryl)disulfane, $[(PhO)_2P(S)S]_2$ [41,42], bis(4,4,5,5-tetramethyl-2-thioxo-1,3,2-λ^5-dioxaphospholan-2-yl)-disulfane, $[OCMe_2CMe_2OP(S)S]_2$ [43] and bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfane [44].

Some bis(thiophosphonyl)disulfanes have also been crystallographically analyzed, namely $(MeO)^tBuP(S)$-$SSP(OMe)^tBu$ [41] and (menthylO)PhP(S)SSP-(Omenthyl)Ph [45].

2.3. Spectroscopic characterization

NMR spectroscopy has been extensively used for the characterization of the bis(thiophosphoryl)disulfanes and for the elucidation of some structural details, e.g. molecular conformations. Both solution and CP MAS ^{31}P-NMR spectroscopic studies are reported and the data are correlated with X-ray diffraction structure determinations [46], in addition to detailed ^{1}H- and ^{13}C-NMR studies [38,41,46b,47].

The ^{31}P chemical shifts of bis(thiophosphoryl)disulfanes appear at ca. 80 ppm (relative to 85% H_3PO_4), close to the values observed for the dithiophosphoric acids, and at clearly different values from those observed for metal complexes containing bidentate or ionic dithiophosphato groups [48].

Vibrational (infrared and Raman) spectroscopy was more popular in the earlier years and was used for the characterization of some bis(dialkyl- and diarylthiophosphoryl) disulfanes, $(RO)_2P(S)SSP(S)(OR)_2$ [R = Me, Et, ^{n}Pr, ^{i}Pr, Bu, EtCHMe, $^nC_5H_{11}$, cyclohexyl $^nC_8H_{17}$, Ph, $PhCH_2$, 5,2-$Me(Me_2CH)C_6H_3$, etc.]; the P=S stretching vibration at 640–670 cm^{-1} is intense and may be used for their qualitative and quantitative determination. The P–O–C group absorbs at 960–1050 and 1180–1250 cm^{-1}, and the P–O and S–S bonds absorb at 750–800 and 480–520 cm^{-1}, respectively [49]. Other authors reported that the P–S stretching frequency appears in the 490–540 cm^{-1} region in both Raman and IR spectra as weak or moderate intensity bands. The S–S stretching frequency appears at ca. 478 cm^{-1} as a strong band in the Raman spectra only [50].

A comparative analysis of the IR spectra was conducted for metal complexes with phosphoric, phosphinic and phosphonic dithio acids and the corresponding disulfanes, in the range of vibrational coupling of phosphorus with sulfur. The substitution of alkoxy groups by alkyls gives a low frequency shift of the ν(PS) absorption band [51].

2.4. Thermal stability

Bis(thiophosphoryl)disulfanes are thermally stable under normal conditions. The thermal decomposition of bis(dimethylthiophosphoryl)disulfane, $(MeO)_2P(S)$-$SSP(S)(OMe)_2$ was studied in some detail, by using differential thermal analysis. An exothermic reaction started at ca. 140 °C and reached a maximum at 174 °C. The evolved gaseous mixture contained MeSH, Me_2S, Me_2S_2, $(MeO)_2P(O)SMe$, and $(MeO)_2P$-(S)SMe, as shown by gas chromatography and mass spectral analysis [52]. DTA studies showed that in the presence of H_2O, $(MeO)_2P(S)SSP(S)(OMe)_2$ decomposed at a lower temperature and reached a maximum at 100 °C [53]. During thermal decomposition, $(BuO)_2P(S)SSP(S)(OBu)_2$ at 184 °C and Bu(BuO)P-(S)SSP(S)(OBu)Bu at > 215 °C gave 1-butene, BuSH and BuSSBu as main products with *cis*-, *trans*-2-butene, Bu_2S, Me_2CHCH_2SH and $(Me_2CHCH_2)_2S$ as minor products. The disulfanes are considerably less stable than the zinc salts of the corresponding acids (used as lubricant oil additives) [54].

2.5. Photolysis

The photolytic properties of the bis(thiophosphoryl)disulfanes can be important in some photochemically activated reactions, e.g. with metal carbonyl derivatives and other organometallic species. Their understanding can also contribute to clarification of the reaction mechanisms.

The photolysis and radiolysis have been investigated by electron spin resonance spectroscopy; formation of thio and dithio radicals, radical ions, and phosphorus-centered radicals was observed. Isotropic and anisotropic ESR parameters are reported for $(RO)_2P(S)S$

[R = Et, ^{n}Pr,^{i}Pr, CH_2CHMe_2,CHMeEt, CH_2CMe_3, C_6H_4Me and $(RO)_2 = O(CH_2)_3O$] generated by photolysis of $(RO)_2P(S)SH$ and their salts or the corresponding disulfanes [in some cases in the presence of $(Me_3C)_2O_2$]. The unpaired electron in these radicals is shared equally between the two sulfur atoms in an in-plane orbital. The radicals are very short-lived [55].

Laser flash photolysis has been used to record the optical spectra of sulfur-containing radicals formed during photodissociation of bis(diisobutylthiophosphoryl)disulfane. The rate constant of this reaction is close to 109 $M^{-1}\,s^{-1}$ and successfully competes with the reaction of recombination [56].

3. Reactions of bis(thiophosphoryl)disulfanes with metals and metal compounds

3.1. Group 1: Li, Na, K, Rb, Cs, Fr

The reactions of bis(thiophosphoryl)disulfanes with alkali metal species afford esters of dialkyldithiophosphoric acids [12] and are outside the scope of this review.

3.2. Group 2: Be, Mg, Ca, Sr, Ba, Ra

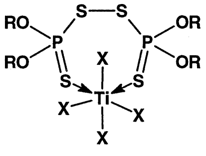
Reactions of bis(thiophosphoryl)disulfanes $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr, Ph) with organomagnesium compounds PhNHMgX (X = Br, I) in absolute ether at 30–34 °C, yield 78–85% $(RO)_2P(S)NHPh$, $Mg[S_2P(OR)_2]_2$, MgX_2 and free sulfur [57].

3.3. Group 3: Sc, Y

No reaction of scandium or yttrium species with bis(thiophosphoryl)disulfanes has been reported.

3.4. Group 4: Ti, Zr, Hf

The reactions of titanium(IV) halides, TiX_4 (X = Cl, Br) with bis(thiophosphoryl)disulfanes, L = $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr), gave air- and moisture-sensitive, hexacoordinate $TiX_4 \cdot L$ complexes of the bidentate ligands. The compounds were characterized by IR spectra, which suggest *cis*-octahedral symmetry. Probably the compounds are cyclic chelates, **1**, containing seven-membered rings [58].

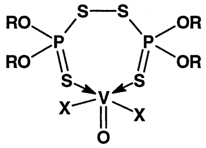


1

No reaction of any zirconium or hafnium species has been reported.

3.5. Group 5: V, Nb, Ta

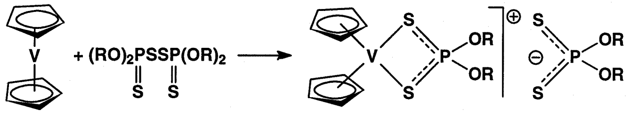
The reactions of bis(thiophosphoryl)disulfanes, L = $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr), with $VOCl_3$ led to the reduction of vanadium and the formation of $VOCl_2L$, cyclic chelate complexes, **2**, without cleavage of the S–S bonds.



2

All compounds were characterized by elemental analyses and IR, visible and ESR spectra. The occupation of the sixth coordination position in $VOCl_2L$ by different donor solvents was studied by visible and ESR spectra [58].

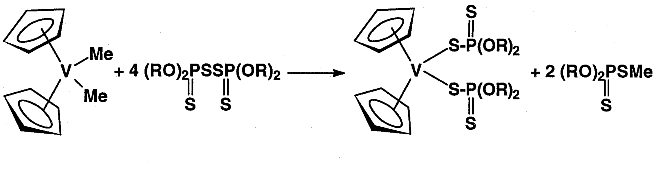
The green dithiophosphate ionic complexes $[Cp_2V\{S_2P(OR)_2\}]^+[S_2P(OR)_2]^-$ can be conveniently prepared, in quantitative yield, by oxidative addition (insertion) of vanadocene, VCp_2, with the disulfanes $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr) in THF [Eq. (5)].



(5)

The EPR spectra of the complexes have been recorded in solution at room temperature and in solid glasses; they show isotropic interaction of the unpaired electron with the ^{51}V and ^{31}P nuclei, which can be accounted for in terms of delocalization through the sulfur atoms. The salt-like character of the products was demonstrated by conductivity measurements in nitromethane solution [59].

Dimethylniobocene, Cp_2NbMe_2, reacted with $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr) in benzene, under UV irradiation at room temperature, to give after 48 h a 10% yield of pink, purple, paramagnetic $[Cp_2Nb\{S_2P(OR)_2\}_2]$ via S–S bond cleavage [Eq. (6)].



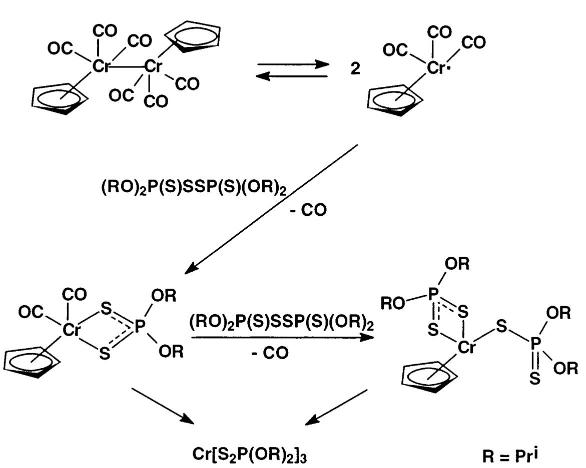
(6)

The EPR of the compounds were recorded at 130 and 295 K. They show that the unpaired electron lies essentially in the $4d_{x^2-y^2}$ metal-ion orbital mixed with a small amount of the corresponding metal-ion $4d_{z^2}$ orbital, the z axis coinciding with the C_2 axis of the compound; a weaker delocalization than in $[Cp_2Nb\{S_2P(OR)_2\}]^+$ is deduced [60].

3.6. Group 6: Cr, Mo, W

The reaction of cyclopentadienyl tricarbonylchromium dimer, $[CpCr(CO)_3]_2$, with bis(diisopropylthiophosphoryl)disulfane, $(^iPrO)_2P(S)S{-}SP(S)(O^iPr)_2$, in 1:1 molar ratio, at room temperature in toluene, produced after 5 h, a greenish blue solution, from which dark purple $CpCr(CO)_2\{S_2P(O^iPr)_2\}$ and blue $CpCr\{S_2P(O^iPr)_2\}_2$, were isolated in 32 and 30% yields, respectively. At 70–80 °C the reaction afforded $CpCr\{S_2P(O^iPr)_2\}_2$ and purple $Cr\{S_2P(O^iPr)_2\}_3$, in 35 and 11% yields, respectively. In both cases a small amount (ca. 5%) of $Cp_2Cr_2(CO)_4S$ was also isolated. The reaction was monitored by NMR and it was established that $CpCr\{S_2P(O^iPr)_2\}_2$ and $Cr\{S_2P(O^iPr)_2\}_3$ derive from $CpCr(CO)_2S_2P(O^iPr)_2$, which is the primary reaction product (Scheme 3). It was also found that the Cr≡Cr triple bond dimer $[CpCr(CO)_2]_2$ reacts with the disulfane $(^iPrO)_2P(S)SSP(S)(O^iPr)_2$, albeit much less readily, generating $CpCr\{S_2P(O^iPr)_2\}_2$. The reaction is 90% complete after 5 days [61].

The X-ray investigation showed that $CpCr(CO)_2S_2P(O^iPr)_2$ contains two *cis* CO ligands and a bidentate $S_2P(OR)_2$ ligand, whereas in $CpCr\{S_2P(O^iPr)_2\}_2$ one ligand is unidentate and the second one is bidentate chelating. The latter compound is fluxional in solution and ^1H- and ^{31}P-NMR spectra show a rapid unidentate–bidentate exchange between the ligands in the temperature range between −40 and 80 °C. Compound $Cr\{S_2P(O^iPr)_2\}_3$ is a symmetrically coordinated octahedral complex [61].



