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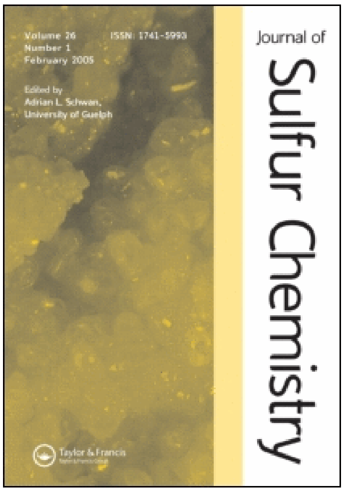

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THE CHEMISTRY OF THIONITROSO COMPOUNDS

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This review will deal with the generation, reactions and theoretical calculations of both *C*- and *N*-bonded thionitroso compounds, including the spectroscopic detection of unstable *C*-thionitroso compounds. Several types of transition metal complexes of thionitroso compounds are also addressed.

Key words: [2+3] cycloaddition, [2+4] cycloaddition, ene reaction, metal complexes, spectroscopic detection, sulfurization, theoretical calculations, *N*-thionitrosoamines, thionitroso compounds.

CONTENTS

1. INTRODUCTION

Organic compounds containing double bonded sulfur atoms have been extensively studied during the last thirty years. Among them the most documented are the thiocarbonyl compounds (with a C═S bond) which are widely utilized in organic synthesis.[1]

As for compounds containing an N═S bond much less work has been reported than with thiocarbonyl compounds in spite of their interesting properties. Among them thiocumulenes of the type R—N═S═X with a central tetravalent sulfur atom have been relatively well investigated and their chemistry has been occasionally reviewed.[2–7] Recently, the chemistry of *N*-sulfides was also reviewed.[8] Thionitroso compounds, with their divalent monocoordinate sulfur atom, however, have been much less studied. Although the parent system HN═S has been calculated by several workers HN═S has not been detected so far. Its existence has only been postulated in the reactions of intermediary sulfenylnitrenes (ArSN) and arylthioamines ($ArSNH_2$),[9] although the NS radical[10] and the NS^+ cation[11] have been detected spectroscopically. A compound of formula FNS was reported in 1963, but its structure was found to be that of the isomer F—S≡N.[12,13] The only example of an isolated thionitroso compound is Me_2NN═S,[14] but the electronic structure of Me_2NN═S is concluded to be Me_2N^+═N—S^-, both experimentally and according to theoretical calculations (see Section 6). Thus, the character of the N═S bond in the *N*-thionitroso compound Me_2NN═S is considered to be substantially changed. Otherwise unstable N═S bonds are also known to be stabilized by complexation with metals (see Section 7). *C*-Bonded thionitroso compounds have only become known as reactive intermediates so far.

The present review will focus on the chemistry of organic thionitroso compounds and the papers discussed in this review are confined to those reported before June, 1992.

2. COMPUTATIONAL STUDIES

Theoretical investigations of thionitroso compounds started in 1978, when Collins and Duke reported the theoretical structures of FSN and HNS by ab initio calculation.[15] They optimized the structure of HNS using STO-3G and some polarization functions for p- and d-orbitals. As a result, of the two possible isomers, HNS was more stable than HSN by 25.6 kcal/mol, whereas FNS was less stable than FSN. This result suggested the existence of HNS (or RNS) in the thionitroso form, although the structure of FNS was experimentally determined to be F—S≡N. The calculated NS bond length was 1.5499 Å and the H—N—S angle was 100° (Table 1).

As for organic thionitroso compounds, quantum chemical calculations were performed by Mehlhorn *et al.*[16] They described the electronic structure and various physical properties of HNS, PhNS and R_2NNS using INDO, CNDO/S and

TABLE 1 Optimized structures of RNS and net charges on N and S

R	bond length/Å N—S	R—N	angle <RSN	calculation method	net charges N	S	ref.
H	1.550	1.005	100°	STO-3G	—	—	15
H	1.618	—	—	SCF/3-21G	—	—	16
H	1.549	1.017	110°	SCF/D11	−0.26[a)]	+0.06[a)]	17
H	1.539	1.010	111°	SCF/6-31*	—	—	18
H	1.541	—	—	SCF/3-21G(d)	—	—	19
H	1.600	1.010	108°	MRD-CI	—	—	20
H	1.54	1.01	110°	RMP2/6-31G**	−0.49	+0.18	21
H	1.552	—	—	INDO	−0.15[b)]	+0.03[b)]	16
Me_2N	1.582	—	—	INDO	−0.06[b)]	−0.30[b)]	16
Ph	—	—	—	CNDO/S	−0.12	−0.11	16
H	1.491	1.013	—	MNDO	—	—	22
Me	1.495	1.456	—	MNDO	—	—	22
Ph	1.505	1.404	—	MNDO	—	—	22

a) SCF/F32 basis
b) CNDO/S

ab initio SCF methods. The NS bond length of an optimized structure of ground state HNS by INDO was 1.552 Å, similar to that of Collins and Duke, but somewhat longer (1.618 Å) by the SCF-method (STO-3-21G). The NS distance was lengthened considerably in the lowest triplet state T_1 (1.717 Å/SCF) compared to the S_0 ground state. In the case of Me_2NNS, the NS distance was 0.030 Å (INDO) longer, indicating single bond character of the N=S bond in the thionitrosoamine. The electronic structure of the thionitroso compounds was predicted to be polarized in the sense $N^{\delta-}{=}S^{\delta+}$ when the NS bond is attached to hydrogen or carbon. This electronic structure of the NS moiety was substantially different from that of Me_2NNS, which was predicted to have a zwitterionic structure of $Me_2N^+{=}N{-}S^-$. These polarizations are different from the electronic structure of HNO, indicating different chemical behavior of thionitroso compounds and nitroso compounds. From the viewpoint of frontier orbitals, the LUMO energy of thionitrosobenzene was considerably lower than that of nitrosobenzene, whereas the HOMO enegies were very similar. Hence thionitrosoarenes are expected to have a strong electron affinity and their facile acceptance of electrons should drastically diminish the chance of isolating thionitroso compounds in the presence of electron donors. Significant changes of the frontier orbitals of thionitroso compounds by substituents are also pointed out. A transition state calculation by CNDO/S shows that the UV-VIS spectrum of a thionitroso compound has weak n-π^* absorption bands, for instance at 1282 and 426 nm for HNS (1234 and 491 nm for thionitrosobenzene). Mehlhorn's calculations also suggest that the lowest triplet state of a thionitroso compound lies close to the singlet ground state and, specifically, the T_0 state of HNS was estimated to be slightly more stable than the S_0 state in simple basis set calculations (STO-3-21G).

More sophisticated calculations of HNS were carried out by Wasilewski and Staemmler.[17] Their calculations were performed at the SCF level with inclusion of electron correlation effects by means of the CEPA method for the excited states. The optimized structure of HNS by SCF/D11 showed a similar NS bond length (1.549 Å) and a widened H—N—S angle of 110° in comparison with the calculations by Mehlhorn, but very similar to those calculated by Hess *et al.* (SCF/6-31*).[18] The harmonic vibration frequencies of HNS were estimated to be 1231, 1338 and 3607 (NH stretching) cm^{-1}. Also calculations of the excited states were performed in this report. As a result, the number and relative energetic order of the low-lying states agreed with those of HNO, but the energy separations were much smaller for HNS than for HNO, and a pair of low-lying excited A'' states possess excitation energies of 1–2 eV. Wasilewski and Staemmler suggested that although the HNS molecule has a closed-shell $^1A'$ ground state, it has to be considered as a highly reactive radical. With regard to the NS bond, the bond order was estimated to be two and polarized as $N^{\delta-}{=}S^{\delta+}$ (net charge on N: -0.26, on S: $+0.06$; D21 basis set).

The π bond strength of HNS was calculated by Schmidt *et al.* with the ab initio MCSCF method (3-21G(d)).[19] The calculated length of the N=S bond in HNS was 1.541 Å and the stretching wavenumber 1245 cm^{-1}. The estimated π bond strength was 42 kcal/mol, i.e. it is less stable than the N=O and the P=O bond by 20 and 10 kcal/mol, respectively, and close to the N=P and the P=S bond (Table 2). These facts are suggestive of thermal instability of thionitroso compounds, and of the necessity of some features stabilizing N=S bonds for the isolation of thionitroso compounds.

Recently, Mehlhorn *et al.* reported a theoretical study of RNS involving excited states.[20–22] For HNS an MRD-CI calculation was carried out.[20] As a result, HNS is expected to have a singlet ground state in agreement with the conclusion

TABLE 2 A = B π-bond strengths[19]

A	B	estimated value (kcal/mol)	experimental (kcal/mol)
C	C	65	59, 65
Si	C	38	38, 39
Si	Si	25	26
N	N	60	55, 64
P	N	44	
P	P	34	
C	N	63	
Si	N	36	
Si	P	29	
C	O	77	
Si	O	50	
C	S	53	
Si	S	50	
N	O	62	
P	O	53	
N	S	42	
P	S	40	

of Wasilewski *et al.* The calculated molecular geometry was: d(NH) 1.010 Å, d(NS) 1.600 Å, and <HNS 108.0° (MRD-CI(DC/DZP)). The NS bond length increased when the basis set was improved to take some electron correlation into account. The excited states S_1 and T_1 lie close to the singlet ground state. The energy gap between the S_0 and the T_1 state is small (25 kJ/mol). The low-energy S–S transition of the type $^1A'$-$^1A''$ had a very low dipole strength ($n\pi^*$) and its transition energy was in the near infrared region (1305 nm). The S_0–S_2 transition should give rise to a second weak band in the visible region at 432 nm, suggesting that thionitroso compounds are orange or yellow colored. The S_1–T_1 splitting (4436 cm^{-1}) was estimated to be larger than the S_0–T_1 energy difference (3326 cm^{-1}). Ab initio calculations on $CH_3N{=}S$ were also carried out and the result was similar to that with HNS. The S_1 and T_1 states (T_1 was lower than S_1) lay close to the singlet ground state, the energy gap of S_0–S_1 being 7000 cm^{-1}.[21]

MNDO calculations on $RN{=}S$ ($R = H, CH_3, Ph$) have also been carried out.[22] The calculated NS bond lengths are 1.491 Å ($R=H$), 1.495 Å ($R=CH_3$) and 1.505 Å ($R=Ph$). The NS bond length was not dramatically affected by substituents, but became slightly stretched when R was an alkyl or aryl group. The calculated frontier orbital energies are E_{HOMO}: $-10.06 \sim -9.44$ eV and E_{LUMO}: $-1.76 \sim -1.37$ eV ($R=H, CH_3, Ph$). The estimated non-vertical ionization potential of HNS was 9.55 eV, the electron affinity -1.86 eV and the dipole moment $4.77 \cdot 10^{-3}$ Cm.

A theoretical study of the radical cation HNS^+ has been reported by Redondo *et al.*[23] In their report, the UHF wave function was used for three solutions of the HNS^+ radical and two of these structures were estimated to be more stable than the other.

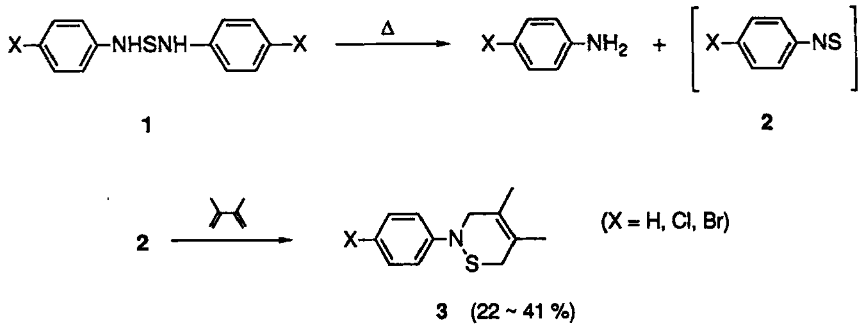
3. GENERATION OF THIONITROSO COMPOUNDS

Thionitroso compounds are considered to be unstable species based on the theoretical studies mentioned above. In fact, thionitroso compounds which are stable under ambient conditions have not been reported so far except for an *N*-thionitrosoamine. The parent compound HNS has still not been detected. However, *C*-thionitroso compounds as reaction intermediates have been occasionally reported in various reactions.

3.1. *Thermal Reactions of* N,N′-*Thiodianiline*

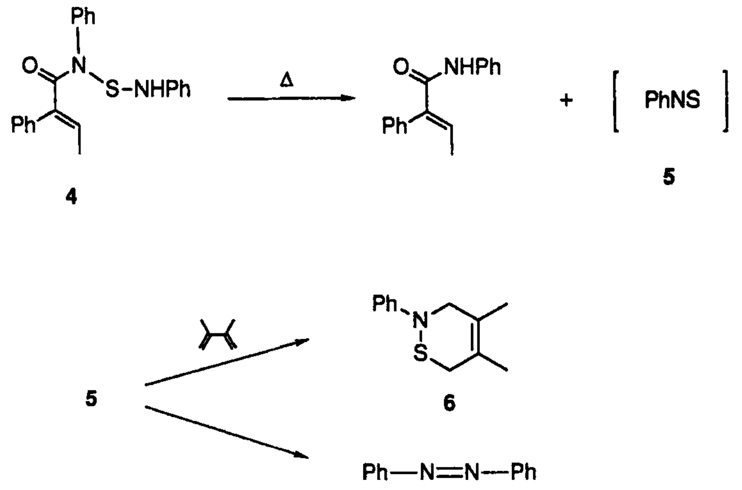
The first thionitroso intermediate was reported in 1966 by Tavs in thermal reactions of *N,N′*-thiodianilines.[24] *N,N′*-Thiodianilines **1** decompose slowly at room temperature with the appearance of a blue color. When heated at 80°C for 6 h with excess 2,3-dimethylbutadiene, 2-aryl-4,5-dimethyl-3,6-dihydro-1,2-thiazines **3**, the corresponding Diels-Alder adducts, are obtained in 22–41% yield (Scheme 1), suggesting the intermediacy of thionitrosoarenes **2**.

