Sulfenato, Thiosulfinato, and Thiosulfonato Transition Metal Complexes☆

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The synthesis and coordination chemistry of sulfenic, thiosulfinic, and thiosulfonic acid anions are reviewed. Different approaches, which yield the platinum(II) and ruthenium(II) complexes containing the anionic sulfur(0), sulfur(II), and sulfur(IV) oxid ligands, are described. The oxidative addition of thiosulfinates or *N*-sulfinyl phthalimides to platinum(0) complexes $L_2Pt(C_2H_4)$ [L = PPh_3, 1/2 $PPh_2CH_2CH_2PPh_2$, 1/2 (*R*,*R*)-(−)-DIOP, 1/2 $(C_5H_4PPh_2)Fe(C_5H_4PPh_2)$] leads to sulfenato complexes; those of *N*-thiosulfinyl phthalimides or trisulfid 1-oxides afford the thiosulfinato complexes. Moreover, the reactions of $CpRu(PPh_3)(L)(SH)$ (L = CO, PPh_3) with *N*-sulfinyl phthalimides forming the thiosulfinato moiety, are reported. The spectroscopic, structural and chemical properties of these complexes are discussed.

1. Introduction

Sulfur compounds are widely spread in nature. Although the sulfur content (of about 2%) in organisms is comparatively small, sulfur-containing substances are of great biological importance. Thiols have one of the most reactive functional groups to be found in cells[1]. Biologically, the most important reaction of thiols is their oxidation to disulfides and higher sulfur oxides. In all these conversions *sulfenic acids RSOH* might be involved[2]. These acids have been proposed as key intermediates in a number of biochemical reactions: the occurrence of protein sulfenic acids in certain enzymes results from oxidation of the cysteine residues in proteins[3]; it is also known that some acylsulfenic acids are generated in the process converting carboxylic groups to thio acids by bacterium[4].

Sulfenic acids play an important role in reactions occuring in extracts of *Allium* plants. In 1948 Stoll and Seebeck detected three cysteine *S*-oxide $RS(O)CH_2CH(NH_2)COOH$ (R = methyl, propyl, 2-propenyl) in *Allium sativum* L (garlic)[5]. Upon cutting these plants, alliinase-induced cleavage of the sulfur−carbon bond leads to the corresponding sulfenic acids RSOH. These condense very quickly giving the relatively stable thiosulfinic-S esters (*thiosulfinates*) RS(O)SR[6]. Most attention has been

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Ralf Wünsch (right) was born in Gräfelfing/München in 1967 and received his Diploma degree in 1993 as well as his doctoral degree in 1995 from the Universität München with Priv.-Doz. Wolfgang Weigand. He joined the group of Prof. Dr. Dr. h.c. Dieter Seebach, ETH-Zürich, in 1996 as a DFG Postdoctoral Fellow.

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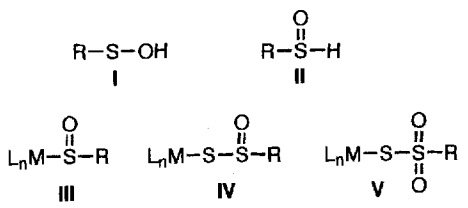
focused on thiosulfinates because of their biological and pharmacological activities[7]. The manifold chemistry of these compounds has also been investigated recently[8].

Sulfenic acids are generally very unstable and highly reactive. Very few compounds have been synthesized and isolated at room temperature to date[9]; they can act as either a nucleophile or an electrophile under different reaction conditions. The main cause of their instability is a facile self-condensation reaction to form the corresponding thiosulfinic-S esters RS(O)SR (thiosulfinates) involving nucleophilic attack by one sulfenic acid sulfur on that of the second RSOH[10]. Sulfenic acids can be stabilized either by steric inhibition or by formation of intramolecular hydrogen bonding between the sulfenic acid moiety and a suitable hydrogen bond acceptor[9]. Two possible tautomeric structures have been considered [R–S–O–H **I**, R–S(O)H **II**] (Scheme 1). Microwave spectroscopic analysis, mass spectrometry and photoelectron studies of the products obtained on flash vacuum pyrolysis of *t*butyl-methyl sulfoxide confirmed structure **I** for the methane-sulfenic acid[8,11].

Scheme 1



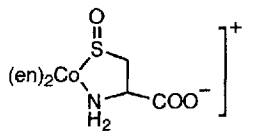
Thiosulfinates can be viewed as the S esters of the unknown thiosulfinic acid RS(O)SH. Mikolajczyk et al. have synthesized and characterized the first relatively stable salts of thiosulfinic acids starting from the corresponding sulfinyl chloride and hydrogen sulfide in the presence of triethylamine[12]. The stability of these salts is attributed to steric protection by bulky groups bonded to the central sulfinyl sulfur atom. The adamantyl thiosulfinic acid anion has been characterized by X-ray structure determination[12]. It was found that the free acids, generated from their salts upon acidification, are very unstable. They undergo a fast elimination of sulfur and subsequent conversion into the corresponding thiosulfinate RS(O)SR. Ab initio calculations[13] predict the thionosulfinic acid [HS(S)OH] to be more stable than the thiolo form [HS(O)SH] by 9.2 kcal/mol when the 6-31G* basis set is used, and by 4.3 kcal/mol at the MP2/6-31G* level.

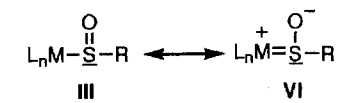
At the beginning of our own work in 1991 there were surprisingly few reports on the coordination chemistry of these unstable sulfur oxygen acid anions. Our intention has been focused on stabilizing anions of sulfenic, thiosulfinic and thiosulfonic acids, by transition metal complexes (Scheme 1). This review describes synthetically useful paths leading to sulfenato (**III**), thiosulfinato (**IV**) and thiosulfonato metal complexes (**V**); some stereochemical aspects of these reactions will also be discussed.

2. Stabilization of Anions of Sulfenic Acids by Platinum(II) Complexes

The syntheses of coordinated sulfenates are currently limited to just a few complexes. The first reports of a metal-sulfenato complex were published by George et al., who prepared the iridium compound $IrCl_2[S(O)CH_3](CO)(PR_3)_2$ by reaction of methyl sulfinyl chloride $H_3CS(O)Cl$ with $IrCl(CO)(PR_2R')_2$ (R = Ph, R' = Me, Ph)[14]; Blake et al. investigated reactions of sulfinylsulfonates and thionyl dichloride with $IrCl(CO)(PMePh_2)_2$[15]. The controlled monooxidation of thiolates coordinated to cobalt(III) led to coordinated, *S*-bonded sulfenic acid anions; for example, oxidation of (cysteinato)-*N*,*S*-bis(ethylen diamine)cobalt(III) perchlorate with hydrogen peroxide yielded the corresponding sulfenato complex **1** (Scheme 2). By this oxidative route Deutsch[16] and Sargeson[17] were able to synthesize and characterize independently several (sulfenato)-bis(ethylendiamine) cobalt(III) complexes. Efforts to prepare derivatives of more electron-rich, low-valent metal fragments, e.g. $CpW(CO)_3$[18], $CpRu(PR_3)_2$[19], $(Ph_3P)_2Pt$[20], could not be realized because of further oxidation of the coordinated sulfenate or disproportionation yielding the thiolate and sulfinato ligands RSO_2^-. In contrast, oxygenation of ruthenium-bound thioethers selectively yields the sulfoxides as recently shown by W. A. Schenk et al.[21]. How can this unexpected behavior be explained? It has been suggested that the primary attack on sulfoxides by electrophilic oxidation reagents occurs at oxygen rather than at the sulfur atom[22]. Transition metal fragments in lower oxidation states exhibit excellent π-donor ability; therefore the mesomeric structure **VI** has to be taken into account (Scheme 2). This type of resonance structure can be neglected in the case of positively-charged sulfenato complexes or with metal ions in higher oxidation states[19].