Scheme 3.

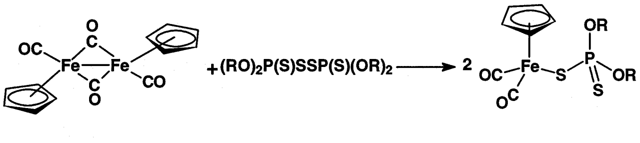
The reactions of $MoCl_5$ and $MoOCl_3$ with $(BuO)_2P(S)SSP(S)(OBu)_2$ (L), in non-aqueous medium were studied by ESR. $MoCl_5$, and L formed $[MoOCl\{S_2P(OBu)_2\}_2]$ and $[MoOCl_4L]^-$, whereas $MoOCl_3$ and L gave MOL_n^{5+} ($n = 3$–6). Extraction of MoO^{3+} from the aqueous phase in methylphenyldisulfane solution led to the formation of $MoOL_n^{3+}$, $MoOClL_n^{2+}$, $MoOCl_2L_n^{+}$, $MoOCl_3L_n$, and $MoOCl_4L^-$ [62].

3.7. Group 7: Mn, Tc, Re

No reaction of bis(thiophosphoryl)disulfanes with chemical species of this triad has been reported.

3.8. Group 8: Fe, Ru, Os

Only iron species were reacted with bis(thiophosphoryl)disulfanes. Red–orange, monodentate dithiophosphate complexes $Cp^*Fe(CO)_2[\eta^1\text{-}SP(S)(OR)_2]$, ($Cp^* = \eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$, $\eta\text{-}C_5Me_5$) were prepared in 70–88% yields, by oxidative cleavage of $[Cp^*Fe(CO)_2]_2$ with $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, ^{i}Pr) in cyclohexane, at 50–60 °C [Eq. (7)] [63].



(7)

3.9. Group 9: Co, Rh, Ir

Oxidation of cobalt(II) di(2-ethylhexyl)dithiophosphate by the corresponding disulfane was studied, using the isomolar series method. It was shown that the stoichiometric coefficients correspond to reaction (8):

$$2Co\{S_2P(OR)_2\}_2 + (RO)_2P(S)SSP(S)(OR)_2 \rightleftarrows 2CO\{S_2P(OR)_2\}_3 \quad (8)$$

The reversibility of the reaction was demonstrated and the equilibrium constant was evaluated. Iodine was found to exert a catalytic effect on the oxidation of cobalt(II) di(2-ethylhexyl)dithiophosphate by disulfane [64].

3.10. Group 10: Ni, Pd, Pt

Violet, crystalline, nickel(II) dithiophosphate complexes, $Ni\{S_2P(OR)_2\}_2$, are formed in 70% yields in the reaction of $[Ni\{P(OPh)_3\}_4]$ with $(RO)_2P(S)SSP(S)(OR)_2$ (R = ^{i}Pr, Ph) in refluxing chloroform for 3 h [65].

Liquid bis(dialkyldithiophosphato)platinum(II) complexes, $Pt\{S_2P(OR)_2\}_2$, with C1–C18 alkyl chains (R = Me, Et, Pr, Bu, pentyl, hexyl, heptyl, dodecyl, and octadecyl), were prepared by oxidative addition of bis-

(dialkylthiophosphoryl)disulfanes to tris(styrene)-platinum(0) and alternatively, by the reaction of tetrachloroplatinate(II) with ammonium-*O*,*O′*-dialkyldithiophosphates. The complexes obtained contain a ligand with alkyl chains that attach to the coordination plane perpendicularly and thus render a close packing of the molecules difficult, hence their non-crystallization [66].

3.11. Group 11: Cu, Ag, Au

Copper *O*,*O*-dialkyl dithiophosphate complexes, $Cu_4\{S_2P(OR)_2\}_4$ (R = alkyl), were claimed in a patent as products formed by treating $(RO)_2(S)PSSP(S)(OR)_2$ with an excess of activated copper at 25–125 °C. As an example, the formation of the *n*-butyl derivative (R = Bu) formed from the disulfane and copper metal in refluxing hexane for 1 h in 98% yield, is given. Obviously, the reaction deserves further study and a complete characterization of the products [67].

An EPR study was carried on the interaction between CuX_2 (X = Cl, Br, NO_3, ClO_4) and $(RO)_2P(S)SSP(OR)_2$ (R = Me, ^{i}Pr, cyclohexyl, Ph) and showed that a reaction occurred only after the addition of reducing agents (ascorbic acid, KSCN, hydroxylamine hydrochloride, α-tocopherol, α-tocotrienol); in aqueous solution and benzene, Cu(II) was quantitatively reduced to Cu(I) and $CuS_2P(OR)_2$ was formed. When the concentration of the reducing agent was less than that of Cu(II) mixed ligand complexes $CuXS_2P(OR)_2$ were obtained [68].

Silver complexation was demonstrated by solvent extraction and was assigned to redox reactions and/or insertion of metal ion or metal halide into the S–S group of bis(2-ethylhexylthiophosphoryl)disulfane [69].

3.12. Group 12: Zn, Cd, Hg

The disulfanes $(RO)_2P(S)SSP(S)(OR)_2$ (R = Et, Bu) react with $HgCl_2$ in 1:1 or 1:2 molar ratio at room temperature to give $[(RO)_2P(S)S]_2 \cdot HgCl_2$ or $[(RO)_2P(S)S]_2 \cdot 2HgCl_2$, apparently without sulfur–sulfur bond cleavage. The reaction of $(EtO)_2P(S)SSP(S)(OEt)_2$ with $HgCl_2$ (1:1) gave also the dithiophosphate $Hg[S_2P(OEt)_2]_2$, the trisulfane $[(EtO)_2P(S)SSSP(S)(OEt)_2$ and HCl as byproducts. Both 1:1 and 1:2 addition compounds (R = Et) could be converted to dithiophosphates, $Hg[S_2P(OEt)_2]_2$ when refluxed in EtOH with small amounts of HCl. The reaction deserves further study [70].

The reaction of $(RO)_2P(S)SS(S)P(OR)_2$ (R = Et, ^{i}Pr, Bu) with $HgEt_2$ in benzene at 60–70 °C during 8–10 h gave $(RO)_2P(S)SHgEt$ and $(RO)_2P(S)SEt$ [Eq. (9)] [71].

$$(RO)_2P(S)SSP(S)(OR)_2 + HgEt_2 \rightarrow (RO)_2P(S)SHgEt + (RO)_2P(S)SEt \qquad (9)$$

Mercury complexation, assigned to redox reactions and insertion of metal ions or metal halides into the S–S group of bis(di-2-ethylhexylthiophosphoryl)disulfane, was investigated by solvent extraction [69].

No reactions of zinc or cadmium species with bis(thiophosphoryl)disulfanes have been reported. It can be speculated that the metal powders of these active metals would react to form the corresponding dithiophosphates.

3.13. Group 13: B, Al, Ga, In, Tl

No reactions of chemical species of this triad with bis(thiophosphoryl)disulfanes have been reported.

3.14. Group 14: Si, Ge, Sn, Pb

Insertion of tin dihalides SnX_2 (X = Cl, Br) in the sulfur–sulfur bond of bis(diisopropylthiophosphoryl) disulfane, $(^iPrO)_2P(S)SSP(S)(O^iPr)_2$, occurs when the compounds react in dichloromethane, at room temperature. The primary products are $[(^iPrO)_2P(S)S]_2 \cdot SnX_2$ which undergo a redistribution to form $X_2Sn\{S_2P(O^iPr)_2\}_2$ in which tin is oxidized to a tetravalent state and is hexacoordinated. The latter compounds were characterized by IR and ^{31}P-NMR spectra [72].

3.15. Group 15: As, Sb, Bi

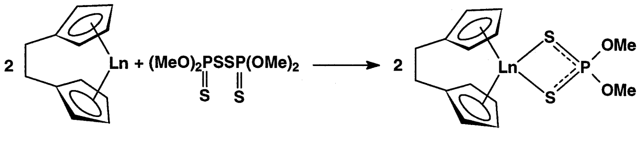
No reaction of the Group 15 element species with bis(thiophosphoryl)disulfanes have been reported.

3.16. Group 16: Te, Po

There is no reaction reported for this group.

3.17. Lanthanides

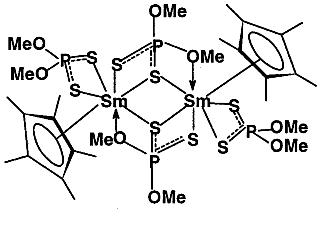
Low valent lanthanide species readily insert into the S–S bond of bis(thiophosphoryl)disulfanes, to form interesting compounds. *ansa*-Metallocene derivatives of samarium and ytterbium with a dimethyldithiophosphate ligand $[Me_4C_2(C_5H_4)_2]Ln\{S_2P(OMe)_2\}$ (Ln = Sm, Yb) were obtained by reacting the organolanthanide(II) complexes $[Me_4C_2(C_5H_4)_2]Ln$ with the disulfane $(MeO)_2P(S)SSP(S)(OMe)_2$, resulting in the oxidative insertion of the lanthanide, with the cleavage of the S–S bond [Eq. (10)] [73].



(10)

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with $(MeO)_2P(S)SSP(S)(OMe)_2$ results in elimination of a C_5Me_5

ligand and formation of the dinuclear organosamarium(III) complex $[(C_5Me_5)Sm\{S_2P(OMe)_2\}_2]_2$, **3**, by oxidative insertion of the metal-containing moiety into the S–S bond. The molecular structure of **3** was determined by X-ray diffraction. The most notable structural feature is the presence of triply bridging *O*,*O*′-dimethyldithiophosphate ligands in which one of the methoxy groups is involved in the coordination to samarium [74].



3

3.18. Analytical applications

Several analytical applications of bis(thiophosphoryl)disulfanes, based upon their interactions with metal species, are reported in the literature. In most cases the nature of the compounds involved is not clearly established. These are briefly mentioned here, as further illustration of the interactions of bis(thiophosphoryl)disulfanes with metal species.

An extraction–photometric determination of palladium(II) by using some bis(thiophosphoryl)disulfane unidentified complexes formed with $(RO)_2P(S)SSP(S)(OR)_2$ (R = Me, ^{i}Pr, Ph, cyclohexyl) was developed, based upon their UV absorption. The complexes are extracted into chloroform, dichloroethane or carbon tetrachloride from acidic solutions. Palladium is said to react with the reagents in a 1:3 molar ratio. Platinum metals (with the exception of Os), Cu(II), Co(II), Ni(II), Fe(III), Cr(III), Bi(III), Mn(III), Cd(II), Mg(II), Al(III), Sn(IV), As(III,V), Se(IV), Mo(VI), In(III), Th(IV), and alkali and alkaline earth metals do not interfere in the extraction–spectrophotometric determination of Pd described in this work [75]. A similar method, based upon extraction and atomic absorption determination of palladium(II) using bis(diisopropylthiophosphoryl)disulfane as reagent was developed for determining palladium in a platinum-group metal mixture and a Pb–Zn ore concentrate [76].

Copper(II) can be rapidly determined in carbonated water, fruit juices, and fruit jams after extraction in the presence of a 0.02% solution of bis(diisopropylthiophosphoryl)disulfane and 10% ascorbic acid, based upon the formation of a colored complex [77]. Bis(thiophosphoryl)disulfanes $(RO)_2P(S)SSP(S)(OR)_2$, where R = Me, ^{i}Pr, Ph, cyclohexyl, were also examined as reagents for photometric and extraction–photometric determination of copper. These reagents form colored complexes in 60% EtOH solutions. In aqueous solutions, insoluble complexes are formed which can be extracted with organic solvents. An extraction–photometric procedure has been developed for Cu determination. The extraction is carried out from 0.5 N HCl with a ten-fold excess of disulfane [78].

A highly selective and sensitive method for the extraction–flame atomic absorption determination of copper with bis(dimethylthiophosphoryl)disulfane-methyl methacrylate was developed. The presence of 34 other ions do not impede the determination of copper [79]. Another extraction–spectrophotometric determination of copper with bis(dithymylthiophosphoryl)disulfane was developed for the determination of microquantities of copper in ore concentrates [80]. Presumably, in all these methods the extracted species is a copper(I) dithiophosphate formed in the reduction of copper(II) by the bis(thiophoshoryl)disulfane.