Scheme 1



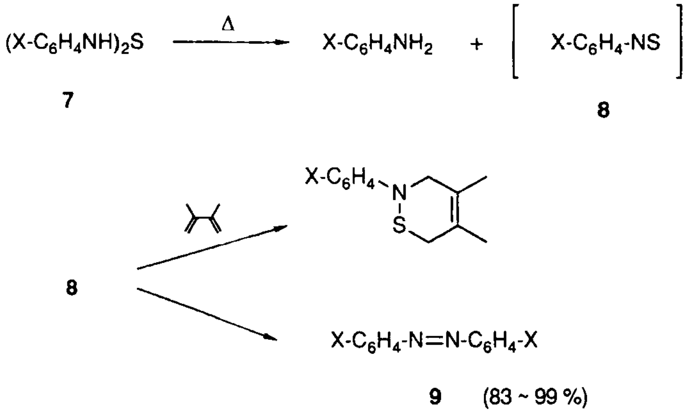
The generation of thionitroso compounds in this type of reaction was also reported by Minami *et al.*[25] and by Davis and Skibo.[26] Minami obtained the Diels-Alder adduct of thionitrosobenzene (**5**) with 2,3-dimethylbutadiene in the thermal reaction (140°C) of the thiobisamine **4** in 35% yield (Scheme 2), but when tetraphenylcyclopentadienone was used as a diene, azobenzene was obtained (65%) instead of the Diels-Alder adduct. Davis and Skibo obtained azo compounds, aniline, and sulfur in high yields in the absence of a trapping agent, and Diels-Alder adducts in the presence of 2,3-dimethylbutadiene in the thermal reaction of *N*,*N*′-thiodianilines **7** and arylaminothiopiperidines **10** (Schemes 3 and 4). They explained the formation of these products as shown in Schemes 3 and

Scheme 2



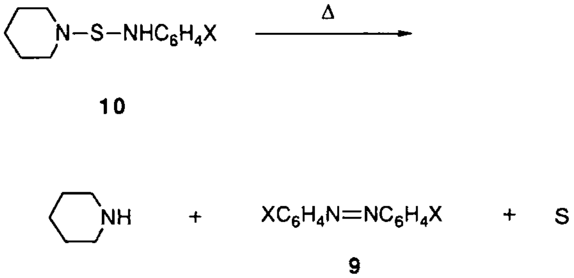
5. First, a thiodianiline disproportionates to an aniline and a thionitrosoarene, and the latter undergoes dimerization, followed by desulfurization to give an azobenzene and elemental sulfur.

Scheme 3



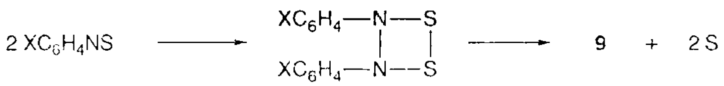
(X = 4-MeO, H, 4-Br, 4-Cl, 3-NO$_2$)

Scheme 4



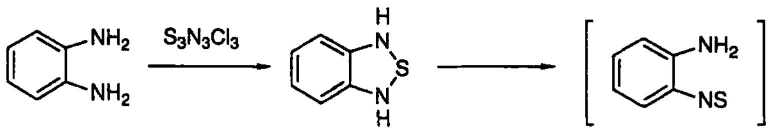
(X = 4-MeO, H, 4-Br, 4-Cl)

Scheme 5



The intramolecular generation of the thionitroso compound **12** was postulated in the reaction of 1,2-diaminobenzene and trithiazyl trichloride ($N_3S_3Cl_3$) via **11** (Scheme 6).[27]

Scheme 6



11 12

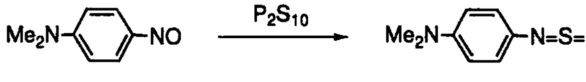
3.2. *Sulfurization of Amines*

The preparation of thionitroso compounds by sulfurization of anilines has been attempted from early years. The simple reaction of anilines and SCl_2, however, did not afford thionitroso compounds, but instead gave *N*-thiosulfinylanilines **13** or sulfur diimides **14** (Scheme 7).[28]

Scheme 7

$$\mathrm{RNH_2} \xrightarrow{\mathrm{SCl_2}} \underset{\mathbf{13}}{\mathrm{R{-}N{=}S{=}S}} \quad \text{and/or} \quad \underset{\mathbf{14}}{\mathrm{R{-}N{=}S{=}N{-}R}}$$

Scheme 8



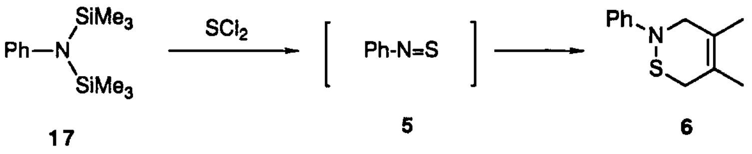
15 16

Barton and Robson's sulfurization of *p*-(dimethylamino)nitrosobenzene (**15**) with phosphorus pentasulfide resulted in the formation of *N*-thiosulfinylaniline **16** (Scheme 8).[29] Although these studies failed to yield isolated thionitroso compounds, this represented the first isolation of a stable *N*-thiosulfinylamine. The sulfur diimide was regarded to be formed via dimerization and subsequent desulfurization of a thionitroso intermediate.

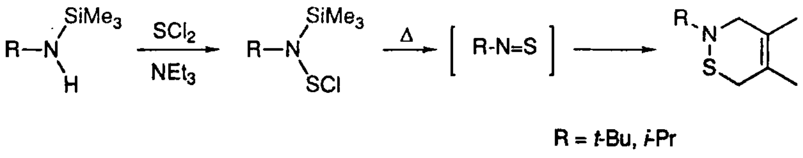
When *N*,*N*-bis(trimethylsilyl)aniline (**17**) was employed, the reaction with SCl_2 resulted in the successful trapping of the intermediary thionitrosobenzene (**5**) as the Diels-Alder adduct **6** (Scheme 9).[30]

The sulfurization of silylated amines could be achieved by reaction with SCl_2, followed by thermolysis (Scheme 10),[31] and the thionitroso intermediates were trapped with 2,3-dimethylbutadiene.

Scheme 9

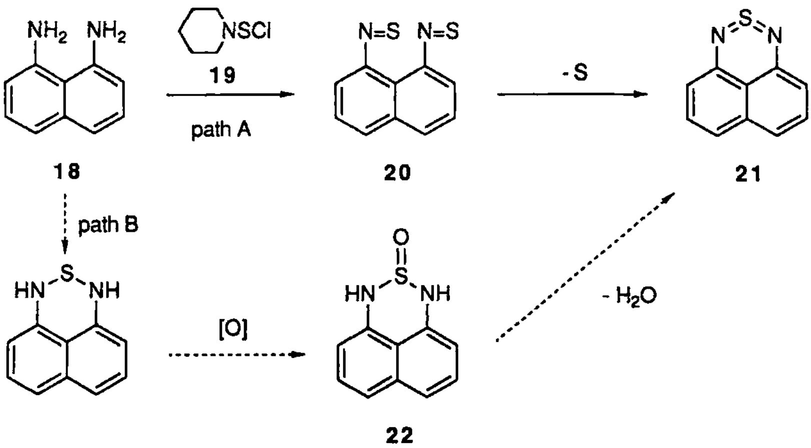


Scheme 10



Diaminonaphthalene **18** also underwent sulfurization by piperidine-1-sulfenyl chloride (**19**) (Scheme 11).[32] Although the thionitroso compound **20** was not trapped, this reaction was considered to proceed via bis(thionitroso)naphthalene **20** (pathway A), since the alternative reaction pathway B was disproved by the fact that the authentic sulfoxide **22** did not yield the thiadiazine **21** when treated with **19** under similar conditions.

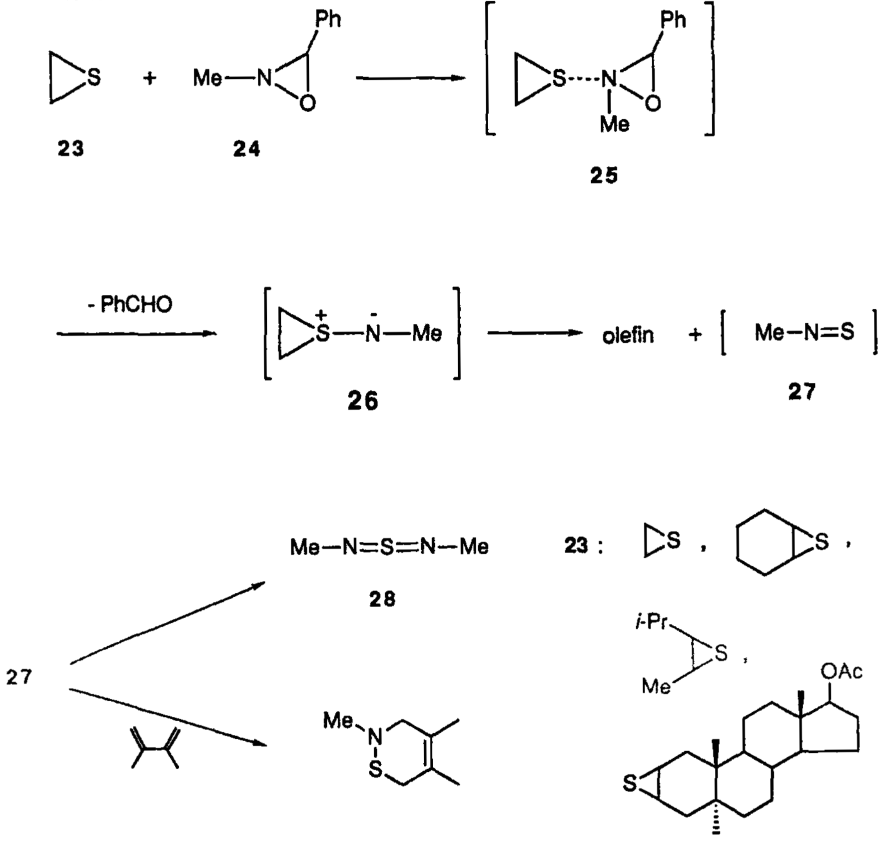
Scheme 11



3.3. *Fragmentation of S—N Ylides*

Hata and Watanabe found that the fragmentation of an S—N ylide led to an intermediary thionitroso compound (Scheme 12).[33] They prepared the S—N ylide **26** *in situ* by the reaction of thiirane **23** with oxaziridine **24**, and the ylide **26** formed from **25** fragmented at room temperature into an olefin and thionitrosomethane **27** which in turn gave the sulfur diimide **28** in the absence of a trapping reagent and could be trapped by Diels-Alder reaction with 2,3-dimethylbutadiene.

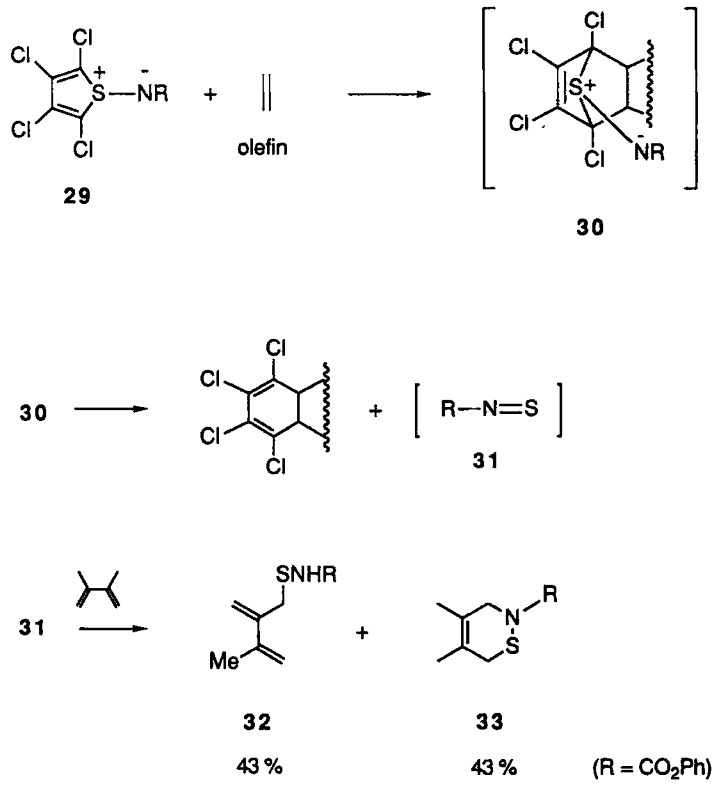
Scheme 12



Meth-Cohn and van Vuuren found that a similar fragmentation of an appropriate S—N ylide generates an electron-poor thionitroso compound.[34,35] Reaction of the starting S—N ylide **29** with an olefin afforded another S—N ylide **30** which led to a thionitroso intermediate **31** under the reaction conditions (Scheme 13).

Interestingly, the trapping of **31** in the presence of 2,3-dimethylbutadiene gave not only the Diels-Alder adducts **33** but also the ene products **32** in comparable yields.