Scheme 2

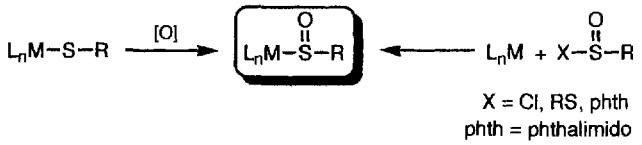




In order to circumvent this problem we employed reagents containing the sulfenato unit RS(O) from which this group can transfer to low-valent metal complexes. Thiosulfinates [RS(O)SR] and *N*-sulfinyl phthalimides [RS(O)-phth] seem to be the reagents of choice (Scheme 3). The sulfur–sulfur bond energies of thiosulfinates are unusually weak (46 kcal/mol for dimethyl thiosulfinate and 36 kcal/mol for the diphenyl derivate), and about 20–30 kcal/mol less than those of the corresponding disulfides and thiosulfonates[23].

Therefore thiosulfinates should be predestined for reactions which result in cleavage of the sulfur–sulfur bond.

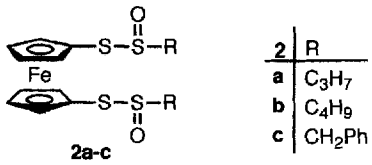
Scheme 3



2.1. Syntheses of (a)cyclic thiosulfinates

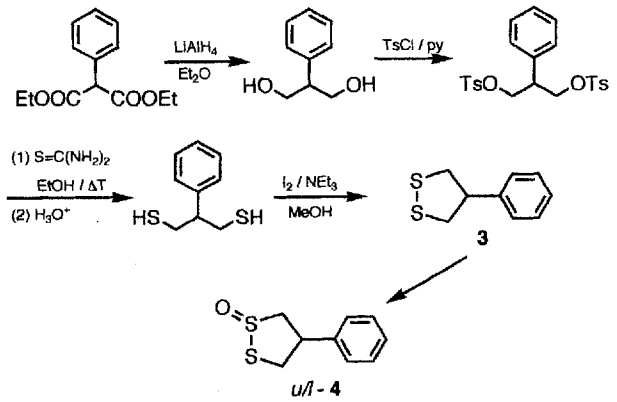
The most general method of preparing symmetrically (a)cyclic thiosulfinates as racemic mixtures consists of the selective monooxidation of the corresponding disulfides by peroxides or peroxyacids[23c,24]. We have reported the syntheses and the separation of racemic mixtures of some aliphatic as well as aromatic substituted thiosulfinates by HPLC methods using chiral stationary phases[25]. The unsymmetrically ferrocenyl-substituted thiosulfinates **2a–c** were obtained by the reaction of 1,1′-bishydrogensulfide ferrocene with sulfinyl phthalimides[26] (Scheme 4). The oxidation of the unusually stable cyclic five-membered disulfide **3** using peroxyacetic acid yields the thiosulfinate as a mixture of the *u/l*-diastereoisomers **4** in a ratio of 10:1 (Scheme 5). By using a half equivalent of singlet oxygen $^1\Delta_gO_2$, we obtained a mixture of disulfide **3** (15%), *u/l*-thiosulfinates **4** (70%), and thiosulfonate (15%); the reaction with one equivalent gives the thiosulfonate exclusively[27]. The oxidation reactions of 1,2-dithian and its derivatives to the corresponding 1,2-dithian mono-*S*-oxides **5–9** (Scheme 6) were carried out respectively with peracetic acid, *m*-chloroperoxybenzoic acid (*m*CPBA) and trifluoroperoxyacetic acid, at −50 °C. In this way we synthesized the TADDOL derivative (R_{SO},*R*,*R*)-**10**[28] in a collaboration with Seebach's group[29].