A membrane extraction of mercury(II) and silver(I) with bis(di-2-ethylhexyl-thiophosphoryl)disulfane has been described, which shows selectivity for mercury and silver over zinc, nickel, cadmium and copper of the order of 103 [81]. Poly(vinyl chloride) (PVC) membrane electrodes sensitive to Ag^+ were prepared with bis(thiophosphoryl)disulfanes as carriers. The electrode was highly selective to Ag^+ and not sensitive to the change of acidity in the system [82]. This is a fast and simple analytical method and it was successfully applied for the determination of silver ions in electroplating wastewaters [83]. A modified graphite electrode was produced by adsorption of bis(diisopropylthiophosphoryl)disulfane $(^{i}PrO)_2P(S)SSP(S)(O^{i}Pr)_2$ under vacuum. The modified electrode was used for the simultaneous determination of Cu(II) and Ag(I) by flow injection anodic stripping voltammetry [84].

4. Bis(thiophosphinyl)disulfanes

4.1. Preparation and formation

Bis(thiophosphinyl)disulfanes can be best prepared by oxidation of the dithiophosphinic acids or their salts with iodine or polyiodide solutions (I_2 in KI 10%), in very good yields (e.g. R = Et, 95%; R = ^{n}Pr, 90%) [Eqs. (11) and (12))] [85–87].

$$2NaS_2PR_2 + I_2 \rightarrow R_2P(S)SSP(S)R_2 + 2NaI \quad (11)$$

$$2HS_2PR_2 + I_2 \rightarrow R_2P(S)SSP(S)R_2 + 2HI \quad (12)$$

Oxidation of sodium salts of dialkyldithiophosphinic acids, RR′P(S)SH, with iodine in 10% KI solutions, followed by extraction in diethyl ether, afforded the disulfanes RR′P(S)SSP(S)RR′ (R = R′ = ^{n}Bu; R = Et, R = ^{s}Bu; R = ^{n}Bu, R′ = Cyh) in 88–100% yields [88].

Oxidation with bromine is also possible; thus, the trifluoromethyl derivative $(CF_3)_2P(S)SSP(S)(CF_3)_2$ was best prepared, in 94% yield, by bromination of sodium or ammonium salts of $(CF_3)_2P(S)SH$ [89].

Oxidation of dithiophosphinic acids with sulfoxides affords bis(thiophosphinyl)disulfanes in excellent yields [90].

In some cases even the air may serve as an oxidant. Thus, the boron compound $Me_2NCH_2P(S)(Ph)SB(OR)_2$ [derived from $(HOR)_2$ = pyrocatechol] was oxidized by air to give a mixture of $Me_2NCH_2P(S)(Ph)SSP(S)CH_2NMe_2$ and $(RO)_2BOB(OR)_2$ [91].

Oxidation of dithiophosphinic acids with nitric acid seems to be unsuitable, since treatment of $R_2P(S)SH$ (R = alkyl, Ph) with 6 N HNO_3 gave the corresponding phosphinic acids, $R_2P(O)OH$ [86,92].

Some metals in their higher oxidation states (Cu(II), Au(III), Tl(III)) are reduced by dithiophosphinate anions, which in turn are oxidized to bis(thiophosphinyl)disulfanes [Eqs. (13) and (14)] [93].

$$4Cu^{2+} + 8R_2PS_2^- \rightarrow [CuS_2PR_2]_4 + 2R_2P(S)SSP(S)R_2 \quad (R = Et, {}^nPr, Ph) \qquad (13)$$

$$Tl^{3+} + 3R_2PS_2^- \rightarrow TlS_2PR_2 + R_2P(S)SSP(S)R_2 \quad (R = Et, {}^nPr) \qquad (14)$$

Presumably, the high oxidation state dithiophosphinates, $M(S_2PR_2)_n$ are first formed as intermediates, followed by their disporportionation.

The reactions between diorganodithiophosphinates and dimeric diphenylantimony(V) bromide oxide $(SbPh_2OBr)_2$ led to reduction of antimony, while the oxidation of dithiophosphinate followed a complex path varying in detail with the nature of the organic groups on dithiophosphinate. The reaction products were antimony(III) dithiophosphinates, $SbPh_2(S_2PR_2)$ and bis(thiophosphinyl)disulfanes, $R_2P(S)SSP(S)R_2$, where R = Me, Et and Ph [94].

When Ph_2TeCl_2 was reacted with $MS_2PR_2 \cdot xH_2O$ (R = Me, Et, M = Na, $x = 2$; R = Ph, M = NH_4, $x = 0$) in a 1:2 molar ratio, to form dithiophinato derivatives, $Ph_2Te(S_2PR_2)_2$, the alkyl derivatives disproportionated rapidly to $TePh_2$ and the corresponding disulfane, $R_2P(S)SSP(S)R_2$, as proved by multinuclear (^1H, ^{13}C, ^{31}P) NMR studies. In contrast, with diphenyldithiophosphinate salts the desired diphenyltellurium(IV) compound $Ph_2Te(S_2PPh_2)_2$ could be isolated and its crystal and molecular structure was determined by single-crystal X-ray diffractometry [95].

4.2. Molecular structure (X-ray diffraction)

The molecular structures of a number of bis(thiophosphinyl)disulfanes have been determined by X-ray diffraction; these include alkyl derivatives $R_2P(S)SSP(S)R_2$, R = Me, ^{i}Pr [96], R = Et [97], R = Ph [98], R_2 = ^{t}BuPh [41] and two modifications of bis(dicyclohexylthiophosphinyl)disulfane [99].

4.3. Spectroscopic characterization

Bis(thiophosphinyl)disulfanes were well characterized through NMR spectroscopy in solid state [41,100] and in solution [101].

Infrared spectroscopy was used for comparative characterization of bis(thiophosphinyl)disulfanes, dithiophosphinic acids and metal dithiophosphinates [102].

Among other physical properties of bis(thiophosphinyl)disulfanes measured, dipole moments are mentioned [103].

5. Reactions of bis(thiophosphinyl)disulfanes with metals and metal compounds

5.1. Group 1: Li, Na, K, Rb, Cs, Fr

The reactions of bis(thiophosphinyl)disulfanes with alkali metal derivatives (e.g. LiR, etc.) can be used for the preparation of dithiophosphinic acid esters, but are outside the scope of this review.

5.2. Group 2: Be, Mg, Ca, Sr, Ba, Ra

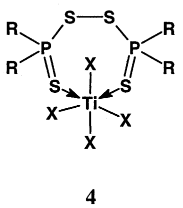
Apparently, no reactions of Group 2 metal species with bis(thiophosphinyl)disulfanes have been reported.

5.3. Group 3: Sc, Y

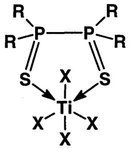
No reactions of bis(thiophosphinyl)disulfanes with Group 3 metal species have been reported.

5.4. Group 4: Ti, Zr, Hf

The reactions of titanum(IV) halides, TiX_4 (X = Cl, Br) with $R_2P(S)SSP(S)R_2$ (R = Me, Et) are similar to those of bis(thiophosphoryl)disulfanes and give hexacoordinate $TiX_4 \cdot L$ chelate ring complexes, **4**, without S–S bond cleavage. The compounds were characterized by elemental analyses and IR, visible and EPR spectra [58]. This behavior is similar to that of dithiodiphosphanes, $R_2(S)P–P(S)R_2$, which form five-membered chelate rings, **4a** [104].



4

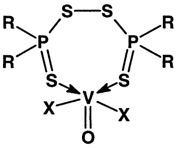


4a

No reaction of zirconium or hafnium species with bis(thiophosphinyl)disulfanes has been reported so far.

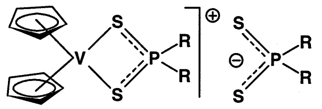
5.5. Group 5: V, Nb, Ta

As in the case of titanium halides, the reaction of $R_2P(S)SSP(S)R_2$ (R = Me, Et) with VCl_4 and $VOCl_3$ occured without S–S bond cleavage, and led to reduction of vanadium and formation of $VOCl_2L$, **5**. Again, the product was characterized only by IR, visible, and ESR spectra [58].



5

Bis(diethylthiophosphinyl)disulfane, $Et_2P(S)SSP(S)$-Et_2, reacts quantitatively with vanadocene, VCp_2, in THF, in a manner similar to the corresponding dithiophosphoryl analogues, to form a green, air-stable dithiophosphinate ionic complex of dicyclopentadienylvanadium(IV), $[Cp_2V(S_2PEt_2)]^+[S_2PEt_2]^-$, **6**, which was investigated by IR and EPR spectroscopy, in methylene chloride solution at room temperature and in solid glass at − 160 °C [59].



6

No reaction of bis(thiophosphinyl)disulfanes with a tantalum species has been reported so far.

5.6. Group 6: Cr, Mo, W

The reaction of chromium hexacarbonyl, $Cr(CO)_6$, with $Et_2P(S)PSSP(S)Et_2$ was briefly mentioned, without experimental details [93], to form $Cr(S_2PEt_2)_3$ [Eq. (15)], a compound previously obtained from NaS_2PEt_2 and chromium(III) chloride [105].

$$3Et_2P(S)SSP(S)Et_2 + 2Cr(CO)_6 \rightarrow 2Cr(S_2PEt_2)_3 + 12CO \quad (15)$$

The facile reaction of $[CpCr(CO)_3]_2$ with one mole equivalent of $Ph_2P(S)SSP(S)Ph_2$, led to the isolation of dark, purplish brown $CpCr(CO)_2(S_2PPh_2)$ and blue $CpCr(S_2PPh_2)_2$ in 50 and 10% yields, respectively [Eq. (16)] [106].

$$[CpCr(CO)_3]_2 + Ph_2P(S)SSP(S)Ph_2 \underset{-CO}{\rightarrow} 2CpCr(CO)_2(S_2PPh_2) \rightarrow CpCr(S_2PPh_2)_2 \quad (16)$$

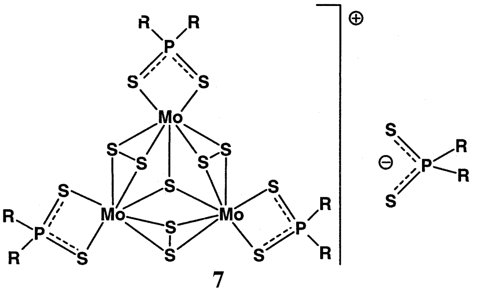
Proton NMR spectral studies demonstrated that $CpCr(S_2PPh_2)_2$ is derived from $CpCr(CO)_2(S_2PPh_2)$, the primary product. IR spectral data indicated that $CpCr(CO)_2(S_2PPh_2)$ possesses *cis*-CO ligands and a bidentate S_2PPh_2 ligand, while $CpCr(S_2PPh_2)_2$ contains both a unidentate and a bidentate ligand, as confirmed by its X-ray diffraction analysis. Variable temperature ^1H and ^{31}P spectral studies showed the occurrence of very rapid unidentate–bidentate exchange between the ligands in $CpCr(S_2PPh_2)_2$ in the temperature range − 80 to + 60 °C. In this case, the tris-complex $Cr(S_2PPh_2)_3$ was not observed [106].

Numerous reactions of bis(thiophosphinyl)disulfanes with molybdenum and tungsten species have been reported, and they provide some readily available molybdenum–sulfur cubane derivatives or precursors.

In the oxidative decarbonylation reactions with $M(CO)_6$ the bis(thiophosphinyl) disulfanes $R_2P(S)SSP$-$(S)R_2$ act both as oxidizing and sulfur transfer reagents, with the formation of $R_2P(S)SP(S)R_2$ and trinuclear chelate complexes. Thus, $Mo(CO)_6$ reacts in refluxing toluene, with $R_2P(S)SSP(S)R_2$ in 1:3 molar ratio, to afford the red salts $[Mo_3S_7(S_2P_2)_3]^+[S_2PR_2]^-$ (**7**, R = Et, ^{n}Pr [93a,107]; R = ^{n}Bu [107]), in high yields [Eq. (17)]. A reliable procedure for the preparation of $[Mo_3S_7(S_2PEt_2)_3][S_2PEt_2]$, from $Mo(CO)_6$ and $Et_2P(S)SSP(S)Et_2$ is described in *Inorganic Syntheses* [108].