Scheme 13



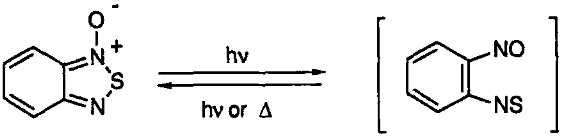
R = CO$_2$Ph, 4-MeC$_6$H$_4$SO$_2$, CO$_2$Et

olefin : cyclohexene, acenaphthylene

3.4. *Ring Opening Reactions of Benzothiadiazoles and Benzisothiazoles*

Transient thionitroso compounds are also formed by ring opening reactions of benzothiadiazoles[36] and benzisothiazoles.[37,38] Pedersen observed a photochemical ring opening reaction of benzo[c]-1,2,5-thiadiazole 2-oxide (**34**) at low temperature by UV-VIS spectroscopy to form 2-thionitrosonitrosobenzene (**35**) (details to be described in Section 4) (Scheme 14).[36]

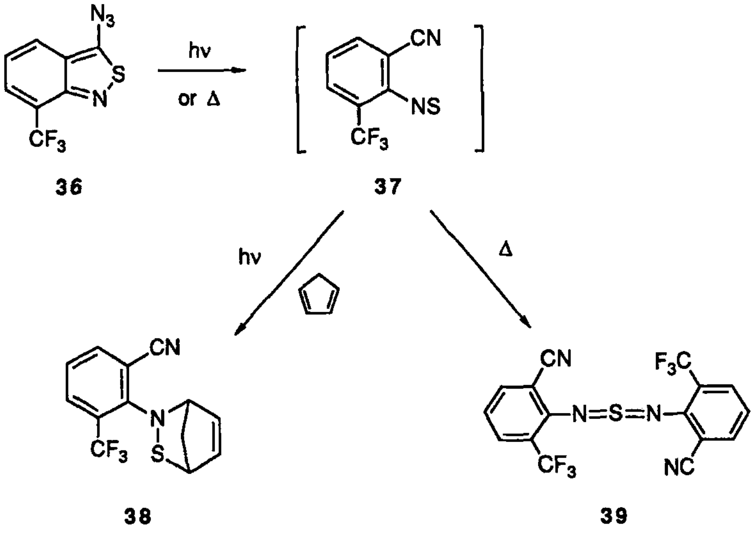
Scheme 14



34 **35**

Joucla and Rees reported thermal and photochemical reactions of the azidobenzisothiazole **36** with loss of molecular nitrogen and a subsequent ring opening reaction to form the thionitrosoarene **37** (Scheme 15).[37] The thionitroso compound formed in this reaction afforded the sulfur diimide **39** in a thermal reaction at 180°C and a Diels-Alder adduct **38** in a photochemical reaction in the presence of cyclopentadiene.

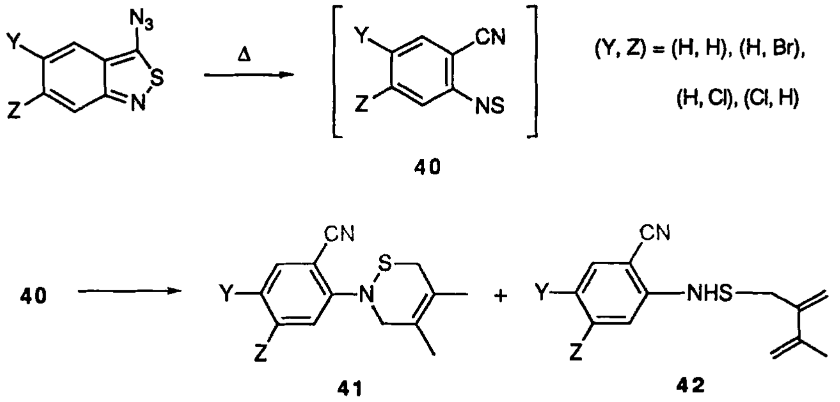
Scheme 15



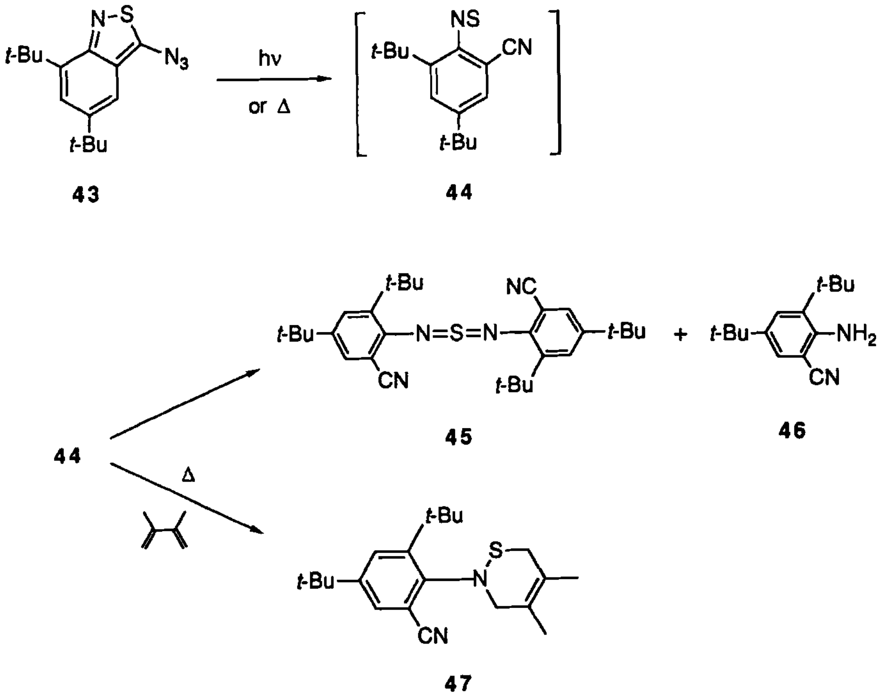
36 **37** **38** **39**

Similar reactions were reported by Bryce and Heaton (Scheme 16)[38] and by us (Scheme 17).[39] The thionitroso intermediates **40** and **44** were trapped as the Diels-Alder adducts **41** and **47**, and as the ene adducts **42**. These ring opening reactions proceed readily to form thionitrosoarenes cleanly with elimination of nitrogen and have become an efficient method for the generation of *o*-cyanothionitrosobenzenes.

Scheme 16



Scheme 17



3.5. *Desulfurization of* N-*Thiosulfinylamines*

N-Thiosulfinylanilines (R—N═S═S) can also be precursors of thionitroso intermediates. Inagaki *et al.* reported that the sterically hindered *N*-thiosulfinylanilines **48a,b** undergo desulfurization reactions in the presence of light or tertiary phosphines to give the sulfur diimides **49a,b**, the anilines **50a,b** and the *N*-sulfinylanilines **51a,b** probably via thionitroso compounds (Schemes 18 and 19).[40,41] A similar reaction was reported by Unno *et al.* for the highly sterically hindered *N*-thiosulfinylaniline **48c**.[42]

Scheme 18

$$\underset{\mathbf{48}}{\text{Ar-N=S=S}} \xrightarrow{h\nu} \left[\,\text{Ar-N=S}\,\right]$$

$$\longrightarrow \underset{\mathbf{49}}{\text{Ar-N=S=N-Ar}} + \underset{\mathbf{50}}{\text{ArNH}_2} + \underset{\mathbf{51}}{\text{Ar-N=S=O}}$$

Ar = a) 2,4-di-*t*-butyl-6-methylphenyl
b) 2,4,6-tri-*t*-butylphenyl
c) 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl

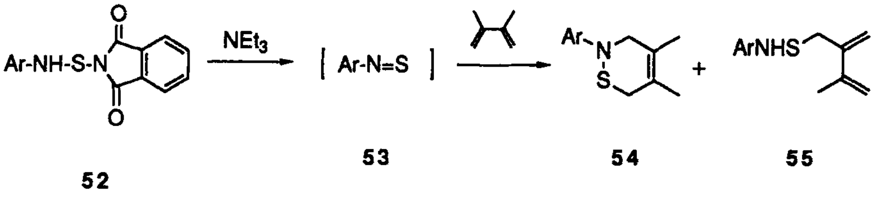
Scheme 19

$$\underset{\mathbf{48}}{\text{Ar-N=S=S}} \xrightarrow{\text{PPh}_3} \left[\,\text{Ar-N=S}\,\right] \longrightarrow \underset{\mathbf{49a,b}}{\text{ArNSNAr}} + \underset{\mathbf{50a,b}}{\text{ArNH}_2} + \underset{\mathbf{51a,b}}{\text{Ar-N=S=O}}$$

3.6. *1,2-Elimination from* N-*(Arylaminothio)phthalimides*

Bryce and Taylor reported the generation of the thionitrosoarenes **53** by 1,2-elimination reactions of *N*-(arylaminothio)phthalimides **52** in the presence of triethylamine.[38,43–45] Their reports are concerned with the reactivity of thionitrosoarenes towards dienes (details to be discussed in Section 5) and the thionitroso intermediates **53** were trapped as Diels-Alder adducts **54** and ene products **55** (Scheme 20). By their method, thionitrosoarenes are generated in high yield (deduced from the yields of Diels-Alder and ene products) and the precursors are easily prepared. Their method can be used for the generation of various types of thionitrosoarenes.

Scheme 20

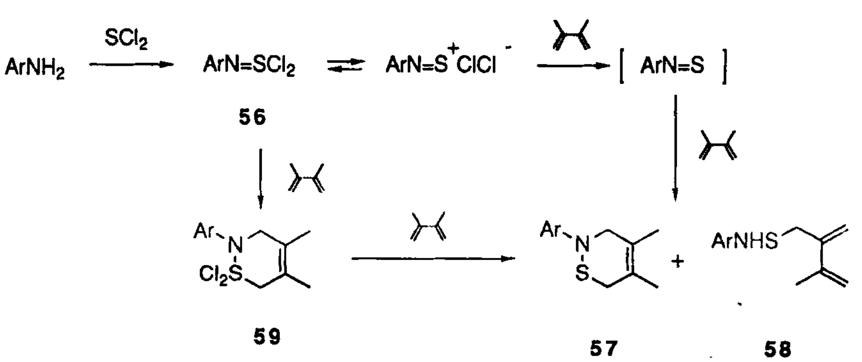


Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$,
4-NCC_6H_4, 2-MeC_6H_4, 2-BrC_6H_4, 2-NCC_6H_4, 1-naphthyl, 3-pyridyl

3.7. *Dehalogenation of N-Aryliminosulfur Dichlorides*

N-Aryliminosulfur dichlorides are known as very unstable compounds, but they can nevertheless be used as precursors of thionitroso compounds. Bryce and Taylor reported the reaction of *N*-aryliminosulfur dichlorides **56** with 2,3-dimethylbutadiene (Scheme 21).[45] They obtained both the Diels-Alder adducts **57** and the ene adducts **58** of the corresponding transient thionitrosoarenes. The reaction is clean and efficient (ca. 70% yield) and considered to proceed by 1,1-elimination of chlorine from sulfur. Although 2,3-dimethylbutadiene was considered to act both as dechlorinating agent and diene, a reaction pathway via intermediate **59** cannot be ruled out.

Scheme 21



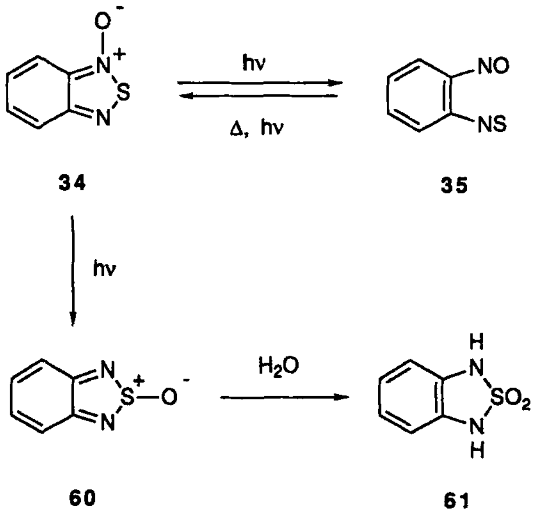
Ar = 4-$MeOC_6H_4$, 4-ClC_6H_4

4. SPECTROSCOPIC DETECTION OF THIONITROSO COMPOUNDS

There have been only a few reports concerning the spectroscopic detection of thionitroso compounds. Their paucity is due to the instability of thionitroso compounds and the scarcity of generation methods compatible with spectroscopic detection at cryogenic temperatures.

The first study of spectroscopic detection of thionitroso compounds was done by Pedersen *et al.*,[36] who used the thiadiazole *N*-oxide **34** as precursor. When **34** was irradiated at room temperature and then hydrolyzed, the thiadiazoline **61** was obtained, presumably via the thiadiazole *S*-oxide **60** (Scheme 22). In the flash photolysis of **34** one observed a transient absorption band at 467 nm (in ethanol) or 493 nm (in cyclohexane), which disappeared with concomitant regeneration of the starting material, suggesting the formation of a reversible intermediate. The transient species decayed in a first-order process with k ~ 100 s^{-1} at ambient temperature both in the presence or the absence of oxygen, the thermodynamic data being E_a = 16.1 kcal/mol, A = $1.06 \cdot 10^{14}$ s^{-1}, $\Delta S^{\ddagger}$ = 3.7 cal/K·mol, $\Delta H^{\ddagger}$ = 15.5 kcal/mol (at 25°C) and $\Delta G^{\ddagger}$ = 14.4 kcal/mol (at 25°C) (in cyclohexane).