Scheme 4

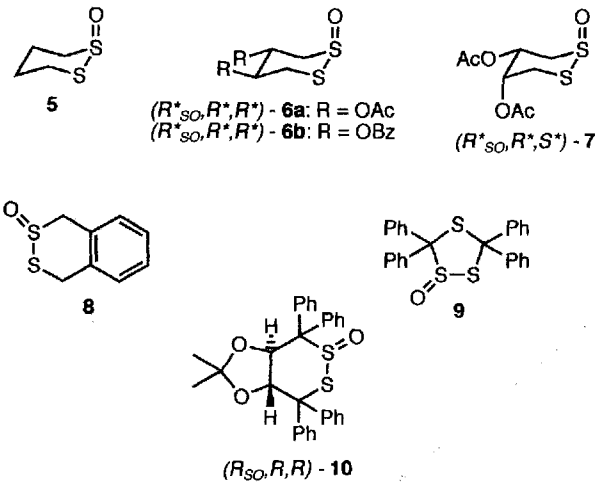


2	R
a	C_3H_7
b	C_4H_9
c	CH_2Ph

Scheme 5



Scheme 6

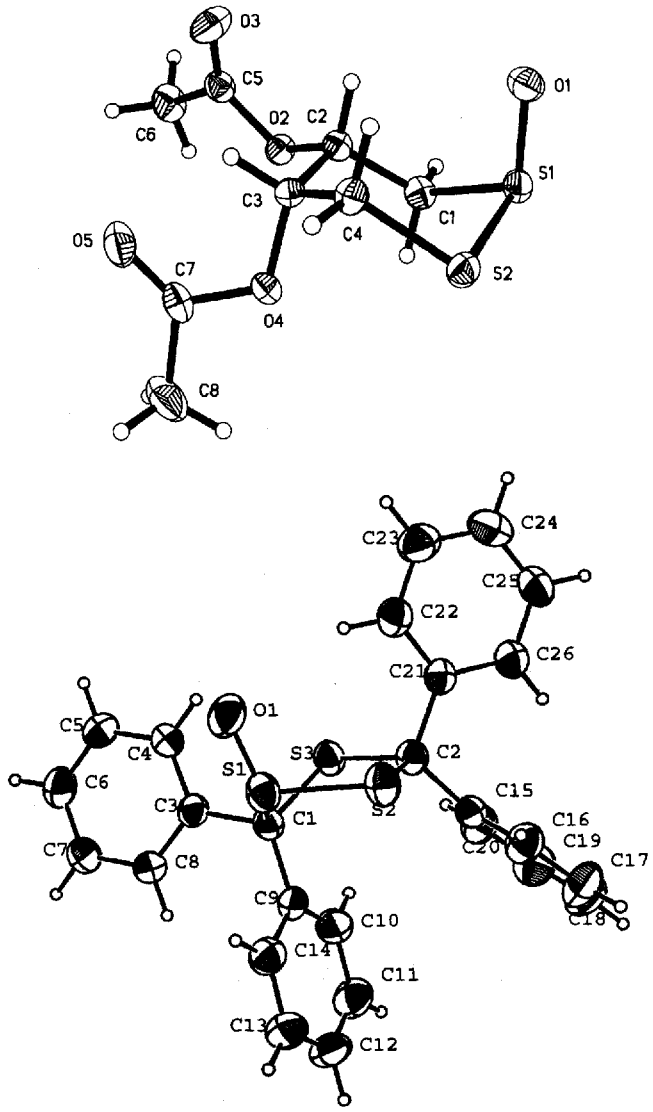


Thiosulfinate **7** has been characterized by X-ray determination (Figure 1)[28]. The sulfur–sulfur distance is 209.95(9) pm; the crystallographic study shows the diaxial (antiperiplanar) orientation of the S=O group and the lone pair of electrons at sulfur; this is characteristic of 1,2-dithian mono-S-oxides. In particular, a stereoelectronic effect [n(S) → σ*(SO) interaction] might be responsible for this orientation[30]. The relative configuration of this diastereoisomer is *l,u* (R^*_{SO},*R**,*S**). The peroxyacid oxidation of 3,3,5,5-tetraphenyl 1,2,4-trithiolan gives the thiosulfinate regioselectively (Figure 1). In the IR spectra of the thiosulfinates, characteristic bands in the range of 1060–1100 cm^{-1} are attributed to the ν(S=O) mode[23c].

2.2. Synthesis of Platinum(II) Sulfenato and Thiosulfonato Complexes

In preliminary work, it was shown that oxidative addition of acyclic thiosulfinates to $(Ph_3P)_2Pt(C_2H_4)$ (**11**) in toluene led to monomeric *trans*-configured complexes, which lost one equivalent of triphenyl phosphine in solution to form the dimetallic thiolate-bridged sulfenato complexes[31]. The cyclic five- and six-membered thiosulfinates **4–8** also react readily via oxidative addition with the platinum(0) compounds **11–15** (Scheme 7) to give six- and seven-membered chelate complexes[27,31,32]. These compounds contain the new 1-sulfenato-3-thiolato (Scheme 8) and 1-sulfenato-4-thiolato ligands (Scheme 9), which arise by insertion of platinum into the sulfur–sulfur bond. Complexes **16**, **18d**, **e**, and **20** are formed as 1:1 mixtures of both possible diastereoisomers; no diastereoselectivity has been observed. The sulfenato complexes **16–20** show ν(SO) vibrations as a single absorbance between 960 and 1000 cm^{-1}, while the thiosulfinates **5–10** show ν(SO) in the 1060–1100 cm^{-1} range[23c]. The ^{31}P NMR spectra of the sulfenato thiolato platinum(II) complexes confirm that the *trans* influence of the sulfenato ligand is higher than that of the thiolato group [$\Delta^1J(^{31}P^{195}Pt) = {}^1J(^{31}P_{trans\text{-}S}{}^{195}Pt) - {}^1J(^{31}P_{trans\text{-}SO}{}^{195}Pt) \approx 1000$ Hz].

Figure 1. Molecular structures of (R^*_{SO},R^*,S^*)-**7** (top) and **9** (bottom) in the crystal. Selected bond lengths [pm] and angles [°]: (R_{SO},R^*,S^*)-**7**: S(1)–O(1) 148.6(2), S(1)–S(2) 209.95(9); C(1)–S(1)–S(2) 97.40(8), C(4)–S(2)–S(1) 98.48(8), O(1)–S(1)–S(2) 108.90(7). **9**: S(1)–O(1) 146.6(2), S(1)–S(2) 206.2(12); C(1)–S(1)–S(2) 94.16(9), C(2)–S(2)–S(1) 104.05(9), O(1)–S(1)–S(2) 106.69(12)

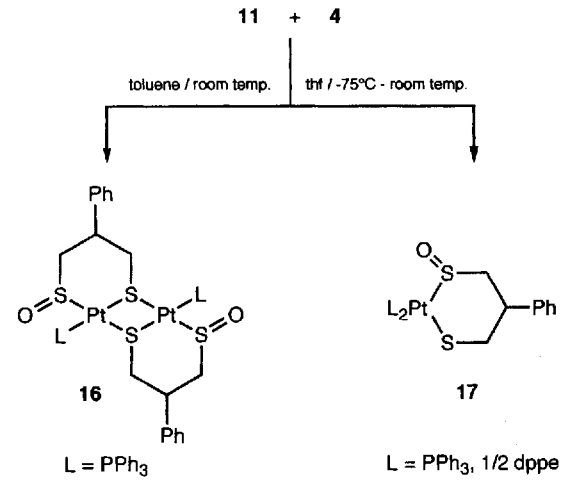


Scheme 7

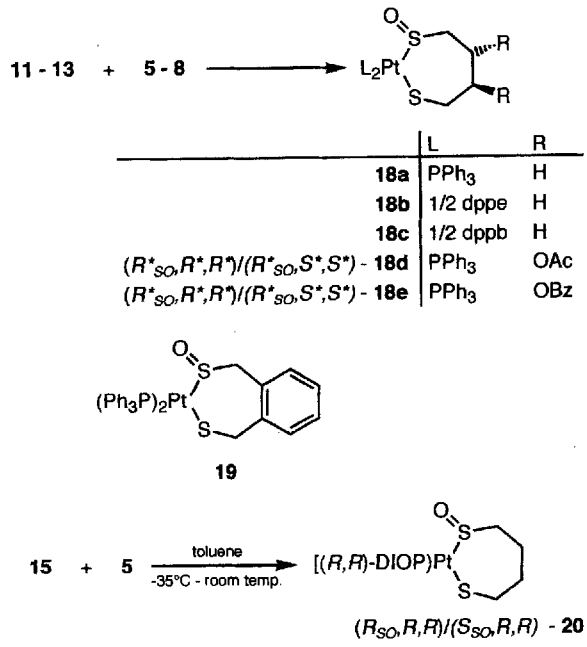
$L_2Pt(C_2H_4)$

	L
11	PPh_3
12	1/2 $Ph_2P(CH_2)_2PPh_2$ (dppe)
13	1/2 $Ph_2P(CH_2)_4PPh_2$ (dppb)
14	1/2 (η^5-$C_5H_4PPh_2)_2Fe$ (dppf)
15	1/2 (*R*,*R*)-(-)-DIOP

Scheme 8



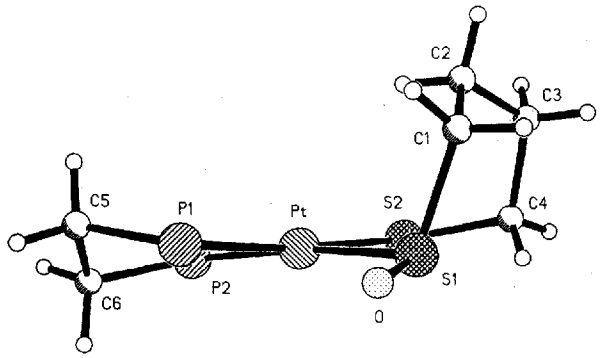
Scheme 9



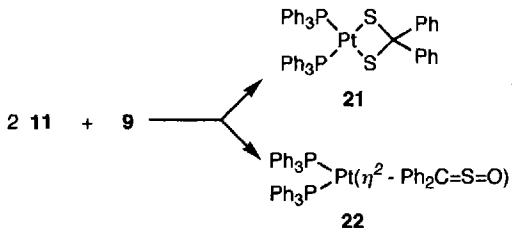
The X-ray structure of **18a** shows the explicit boat conformation of the seven-membered ring and a strong distortion of the square-planar coordination at the platinum(II) center: the planes Pt,P(1),P(2) and Pt,S(2),S(2) make an angle of 16.1°[31]. Another X-ray crystal structure determination has been carried out for the platinum complex **18b** containing the chelating dppe ligand (Figure 2); here the tetrahedral distortion of 6° is much smaller[33]. The key bond lengths in complex **18b** are S(1)-O 150.1(9) pm, Pt-P(1) 225.9(3) pm, which is *trans* to S(2), and Pt-P(2) 230.1(3), which is *trans* to the sulfoxidic S(1) atom. The latter value is an additional manifestation of the high *trans* influence of the sulfenato ligand.