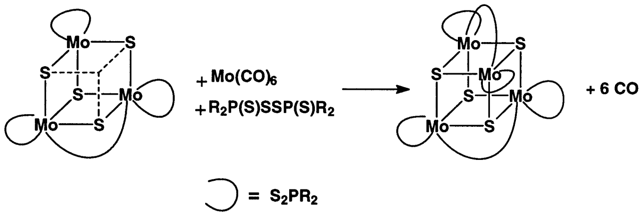
$$3Mo(CO)_6 + 9R_2P(S)SSP(S)R_2 \rightarrow [Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^- + 7R_2P(S)SP(S)R_2 + 18CO \quad (17)$$

The trinuclear complex is a 1:1 electrolyte and its $^{31}P(^1H)$-NMR spectrum displays two signals in 3:1 intensity ratio ($\delta_P = 110.1$ and 73.5 ppm relative to 85% H_3PO_4). The composition of the cation is confirmed by field desorption mass spectrometry (*m*/*z* 977) and an X-ray crystal structure determination of $[Mo_3S_7$-$(S_2PEt_2)_3]^+[S_2PEt_2]^-$ [93a,109]. The complex **7** contains three chelating and one anionic dithiophosphinato groups.



7

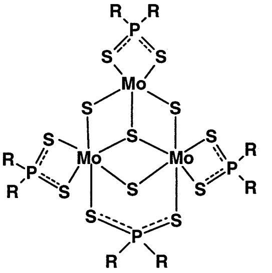
The reaction provides convenient access to Mo_3S_7 clusters, as well as to neutral, non-electrolyte $Mo_3S_4(S_2PR_2)_4$ compounds, **8** (e.g. R = Et), which can be obtained by treating $[Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^-$ with triphenylphosphine [Eq. (18)] [93a,107].



Scheme 4.

$$[Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^- + 3PPh_3 \rightarrow Mo_3S_4(S_2PR_2)_4 + 3Ph_3PS \tag{18}$$

The trinuclear complexes, **8**, contain three chelating and one bridging dithiophosphinato ligands:



8

The trinuclear complex can also be obtained by reacting $Mo(CO)_6$ with bis(alkylthiophosphinyl)-trisulfanes (R = Et) [Eq. (19)] [107],

$$6Mo(CO)_6 + 9R_2P(S)SSSP(S)R_2 \rightarrow 2[Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^- + 5R_2P(S)SP(S)R_2 + 36CO \tag{19}$$

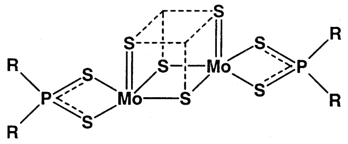
or a mixture of $R_2P(S)SSP(S)R_2$ and elemental sulfur (in situ formation of the trisulfane) [110]. Treatment of $Mo_3S_4(S_2PR_2)_4$ with disulfanes $R_2P(S)SSP(S)R_2$ or with S_8, regenerates the ionic compound $[Mo_3S_7(S_2PR_2)_3]^+$ $[S_2PR_2]^-$ [107].

In the ionic compound $[Mo_3S_7(S_2PEt_2)_3]^+[S_2PEt_2]^-$ the anion can be easily exchanged and $[Mo_3S_7(S_2PEt_2)_3]^+X^-$ with $X^- = Ph_2PS_2^-$, $Me_2PS_2^-$, $Et_2NCS_2^-$ and ClO_4^- have been prepared [107].

Under milder conditions (refluxing in acetone) $Mo(CO)_6$ reacts with a disulfane $R_2P(S)SSP(S)R_2$ (1:2.5 molar ratio) to form red, air-stable, dinuclear compounds $Mo_2S_4(S_2PR_2)_2$, **9** [Eq. (20)] [107]:

$$2Mo(CO)_6 + 5R_2P(S)SSP(S)R_2 \rightarrow Mo_2S_4(S_2PR_2)_2 + 12CO + 4R_2P(S)SP(S)R_2 \tag{20}$$

The dinuclear complexes have an incomplete cubane structure **9** [107].



9

These dinuclear species are intermediates in the formation of $[Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^-$, since prolonged heating of the reaction mixture yields the trinuclear complex [107]. Heating the dinuclear complex with $Mo(CO)_6$ and additional disulfane leads to the quantitative formation of the trinuclear compound $[Mo_3S_7(S_2PR_2)_3]^+[S_2PR_2]^-$ [Eq. (21)] [107].

$$Mo_2S_4(S_2PEt_2)_2 + Mo(CO)_6 + 4Et_2P(S)SSP(S)Et_2 \rightarrow [Mo_3S_7(S_2PEt_2)_3]^+[S_2PEt_2]^- + 3Et_2P(S)SP(S)Et_2 + 6CO \tag{21}$$

Air-stable, black–red tetranuclear cluster compounds with cubane skeletons, $Mo_4S_4(S_2PR_2)_6$ (R = Et, ^{n}Pr) are conveniently prepared by reacting equimolar amounts of $Mo_3S_4(S_2PR_2)_4$, $Mo(CO)_6$ and $R_2P(S)SSP(S)R_2$, in refluxing toluene, for 5 h [Eq. (22)] [110].

$$Mo_3S_4(S_2PR_2)_2 + Mo(CO)_6 + R_2P(S)SSP(S)R_2 \rightarrow Mo_4S_4(S_2PR_2)_6] + 6CO \tag{22}$$

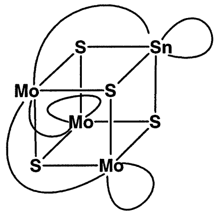
The crystal structure of the ethyl derivative, $Mo_4S_4(S_2PEt_2)_6$, has been established by X-ray diffraction [110] and is maintained in solution, as shown by the ^{31}P-NMR spectrum (two singlets with 2:1 intensity ratio). In the cubane complex two S_2PEt_2 ligands are bridging and two are chelating. The formation of $Mo_4S_4(S_2PEt_2)_6$ implies the insertion of a fourth molybdenum atom into an incomplete cubane structure (Scheme 4).

The incorporation of other metals into the incomplete cubane cluster of $Mo_3S_4(S_2PR_2)_4$ is possible under certain conditions and affords bimetallic heterocubanes. A reaction of incomplete cubane $Mo_3S_4(S_2PEt_2)_4$ with tin powder and $Et_2P(S)SSP(S)Et_2$ [Eq. (23)] (50% yield) or directly with $Sn(S_2PEt_2)_2$ [Eq. (24)] (64% yield) leads to a new bimetallic heterocubane air-stable, black, diamagnetic complex $Mo_3SnS_4(S_2PEt_2)_6$, **10** [111]:

$$Mo_3S_4(S_2PEt_2)_4 + Sn + Et_2P(S)SSP(S)Et_2 \rightarrow Mo_3SnS_4(S_2PEt_2)_6 \tag{23}$$

$$Mo_3S_4(S_2PEt_2)_4 + Sn(S_2PEt_2)_2 \rightarrow Mo_3SnS_4(S_2PEt_2)_6 \tag{24}$$

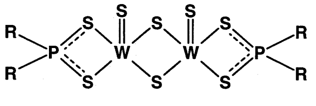
The crystal and molecular structure of $Mo_3SnS_4(S_2PEt_2)_6$ was established by X-ray diffraction and is supported by its ^{31}P-NMR spectrum (four singlets in 2:2:1:1 intensity ratio) in solution [111]. It contains three bridging and three chelating dithiophosphinato ligands.



10

The reaction of $W(CO)_6$ with disulfanes $R_2P(S)SSP(S)R_2$, in refluxing 1,2,4-trimethylbenzene, affords red, dinuclear tungsten complexes $W_2S_4(S_2PR_2)_2$ (**11**, R = Et, ^{n}Pr) [Eq. (25)] and does not proceed further to a trinuclear cluster [93a,b]. A similar compound, $W_2S_4(S_2PPh_2)_2$, was prepared from $[NEt_4]_2[WS_4]$ and $Ph_2P(S)SSP(S)Ph_2$ [111a].

$$2W(CO)_6 + 5R_2P(S)SSP(S)R_2 \rightarrow W_2S_4(S_2PR_2)_2 + 12CO + 4R_2P(S)SP(S)R_2 \quad (25)$$



11

The structure **11** is supported by the $^{31}P(^1H)$-NMR spectrum, electron impact mass spectrum and infrared spectrum [93].

A better procedure for the synthesis of $W_2S_4(S_2PR_2)_2$ uses the more reactive acetonitrile complex and a trisulfane (generated in situ from the disulfane and elemental sulfur) in refluxing toluene (R = Et, ^{n}Pr, ^{n}Bu) [Eqs. (26) and (27)] [107]:

$$R_2P(S)SSP(S)R_2 + S \rightarrow R_2P(S)SSSP(S)R_2 \quad (26)$$

$$4W(CO)_3(MeCN)_3 + 5R_2P(S)SSSP(S)R_2 \rightarrow 2W_2S_4(S_2PR_2)_2 + 3R_2P(S)SP(S)R_2 + 12CO + 12MeCN \quad (27)$$

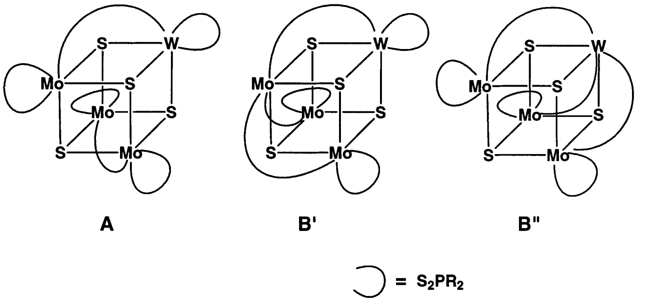
The photochemical reaction of $W(CO)_6$ with $R_2P(S)SSP(S)R_2$ (R = Et, ^{n}Pr), under UV irradiation at room temperature, gives only mononuclear complexes $W(CO)_3(S_2PR_2)_2$ [Eq. (28)] [112].

$$W(CO)_6 + R_2P(S)SSP(S)R_2 \rightarrow W(CO)_3(S_2PR_2)_2 + 3CO \quad (28)$$

By refluxing the incomplete cubane compound $Mo_3S_4(S_2PEt_2)_4$ with $W(CO)_3(MeCN)_3$ and $Et_2P(S)SSP(S)Et_2$ in toluene, during 1.5 h, the heterobimetallic cubane $Mo_3WS_4(S_2PEt_2)_6$ is obtained in 70% yield [Eq. (29)] [113]:

$$Mo_3S_4(S_2PEt_2)_4 + W(CO)_3(MeCN)_3 + Et_2P(S)SSP(S)Et_2 \rightarrow Mo_3WS_4(S_2PEt_2)_6 + 3CO + 3MeCN \quad (29)$$

The compound occurs in two forms: **A**—with two bridging and four chelating S_2PEt_2 ligands, and **B**—with three bridging and three chelating ligands. The **A**–**B** isomers can be separated by fractional crystallization. Then, fraction **B** can be further separated into two isomers by chromatography (Scheme 5) [113].



Scheme 5.

The structure of form **B** was established by X-ray diffraction [113]. In the two isomers the Mo and W atoms are statistically distributed between the four corners of the cube. The same structure is confirmed by ^{31}P-NMR spectroscopy in solution. Prolonged heating of form **A** results in isomerization to form **B** [113].