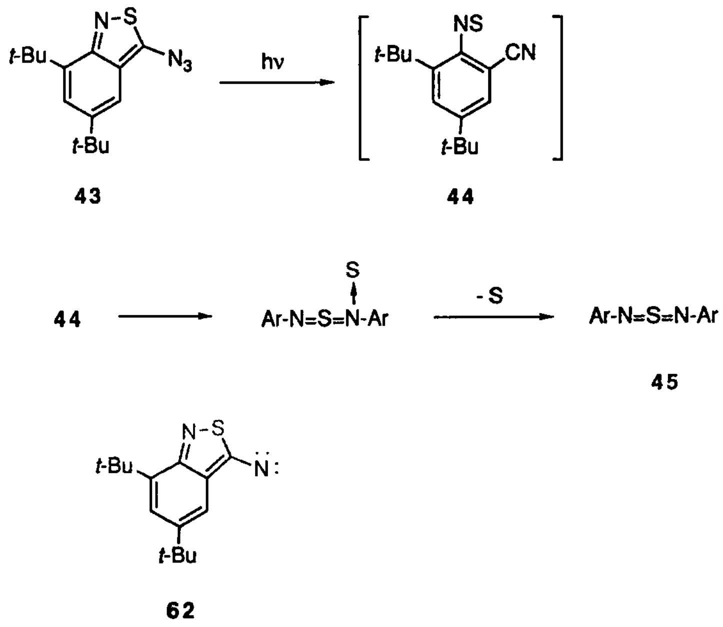
Scheme 22



A similar absorption band was observed when the photoreaction was carried out in matrices at cryogenic temperatures. When **34** was irradiated at 85 K in an EPA matrix, a transient species with absorption maxima at 458 and 485 nm (ε 8000–9000) and a compound assignable as the *S*-oxide **60** were observed in the ratio 2:1, the former being reverted to a mixture of the starting material and the *S*-oxide **60** when the matrix was warmed or photolyzed (400 nm) for a prolonged time. Pedersen concluded that the transient species with absorption maxima at 458 and 485 nm was *o*-thionitrosonitrosobenzene (**35**) on the basis of its reversibility to starting material, the absence of a triplet oxygen effect on its lifetime, and the comparison of the products at both ambient and cryogenic temperatures.

We recently attempted the matrix isolation of a thionitroso compound in the photochemical reaction of the azidoisothiazole **43** and succeeded in the observation of the UV-VIS and IR spectra of the thionitroso compound **44** (Scheme 23).[46,47] When the photolysis of the azidoisothiazole **43** at 12 K in an argon matrix was monitored by UV-VIS spectroscopy, a transient species with absorptions at 456 and 483 nm (ε 4000–5000) was observed, with isosbestic points. A similar absorption was also observed in some organic glass matrices such as EPA, 2-methyltetrahydrofuran and isopentane at 70 K. The transient species disappeared below 100 K to give another intermediate assignable to a dimer of the thionitroso compound which afforded the sulfur diimide **45** upon warming of the matrices to 195 K. When the photochemical reactions in argon and undecane matrices were followed by IR spectroscopy, an absorption due to a cyano group (2225 cm^{-1}) was observed at the expense of the azide absorption. The transient species also had absorptions at 1120 and 1200 cm^{-1} which disappeared at 110 K. The observation of the cyano group in the IR spectra, diagnostic of the formation of **44**, under conditions similar to those for the observation of the electronic spectra led us to conclude that the transient species with absorption at 456 and 483 nm was the thionitrosoarene **44**.

Scheme 23



A similar absorption was observed in solution in the desulfurization reaction of the highly sterically hindered *N*-thiosulfinylaniline **48c**.[48] When **48c** was desulfurized with $(Me_2N)_3P$ at −90°C an absorption around 475 nm (ε 200–300) was observed in ethereal solution and this spectrum disappeared at −70 ~ −40°C with emerging absorption of the corresponding sulfur diimide. Because *N*-thiosulfinylanilines are known to produce anilines and sulfur diimides via a thionitroso intermediate, the observed transient species is assignable to the corresponding thionitrosoarene.

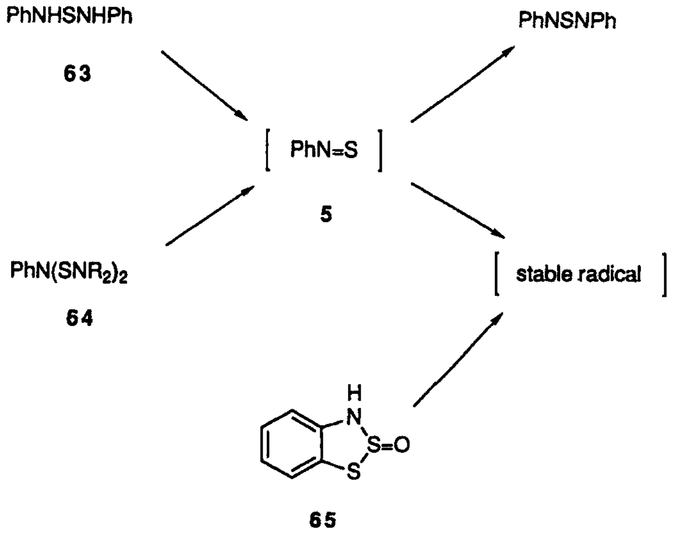
Theoretical calculations predict that the vibrational wavenumber of the N═S stretching in HNS (see Section 2) is 1231 cm^{-1} (Wasilewski[17]) or 1245 cm^{-1} (Schmidt[19]). Since it is known that the experimental values of stretching wavenumbers can be estimated by multiplication of the calculated value by 0.9, the experimental stretching wavenumber of HN═S is estimated to be about 1100 cm^{-1}. Although the assignment of the above mentioned IR spectra observed with the thionitrosoarene **44** was difficult because of the complexity of the spectra, the absorption at 1120 or 1200 cm^{-1} is reasonably assigned to the N═S stretching of the thionitrosoarene. Accurate assignments of experimental stretching frequencies of N═S bonds, however, are still outstanding.

As for UV-VIS spectra, theoretical values have only been reported by Mehlhorn who used a semiempirical method. The estimated absorption maxima of the weak n-π* band were 1282 and 426 nm for HN═S, 1234 and 491 nm for PhN═S, and 657 and 408 nm for Me_2NN═S, whereas the wavelengths of the absorption maxima of the π—π* transition for PhN═S were predicted to be shorter than 350 nm.[16] On the other hand, experimentally, Me_2NN═S has absorption maxima at 306, 587 and 705 nm (in cyclohexane), while *C*-thionitrosoarenes have absorption maxima at 458 and 485 nm (for **35**) and 456 and 483 nm (for **44**). Although these values are close to the 491 nm predicted by Mehlhorn, the observed absorption coefficients [ε 8000–9000 (for **35**) and 4000–5000 (for **44**)] indicate that these absorptions should be assigned to the π—π* transition. The possibility of the presence of a forbidden weak absorption due to an S_0–S_2 transition[20] in this region can not be excluded.

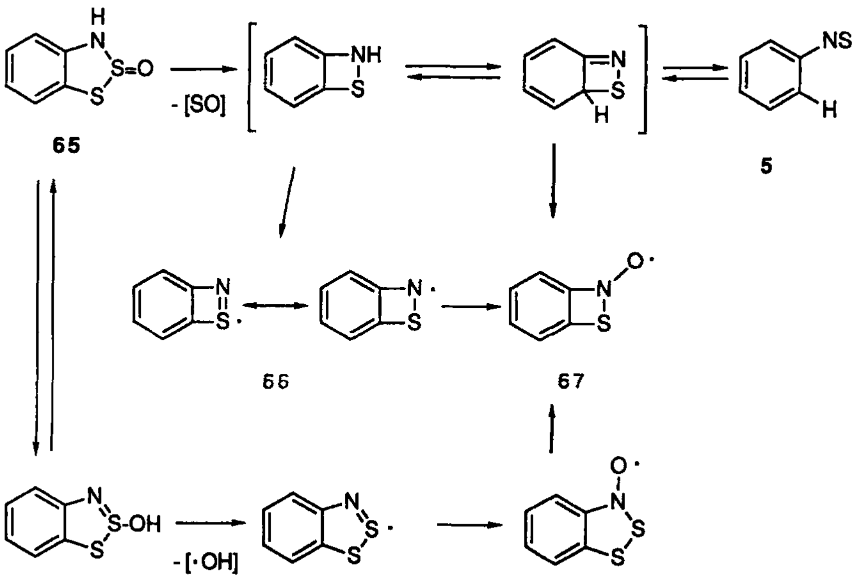
ESR studies of thionitroso compounds have also been carried out because thionitroso compounds may have a triplet ground state or biradical character. Although we attempted an ESR study of the ring opening reaction of the azidoisothiazole **43** in organic glass matrices, no ESR signals of the thionitrosoarene **44** nor the nitrene intermediate **62** could be detected.[47] This fact suggests a singlet ground state of the thionitrosoarene **44**.

Mayer *et al.* reported an ESR study of transient thionitrosobenzenes in the pyrolysis of **63** and **64**.[49] Instead of the signals of the thionitrosobenzenes they observed signals due to the stable radicals **66** and **67**, probably formed via thionitrosobenzenes. These radicals were also observed when formed from **65** (Schemes 24 and 25). The fact that **66** was formed from Ph—N═S despite the accompanying loss of aromaticity was considered as due to the biradical character of the thionitrosobenzene.

Scheme 24



Scheme 25

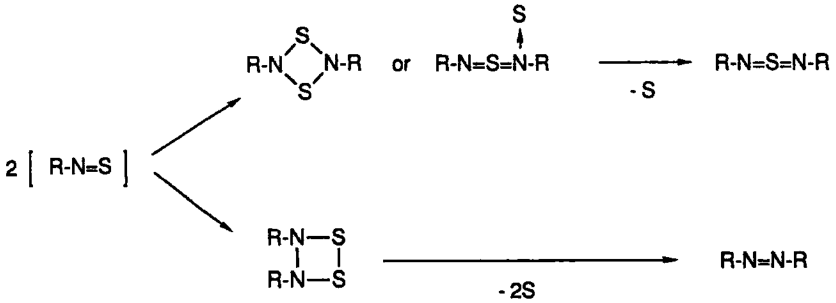


5. REACTIONS OF THIONITROSO COMPOUNDS

5.1. *Dimerizations*

Thionitroso compounds R—N═S are known to give azo compounds or sulfur diimides in the absence of trapping reagents. The reaction is considered to proceed via dimerization of the thionitroso compound, followed by desulfurization (Scheme 26). Azo compounds are formed when R is phenyl or monosubstituted phenyl,[25,26] while sulfur diimides are produced when R is methyl (85%),[33] 2-trifluoromethyl-5-cyanophenyl (58%),[37] or 2,4-di-*t*-butyl-6-cyanophenyl (78%).[39,46,47] The formation of azo compounds and sulfur diimides can be explained in terms of head-to-head dimerization of the thionitroso compounds, followed by loss of two sulfur atoms and by head-to-tail dimerization, followed by loss of one sulfur atom, respectively. In some cases the azo compounds can also be produced from the sulfur diimides when these are unstable under the reaction conditions. However, the exact reason for the selectivity of these dimerization reactions is not clear at present.

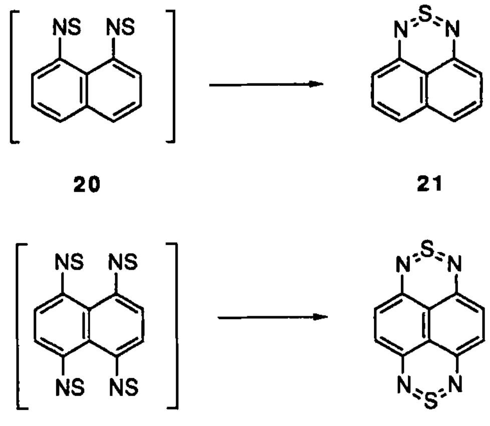
Scheme 26



The dimerization of thionitroso compounds seems to be very fast since 2,4-di-*t*-butyl-6-cyanothionitrosobenzene (**44**) undergoes dimerization even at about 100 K in organic glass matrices as evidenced by monitoring of the UV-VIS spectra,[47] although the dimerization would be anticipated to be rather slow because of steric congestion.

Intramolecular dimerizations of thionitroso groups can also take place. When thionitroso groups were generated in the 1,8-positions of naphthalene via sulfurization of the corresponding diamine **20**, the cyclic sulfur diimide **21** was obtained (62%) (Scheme 27). A similar reaction proceeded when the thionitroso groups were introduced in the 1,4,5,8-positions of naphthalene (25%). The intramolecular dimerization of *peri*-positioned thionitroso groups is considered to be

Scheme 27



20 21

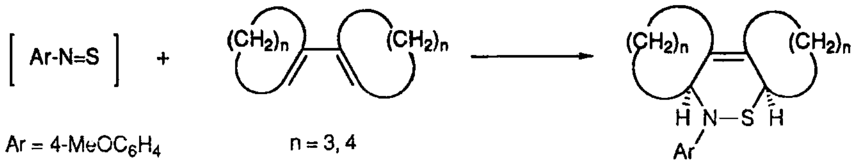
faster than Diels-Alder trapping, since only the cyclic sulfur diimide was obtained, even in the presence of 2,3-dimethylbutadiene or cyclopentadiene.

5.2. *[2+4] Cycloaddition Reactions*

Thionitroso compounds react with dienes to form [2+4] adducts. This reaction has often been used as a proof of the intermediacy of thionitroso compounds. Aromatic and aliphatic thionitroso compounds react with 2,3-dimethyl-1,3-butadiene and 1,3-butadiene (see Section 3).

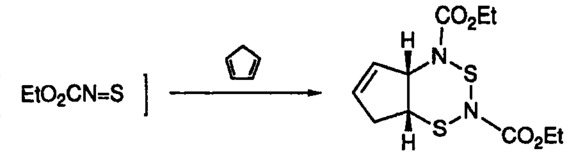
Cyclic dienes react with thionitroso compounds in a similar fashion. Cyclopentadiene and cyclohexadiene react with simply substituted thionitrosoarenes or electron-poor thionitroso compounds to give [2+4] adducts.[35,37] Bicyclic dienes such as 1,1'-bicyclopentene or 1,1'-bicyclohexene also react with a thionitrosoarene ($4\text{-}MeOC_6H_4\text{-}N{=}S$) to give the [2+4] cycloadducts **68** (75% yield) (Scheme 28).[44,45] These results are suggestive of the high reactivity of simply substituted thionitrosoarenes even toward highly substituted dienes. Steric congestion of cyclic dienes or thionitroso compounds, however, seems to prevent the [2+4] cycloaddition in some cases. Meth-Cohn reports that $EtO_2C\text{-}N{=}S$ gives [2+4] adducts with butadiene in 82% yield and with cyclohexadiene in 40% yield.[35] This difference can be explained in terms of the difference in the steric congestion of the dienes. Furthermore, although 2-trifluoromethyl-5-cyanothionitrosobenzene gave a [2+4] adduct with cyclopentadiene,[37] 2,4-di-*t*-butyl-6-cyanothionitrosobenzene afforded no [2+4] adduct with cyclopentadiene, furan, or anthracene.[47] With cyclopentadiene, an interesting reaction forming an adduct **69** of two molecules of thionitroso intermediate with one molecule of cyclopentadiene has been reported (Scheme 29).[35] The reaction was considered to proceed in a [2+2+2] manner.