Another coordination mode was found during an investigation of the reaction of 3,3,5,5-tetraphenyl 1,2,4-trithiolane-1-*S*-oxide (**9**) with platinum(0) complexes (Scheme 10). The reaction of **11** with **9** induces fragmentation of the thiosulfinate and gives a 1:1 mixture of the well-known η^2-sulfine platinum(0) **22**[34] and the diphenylmethylene dithiolate platinum(II) complex **21**[28]; **21** can be regarded as the product of a formal oxidative addition of the hypothetical diphenyl dithiirane[35] to platinum(0) compounds.

Figure 2. Molecular structure of **18b** in the crystal. Selected bond lengths [pm] and angles [°]: Pt–P(1) 225.9(3), Pt–P(2) 230.1(3), Pt–S(1) 234.1(3), Pt–S(2) 234.8(1), O–S(1) 150.1(9); S(1)–Pt–S(2) 91.7(1), Pt–S(1)–O 112.3(4), O–S(1)–C(1) 104.7(6)

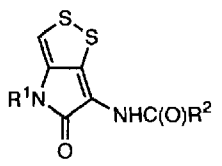


Scheme 10



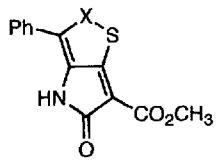
We have also studied the reactivity of derivatives of dithiolo **23**–**27**[36] and isothiazolo pyrrols **28** and **29**[37] towards platinum(0) complexes **11**, **14** and **15** in a collaboration with Stachel's group. Some of these dithiolo pyrrols are antibiotics (thiolutin, holomycin, aureothricin), which are produced in streptomyces bacterial cultures (Scheme 11). They are active against Gram-positive and Gram-negative bacteria[38]. It was shown that insertion of platinum(0) takes place selectively into the sulfur–sulfur as well as into the sulfur–nitrogen linkage in the case of the disulfides **23** and **26**, thiosulfinates **24** and **27**, and sulfinamides **28** and **29**, yielding respectively the dithiolato **30** and **31**, sulfenato–thiolato **32**–**34**, and amido–sulfenato complexes **35**–**38** (Scheme 12, 13). In contrast, **11** reacts with the thiosulfonate **25** via C–S cleavage in toluene at room temperature, involving insertion of platinum(0) into the C–S bond (Scheme 14). While complex **39** is an unusual compound, it was not the first thiosulfonato complex to be prepared. Shaver and coworkers isolated $Cp(Ph_3P)(OC)Ru[SS(O)_2CH(CH_3)_2]$ by a disproportionation reaction of the corresponding thiosulfinato complex (vide infra)[39]. However, this is to our knowledge the *first example of insertion of a metal atom into a C–S bond in the presence of the S–SO$_n$ (n = 0–2) moiety.* Activation and cleavage of the C–S bond in condensed thiophenes and other heterocycles by low-valent transition-metal complexes have been studied intensively for their role in catalytic hydrodesulfurization[40]. The ^{31}P NMR spectrum of **39** shows the coupling pattern of an AB spin system and is consistent with a C,S-bound species [$^1J(^{31}P^{195}Pt)$ = 3724, 2054 Hz]; the formation of a C–S insertion product was confirmed by X-ray analysis of **39** (Figure 3), which shows the six-membered platinum-containing ring in a boat conformation and a strong distortion of the square planarity around the platinum(II) ion with a P(1)PtP(2)/S(2)PtC(3) dihedral angle of 22.9°. The short sulfur–sulfur bond length of 203.4(2) pm is quite remarkable considering that the S–S distance is much longer in the educt **25** [213.9(2) pm]. We observed that complex **39** reacts with carbon monoxide (100 atm, 24 h) yielding **40**; in doing so one phosphine ligand is substituted by carbon monoxide (Scheme 14). Within several hours the free phosphine removes one sulfur atom, affording the bicyclic sulfinato platinum(II) complex **41** and $Ph_3P{=}S$. The ^{31}P NMR spectrum [$^1J(^{31}P^{195}Pt)$ = 2144 Hz] indicates that the phosphine ligand is bound *trans* to the carbon atom. The desulfurization reactions of these thiosulfonato complexes **39** and **40** are currently under investigation.

Scheme 11

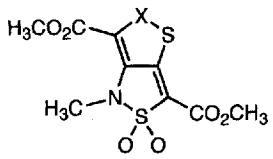


	R^1	R^2
Thiolutin	CH_3	CH_3
Holomycin	H	CH_3
Aureothricin	CH_3	C_2H_5

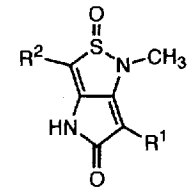
Scheme 12



	X
23	S
24	SO
25	SO_2



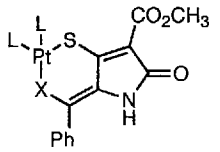
	X
26	S
27	SO



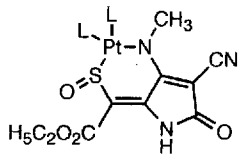
	R^1	R^2
28	COOMe	Ph
29	CN	COOEt

Recently we reported that platinum(II) sulfenato complexes are accessible from *N*-(alkyl- and arylsulfinyl) phthalimides and platinum(0) reagents **11**–**13**[41] (Scheme 15). In the first step, sulfenyl phthalimides may be oxidized to the corresponding sulfinyl phthalimides with *m*CPBA[42]. The sulfenyl-transfer reagents of the type RS(O)-phth add oxidatively to $(Ph_3P)_2Pt(C_2H_4)$ (**11**) with cleavage of the S–N bond, giving the *trans*-$(Ph_3P)_2Pt(phth)[S(O)R]$ **42**–**47**. The *trans* geometry has been confirmed on the basis of the ^{31}P NMR spectra. By analogy, the *cis*-$L_2Pt(phth)[S(O)R]$ [L = 1/2 $Ph_2P(CH_2)_nPPh_2$, *n* = 2, 4] **48**–**50** were also prepared via oxidative addition. However,