Under slightly different conditions, the dinuclear complexes $Mo_2S_4(S_2PR_2)_2$ react with $R_2(S)PSSP(S)R_2$ and $W(CO)_3(MeCN)_3$ (1:2 molar ratio, 3 h in refluxing toluene) [Eq. (30)] to form the complete cubane $Mo_2W_2S_4(S_2PR_2)_6$ (R = Et, ^{n}Pr), which can be alternatively obtained from $Mo_2S_4(S_2PR_2)_2$ and $W(CO)_3(S_2PR_2)_2$ [Eq. (31)] [112]:

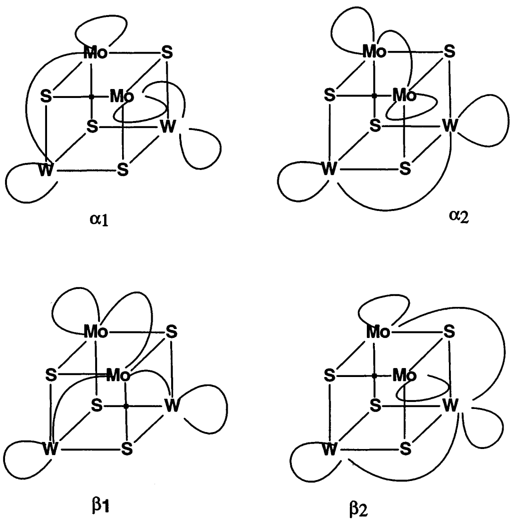
$$Mo_2S_4(S_2PR_2)_2 + 2R_2P(S)SSP(S)R_2 + 2W(CO)_3(MeCN)_3 \rightarrow Mo_2W_2S_4(S_2PR_2)_6 + 6CO + 6MeCN \quad (30)$$

$$Mo_2S_4(S_2PR_2)_2 + 2W(CO)_3(S_2PR_2)_2 \rightarrow Mo_2W_2S_4(S_2PR_2)_6 + 6CO \quad (31)$$

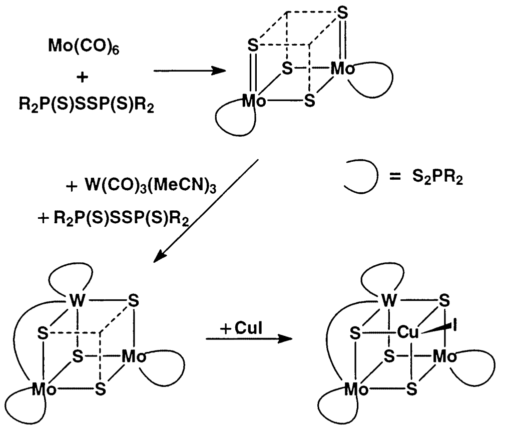
The cubane complex occurs in four isomeric forms: two α-isomers, containing two bridging and four chelating S_2PR_2 ligands, and two β-isomers, with three bridging and three chelating S_2PR_2 ligands (Scheme 6). All were characterized by ^{31}P-NMR spectroscopy and X-ray diffraction of a β1–β2 mixed crystal (R = Et) [112].

Stepwise synthesis of a trimetallic cubane cluster, containing molybdenum, tungsten and copper, is possible starting from $Mo(CO)_6$ and bis(thiophosphinyl)-disulfanes, via dinuclear $Mo_2S_4(S_2PR_2)_2$ (incomplete cubane with two vacant sites) and $Mo_2W(S_2PR_2)_4$ (incomplete cubane with one vacant site), according to the sequence shown in Scheme 7 [114].

The resulting compounds, $Mo_2WCuI(S_2P_2)_4$ (R = Et, 66% yield; R = ^{i}Pr, 59% yield) form diamagnetic, red–brown crystals. The crystal structure of the *n*-propyl



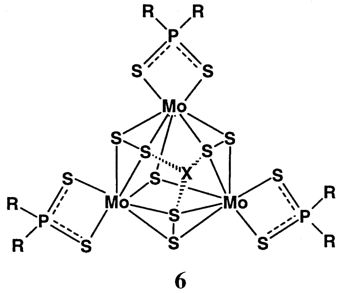
Scheme 6.



Scheme 7.

derivative has been established by X-ray diffraction. No isomeric forms of the trimetallic complex were observed [114].

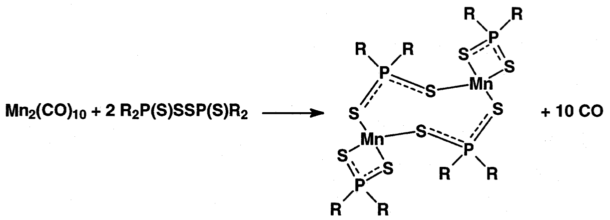
The vacant site in the incomplete cubane structure of $[Mo_3S_7(S_2PR_2)_3]^+$ cation can be occupied by a halogen, when it reacts with tetraalkylammonium halides, $[NR_4]^+X^-$, or even with alkyl halides, RX, to give orange, neutral cubane-type compounds **12**, $Mo_3S_7X(S_2PR_2)_3$, with R = Et, ^{n}Pr, ^{n}Bu and X = Cl, Br, I (not all combinations). Alternatively, the reaction between $K_4[Mo_2Cl_8]$ with the disulfane $Et_2P(S)SSP(S)Et_2$ in refluxing 1,2,4-trimethylbenzene for 5 h, gives $Mo_3S_7Cl(S_2PEt_2)_3$ in 80% yield. Curiously, the halogen is bonded to three sulfur atoms, as found by X-ray diffractometry [115].



6

5.7. Group 7: Mn, Tc, Re

The oxidative addition reaction of $Mn_2(CO)_{10}$ with $R_2P(S)SSP(S)R_2$ (R = Et, ^{n}Pr), in refluxing 1,2,4-trimethylbenzene at 125 °C, gives after 1.5 h, colorless crystalline manganese dithiophosphinates, $Mn(S_2PR_2)_2$, which are dimerized in solution and in the solid state via bridging ligands. The yields are excellent (79%, R = Et; 73%, R = ^{n}Pr) [Eq. (32)] [116].



(32)

The metal carbonyl can be replaced by powdered manganese [Eq. (33)], but in this case the reaction requires much longer reaction times (15 h) and the yields are lower.

$$Mn + R_2P(S)SSP(S)R_2 \rightarrow Mn(S_2PR_2)_2 \qquad (33)$$

The crystal structure of the ethyl complex was determined by X-ray diffraction. The compound contains a $Mn_2P_2S_4$ chair-shaped, eight-membered ring involving two bridging dithiophosphinato groups, while two other ligands are bidentate chelating. The effective magnetic moments at 295 K of 5.85 BM (R = Et) and 5.82 BM (R = ^{n}Pr) correspond to spin-only values of five unpaired electrons (5.92 BM), indicating a Mn(II) oxidation state of the metal [116].

No reaction of technetium or rhenium species has been reported.

5.8. Group 8: Fe, Ru, Os

Formation of an air-sensitive iron(III) diethyldithiophosphinate, $Fe(S_2PEt_2)_3$ (previously prepared from NaS_2PEt_2 and $FeCl_3$) [117] in a reaction of iron pentacarbonyl with $Et_2P(S)PSSP(S)Et_2$ [Eq. (34)], has been mentioned without experimental details [93].

$$2Fe(CO)_5 + 3Et_2P(S)PSSP(S)Et_2 \rightarrow 2Fe(S_2PEt_2)_3 + 4CO \qquad (34)$$

5.9. Group 9: Co, Rh, Ir

Surprisingly, no reaction of bis(thiophosphinyl)disulfanes with metal species of this triad has been reported.

5.10. Group 10: Ni, Pd, Pt

The reaction of nickel tetracarbonyl, $Ni(CO)_4$, with bis(diethylthiophosphinyl)disulfanes [Eq. (35)], to form the known $Ni(S_2PEt_2)_2$ [117], was mentioned without experimental details [93].

$$Ni(CO)_4 + Et_2P(S)PSSP(S)Et_2 \rightarrow Ni(S_2PEt_2)_2 + 4CO \tag{35}$$

A new synthesis of the nickel(II) dithiophosphinate complex, $Ni(S_2PEt_2)_2$, using a reaction of the nickel(0) complex $Ni[P(OPh)_3]_4$ with $Et_2P(S)SSP(S)Et_2$ in refluxing chloroform, has been described [65].

The reaction of $Pd_2(\mu\text{-dcpe})_2$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] with bis(thiophosphinyl)-disulfanes, $R_2P(S)SSP(S)PR_2$ (R = Et, Ph), gives the ionic complexes $[(dcpe)Pd(S_2PR_2)]^+[S_2PR_2]^-$ in very good yields (60%, R = Et and 72%, R = Ph). A dimeric compound $[(Et_2PS_2)Pd(\mu\text{-}S_2PEt_2)]_2$, is also isolated in low yield for R = Et [118] (Scheme 8).

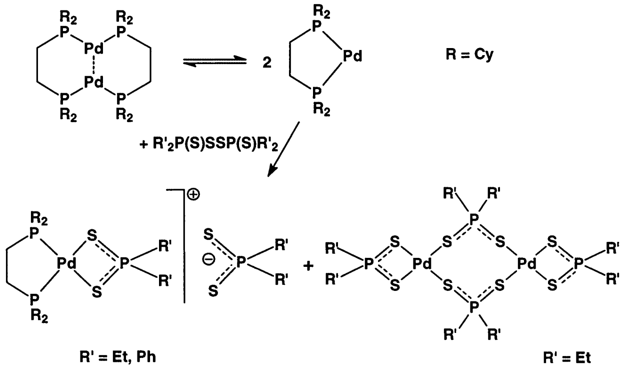
The X-ray structure of a benzene solvate of $[(dcpe)Pd(S_2PEt_2)]^+[S_2PEt_2]^-$ shows a nearly planar spirocyclic palladium atom in the cation and a free $Et_2PS_2^-$ anion. Variable-temperature ^{31}P-NMR spectra of $[(dcpe)Pd(S_2PEt_2)]^+[S_2PEt_2]^-$ indicate rapid interchange of the coordinated and free $Et_2PS_2^-$ counterion in solution at room temperature [118].

5.11. Group 11: Cu, Ag, Au

No reaction of Group 11 metal species with bis(thiophosphinyl)disulfanes has been reported.

5.12. Group 12: Zn, Cd, Hg

The electrochemical behavior of bis(diphenylthiophosphinyl)disulfane was studied by classical polarography. The data obtained show that $Ph_2(S)PSSP(S)Ph_2$ is not reduced directly on the dropping mercury electrode but is adsorbed. It then undergoes a rapid chemical reaction causing the formation of $Hg(S_2PPh_2)_2$ [119]. The disulfane $(CF_3)_2P(S)SSP(S)(CF_3)_2$ also reacts with mercury metal to give $Hg\{S_2P(CF_3)_2\}_2$ [Eq. (36)] [120]:



Scheme 8.

$$Hg + (CF_3)_2P(S)SSP(S)(CF_3)_2 \rightarrow Hg\{S_2P(CF_3)_2\}_2 \tag{36}$$

The reaction of $Ph_2P(S)SS(S)PPh_2$ with diethylmercury, $HgEt_2$, in benzene at 60–70 °C, gave $Ph_2P(S)SHgEt$ (80% yield) and $Ph_2P(S)SEt$ [Eq. (37)] [71].

$$Ph_2P(S)SS(S)PPh_2 + HgEt_2 \rightarrow Ph_2P(S)S-HgEt + Ph_2P(S)SEt \tag{37}$$

5.13. Group 13: Al, Ga, In, Tl

Among the metals of Group 13, only gallium has been involved in a reaction related to bis(thiophosphinyl)disulfane chemistry. Thus, the reaction of tri-*tert*-butylgallium, Ga^tBu_3 with $Ph_2P(S)(SH)$ surprisingly yields $Ph_2P(S)SSP(S)Ph_2$ and only traces of the expected product $[^tBu_2Ga(\mu\text{-}S_2PPh_2)]_2$, in contrast to the reaction of Ga^tBu_3 with $HO(S)PPh_2$ (E = S, O) which yields the dimeric compounds $[^tBu_2Ga(\mu\text{-}OEPPh_2)]_2$, E = S and O [121].