Scheme 28



68

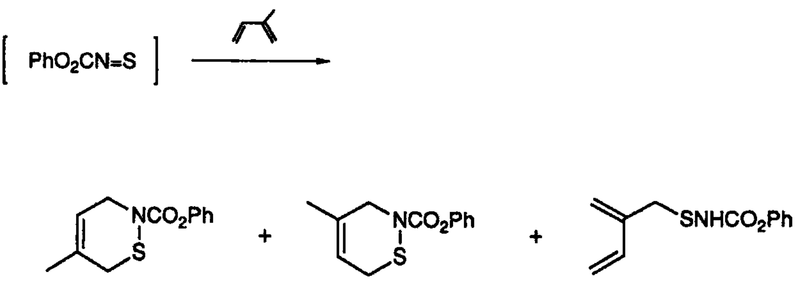
Scheme 29



69

The regioselectivity of [2+4] cycloadditions of thionitroso compounds shows a dependence upon their electronic nature. Meth-Cohn reported that the reaction between electron-poor thionitroso compounds and isoprene gave two isomeric [2+4] adducts (**70** and **71**; 25% yield each) and the ene adduct **72** (50% yield) (Scheme 30),[35] while 3:1 regioselectivity was observed in the reaction of 4-methoxythionitrosobenzene with isoprene (Scheme 31).[43] The change in regioselectivity is considered to be due to the change in the reactivity of the thionitroso compound: regioselectivity was observed for electron-rich, stabilized thionitroso compounds, but not for electron-poor, destabilized thionitroso compounds.

Scheme 30

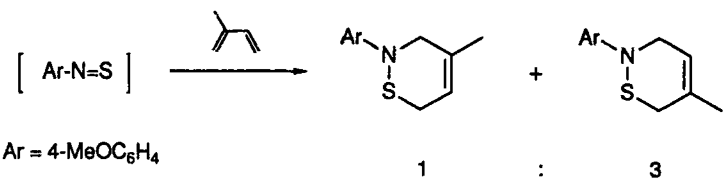


70 25%

71 25%

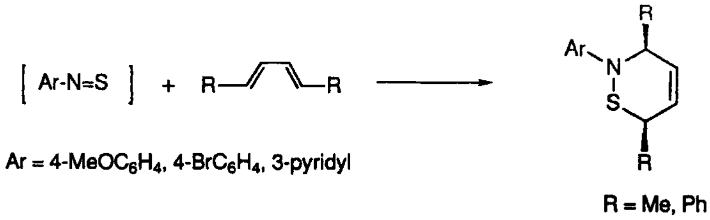
72 50%

Scheme 31



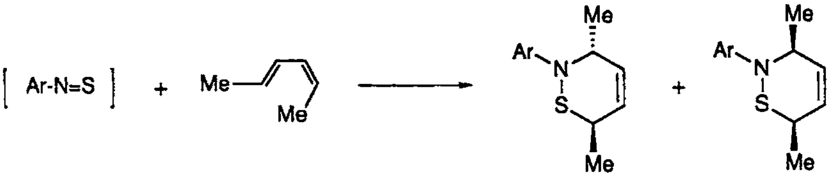
The stereochemistry of [2 + 4] cycloaddition reactions of thionitroso compounds has been investigated by Bryce and Taylor.[38,45] When thionitrosoarenes (Aryl = 4-MeOC$_6$H$_4$, 4-BrC$_6$H$_4$) were treated with (*E*,*E*)-hexa-2,4-diene, [2+4] adducts with a *cis*-structure were obtained stereoselectivity (> 98% diastereomeric excess, 70% yield). A similar stereochemical outcome was observed in the reaction of thionitrosoarenes (Aryl = 4-MeOC$_6$H$_4$, 3-pyridyl) with 1,4-diphenylbutadiene (Scheme 32).

Scheme 32



However, when (*E*,*Z*)-hexa-2,4-diene was allowed to react with thionitrosoarenes, the products were not only the expected *trans*-[2+4] adducts **73**, but also the *cis*-adducts **74** (Scheme 33). The ratio of *cis*- and *trans*-isomers was dependent upon the electronic nature of the substituents of the thionitrosoarenes. With thionitrosoarenes with electron-withdrawing substituents (Ar = 4-BrC$_6$H$_4$, 4-ClC$_6$H$_4$) the formation of the *trans*-products was favored (> 90% d. e.), while those with electron-donating group (Ar = 4-MeOC$_6$H$_4$) gave a 1:1 mixture of *cis* and *trans* products. They explained these facts by a possible (*E*,*E*) impurity in the diene and the changes in selectivity by the substituent of the thionitrosoarene to (*E*,*Z*)- and (*E*,*E*)-diene isomers. The higher reactivity of the less hindered (*E*,*E*)-diene and the large excess of dienes used in the reactions allowed even a small percentage of an (*E*,*E*)-diene impurity to give a considerable amount of the corresponding products. Indeed, when they treated thionitrosoarenes with 1:1 mixtures of (*E*,*E*)- and (*E*,*Z*)-dienes, the *cis*-adducts were obtained with high stereoselectivity (> 80% d. e.). The change in selectivity by the aryl substituent was explained as follows: thionitrosoarenes which are electronically stabilized by electron-donating groups are less reactive and hence more selective toward (*E*,*E*)-dienes to give *cis*-adducts, whereas highly reactive thionitrosoarenes bearing electron-withdrawing substituents are relatively indiscriminate and react with (*E*,*Z*)-dienes to afford predominantly *trans*-adducts. These results show the retention of the stereochemistry of dienes in [2+4] cycloaddition reaction of thionitroso compounds and suggest that the cycloaddition proceeds not in a stepwise manner, as observed in the reaction of sulfinylamines (R—N=S=O), but in a concerted manner.

Scheme 33



trans *cis*

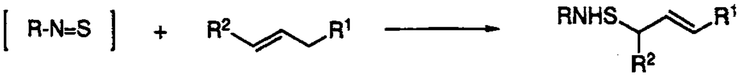
73 **74**

Asymmetric [2+4] reactions with chiral thionitroso dienophiles have been attempted by Dillen *et al.*,[50] but trapping with chiral thionitroso compounds (RO_2C—N=S, R = a: (−)-menthyl; b: (+)-fenchyl) resulted in the formation of thiazines with no diastereodifferentiation, and the adducts were obtained as inseparable mixtures of diastereomers.

5.3. *Ene Reactions*

An ene reaction of thionitroso compounds was first reported by Meth-Cohn and van Vuuren.[34,35] When the electron-poor thionitroso compounds PhO_2C—N=S and $4\text{-}MeC_6H_4SO_2$—N=S were generated in the presence of cyclohexene, ene products were obtained in 72 and 64% yield, respectively. A similar reaction proceeded also in the case of EtO_2C—N=S to give ene adducts in moderate to high yields from various acyclic and cyclic alkenes (Scheme 34, Table 3). Thionitrosoarenes also react with alkenes in the ene reaction mode. Bryce and Taylor report the reaction of thionitrosoarenes (Ar = $4\text{-}MeOC_6H_4$, 1-naphthyl and 3-pyridyl) with α-methylstyrene and isobutene to give the ene adducts **75** (45 ~ 65%).[43,45]

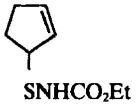
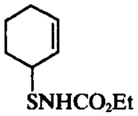
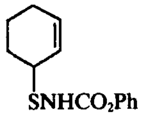
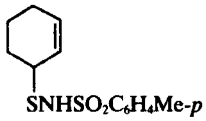
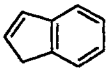
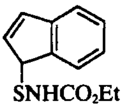
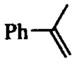
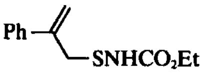
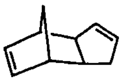
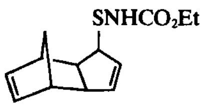
Scheme 34



75

R = PhO_2C, EtO_2C, $4\text{-}MeC_6H_4SO_2$

TABLE 3 Ene adducts of RNS with olefins[35]

alkene	ene adduct	yield/%
	 SNHCO$_2$Et	98
	 SNHCO$_2$Et	98
	 SNHCO$_2$Ph	72
	 SNHSO$_2$C$_6$H$_4$Me-*p*	64
	 SNHCO$_2$Et	18
	 SNHCO$_2$Et	79
 Ph	 Ph SNHCO$_2$Et	92
 Br	 EtO$_2$CNHS Br	95
	 SNHCO$_2$Et	59

The regioselectivity of the ene reaction of thionitroso compounds is very high. The structure of the isolated ene products is always that of an *S*-allylthioamine and no *N*-allylhydrothioamines have been isolated so far. The selectivity of the ene reaction of thionitroso compounds is different from that of thioaldehydes, which yield both regioisomers in their ene reactions, but similar to that of *N*-

sulfinylamines. The regioselectivity of the reaction may be due to the steric congestion of the transition state, but electronic effects involving the lowest triplet state may also play an important role. Theoretical considerations will be necessary to elucidate this point.

Meth-Cohn also reports that electron-poor thionitroso compounds undergo competitive [2+4] cycloaddition and ene reaction with 2,3-dimethylbutadiene and isoprene. In the reaction of $PhO_2C—N═S$ with 2,3-dimethylbutadiene, both the [2+4] adduct and the ene adduct were obtained in 1:1 ratio (43% yield each) (Scheme 13).[34] Similar results were observed in the reaction with isoprene. In this case, two isomeric [2+4] adducts (25% each) and an ene adduct (50%) were obtained.

They reported that the ene reaction is not observed to compete with the [2+4] cycloaddition in the case of any of the isosteres ($EtO_2CCH═S$, $EtO_2CN═O$ or $ArSO_2N═S═O$) of the thionitroso compounds and that the only other examples in which methylbutadienes undergo competitive ene and [2+4] cycloaddition are reactions with reactive intermediates such as benzyne, $PhS^+═O$ or certain reactions with diethyl azodicarboxylate.[35]

The selectivity of the [2+4] cycloaddition and the ene reaction has been well documented by Bryce and Taylor.[38,43,45] They generated simply substituted thionitrosoarenes in the presence of dienes. The thionitrosoarenes afforded [2+4] adducts **76** and ene adducts **77** in their reactions with 2,3-dimethylbutadiene (Scheme 35). The ratio of the products was affected by the substituent of the thionitrosoarenes. The changes in this ratio by the substituents are summarized in Table 4. Based on these results, electron-poor thionitroso compounds tend to predominantly give ene adducts, whereas electron-rich ones give [2+4] adducts. We also studied the reaction of 2,4-di-*t*-butyl-6-cyanothionitrosobenzene (**44**) with 2,3-dimethylbutadiene. Only the [2+4] adduct **47** was obtained (14%) without any formation of the ene adduct, but the aniline **46** was obtained (75%) instead (Scheme 17),[47] which is in contrast to Bryce's result. The difference may be due to the steric or electron-donating effect of the *t*-butyl groups, although the possibility can not be excluded that some ene product was actually formed, but decomposed to give the aniline under our reaction conditions or during the work-up, since the aniline was not formed in high yield in the absence of the diene.

Scheme 35

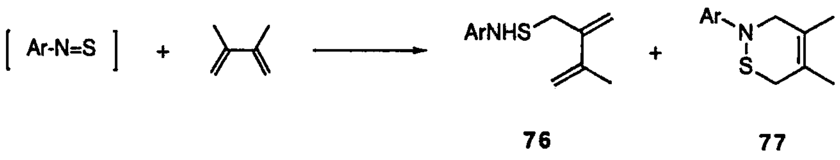


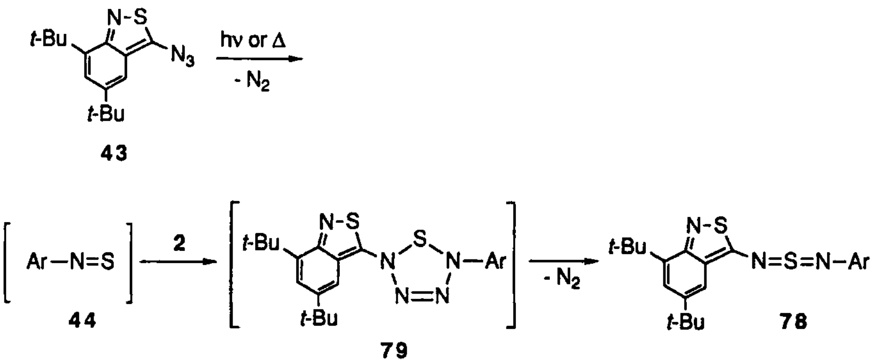
TABLE 4 Product isomer ratios from 2,3-dimethylbutadiene trapping of Ar—N=S intermediates[38,45]

Ar	product isomer ratio	
	76	**77**
4-$MeOC_6H_4$	15	85
4-MeC_6H_4	40	60
2-MeC_6H_4	65	35
C_6H_5	45	55
1-naphthyl	55	45
4-BrC_6H_4	75	25
2-BrC_6H_4	88	12
4-ClC_6H_4	75	25
3-pyridyl	75	25
4-NCC_6H_4	80	20
2-NCC_6H_4	90	10
4-$O_2NC_6H_4$	80	20
2-NC-5-BrC_6H_3	78	22
2-NC-5-ClC_6H_3	78	22
2-NC-4-ClC_6H_3	80	20

5.4. *[2+3] Cycloaddition Reactions*

A thionitrosoarene reacts with 1,3-dipoles to give [2+3] adducts. We have studied the possibility of [2+3] cycloaddition to thionitroso compounds.[39,47] In both thermal and photochemical reactions of the azidoisothiazole **43**, a small percentage of the unsymmetrical sulfur diimide **78** was isolated (Table 5). The most plausible mechanism for the formation of **78** is a [2+3] cycloaddition of the thionitrosoarene **44** to the starting azide **43**, followed by loss of nitrogen from the unstable thiatetrazoline intermediate **79** (Scheme 36).