Scheme 13

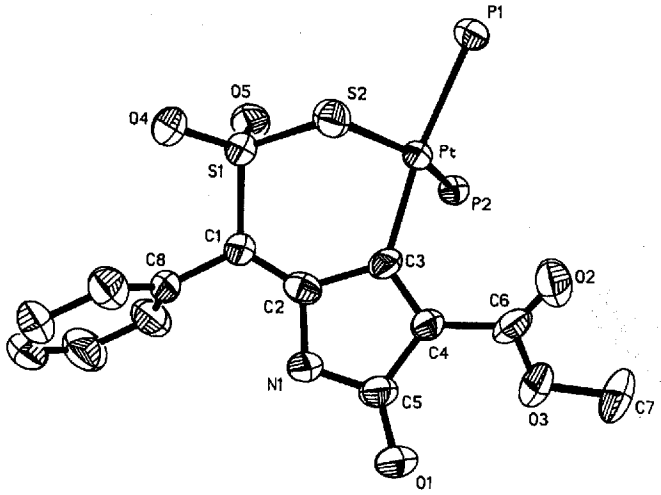


	X	L
30	S	PPh_3 ⌐ PBu_3
31	S	PBu_3 ← ⌙
32	SO	PPh_3
33	SO	1/2 dppf
34	SO	1/2 (*R,R*)-DIOP

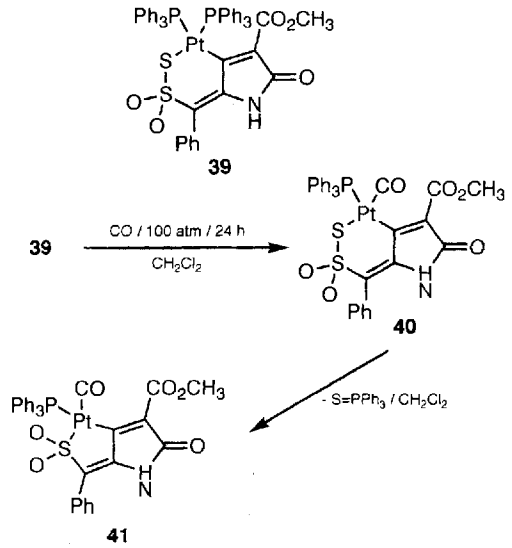


	L
35	PPh_3 ⌐ PBu_3
36	PBu_3 ← ⌙
37	1/2 dppf
38	1/2 (*R,R*)-DIOP

Figure 3. Molecular structure of **39** in the crystal. Selected bond lengths [pm] and angles [°]: Pt–P(1) 235.8(2), Pt–P(2) 227.3(2), Pt–S(2) 236.2(2), Pt–C(3) 204.6(7), S(1)–S(2) 203.4(2), S(1)–O(4) 143.4(4), S(1)–O(5) 144.2(5); S(2)–Pt–C(3) 86.9(2), P(1)–Pt–P(2) 102.9(1), O(4)–S(1)–O(5) 115.5(3)

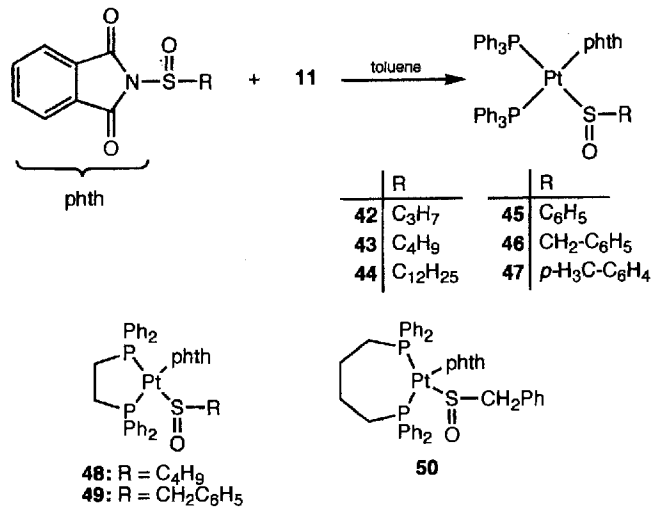


Scheme 14



these complexes exhibit a high tendency to decompose in solution. The IR spectra display bands attributed to SO stretching modes in the range 965–995 cm^{-1}. These reactions are similar to the reported oxidative addition of the corresponding thiophthalimides RS-phth to **11**[43].

Scheme 15

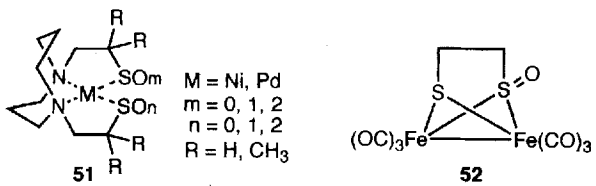


	R
42	C_3H_7
43	C_4H_9
44	$C_{12}H_{25}$

	R
45	C_6H_5
46	CH_2-C_6H_5
47	*p*-H_3C-C_6H_4

In recent studies M. Y. Darensbourg and coworkers[44] have prepared a series of nickel(II) and palladium(II) complexes **51** containing sulfenato/thiolato, disulfenato, and sulfenato/sulfinato ligands by careful oxidation of bis(2-mercaptoethyl)-1,5-diazacyclooctane-nickel(II) and palladium(II) as well as *N,N'*-bis(2-methyl-2-mercaptopropyl)-1,5-diazacyclooctane-nickel(II)[44a–e] with both molecular oxygen ($^3\Sigma$ O_2 and $^1\Delta$ O_2) and hydrogen peroxide (Scheme 16). The ease of synthesis and accessibility of the sulfenato [–S(=O)R] moiety is dependent on both the metal and the substituent R. For nickel, steric encumbrance about the sulfur appears to inhibit the addition of a second oxygen atom at the sulfenate group to produce sulfinate. For palladium, the sulfenate is quite stable even in the non-sterically-hindered thiolates. The whole series was characterized by cyclic voltammography (to explore correlations of S-donor ability to M(II) (M = Ni, Pd) and resultant potentials with S-oxygenation level) and X-ray diffraction. The authors report that the observed reduction-promoted, intermolecular oxygen transfer from [Ni(II)S(=O)R] could be consistent with the reductive activation observed in oxygen-degraded S-rich catalytic sites such as found in [NiFe] hydrogenase enzymes[44b].

Scheme 16

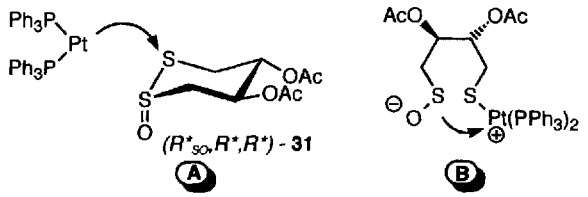


Lorenz and coworkers[45] were able to oxidize one of the two sulfur atoms in the diiron complex $(OC)_3Fe\overline{SC_2H_4S}Fe(CO)_3$ to form **52**; here the sulfenato moiety acts as a bridging ligand and thus a second oxidation yielding the sulfinato group is prevented (Scheme 16).