5.14. Group 14: Sn, Pb

Tin powder is oxidized by $Et_2P(S)SSP(S)PEt_2$ to tin(II) diethyldithiophosphinate, with insertion of the metal into the S–S bond [Eq. (38)]. The reaction takes place in refluxing toluene and affords a 70% yield [111]:

$$Sn + Et_2P(S)SSP(S)PEt_2 \rightarrow Sn(S_2PEt_2)_2 \tag{38}$$

Tin(II) chloride undergoes oxidative insertion into the S–S bond of bis(diethylthiophosphinyl)disulfanes [Eq. (39)], to form dichlorotin(IV) diethyldithiophosphinate [93], which has been prepared before from $SnCl_4$ and sodium diethyldithiophosphinate [122].

$$SnCl_2 + Et_2P(S)SSP(S)Et_2 \rightarrow Cl_2Sn(Sn_2PEt_2)_2 \tag{39}$$

The reaction between $SnCl_2$ and $Ph_2P(S)SSP(S)Ph_2$ was studied by multinuclear (^{1}H, ^{13}C, ^{31}P, ^{119}Sn) NMR spectroscopy. The previously reported *cis*-dichlorobis(-diphenyldithiophosphinato)tin(IV) was isolated as $Cl_2Sn(S_2PPh_2)_2 \cdot 0.5Me_2CO$ and its crystal structure was determined. The dithiophosphinato groups are isobidentate coordinated [P–S 2.044(2) and 2.021(2) Å] through both S atoms [Sn–S 2.530(1) and Sn–S 2.596(2) Å]. The Cl atoms are in *cis* positions [Cl–Sn–Cl 92.8(1)°] in a distorted octahedral tin complex [123].

No reaction of any lead species has been reported.

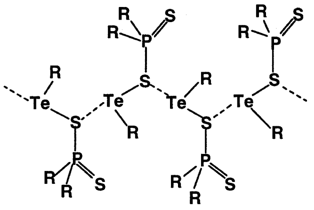
5.15. Group 15: As, Sb, Bi

The redistribution reaction between tetramethyldistibane, $Me_2SbSbMe_2$, and $Me_2P(S)SSP(S)Me_2$ [Eq. (40)], gives a complex mixture of compounds, from which crystals of $Me_2SbS_2PMe_2$, suitable for X-ray diffraction studies, can be isolated. The structure contains $Me_2SbS_2PMe_2$ units associated into infinite polymeric chains, through intermolecular, Sb···S secondary bonds. The dithiophosphinato ligand can be described either as bimetallic biconnective [intramolecular Sb–S 2.555(2) Å and intermolecular S···Sb 3.158(2) Å] or bimetallic triconnective [if the weak intramolecular Sb···S contact of 3.822(2) Å is considered] [124].

$$Me_2Sb-SbMe_2+Me_2P(S)SSP(S)Me_2 \rightarrow 2Me_2SbS_2PMe_2 \quad (40)$$

5.16. Group 16: Te, Po

Aryltellurium(II) diorganodithiophosphinates, $ArTeS_2PR_2$, were prepared by the redistribution of ArTeTeAr with $R_2P(S)SSP(S)R_2$ (Ar = Ph, *p*-tolyl; R = Me, Et, Ph) and, alternatively, from $PhTeCl_3$ with $NaS_2PR_2 \cdot 2H_2O$ (R = Me, Et). The compounds were characterized by IR, ^{1}H- and ^{31}P-NMR, and mass spectroscopy. The derivative $PhTeS(S)PPh_2$ displays thermochromism; a yellow form is observed at < -60 °C and a red form at room temperature. The crystal structure of $PhTeS(S)PPh_2$ was studied using X-ray diffraction, at both low and room temperatures. In both cases the molecules are associated in supramolecular polymeric chains, **13**, through monodentate biconnective dithiophosphinato bridges, in which the sulfur atom single bonded to phosphorus is involved in secondary bonding to the tellurium atom of a symmetry related molecule (Te–S(–P) 2.406 Å, Te···S(–P) 3.383 Å at 173 K and, respectively, Te–S(–P) 2.401 Å, Te···S(–P) 3.422 Å at 294 K) [125].



13

The sulfur atoms doubly bonded to phosphorus are not involved in coordination to tellurium. This unusual zigzag chain-like structure in which the phosphinodithioato group acts as a monodentate biconnective bridge, represents a unique coordination pattern, not observed before in any metal compounds containing dithiophosphorus ligands.

5.17. Lanthanides and actinides

No reactions of lanthanide and actinide species with bis(thiophosphinyl)disulfanes have been reported.

5.18. Analytical applications

As in the case of bis(thiophosphoryl)disulfanes discussed in Section 3.18, some interactions of bis(thiophosphinyl)disulfanes with metal species (usually cations) were used in several analytical applications, without isolation or identification of the species formed.

The interactions of $R_2P(S)SSP(S)R_2$ (R = Et, Pr, Ph) have been visually studied by using over 30 ions of elements. A high level of selectivity has been established for the interactions involving the ions of Cu(I,II), Pd(II), Hg(II), Os(VIII), Au(III), Se(IV) and Tl(I). The extraction of some of the compounds formed, with organic solvents, was also studied and can be used for analytical purposes [126].

The disulfanes $R_2P(S)SSP(S)R_2$ (R = Et, Pr, C_5H_{11}, Ph) form colored complexes of 3:1 stoichiometry with palladium(II), which can be extracted from aqueous solutions in dichloromethane and serve for the spectrophotometric determination of the metal, in the presence of Pt, Ir, Rh, Ru, Cr, Mo, Zn, Cd, Ni, Al, but Ag(I), Sb(III) and Os severely interfere and must be absent [127].

Bis(diphenylthiophosphinyl)disulfane was recommended for the photometric determination of copper [128].

6. Conclusions and outlook

The survey of the literature presented in this review clearly illustrates the synthetic usefulness of compounds containing the $>P(S)SSP(S)<$ skeleton, not only as an alternative route to the synthesis of metal complex and organometallic dithiophosphates, dithiophosphinates and dithiophosphonates, but also for the synthesis of new types of compound which cannot be obtained by other procedures. Such reagents could be very useful in cases when an aqueous system is to be avoided and when the metal species are not water-soluble. The potential of these reagents has not been fully explored and many reaction types, which have not been sufficiently investigated or not at all, can be identified.

Among the most promising substrates for reactions with the title reagents should be many simple organometallic compounds [129]. An attractive set would be the reactions of $>P(S)SSP(S)<$ reagents with metal carbonyls. The reactions with $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ were barely mentioned in the literature, with no experimental details, but those of heavier transition metal carbonyls (e.g. those of ruthenium, osmium, rhodium, iridium), dinuclear carbonyls, such as $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, polynuclear carbonyl clusters, e.g. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$ etc., certainly deserve attention. The experience available so far also suggests that cyclopentadienylmetal carbonyls, such as $CpTi(CO)_2$, $CpMn(CO)_3$, $CpRe(CO)_3$, $CpCo(CO)_2$, $CpNi(CO)$ and dimeric $[CpMo(CO)_3]_2$, $[CpW(CO)_3]_2$ etc., as well as more complex cluster cyclopentadienylmetal carbonyls, e.g. $[CpFeCO)]_4$, $Cp_3Ni_3(CO)_2$, $[CpRh(CO)]_3$, to name only a few, should provide interesting chemistry.

In view of the fascinating chemistry of the compounds containing metal–metal multiple bonds [130] the reactions of dinuclear reagents such as $[CpCr(CO)_2]_2$, $[CpMo(CO)_2]_2$, $[CpW(CO)_2]_2$, or inorganic species such as $[Mo_2Cl_8]^{2-}$, $Mo_2(OOCR)_4$, or dinuclear and trinuclear rhenium derivatives, would be of very great interest for the study of potential addition reactions.

Organometallic olefin complexes of metals in zero oxidation state, such as $(R_3P)_2M(C_2H_4)$, $Pt(COD)_2$ ($M = Ni$, Pd, Pt), $Mo(CO)_4(COD)$, metal(0) phosphine complexes, e.g. $M(PR_3)_4$ ($M = Ni$, Pd, Pt) and many other related species in which an olefin is a good leaving group, could provide interesting sources of L_2M: moieties capable of insertion into the S–S bond. In this respect the carbene-like molecules, such as stannylenes, $:SnR_2$ and plumbylenes, $:PbR_2$ [131], should also be considered.

No less interesting would be the reactions of $>P(S)SSP(S)<$ reagents with reactive organometallics, such as ZnR_2, CdR_2, AlR_3, GaR_3, InR_3, SnR_4, PbR_4, BiR_3 etc. or the potential redistribution reactions of Main Group metal dinuclear species, such as $R_2Ga–GaR_2$, $R_3Sn–SnR_3$, $R_3Pb–PbR_3$, $R_2Sb–SbR_2$, $R_2Bi–BiR_2$, etc.

Even the reaction of $>P(S)SSP(S)<$ derivatives with (activated) metals deserve attention, for comparative studies of metal reactivity towards the S–S bond of these reagents.

Further developments can be expected by extending this chemistry to seleno analogues, $>P(Se)SeSeP(Se)<$ [132] and perhaps to similar dithioarsenic compounds, such as $R_2As(S)SSAs(S)R_2$ (little known to date) or $R_2AsSSAsR_2$ [133].

It can be anticipated that a very vast area of synthetic and structural research is open for the use of the disulfanes discussed and the imagination in the exploration of these reagents has no limits.

References

[1] I. Haiduc, D.B. Sowerby, S.F. Lu, Polyhedron 14 (1995) 3389.
[2] I. Haiduc, D.B. Sowerby, Polyhedron 15 (1996) 2469.
[3] L.I. Victoriano, Coord. Chem. Rev. 196 (2000) 383.
[4] I. Haiduc, J. Organomet. Chem. 623 (2001) 29.
[5] (a) O.N. Grishina, L.M. Kosova, Zh. Obshch. Khim. 45 (1975) 1758; Chem. Abstr. 83 (1975) 206380;
(b) J. Michalski, M. Potrzebowski, A. Lopusinski, Angew. Chem. 94 (1982) 134;
(c) A. Lopusinski, L. Luczak, J. Michalski, A.E. Koziol, M. Gdaniec, J. Chem. Soc. Chem. Commun. (1991) 889;
(d) L. Luczak, A. Lopusinski, J. Michalski, Pol. J. Chem. 68 (1994) 2497.
[6] D.A. Wheatland, C.H. Clapp, R.W. Waldron, Inorg. Chem. 11 (1972) 2340.
[7] G.G. Talanova, K.B. Yatsimirskii, I.N. Kuraeva, A.Y. Nazarenko, I.M. Aladzheva, O.V. Bikhovskaya, I.V. Leont'eva, R.M. Kalyanova, J. Coord. Chem. 51 (2000) 21.
[8] (a) A.F. Kopacki, J. Horodecky, US Patent, 3,549,588, 1970; Chem. Abstr. 74 (1971) 64973;
(b) A.F. Kopacki, J. Horodecky, US Patent 3,424,715, 1969; Chem. Abstr. 70 (1969) 69059.
[9] (a) B.T. Ashworth, D. Harper, Ger. Offen. DE 1 906 765, 1969; Chem. Abstr. 71 (1969) 125745;
(b) T. Biswas, N. Naskar, D.K. Basu, J. Appl. Polym. Sci. 58 (1995) 981;
(c) J. Kalil, Ger. Offen. DE 2 223 000, 1972; Chem. Abstr. 78 (1973) 42851.
[10] (a) S. Al-Malaika, M. Coker, P.J. Smith, G. Scott, J. Appl. Polym. Sci. 44 (1992) 1297;
(b) R. Sarin, A.K. Gupta, D.K. Tuli, A.S. Verma, M.M. Rai, A.K. Bhatnagar, Tribol. Int. 26 (1993) 389; Chem. Abstr. 120 (1994) 138836;
(c) O.N. Grishina, V.M. Bashinova, M.I. Potekhina, Neftekhimiya, 20 (1980) 451; Chem. Abstr. 93 (1980) 188792;
(d) A.J. Bridgewater, J.R. Dever, M.D. Sexton, J. Chem. Soc. Perkin Trans. II (1980) 1006;
(e) V. Dinoiu, D. Florescu, C. Stanescu, Rev. Chim. (Bucharest) 47 (1996) 725; Chem. Abstr. 125 (1996) 280341;
(f) R. Wang, K. Li, Runhua Yu Mifeng (1999) 22; Chem. Abstr. 131 (1999) 7588;
(g) O.N. Grishina, V.M. Bashinova, S.M. Klyuchanskaya, Mater. Nauch. Konf., Inst. Org. Fiz. Khim., Akad. Nauk SSSR (1969) 147; Chem. Abstr. 73 (1969) 60469.
[11] W. Chen, M. Tian, Gaodeng Xuexiao Huaxue Xuebao 9 (1988) 525; Chem. Abstr. 111 (1989) 7504.
[12] B.A. Khashin, Usp. Khim. 53 (1984) 1325; Russ. Chem. Rev. (Engl. Transl.) 53 (1984) 768.
[13] Houben-Weyl Methoden der Organischen Chemie, Band XII/2, G. Thieme Verlag, Stuttgart, 1964, p. 811 and references therein.
[14] A.N. Shishkov, N.K. Nikolov, A.I. Busev, A.I. Nauch, Tr., Plovdivski Univ., Mat., Fiz., Khim., Biol. (Bulgaria), 10 (1972) 117; Chem. Abstr. 78 (1973) 83952.
[15] W.J. Stec, B. Uznanski, B.J. Bergot, B.L. Hirschbein, K.L. Fearon, PCT Int. Appl. WO 9 116 331, 1991; Chem. Abstr. 116 (1992) 255979.
[16] N.I. Zemlyanskii, V.P. Kalashnikov, Zh. Obshch. Khim. 39 (1969) 616; Chem. Abstr. 71 (1969) 38924.
[17] A.I. Busev, M.I. Ivanyutin, Zh. Anal. Khim. 14 (1959) 244.
[18] H. Bode, W. Arnswald, Z. Anal. Chem. 185 (1962) 99.
[19] N.I. Zemlyanskii, L.V. Glushkova, Zh. Obshch. Khim. 36 (1966) 2193; Chem. Abstr. 66 (1967) 75776.
[20] N.M. German, T.I. Limasova, S.N. Ryabchenko, I.S. Levin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk (1981) 150; Chem. Abstr. 95 (1981) 114711.
[21] L. Bromberg, I. Lewin, H. Gottlieb, A. Warshawsky, Inorg. Chim. Acta 197 (1992) 95.
[22] D.B. Graves, O.W. Maender, US Patent US 3,885,001, 1975; Chem. Abstr. 83 (1975) 58104.
[23] Y. Sasaki, S. Tagashira, Y. Murakami, H. Nakada, Anal. Sci. 10 (1994) 71.
[24] (a) O.A. Cherkasova, N.A. Mukmeneva, E.G. Chebotareva, V.V. Ovchinnikov, D.G. Pobedimskii, P.A. Kirpichnikov, Neftekhimiya, 24 (1984) 76; Chem. Abstr. 101 (1984) 7303;