Scheme 36



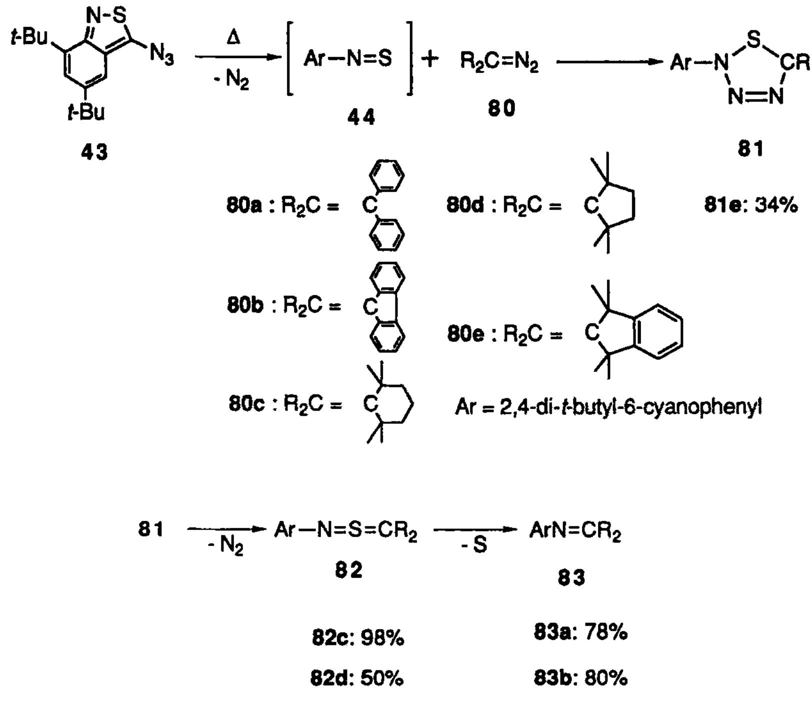
Ar = 2,4-di-*t*-butyl-6-cyanophenyl

TABLE 5 Products of thermal and photochemical reactions of azidoisothiazole **43**[47]

solvent	reaction condition	products/% **45**	**46**	**78**
hexane	hν	78	16	2
hexane	Δ	72	14	11
THF	hν	76	14	2
THF + H_2O	hν	59	14	5
EPA	hν	46	51	trace
ethanol	hν	5	91	3
ethanol	Δ	18	68	10
2-methyl-2-propanol	Δ	15	71	12

Although the thionitrosoarene **44** did not react with aryl azides, it reacted efficiently with diazo compounds (Scheme 37). When the thionitrosoarene **44** was treated with the sterically hindered 2-diazo-1,1,3,3-tetramethylindan **80e**, a [2+3] adduct, the thiatriazoline **81e**, was obtained in 34% yield. The thiatriazoline ring seems to be unstable and undergoes further reactions when other diazo compounds are used. In the corresponding reactions with 2,2,6,6-tetramethyldiazocyclohexane (**80c**) and 2,2,5,5-tetramethyldiazocyclopentane (**80d**),

Scheme 37

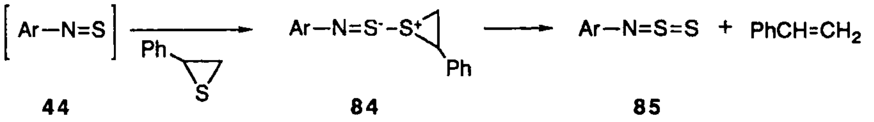


the thiocarbonyl imines **82c,d** were obtained (98 and 50% yield, respectively). They were considered to be formed by denitrogenation of the thiatriazolines **81c,d**. In the case of aromatic diazo compounds **80a,b** without steric protection, the thiocarbonyl imine **82** was not isolated, but the corresponding imine **83** was obtained in about 80% yield. This reaction provides a new route for the preparation of thiocarbonyl imines. We also attempted [2+3] cycloaddition of the thionitrosoarene **44** to other 1,3-dipoles, such as mesitonitrile oxide or *N*,α-diphenylnitrone, but we were unable to obtain any [2+3] cycloadduct. This is thought to be due to the steric congestion in these stable 1,3-dipoles, the only reagents which can be used under the reaction conditions.

5.5. *Sulfurization Reactions*

Thionitroso compounds are expected to be good precursors of thiocumulenes such as RN=S=O, RN=S=S, and RN=S=NR through appropriate functionalization. Indeed, the thionitrosoarene **44** reacted with phenylthiirane to afford the *N*-thiosulfinylamine **85** (Scheme 38).[39,47] The *N*-thiosulfinylamine is thought to be formed via ylide **84** by nucleophilic attack of the thiirane on the sulfur atom of **44**, since the N=S bond is considered to be polarized in the sense of $N^{\delta-}=S^{\delta+}$ according to theoretical calculations.

Scheme 38



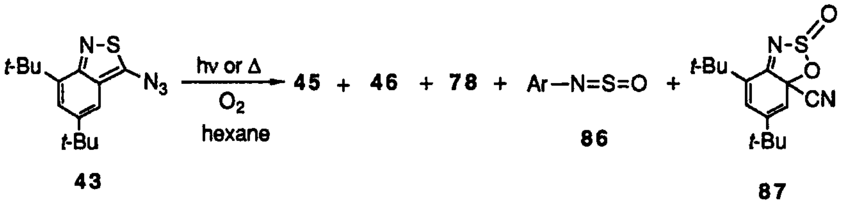
Ar = 2,4-di-*t*-butyl-6-cyanophenyl

5.6. *Reactions with Molecular Oxygen*

The thionitrosoarene **44** also reacts with molecular oxygen under both photochemical and thermal reaction conditions (Scheme 39).[39,47] When **44** was generated in a photochemical reaction in the presence of oxygen, 20% of the *N*-sulfinylaniline **86** was formed. By contrast, the oxathiazoline **87** was formed (30%) in addition to the *N*-sulfinylaniline **86** (11%) in the thermal reaction. The mechanism of these reactions is considered to be as shown in Scheme 40. The primary product of **44** and oxygen is considered to be any of **88–91**. The intermediacy of the *N*-sulfonylaniline **91** was confirmed by its trapping as an ethanol adduct **92** in ethanol as solvent (Scheme 40). The *N*-sulfonylaniline **91** was considered to undergo either reaction with the thionitrosoarene **44** to give the *N*-sulfinylaniline **86** or intramolecular cycloaddition affording the oxathiazoline **87**.

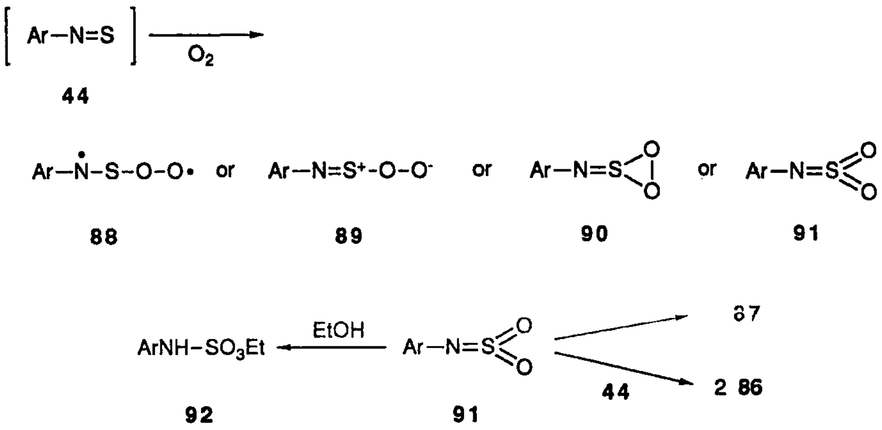
It is remarkable that a thionitrosoarene, which is considered to be a ground-state singlet (see Section 4), reacts easily with triplet oxygen in contrast to nitrosoarenes which are stable to triplet oxygen. This reactivity resembles that of triplet phenylnitrene which reacts readily with triplet oxygen to form nitrosobenzene oxide.[51,52] The cyclization of the *N*-sulfonylaniline **91** to **87** can be regarded as a 1,5-dipolar cyclization or an intramolecular [2+3] cycloaddition.

Scheme 39



	45	46	78	86	87
hν (0 °C)	34 %	17 %	2 %	20 %	
Δ (40 °C)	14 %	15 %	14 %	11 %	30 %

Scheme 40



Ar = 2,4-di-*t*-butyl-6-cyanophenyl

This oxidation reaction in our study obviously indicates the higher reactivity of a thionitrosoarene compared to that of a thiocarbonyl compound. In the case of thiocarbonyl compounds, an oxidation reaction of a thione to a thione *S*-oxide ($R_2C{=}S{=}O$) does not proceed generally with triplet oxygen and needs a stronger oxidizing reagent such as a peracid although thiobenzophenone is known to react rather slowly with triplet oxygen. The high reactivity of thionitrosoarenes toward triplet oxygen may be a consequence of the presence of a low-lying triplet state.

5.7. *Reductions*

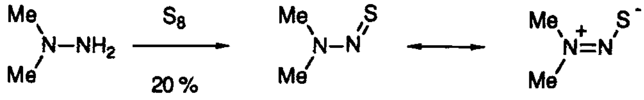
In the case of the thionitrosoarene **44** we found that a considerable amount of the aniline **46** was formed in each reaction (Table 5), especially in the reaction with ethanol as solvent.[47] Even in hydrocarbon solvents, under both thermal and photochemical conditions, the aniline **46** was formed in substantial yield. The possibility of the reduction of the N═S bond by α-hydrogens of ethanol was eliminated by a similar formation of the aniline in the reaction with 2-methyl-2-propanol as solvent. An effect of water can be excluded because no change was observed in the product ratio by addition of water to the solvent. Therefore, the relatively high yield of the aniline is considered to result from the facile addition of ethanol to the thionitrosoarene, followed by hydrolysis. In light of the fact that the aniline was formed also in hydrocarbon solvents, the aniline is considered to be formed also through hydrogen abstraction by the thionitrosoarene and subsequent loss of sulfur. Since theoretical calculations on HN═S have shown a small energy gap between its singlet ground state and lowest triplet state, the thionitroso group might have some biradical character and be able to abstract hydrogen atoms from solvents. In reactions of thionitrosoarenes in alcoholic solvents, the above two pathways to the aniline may be both operative.

6. *N*-THIONITROSOAMINES

N-Thionitrosoamines are the only example of isolable thionitroso compounds.

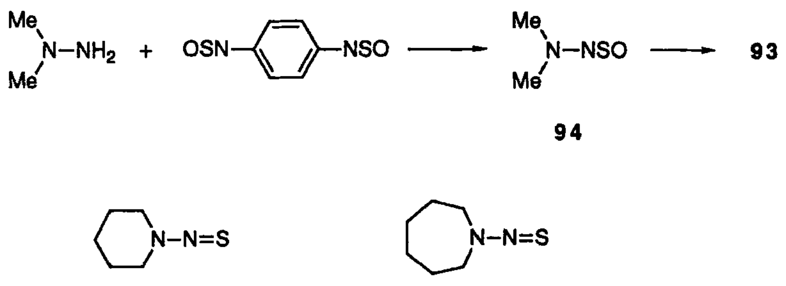
The first *N*-thionitrosoamine was prepared and isolated by Middleton.[14,53] He prepared *N*-thionitrosodimethylamine **93** by two different procedures, one being the sulfurization of a hydrazine and the other the reduction of the *N*-sulfinylhydrazine **94** (Schemes 41 and 42). Compounds **95** and **96** were also prepared by the former method. The preparation of *N*-thionitrosodimethylamine via reduction afforded dimethylhydrazine as a by-product whose formation was considered to be due to further reduction of *N*-thionitrosodimethylamine.

Scheme 41



93 **93'**

Scheme 42



94

95

96

Another N-thionitrosoamine was prepared by Roesky *et al.*[54] They obtained N-thionitrosodiphenylamine in the reaction of N,N-diphenylhydrazine with S_2Cl_2 in the presence of triethylamine. Although this procedure is known for the preparation of N-thiosulfinylanilines from anilines, it successfully affords N-thionitrosoamine in this case (Scheme 43).

Scheme 43

$$Ph_2NNH_2 + S_2Cl_2 + 2\,NEt_3 \longrightarrow Ph_2N\text{-}N{=}S + 2\,Et_3NHCl + S_8$$

N-Thionitrosoamines have a remarkable stability in contrast to C-thionitroso compounds, but are known to decompose under ambient conditions. Neat N-thionitrosodimethylamine decomposes in a few hours at room temperature, but the decomposition is delayed at low temperatures (ca. $< -30°C$) or in dilute solution in nonpolar solvents.[14] Although N-thionitrosodimethylamine could be isolated in pure crystalline form, N-thionitrosopiperidine **95** was not stable enough to be purified by recrystallization or distillation.[14,54] The decomposition of N-thionitrosoamines was significantly accelerated by acidic materials such as boron trifluoride, acetic acid or mineral acids with deposition of elemental sulfur, whereas basic materials such as pyridine, triphenylphosphine, and even aqueous sodium hydroxide did not greatly accelerate the decomposition of N-thionitrosoamines.