2.3. Stereochemical Aspects

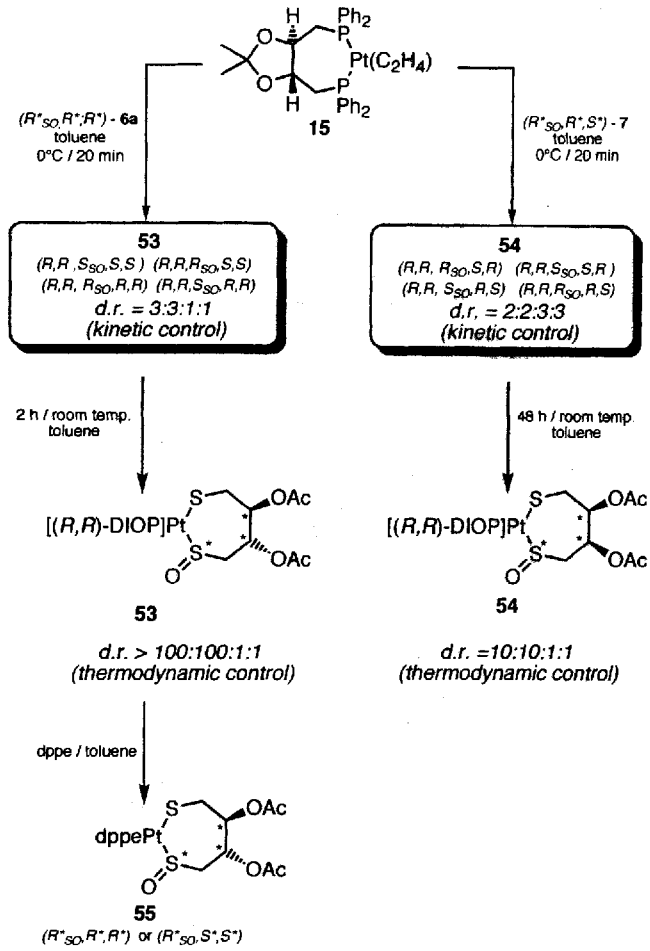
The optically-pure complex [(*R,R*)-(−)-DIOP]Pt(C_2H_4) (**15**) reacts with a fourfold excess of the cyclic thiosulfinate **5** to give a 1:1 mixture of both possible diastereoisomers (R_{SO},*R,R*)/(S_{SO},*R,R*)-**20**; the ^{31}P NMR spectra exhibit two AB splitting patterns. Morevoer **11** inserts into the sulfur–sulfur linkage of (R^*_{SO},*R*,R**)-**6a** resulting also in nearly equal quantities of both diastereoisomers (R^*_{SO}, *R*,R**)/(S^*_{SO},*R*,R**)-**18d** as racemic mixtures (Scheme 9). We assume that addition of the "soft" platinum(0) atom takes place probably at the "soft" thiolate sulfur atom rather than at the "hard" sulfenate sulfur (**A**). The six-membered thiosulfinate is opened to give a quasi-racemization at the sulfenyl sulfur atom (Scheme 17). However, alternative mechanisms are conceivable since the mechanistic work is not yet established.

Scheme 17



We noted that the degree of diastereoselectivity is greatly affected by the structure of the reactants: in contrast to the above observations, oxidative addition of a fourfold excess of (R^*_{SO},*R*,R**)-**6a** {(R^*_{SO},*R*,S**)-**7**} to [(*R,R*)-(−)-DIOP]Pt(C_2H_4) (**15**) at 0°C in toluene (kinetic control) was found to give a mixture of the four possible diastereoisomers with a 3:3:1:1 {2:2:3:3} ratio (Scheme 18). In a thermodynamically-controlled reaction (after stirring the mixtures of the diastereoisomers for two hours {48 h} at room temp.) we observed a ratio of >100:100:1:1 {10:10:1:1} of the four possible diastereoisomers **53** {**54**}. The reaction of a twofold excess of dppe with **53** in toluene leads stereospecifically to one diastereoisomer (R^*_{SO},*R**, *R**)- or (S^*_{SO},*R*,R**)-**55**. The oxidative addition of the enantiomerically-pure thiosulfinate (R_{SO},*R,R*)-**10** to the enantiomerically-pure platinum(0) complex (*R,R*)-**15** proceeded to provide one of the two possible diastereoisomers **56** in a ratio of >100:1 (Scheme 19). The absolute configuration of (R,R,R_{SO},R,R)-**56** has been established by X-ray structure determination (Figure 4) and confirms retention at the sulfoxidic sulfur center. Why is the diastereoselectivity obtained from combination of the optically-pure (*R,R*)-**15** and the thiosulfinates with additional stereogenic centers at the carbon atoms C(2) and C(3) (Figure 1) much higher than from the combination of (*R,R*)-**15** and thiosulfinates **5** and **8** as well as **11** and thiosulfinates **6a**–**7**? We assume that this process is characterized by double chiral induction[46] as the chirality in both (*R,R*)-**15** and **6a**–**7**, (R_{SO},*R,R*)-**10** affects the stereochemical course of the oxidative addition.

Scheme 18



Scheme 19

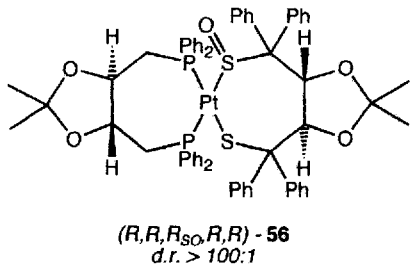
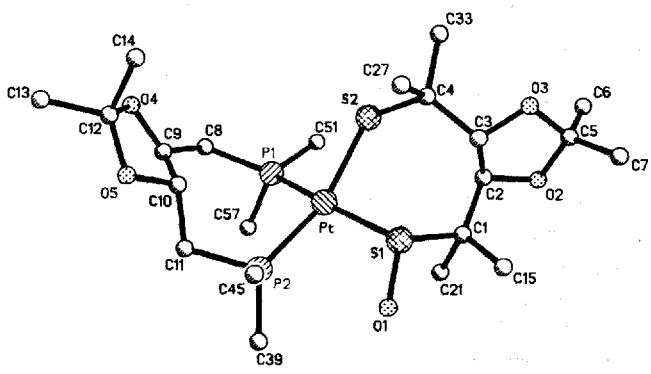
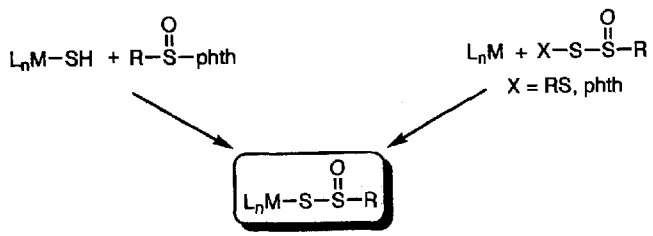


Figure 4. Molecular structure of **56** in the crystal



Scheme 20



3. Stabilization of Anions of Thiosulfinic Acids by Ruthenium(II) and Platinum(II) Complexes

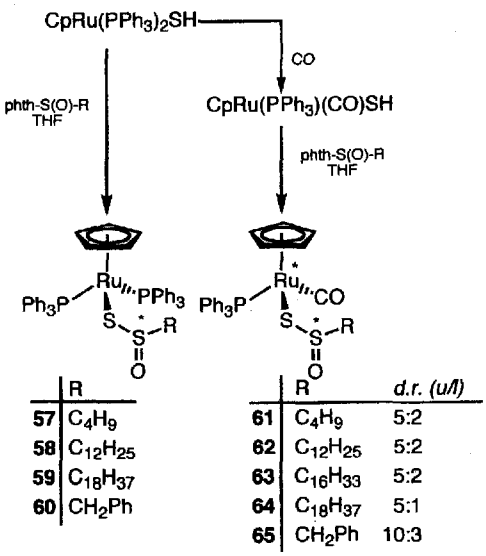
Complexes of the type $L_nMSS(O)R$ containing the thiosulfinato ligand are scarcely known[39,47,48]. Preparation of these complexes via regioselective monooxidation of disulfano complexes L_nMSSR is not practical; here an unseparable mixture of compounds will be generated[47]. The insertion of S_2O into a metal carbon bond would appear to be an elegant method, but such attempts yielded unexpected metal thioester complexes[49].