(b) H. Grossmann, H. Komber, H. Kroschwitz, P.A. Kirpichnikov, N.A. Mukmeneva, D.G. Pobedimskii, Izv. Akad. Nauk SSSR, Ser. Khim. 34 (1989); Chem. Abstr. 111 (1989) 114613;
(c) L. Paddy, N.C.J. Lee, D.N. Waters, W. Trott, Tribol. Trans. 33 (1990) 15; Chem. Abstr. 112 (1990) 219993;
(d) J.L. Paddy, P.S. Brook, D.N. Waters, J. Chem. Soc. Perkin Trans. II (1989) 1703;
(e) R.M. Gainullin, I.E. Ismaev, A.V. Il'yasov, Izv. Akad. Nauk SSSR, Ser. Khim. (1989) 2212; Chem. Abstr. 112 (1990) 198549;
(f) R.M. Gainullin, A.V. Il'yasov, V.M. Bashinova, F.N. Mazitova, Khim. Fiz. 10 (1991) 1109; Chem. Abstr. 115 (1991) 240968.

[25] (a) M. Mikolajczyk, M. Para, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 16 (1968) 295;
(b) Esso Research and Engineering Co., French Patent FR 2 088 991, 1972; Chem. Abstr. 77 (1972) 101215.

[26] K. Maekawa, Y. Shuto, E. Taniguchi, Y. Miyoshi, Bochu-Kagaku 39 (1974) 21; Chem. Abstr. 81 (1974) 49205.

[27] R.L. Blankespoor, Inorg. Chem. 24 (1985) 1126.

[28] (a) I.A. Iankovskii, B.A. Stepanov, O.F. Ryazantseva, N.Y. Serebryakova, Zh. Fiz. Khim. (Russ.) 33 (1959) 1830;
(b) V.F. Toropova, M.K. Saikina, N.I. Guseva, Z. Obshch. Khim. 38 (1968) 2088.

[29] L. Almasi, A. Hantz, Monatsh. Chem. 100 (1969) 798.

[30] (a) L. Almasi, L. Paskucz, Chem. Ber. 98 (1965) 3546;
(b) L. Almasi, L. Paskucz, Monatsh. Chem. 101 (1970) 661;
(c) L. Almasi, A. Hantz, Chem. Ber. 99 (1966) 3288.

[31] G.A. Kutyrev, A.V. Lygin, R.A. Cherkasov, A.N. Pudovik, Zh. Obshch. Khim. 53 (1983) 1009; Chem. Abstr. 99 (1983) 88277.

[32] (a) M.G.B. Drew, G.A. Forsyth, M. Hasan, R.J. Robson, D.A. Rice, J. Chem. Soc. Dalton Trans. (1987) 1027;
(b) W. Rudzinski, Q. Fernando, Anal. Chem. 50 (1978) 472;
(c) V.I. Kuz'min, O.A. Logutenko, A.I. Khol'kin, A.Yu. Erastov, Zh. Neorg. Khim. 31 (1986) 2613; Chem. Abstr. 106 (1987) 60358.

[33] R. Ahmad, G. Srivastava, R.C. Mehrotra, Inorg. Chim. Acta 89 (1984) 41.

[34] T.J. Cardwell, D. Caridi, M.S. Loo, J. Chromatogr. 351 (1986) 331.

[35] E.J. Woo, B.J. Kalbacher, W.E. McEwen, Phosphorus Sulfur 13 (1982) 269.

[36] D. Dakternieks, R. Di Giacomo, R.W. Gable, B.F. Hoskins, J. Organomet. Chem. 349 (1988) 305.

[37] G. Grossmann, B. Schwab, A. John, H. Komber, G. Jeshcke, Phosphorus Sulfur Silicon 78 (1993) 297.

[38] M.J. Potrzebowski, J.H. Reinbenspies, Z. Zhong, Heteroat. Chem. 2 (1991) 455.

[39] S.L. Lawton, Inorg. Chem. 9 (1970) 2269.

[40] V.V. Tkachev, L.O. Atovmyan, S.A. Shchepinov, Zh. Strukt. Khim. 17 (1976) 945; Chem. Abstr. 86 (1976) 120736.

[41] P. Knopik, L. Luczak, M.J. Potrzebowski, J. Michalski, J. Blaszczyk, M.W. Wieczorek, J. Chem. Soc. Dalton Trans. (1993) 2749.

[42] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 49 (1993) 1793.

[43] J.S. Yadav, R. Bohra, R.K. Mehrotra, A.K. Rai, G. Srivastava, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 45 (1989) 308.

[44] M.J. Potrzebowski, G. Grossmann, J. Blaszczyk, M.W. Wieczorek, J. Sieler, P. Knopik, H. Komber, Inorg. Chem. 33 (1994) 4688.

[45] A. Lopusinski, L. Luczak, J. Michalsky, A.E. Koziol, M. Gdaniec, J. Chem. Soc. Chem. Commun. (1991) 889.

[46] (a) M.J. Potrzebowski, K. Ganicz, W. Ciesielski, A. Skowronska, M.W. Wieczorek, J. Blaszczyk, W. Majzner, J. Chem. Soc. Perkin Trans. II (1999) 2163;
(b) P.J. Chu, M.J. Potrzebowski, Magn. Reson. Chem. 28 (1990) 477;
(c) M.J. Potrzebowski, J. Chem. Soc. Perkin Trans. II (1993) 63;
(d) M.J. Potrzebowski, J. Magn. Reson. Chem. 33 (1995) 8;
(e) M.J. Potrzebowski, Wiad. Chem. 49 (1995) 777; Chem. Abstr. 125 (1996) 10940.

[47] (a) H. Komber, G. Grossmann, A. Kretschmer, Phosphorus Sulfur 35 (1988) 335;
(b) G. Grossmann, H. Komber, Phosphorus, Sulfur, Silicon Relat. Elem. 61 (1991) 269;
(c) M.J. Potrzebowski, Magn. Reson. Chem. 30 (1992) 35;
(d) H. Komber, G. Grossmann, Phosphorus, Sulfur, Silicon Relat. Elem. 83 (1993) 233;
(e) M.J. Potrzebowski, G. Grossmann, J. Blaszczyk, M.W. Wieczorek, J. Sieler, P. Knopik, H. Komber, Inorg. Chem. 33 (1994) 4688.

[48] C. Glidewell, Inorg. Chim. Acta 25 (1977) 159.

[49] A.N. Shishkov, N.K. Nikolov, Nauch. Tr., Plovdivski Univ. Mat., Fiz., Khim., Biol.(Bulgaria), 10 (1972) 87; Chem. Abstr. 79 (1973) 4510.

[50] W.J. Chen, X.Y. Jing, S.G. Song, C. R.-Conf. Int. Spectrosc. Raman, 7th Ottawa, Canada, 1980, p. 192; Chem. Abstr. 94 (1981) 74047.

[51] S.V. Usova, E.V. Rakitina, O.N. Grishina, Zh. Neorg. Khim. 29 (1984) 145; Chem. Abstr. 100 (1984) 164520.

[52] K. Maekawa, Y. Shuto, E. Taniguchi, Y. Miyoshi, Bochu-Kagaku, 39 (1974) 21; Chem. Abstr. 81 (1974) 49205.

[53] K. Kamoshita, Y. Nishizawa, Bochu-Kagaku, 39 (1974) 18; Chem. Abstr. 81 (1974) 49211.

[54] O.N. Grishina, M.I. Potekhina, I.A. Elfimova, S.M. Klyuchanskaya, Neftekhimiya, 14 (1974) 905; Chem. Abstr. 82 (1975) 171150.

[55] B.C. Gilbert, P.A. Kelsall, M.D. Sexton, G.D.G. McConnacchie, M.C.R. Symons, J. Chem. Soc. Perkin Trans. II (1984) 629.

[56] V.F. Plyusnin, Y.V. Ivanov, V.P. Grivin, D.Y. Vorobjev, S.V. Larionov, A.M. Maksimov, V.E. Platonov, N.V. Tkachenko, H. Lemmetyinen, Chem. Phys. Lett. 325 (2000) 153.

[57] B.A. Khaskin, T.G. Rymareva, N.N. Mel'nikova, Zh. Obshch. Khim. 47 (1977) 1912; Chem. Abstr. 87 (1977) 184128.

[58] I. Cuadrado, M. Moran, Transition Met. Chem. 9 (1984) 96.

[59] M. Moran, I. Cuadrado, J. Organomet. Chem. 311 (1986) 333.

[60] J. Sala-Pala, J.L. Migot, J.E. Guerchais, L. Le Gall, F. Grosjean, J. Organomet. Chem. 248 (1983) 299.

[61] L.Y. Goh, Z. Weng, W.K. Lee, I. Haiduc, K.M. Lo, R.C.S. Wong, J. Organomet. Chem., in press.

[62] P.M. Solozhenkin, A.V. Ivanov, E.V. Semenov, G.M. Larin, N.V. Gaidaenko, Dokl. Akad. Nauk Tadzh., SSR 21 (1978) 29; Chem. Abstr. 89 (1978) 139639.

[63] M. Moran, I. Cuadrado, J. Organomet. Chem. 295 (1985) 353.

[64] V.I. Kuz'min, T.A. Klimkina, O.A. Logutenko, Zh. Neorg. Khim. 43 (1998) 877; Chem. Abstr. 129 (1998) 114122.

[65] J. Losada, M. Moran, C. Muro, Transition Met. Chem. 14 (1989) 127.

[66] M. Gianini, W.R. Caseri, V. Gramlich, U.W. Suter, Inorg. Chim. Acta 299 (2000) 199.

[67] R.F. Bridger, US Patent US 4,582,920, 1986; Chem. Abstr. 105 (1986) 115214.

[68] N. Iordanov, N. Nicolov, A. Shishkov, D. Shopov, Inorg. Nucl. Chem. Lett. 12 (1976) 527.

[69] L. Bromberg, I. Lewin, H. Gottlieb, A. Warshawsky, Inorg. Chim. Acta 197 (1992) 95.