N-Thionitrosoamines are stabilized by the contribution of the zwitterionic resonance structure **93′** as evidenced by spectroscopic data. The ^{1}H-NMR spectra of N-thionitrosodimethylamine (and N-thionitrosopiperidine, respectively) showed a pair of separated singlets at δ 3.6 and 4.1 (δ 3.8 and 4.3) assignable to N-methyl (N-methylene) groups, indicating restricted rotation around the N—N bond and hence the double bond character of the N—N bond.

The isolated N-thionitrosoamines possess a blue to deep purple color. Their UV-VIS spectra show absorptions at longer wave length (Table 6). The absorp-

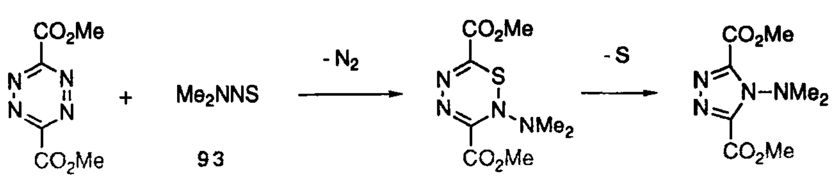
TABLE 6 UV-VIS spectra of *N*-thionitrosoamines[14]

compound	solvent	λ_{max}/nm	ε
93	cyclohexane	705	1.5
		587	27.3
		306	11900
	CCl_4	685	1.8
		576	38
		309	12300
	ethanol	680	1.0
		533	17.5
		306	10800
95	CCl_4	585	13
		318	14500
96	ether	700	—
		584	—
		306	—

tion of **93** (λ_{max} 500–600 nm) shows a large hypsochromic shift by 54 nm between cyclohexane and ethanol solutions. A similar hypsochromic shift was observed in the case of *N*-thionitrosopiperidine (**95**), and this shift was regarded as a dramatic example of a solvent effect on an n-π* band. Thus the hypsochromic shift in **93** is considered to be evidence for extensive hydrogen bonding in ethanol and indicates that the dipolar resonance structure **93′** is an important contribution to the structure of **93**.

N-Thionitrosoamines behave as dienophiles and undergo [2+4] cycloadditions. Although [2+4] cycloadditions of *N*-thionitrosoamines with normal or electron-rich dienes are unknown, an inverse Diels-Alder reaction of **93** with 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine has been reported (Scheme 44) to afford the triazole **97** via [2+4] cycloaddition, followed by loss of nitrogen and sulfur.[55]

Scheme 44



97

7. METAL COMPLEXES OF THIONITROSO COMPOUNDS

It is well-known that unstable π-bonded compounds or open-shell species are stabilized by coordination to transition metals. Thionitroso compounds with their thermodynamically unstable N═S bond can also be stabilized by this method. There are several types of coordination of thionitroso compounds (R—N═S) depending upon the substituent R.

7.1. *Complexes of* N-*Thionitrosoamines*

The most explored complexes of thionitroso compounds are those of *N*-thionitrosoamines, especially those of *N*-thionitrosodimethylamine (**93**) and *N*-thionitrosodiphenylamine with group VIII and group VIA transition metals. Most of the complexes of *N*-thionitrosoamines are more stable than the *N*-thionitrosoamines themselves and isolable in crystalline form.

The first of the complexes reported by Roesky *et al.* was prepared by substitution of $Cr(CO)_5(THF)$ with *N*-thionitrosoamines (Scheme 45).[54,56] The chromium complex **98** was isolated as ruby-red crystals and stable at room temperature, but decomposed above 100°C. The structure of **98** (R = Me) was confirmed by X-ray structure analysis. The coordination structure of **98** is nearly octahedral and the Me_2NNS ligand is coordinated to chromium via the sulfur atom, which is in contrast to the fact that monodentate N—S ligands are generally coordinated to the metal via nitrogen atoms in transition metal complexes with acyclic sulfur-nitrogen compounds. Since the sulfur atom of *N*-thionitrosoamines has a partial negative charge due to the contribution of the resonance structure **93′**, the formation of the sulfur-metal bond takes place readily.

Scheme 45

$$R_2N\text{-}N\text{=}S \;+\; (CO)_5Cr\cdot THF \longrightarrow \underset{\mathbf{98}}{R_2NNS\cdot Cr(CO)_5} \;+\; THF$$

R = a: Me, b: Ph

Indeed, the structure of *N*-thionitrosoamines in complexes shows an enhanced tendency for the resonance structure **93′** as indicated by spectroscopic data as well as X-ray crystallographic data. The $SNNC_2$ atoms of the Me_2NNS ligand and Cr are coplanar in crystals. The N—S distance is 1.635 Å (corresponding to a single bond) and the N—N distance 1.278 Å (remarkably shortened compared to that in hydrazine derivatives). These data indicate that the ligand can best be described in terms of the resonance structure **93′**.

This interpretation is also supported by the IR spectra. In the IR spectrum of **98**, $\nu(NS)$ is shifted from 915 cm^{-1} in neat Me_2NNS to 785 cm^{-1} in the complex, indicative of weakened N—S bonding and η^1—S complexation.[54]

The mean S—Cr—C (*cis*-CO) angle in the crystalline complex is very close to 90°, indicating that the π back donation from chromium to the *N*-thionitroso ligand is similar to that to the carbonyls.

Pd and Pt complexes (both neutral and cationic) of **93** have been investigated by Tresoldi *et al.* Neutral Pd(II) and Pt(II) complexes have been prepared as shown in Schemes 46 and 47.[57] Compound $\mathrm{Me_2NNS}$ reacts with $\mathrm{Pd(diene)Cl_2}$ to give $\mathrm{Pd(SNNMe_2)_2Cl_2}$ **99** and with $\mathrm{M(1{,}5\text{-cyclooctadiene})Cl_2}$ ($\mathrm{M = Pd^{II}, Pt^{II}}$) in the presence of $\mathrm{PR_3}$ ($\mathrm{PPh_3}$, $\mathrm{4\text{-}CH_3C_6H_4PPh_2}$) to give mixed ligand complexes of *cis*-$\mathrm{M(SNNMe_2)(PR_3)Cl_2}$ **101** despite the general formation of *trans*-$\mathrm{PdL_2X_2}$.[57] This reaction is considered to be controlled by the chelate effect of the diene. The *cis*-structure of the complex was confirmed by the far infrared spectrum (ν(Pd—Cl) 320 and 280 $\mathrm{cm^{-1}}$). The complex **99** underwent ligand exchange reactions with triarylphosphines, $\mathrm{AsPh_3}$, and $\mathrm{SbPh_3}$ to give *cis*-$\mathrm{Pd(SNNMe_2)LCl_2}$ **100** (Scheme 46). A bridge cleaving reaction of $\mathrm{[Pd(MeO\text{-}diene)Cl]_2}$ with $\mathrm{Me_2NNS}$ also occurred to form $\mathrm{Pd(MeO\text{-}diene)(SNNMe_2)Cl}$ **102** (Scheme 48). The complexes **99** and **101** underwent metathetical reactions with KSCN and KSeCN to give $\mathrm{Pd(SNNMe_2)_2(YCN)_2}$ and $\mathrm{M(SNNMe_2)(PR_3)(YCN)}$ (Y = S, Se), respectively (Scheme 49).

Scheme 46

$$\begin{tikzcd}
\mathrm{Pd(diene)Cl_2} + 2\,\mathrm{Me_2NNS} \arrow[r] & \mathrm{Pd(Me_2NNS)_2Cl_2} \\
& \mathbf{99} \arrow[d, "\mathrm{L}"] \\
& \mathrm{Pd(Me_2NNS)LCl_2} \\
& \mathbf{100}
\end{tikzcd}$$

diene = 1,5-cyclooctadiene,
norbornadiene,
1,3,5,7-cyclooctatetraene,
dicyclopentadiene

Scheme 47

$$\mathrm{M(1{,}5\text{-cyclooctadiene})Cl_2} \xrightarrow[\mathrm{Me_2NNS}]{\mathrm{PR_3}} \mathrm{M(Me_2NNS)(PR_3)Cl_2}$$

101

$\mathrm{M = Pd^{II}, Pt^{II}}$

$\mathrm{PR_3 = PPh_3}$, *p*-tolyl$\mathrm{PPh_2}$

Scheme 48

$$[\mathrm{Pd(MeO\text{-}diene)Cl}]_2 \xrightarrow{\mathrm{Me_2NNS}} \mathrm{Pd(MeO\text{-}diene)(Me_2NNS)Cl}$$

102

diene = 1,5-cyclooctadiene,
1,3,5,7-cyclooctatetraene,
dicyclopentadiene

Scheme 49

$$\mathbf{99} \xrightarrow{\mathrm{KYCN}} \mathrm{Pd(Me_2NNS)_2(YCN)_2}$$

$$\mathbf{101} \xrightarrow{\mathrm{KYCN}} \mathrm{M(Me_2NNS)(PR_3)(YCN)_2}$$

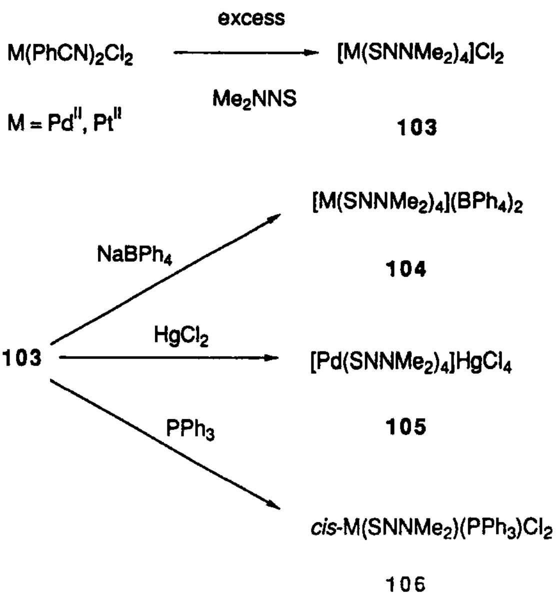
$\mathrm{M = Pd^{II}, Pt^{II}}$
$\mathrm{Y = S, Se}$

The ligands in all the complexes prepared by Roesky were considered to coordinate to Pd and Pt through the sulfur atom as observed with the chromium complex. This interpretation was supported by the higher-frequency shift of ν(N—N) (~1130 cm^{-1}) and the lower-frequency shift of ν(N—S) (~770 cm^{-1}).

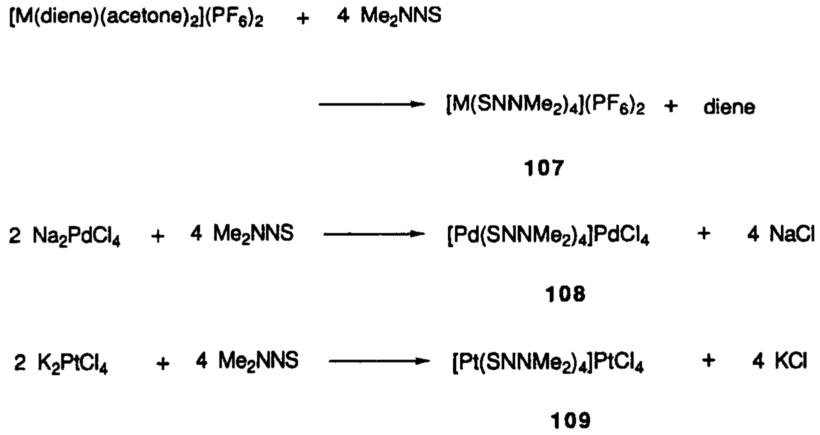
An X-ray crystal analysis was carried out with the complex $\mathrm{Pd(SNNMe_2)(AsPh_3)Cl_2}$. The palladium coordination geometry is nearly square-planar and the ligand $\mathrm{Me_2NNS}$ nearly planar. The ligand $\mathrm{Me_2NNS}$ is located in a *cis*-position relative to $\mathrm{AsPh_3}$. The geometrical features of $\mathrm{Me_2NNS}$ are quite comparable to those found in the chromium complex **98** (d(N—S): 1.639 Å; d(N—N): 1.272 Å). These features indicate that the zwitterionic structure of **93′** is important here as well.

Cationic complexes and binuclear complexes of $\mathrm{Me_2NNS}$ with Pd and Pt have also been reported.[58] The complexes $\mathrm{M(PhCN)_2Cl_2}$ (M = Pd$^{\mathrm{II}}$, Pt$^{\mathrm{II}}$) react with excess $\mathrm{Me_2NNS}$ to give the unstable products $\mathrm{[M(SNNMe_2)_4]Cl_2}$ **103** (Scheme 50). These unstable salts gave the slightly more stable salts **104** and **105** when the counterion was changed to $\mathrm{BPh_4^-}$ or $\mathrm{HgCl_4^{2-}}$. They were diagnosed as bi-monovalent electrolytes by conductivity measurements. The cationic complexes **103** react with triphenylphosphine to give the neutral complexes **106**. The preparation of additional cationic Pd(II) and Pt(II) complexes (**107–109**) is shown in Scheme 51. Also in these complexes the ligand $\mathrm{Me_2NNS}$ coordinates monodentately through the sulfur atom and exhibits spectroscopic properties consistent with the zwitterionic structure **93′**.