Scheme 20 shows two practical methods for the synthesis of thiosulfinato complexes on a preparative scale. The first reaction of metallothiol complexes L_nMSH with the sulfinyl transfer reagent sulfinylphthalimide RS(O)-phth affords the thiosulfinato complexes by formation of a sulfur–sulfur bond. The second synthesis of thiosulfinato complexes involves the oxidative addition of reagents already containing the thiosulfinato unit, e.g. RS(O)SX (X = phth, SR), to low-valent platinum complexes.

3.1. Syntheses of Ruthenium(II) Thiosulfinato Complexes

Shaver's group[47] and our group[48] have found independently a good route to stable ruthenium thiosulfinato complexes from ruthenium(II) hydrogen sulfide complexes $CpRu(PPh_3)(L)(SH)$ (L = CO, PPh_3)[50] with the sulfinyl transfer reagents (Scheme 21). The direct reaction of $CpRu(PPh_3)_2(SH)$ with RS(O)-phth in THF at 0 °C leads, after chromatography on silica, to the thiosulfinato complexes **57**–**60**. The existence of the thiosulfinato moiety is supported by a strong IR absorption in the range of 1020–1030 cm^{-1}. The presence of the thiosulfinato ligands was also confirmed by the AB spin pattern in the ^{31}P NMR spectra. The phosphorus atoms become diastereotopic due to the stereogenic center at the sulfoxidic sulfur atom. Due to the σ/π-donor ability of the thiolate sulfur atom the complexes tend to rapidly dissociate one phosphine group, resulting, for **57**–**60**, in decomposition of the ruthenium compounds. Subsequently, substitution of one phosphine ligand by carbon monoxide causes a greater stability of the complexes **61**–**65**. Thus a further stereogenic center arises at the ruthenium ion. The NMR spectra of these complexes are consistent with the presence of a mixture of the *u/l* diastereoisomers. ^1H and ^{31}P NMR spectra confirm a diastereoselectivity of 3:1 to 5:1, with the *u* diastereoisomers predominating. The diastereoisomers can be separated via fractional crystallization. Complexes **60** and **65** were further characterized by X-ray crystallography[48]. The most interesting aspect of the structures is the thiosulfinato ligand $SS(O)CH_2Ph$. The dihedral angle about the sulfur–sulfur bond in **60** is 170.8°[48b], which is similar to that in the acyclic thiosulfinate tol-S(O)S-tol (174°)[54]. The dihedral angle of 76.2° in **65**[48c] is significantly smaller and very similar to those of $CpRu(PPh_3)(CO)[SS(O)_nCHMe_2]$ (n = 1, 2)[47]. Extended Hückel (EHT) calculations confirm these results, explaining them by stereoelectronic effects[48c]. The S–S bond distances in **60** and **65** [207.5(3); 205.3(4) pm] are slightly longer than those in terminal disulfano ligands (202–205 pm)[51] and in the thiosulfinate anion $RS(O)S^-$ (R = adamantyl) [202.5(9) pm][12].

Scheme 21



	R
57	C_4H_9
58	$C_{12}H_{25}$
59	$C_{16}H_{37}$
60	CH_2Ph

	R	*d.r. (u/l)*
61	C_4H_9	5:2
62	$C_{12}H_{25}$	5:2
63	$C_{16}H_{33}$	5:2
64	$C_{18}H_{37}$	5:1
65	CH_2Ph	10:3

3.2. Reaction of Platinum(0) Complexes with Phthalimido *N*-(thiosulfinyl)phthalimides

Phthalimido disulfides phth-SSR have long been used as disulfido transfer reagents in the synthesis of unsymmetrical di- and trisulfanes[52], and disulfano metal complexes[51]. A regioselective monooxidation (*m*CPBA) of the sulfur atom adjacent to the R group in phthalimido disulfides yields the thiosulfinato transfer reagent phth-SS(O)R (**VII**). Originally, Harpp and coworkers[42b] proposed the formation of the regioisomer phth-S(O)SR (**VIII**) based on ^1H NMR and MS data which were not particularly diagnostic.

An X-ray structural analysis of **67** proves the formation of the regioisomer **VII**[53]; the disulfide **66** has been oxidized at the presumably more electron-rich sulfur atom. The sulfur–sulfur bond lengths [214.0(2)/215.2(2) pm] of **67** are slightly longer than in tol-S(O)S-tol [210.8(2)/212.4(3) pm][54], but significantly longer than those in acyclic disulfides[55].

The oxidative addition of the *N*-(thiosulfinyl)phthalimide **67** to **11** in toluene yields the platinum(II) thiosulfinato complex **68** (Scheme 22). The $\nu(S{=}O)$ absorption band occurs in a range similar to that of the compounds $(C_5H_5)Ru(L)(PPh_3)[SS(O)R]$ (L = CO, PPh_3) [$\nu(S{=}O)$ 1020–1030 cm^{-1}][48b,c]. The ^{31}P NMR spectra exhibit an AB spin system; this non-equivalence of the phosphorus atoms proves the *cis* geometry of **68**[53].

Scheme 22

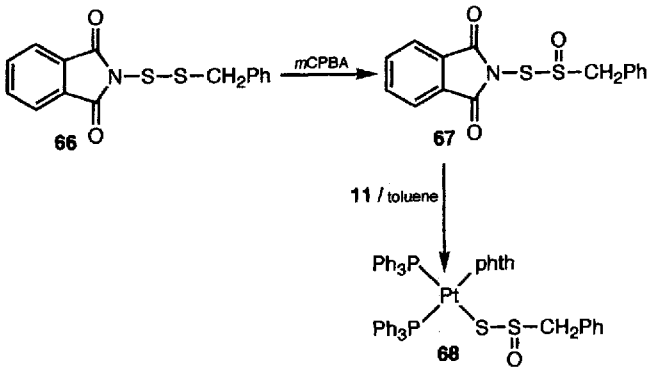
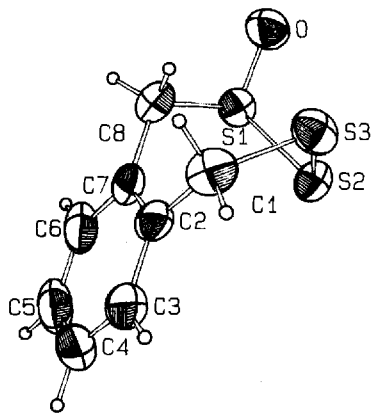


Figure 5. Molecular structure of **69** in the crystal; selected bond lengths [pm] and angles [°]: S(1)–S(2) 214.8(1), S(2)–S(3) 200.9(1), S(1)–O 147.2(2), S(1)–C(8) 181.7(2), S(3)–C(1) 184.3(2); S(2)–S(1)–O 110.61(9), S(1)–S(2)–S(3) 103.64(4)