[70] B. Hu, W. Chen, Gaodeng Xuexiao Huaxue Xuebao 6 (1985) 41; Chem. Abstr. 103 (1985) 133899.

[71] N.N. Mel'nikov, B.A. Khaskin, O.D. Sheluchenko, Zh. Obshch. Khim. 48 (1978) 1657; Chem. Abstr. 89 (1978) 163700; J. Gen. Chem. USSR, Engl. Transl. 48 (1978) 1515.

[72] (a) A.A. Muratova, O.B. Sobanova, E.G. Yarkova, A.S. Khramov, A.N. Pudovik, Zh. Obshch. Khim. 49 (1979) 1903; Chem. Abstr. 91 (1979) 185826;
(b) A.N. Pudovik, A.A. Muratova, O.B. Sobanova, USSR Patent SU 753 851, 1980; Chem. Abstr. 93 (1980) 238830.

[73] F.T. Edelmann, M.R. Riecknoff, I. Haiduc, I. Silaghi-Dumitrescu, J. Organomet. Chem. 447 (1993) 203.

[74] M. Rieckhoff, M. Noltemeyer, F.T. Edelmann, I. Haiduc, I. Silaghi-Dumitrescu, J. Organomet. Chem. 469 (1994) C22.

[75] A.I. Busev, A.N. Shishkov, N.K. Nikolov, Zh. Anal. Khim. 30 (1975) 136; Chem. Abstr. 83 (1975) 52754.

[76] N. Nikolov, Zh. Denchev, Nauchni Tr.-Plovdivski Univ. (Bulgaria) 25 (1987) (Khim.) 87; Chem. Abstr. 111 (1989) 208305.

[77] N. Nikolov, A. Shishkov, Nauchni Tr.-Plovdivski Univ.(Bulgaria) 21 (1983) 75; Chem. Abstr. 102 (1985) 14763.

[78] A.N. Shishkov, N. Nikolov, A.I. Busev, Zh. Anal. Khim. 31 (1976) 454; Chem. Abstr. 85 (1976) 153382.

[79] N. Nikolov, Zh. Denchev, A. Shishkov, Nauchni Tr.-Plovdivski Univ. (Bulgaria) 26 (1988) (Khim.) 119; Chem. Abstr. 115 (1991) 173643.

[80] N. Nikolov, Zh. Denchev, Nauchni Tr.-Plovdivski Univ. (Bulgaria) 26 (1988) (Khim.) 127.

[81] L. Bromberg, I. Lewin, A. Warshawsky, Hydrometallurgy 33 (1993) 59; Chem. Abstr. 119 (1993) 121737.

[82] D. Liu, J. Liu, H. Cai, F. Wang, X. Ren, H. Xu, Huaxue Chuanganqi 19 (1999) 22; Chem. Abstr. 132 (1999) 356149.

[83] D. Liu, J. Liu, D. Tian, W. Hong, X. Zhou, J.C. Yu, Anal. Chim. Acta 416 (2000) 139.

[84] Z.I. Denchev, N.K. Nikolov, L. Ilcheva, Talanta 44 (1997) 749.

[85] L. Malatesta, R. Pizzotti, Gazz. Chim. Ital. 76 (1946) 167.

[86] W. Kuchen, K. Strolenberg, J. Metten, Chem. Ber. 96 (1963) 1733.

[87] W.J. Stec, B. Uznanski, B.J. Bergot, B.L. Hirschbein, K.L. Fearon, PCT Int. Appl., WO 9116331, 1991; Chem. Abstr. 116 (1992) 255979.

[88] O.N. Grishina, L.M. Kosova, S.M. Klyuchanskaya, Zh. Obshch. Khim. 41 (1971) 1995; Chem. Abstr. 76 (1972) 34354.

[89] R.G. Cavell, A.A. Pinkerton, J. Am. Chem. Soc. 93 (1971) 2384.

[90] M. Mikolajczyk, M. Para, Bull. Acad. Pol. Sci. Ser. Sci. Chim. 16 (1968) 295.

[91] B.A. Arbuzov, O.A. Erastov, A.S. Ionkin, S.N. Ignat'eva, Yu.Ya. Efremov, V.M. Nekhoroshkov, Izv. Akad. Nauk SSSR, Ser. Khim. (1990) 1871; Chem. Abstr. 114 (1991) 6670.

[92] W.A. Higgins, P.W. Vogel, W.G. Craig, J. Am. Chem. Soc. 77 (1955) 1864.

[93] (a) H. Keck, W. Kuchen, J. Mathow, B. Meyer, D. Mootz, H. Wunderlich, Angew. Chem. 93 (1981) 1019; Angew. Chem. Int. Ed. Engl. 20 (1981) 975;
(b) W. Kuchen, H. Mayatepek, Chem. Ber. 101 (1968) 3454.

[94] M.N. Gibbons, D.B. Sowerby, C. Silvestru, I. Haiduc, Polyhedron 15 (1996) 4573.

[95] A. Silvestru, I. Haiduc, H.J. Breunig, K.H. Ebert, Polyhedron 14 (1995) 1175.

[96] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 48 (1992) 2085.

[97] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 48 (1992) 701.

[98] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 49 (1993) 1793.

[99] T. Buranda, A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 47 (1991) 1414.

[100] (a) M.J. Potrzebowski, J. Blaszczyk, M.W. Wieczorek, J. Klinowski, J. Phys. Chem. A 101 (1997) 8077;
(b) M.J. Potrzebowski, J. Chem. Soc. Perkin Trans. II (1993) 63.

[101] (a) G. Haegele, W. Kuchen, H. Steinberger, Z. Naturforsch. Teil B: Chem. Sci. 29 (1974) 349;
(b) M. Nanjo, Tohoku Daigaku Senko Seiren Kenkyusho Iho, 28 (1972) 191; Chem. Abstr. 79 (1973) 59778.

[102] (a) S.V. Usova, E.V. Rakitina, O.N. Grishina, Zh. Neorg. Khim. 29 (1984) 145; Chem. Abstr. 100 (1984) 164520;
(b) E.V. Rakitina, N.P. Loseva, P.M. Solozhenkin, Dokl. Akad. Nauk Tadzh. SSR 13 (1970) 28; Chem. Abstr. 75 (1971) 12719.

[103] O. Exner, L. Almasi, L. Paskucz, Collect. Czech. Chem. Commun. 38 (1973) 677.

[104] I. Cuadrado, M. Moran, Transition Met. Chem. 6 (1981) 329.

[105] W. Kuchen, J. Metten, A. Judat, Chem. Ber. 97 (1964) 2306.

[106] L.Y. Goh, W.K. Leong, P.-H. Leung, Z. Weng, I. Haiduc, J. Organomet. Chem. 607 (2000) 64.

[107] H. Keck, W. Kuchen, J. Mathow, Z. Anorg. Allg. Chem. 537 (1986) 123.

[108] H. Keck, W. Kuchen, J. Mathow, Inorg. Synth. 23 (1985) 118.

[109] (a) B. Meyer, D. Mootz, H. Wunderlich, Z. Kristallogr. 156 (1981) 82;
(b) B. Meyer, H. Wunderlich, Z. Naturforsch. Teil B: Chem. Sci. 37 (1982) 1437.

[110] H. Keck, A. Kruse, W. Kuchen, J. Mathow, H. Wunderlich, Z. Naturforsch. Teil B: Chem. Sci. 42 (1987) 1373.

[111] (a) H. Keck, A. Kruse, W. Kuchen, D. Mootz, R. Wiskemann, H. Wunderlich, Z. Naturforsch. Teil B: Chem. Sci. 45 (1990) 461;
(b) E.R.T. Tiekink, A.A. Eagle, C.G. Young, Aust. J. Chem. 53 (2000) 779.

[112] H. Diller, H. Keck, A. Kruse, W. Kuchen, D. Mootz, R. Wiskemann, Z. Naturforsch. Teil B: Chem. Sci. 48 (1993) 548.

[113] A. Deeg, H. Keck, A. Kruse, W. Kuchen, H. Wunderlich, Z. Naturforsch. Teil B: Chem. Sci. 43 (1988) 1541.

[114] H. Diller, H. Keck, H. Wunderlich, W. Kuchen, J. Organomet. Chem. 489 (1995) 123.

[115] G. Borgs, H. Keck, W. Kuchen, D. Mootz, R. Wiskemann, H. Wunderlich, Z. Naturforsch. Teil B: Chem. Sci. 46 (1991) 1525.

[116] C. Denger, H. Keck, W. Kuchen, J. Mathow, H. Wunderlich, Inorg. Chim. Acta 132 (1987) 213.

[117] W. Kuchen, A. Judat, J. Metten, Chem. Ber. 100 (1967) 991.

[118] R. Landtiser, J.T. Mague, M.J. Fink, C. Silvestru, I. Haiduc, Inorg. Chem. 34 (1995) 6141.

[119] A. Shishkov, S. Denchev, Kh. Malakova, Talanta 31 (1984) 69.

[120] R.G. Cavell, A.A. Pinkerton, J. Am. Chem. Soc. 93 (1971) 2384.

[121] C.C. Landry, A. Hynes, A.R. Barron, I. Haiduc, C. Silvestru, Polyhedron 15 (1996) 391.

[122] W. Kuchen, A. Judat, J. Metten, Chem. Ber. 98 (1965) 3981.

[123] R.G. Ramirez, R.A. Toscano, C. Silvestru, I. Haiduc, Polyhedron 15 (1996) 3857.

[124] K.H. Ebert, H.J. Breunig, C. Silvestru, I. Haiduc, Polyhedron 13 (1994) 2531.

[125] (a) A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, Inorg. Chem. 33 (1994) 1253;
(b) A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, D.B. Sowerby, J. Organomet. Chem. 482 (1994) 253.

[126] A. Shishkov, Kh. Malakova, Nauchni Tr.-Plovdivski Univ. (Bulgaria), 26 (1988) (Khim.) 109; Chem. Abstr. 115 (1991) 222112.

[127] A. Shishkov, Kh. Malakova, Talanta 25 (1978) 533.

[128] L.K. Kabanova, P.M. Solozhenkin, S.V. Usova, USSR Patent, SU 1 970 107, 1973; Chem. Abstr. 79 (1973) 13260.

[129] I. Haiduc, J.J. Zukerman, Basic Organometallic Chemistry, Walter de Gruyter, Berlin, 1985.

[130] F.A. Cotton, R.A. Walton, Multiple Bonds between Metal Atoms, 2nd ed., Claredon Press, Oxford, 1993.

[131] (a) M. Veith, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Cluster Chemistry, vol. 1, Wiley–VCH, Weinheim, 1999, p. 73;
(b) M.A. Chaubon, H. Ranaivonjatovo, J. Escudié, J. Satgé, Main Group Met. Chem. 19 (1996) 145;
(c) M.P. Egorov, O.M. Nefedov, Main Group Met. Chem. 19 (1996) 367;
(d) M. Weidenbruch, Main Group Met. Chem. 17 (1994) 9;
(e) W.P. Neumann, Chem. Rev. 91 (1991) 311.

[132] (a) M.V. Kudchadker, R.A. Zingaro, K.J. Irgolic, Can. J. Chem. 46 (1968) 1415;
(b) R.D. Gorak, N.I. Zemlyanskii, Zh. Obshch. Khim. 41 (1971) 1994;
(c) W.W. Du Mont, R. Hensel, W. McFarlane, I.J. Colquhoun, M.L. Ziegler, O. Serhadli, Chem. Ber. 122 (1989) 37;
(d) V. Bereau, J.A. Ibers, Acta Crystallogr. Sect.C: Cryst. Struct. Commun. 56 (2000) 584.

[133] (a) L. Silaghi-Dumitrescu, I. Haiduc, J. Organomet. Chem. 252 (1983) 295;
(b) L. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 34 (1989) 305;
(c) L. Silaghi-Dumitrescu, M.N. Gibbons, I. Silaghi-Dumitrescu, J. Zukerman-Schpector, I. Haiduc, D.B. Sowerby, J. Organomet. Chem. 517 (1996) 101;
(d) L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, M.N. Gibbons, D.B. Sowerby, J. Organomet. Chem. 549 (1997) 187.