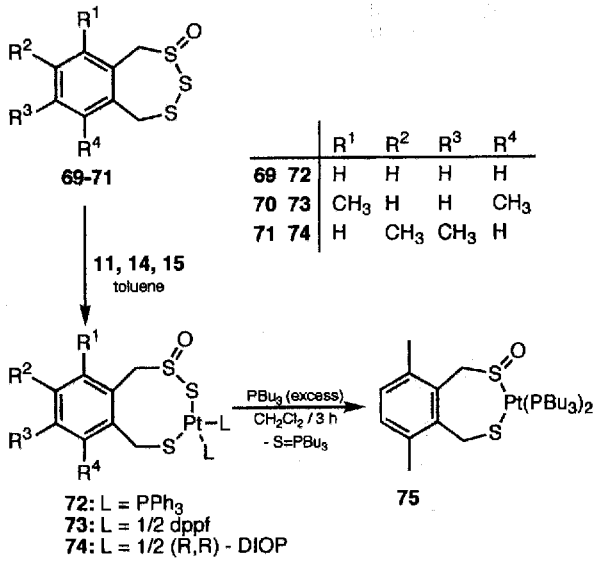
3.3. Reactions of Platinum(0) Complexes with Cyclic Trisulfide-1- and 2-oxides

Whereas the chemical and dynamic properties of (a)cyclic trisulfides have been investigated intensively[56], very little is known about the chemistry of their *S*-oxide derivatives. The regiospecific oxidation of (a)cyclic trisulfides with one equivalent of peroxyacid gives the 1-oxides[57]. The electrophilic oxidation takes place at the more electron-rich sulfur atom bound to the alkyl group. Also ab initio MO calculations on 16 isomers of H_2S_3O show that the 1-oxide (HOS–S–SH) is more stable than the 2-oxide [HS–S(O)–SH] by 67.2 kJmol^{-1}[58]. The linear trisulfide 1-oxide exhibits low stability and its decomposition mechanism has been studied carefully[59]. In contrast, 2,3,4-benzotrithiepin 1-oxides **69–71** (Scheme 23) are remarkably stable compounds, and **69** has been characterized by X-ray diffraction[28] (Figure 5). The crystallographic results illustrate that the molecule exhibits a boat conformation. The presence of an oxygen atom at the terminal sulfur atom has a great effect on the S–S bonds and there is a difference of 14 pm between the lengths of the S(O)–S and S–S bonds. Similar differences have been established in S_8O[60] and *t*Bu-S(O)$_2$SS-*t*Bu[59b] (11 pm). Solutions of platinum(0) complexes in toluene were treated with the 2,3,4-benzotrithiepin 1-oxides **69–71** at −70°C and then the mixtures were warmed to room temp. These reactions are complete after a period of 10–15 h. Compounds **11**, **14** and **15** insert regiospecifically via oxidative addition into the S–S bond, achieving the thiolato thiosulfinato platinum(II) complexes **72–74** (Scheme 23); however, insertion into the S(O)–S bond could not be detected. These results are confirmed by IR and ^{31}P NMR spectroscopic data. The stretching modes of the sulfoxide groups occur at 1027–1054 cm^{-1} which is in agreement with the values observed for the ruthenium(II)[48] and platinum(II)[48] and platinum(II) thiosulfinato complexes[53]. In the case of insertion of platinum(0) species into the S(O)–S bond a disulfano sulfenato complex would result; the S=O stretching mode from these compounds should occur at significantly lower wavenumbers (vide supra). When thiolato thiosulfinato platinum(II) complexes were treated with an excess of tributyl phosphine, in the first step the triphenyl phosphine ligands were substituted. These complexes undergo a partial desulfurization reaction with the phosphines to produce the sulfenato thiolato platinum(II) complexes **75** and Bu_3P=S. The oxidation of benzotrithiols has been found to be not regiospecific; the reaction with oxidation reagents takes place on the external as well as the central sulfur atom yielding a mixture of benzotrithiol 1- (**77**) and 2-oxide (**76**). Thus, benzotrithiol 1-oxides cannot be synthesized directly (Scheme 24): in the first step benzotrithiol 2-oxides are obtained by reaction of (methyl substituted) benzene 1,2-dithiols with thionyl dichloride according to a procedure of M. Schmidt[61]. Irradiation of **76** in acetonitrile with a high-pressure mercury lamp using a Pyrex filter for one hour under an atmosphere of nitrogen gave the benzotrithiol 1-oxides **77** quantitatively. These migrations, however, do not occur thermally. R. Sato and coworkers[62] propose a mechanism for such photochemical rearrangements without ring opening. The authors postulate a strained intermediate, which is converted into the 1-oxides and 2-oxides. The reaction, however, is characteristic of a one-way photochemical rearrangement involving intramolecular oxygen transfer yielding exclusively the benzotrithiol 1-oxides. The 1- and 2-oxides differ in their IR spectra: the stretching modes of the 1-oxides occur at lower wavenumbers (1064–1095 cm^{-1}) than those of the 2-oxides (1100–1125 cm^{-1}). Recently, benzotrithiol 1-oxides derivatives, the antimicrobial marine polysulfides *varacins A–C*, have been isolated from the Far Eastern ascidian *Polycitor sp*[63].

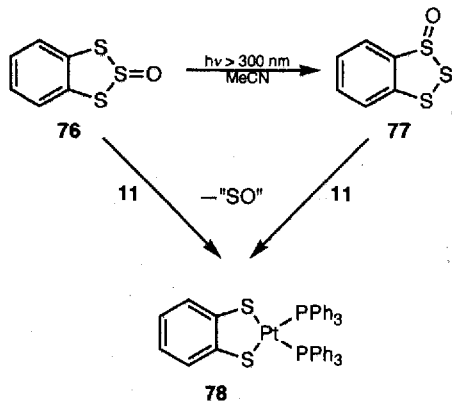
Unexpectedly, the reaction of benzotrithiol 1-oxide **77** with **11** produces quantitatively the 1,2-dithiolate platinum(II) complex **78**. The identical product was isolated when the reaction was carried out with the benzotrithiol 2-oxide **76**. It seems that sulfur monoxide has formally been eliminated from both regioisomers. M. Schmidt reported the thermolysis of benzotrithiol 2-oxid **76**, achieving a polymer $[C_6H_4S_{2.5}]_n$ and sulfur dioxide[61]. This unexpected metal-mediated elimination of sulfur monoxide is not yet understood in detail.

In summary, within the past four years our knowledge of the sulfenate and thiosulfinate anions has been enriched by

Scheme 23



Scheme 24



efficient syntheses of relatively stable complexes containing sulfenato and thiosulfinato ligands, and by X-ray structural characterization of the first thiosulfinato transition metal complexes. Hence it is important to investigate more closely the reactivity of these compounds and their applications. The complexes exhibiting the novel 1-sulfenato-3-thiolato and 1-sulfenato-4-thiolato ligands are interesting starting materials for the stereoselective syntheses of (a)cyclic sulfoxide sulfide compounds such as $RS(CR_2^1)_nS^*(O)R$ (n = 3, 4). Transition metal complexes with sulfenato ligands are also promising candidates for studying the metabolism of metal thiolates, and antioxidation activities in organisms. Undoubtedly, these new results will stimulate research in the field of biologically-active sulfur-oxygen acid anions. We can surely anticipate future significantly developments in this area of classic coordination chemistry.

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* Dedicated to Professor *M. Herberhold* on the occasion of his 60th birthday.

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