Scheme 50

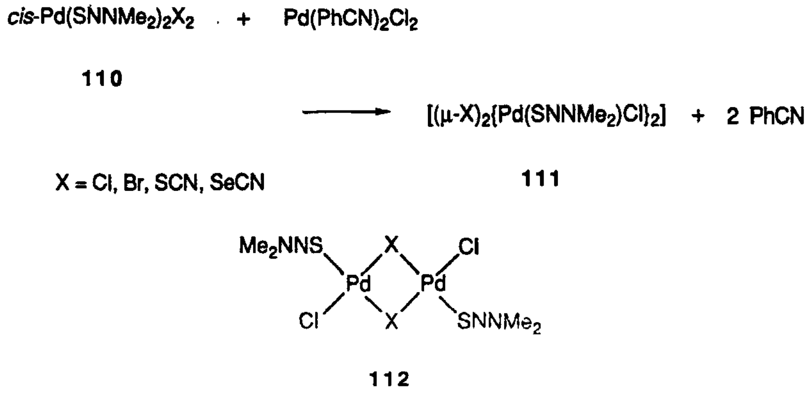


Scheme 51



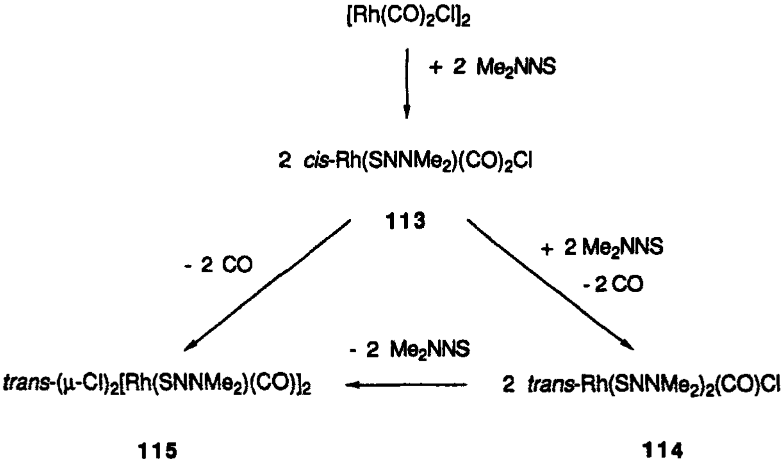
Binuclear Pd(II) complexes **111** have been prepared by reactions of the neutral complexes **110** with $Pd(PhCN)_2Cl_2$ (Scheme 52). The ligand Me_2NNS again coordinates through the sulfur atom in the terminal position and with evidence of back donation (ν(Pd—S): 390 cm^{-1}). The structure of **111** (X = Cl, SCN, SeCN) was shown to correspond to the *trans*-configuration **112** as judged by ν(Pd—Cl) absorptions in the far infrared region (~340 cm^{-1}).

Scheme 52



Complexes of Me_2NNS with rhodium have been reported by Tresoldi *et al.*[59,60] Compound Me_2NNS reacts with $[Rh(CO)_2Cl]_2$ to produce *cis*-$Rh(SNNMe_2)(CO)_2Cl$ **113**, which undergoes reversible CO substitution by Me_2NNS to give *trans*-$Rh(SNNMe_2)_2(CO)Cl$ **114** (Scheme 53). Compounds **113** and **114** spontaneously lose CO and Me_2NNS, respectively to give the binuclear complex trans-$(\mu\text{-}Cl)_2[Rh(CO)(SNNMe_2)]_2$ **115**. Compound **113** was also prepared by the reaction shown in Scheme 54. The complexes **113** and **114** react with EPh_3 (E = P, As, Sb) the Me_2NNS ligand being substituted by EPh_3 to give the neutral complex *trans*-$Rh(EPh_3)_2(CO)Cl$. The reverse of this reaction also takes place and *trans*-$Rh(E'Ph_3)_2(CO)X$ (X = Cl, E′ = As, Sb; X = Br, NCS, E′ = As) undergoes $E'Ph_3$ displacement to give *trans*-$Rh(SNNMe_2)_2(CO)X$ (Scheme 55).

Scheme 53



Scheme 54

$$[\mathrm{Rh(diene)Cl}]_2 \xrightarrow{\mathrm{Me_2NNS}} \mathrm{Rh(SNNMe_2)(diene)Cl} \xrightarrow{\mathrm{CO}} \mathbf{113}$$

diene = 1,5-cyclooctadiene, norbornadiene

Scheme 55

$$\textit{trans}\text{-}\mathrm{Rh(EPh_3)_2(CO)X} \xrightleftharpoons[\mathrm{EPh_3}]{\mathrm{Me_2NNS}} \underset{\mathbf{114}}{\textit{trans}\text{-}\mathrm{Rh(SNNMe_2)_2(CO)X}}$$

X = Cl, Br, NCS E = As, Sb

Oxidation of Rh(I) complexes affords octahedral Rh(III) complexes. The complexes **114** have been oxidized with halogens to give the Rh(III) complexes **116** (Scheme 56). Compounds **113** and **114** react with iodomethane to afford a mixture of $(\mu\text{-Cl})_2[\mathrm{Rh(SNNMe_2)(CO)(CH_3)I}]_2$ and $(\mu\text{-Cl})_2[\mathrm{Rh(SNNMe_2)(CH_3CO)I}]_2$ and a mixture of $\mathrm{Rh(SNNMe_2)(CO)(CH_3)ClI}$ and $\mathrm{Rh(SNNMe_2)(CH_3CO)ClI}$, respectively.

All these complexes are again considered to be *S*-coordinated on the basis of the IR spectra and the two quadruplets (*N*—Me) in their ^{1}H NMR spectra.

Scheme 56

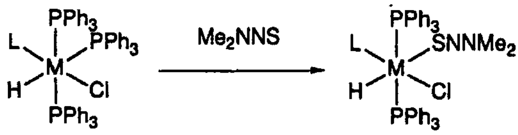
$$\underset{\mathbf{114}}{\textit{trans}\text{-}\mathrm{Rh(SNNMe_2)(CO)Cl}} \xrightarrow[\mathrm{X\,=\,Cl,\,Br,\,I}]{\mathrm{X_2}} \underset{\mathbf{116}}{\mathrm{Rh(SNNMe_2)_2(CO)ClX_2}}$$

Also cationic complexes have been prepared by Tresoldi *et al.*[60] Treatment of $[\mathrm{Rh(diene)Cl}]_2$ (diene = 1,5-cyclooctadiene, norbornadiene), $[\mathrm{Rh(CO)_2Cl}]_2$, $\mathrm{C_5H_5Rh(CO)I_2}$, and $[\mathrm{C_5Me_5RhCl_2}]_2$ with $\mathrm{AgPF_6}$ in acetone or acetonitrile, followed by reaction with a large excees of $\mathrm{Me_2NNS}$, gives the cationic complexes $[\mathrm{Rh(diene)(SNNMe_2)_2}]\mathrm{PF_6}$, $[\mathrm{Rh(CO)_2(SNNMe_2)_2}]\mathrm{PF_6}$, $[\mathrm{C_5H_5Rh(SNNMe_2)_3}](\mathrm{PF_6})_2$, and $[\mathrm{C_5Me_5Rh(SNNMe_2)_3}](\mathrm{PF_6})_2$, respectively. These salts could be converted to the corresponding perchlorate salts by treatment with $\mathrm{AgClO_4}$ (with exception of the $\mathrm{C_5H_5}$ and $\mathrm{C_5Me_5}$ complexes). Also these complexes are *S*-coordinated. The complexes $[\mathrm{Rh(diene)(SNNMe_2)_2}]\mathrm{ClO_4}$ react with $\mathrm{PR_3}$ ($\mathrm{R_3}$ = $\mathrm{Ph_3}$, p-tolyl$\mathrm{Ph_2}$) to give labile products, only $[\mathrm{Rh(1{,}5\text{-}C_8H_{12})(SNNMe_2)(PR_3)}]\mathrm{ClO_4}$ could be isolated. These cationic complexes of $\mathrm{Me_2NNS}$ seem to be more stable than the Pd or Pt complexes.

Ruthenium complexes of Me_2NNS have also been reported by Tresoldi *et al.*[60] Cationic complexes of $[Ru(C_6H_6)(SNNMe_2)_3]X_2$ ($X = PF_6, ClO_4$) have been prepared from $[Ru(C_6H_6)Cl_2]_2$ and Me_2NNS. Their spectroscopic data are very close to those of the cationic rhodium complexes.

Herberhold and Hill, and Gieren *et al.* have reported the hexa-coordinated Me_2NNS complexes of ruthenium, osmium, and iridium.[61,62] They prepared the hydride complexes $(ML)ClH(SNNMe_2)(PPh_3)_2$ **117** from $(ML)ClH(PPh_3)_3$ [ML = Ru(CO), Os(CO), Ir(Cl)] (Scheme 57). The Me_2NNS ligand in these complexes is located in the *trans*-position relative to H since ^1H NMR spectrum contained a triplet assignable to *trans*-H. Bis(thionitrosoamino) cations $[RuH(CO)(SNNMe_2)_2(PPh_3)_2]^+$ and $[IrClH(SNNMe_2)_2(PPh_3)_2]^+$ have been obtained by reaction of Me_2NNS with $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$ and $[IrClH(NCMe)_2(PPh_3)_2]^+_2$.

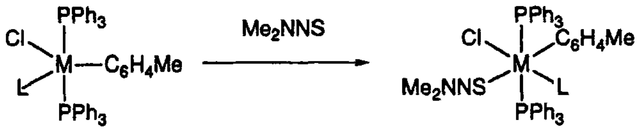
Scheme 57



ML = Ru(CO), Os(CO), Ir(Cl) **117**

The aryl complexes **119** have been prepared from the 16-electron aryl complexes **118** and Me_2NNS (Scheme 58). An X-ray structure analysis of the osmium complex **119** revealed the octahedral structure of the complex with *trans*-coordination of the tolyl and Me_2NNS groups, short bond lengths of Os—S (2.411 Å) and N—N (1.293 Å) and a long N—S bond (1.616 Å). Here again, metal-to-ligand back bonding is operative, and the coordinated Me_2NNS is reasonably described by the canonical structures **120–122** with the major contribution from the resonance form **121** (Scheme 59).

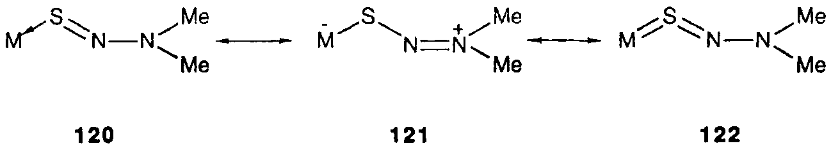
Scheme 58



118 **119**

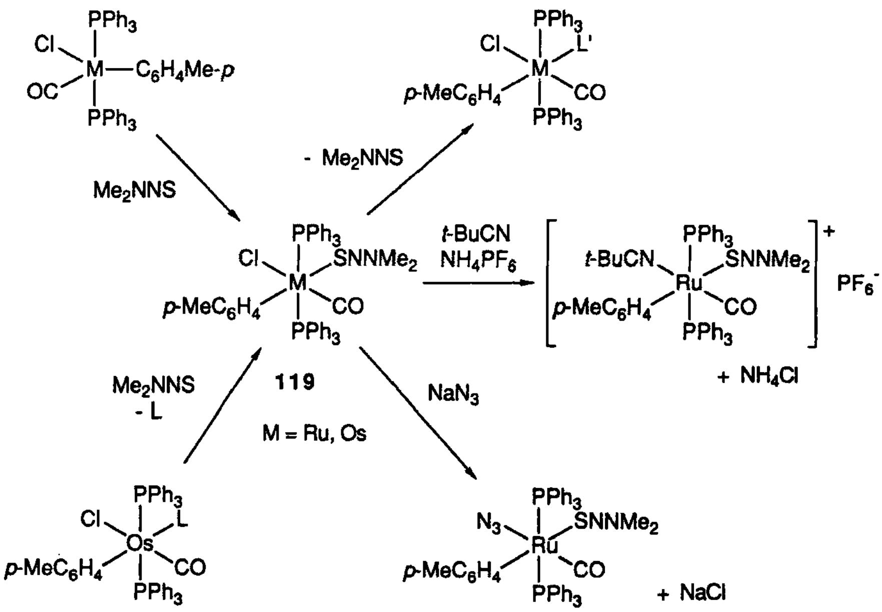
ML = Os(CO), Os(CS), Ru(CO)

Scheme 59



The substitution of these aryl complexes **119** showed the lability of the chlorine ligand, which was readily exchanged by N_3^- or *t*-BuCN (Scheme 60). The Me_2NNS ligand could be substituted by the bulky 2-xylyl isocyanide or by CO which has a large π-acid capacity.

Scheme 60

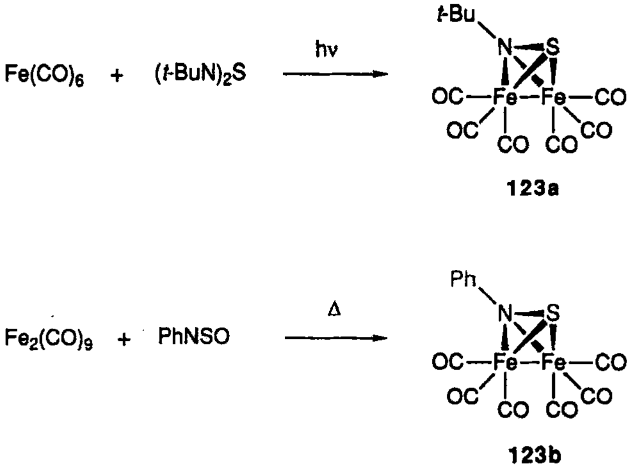


7.2. *Complexes of C-Thionitroso Compounds*

Complexes of *C*-thionitroso compounds have been known even earlier, but only iron complexes have been reported so far. Complexes of *t*-BuNS and PhNS have been reported by Otsuka *et al.*[63] They prepared these complexes from thiocumulenes (sulfur diimides and *N*-sulfinylamines). The iron complex of *t*-BuNS (**123a**) is prepared by the reaction of $(t\text{-BuN})_2S$ with $Fe(CO)_6$ under irradiation with sunlight (Scheme 61). The corresponding Me_3SiNS complex (**123c**) is prepared from the sulfur diimide $(Me_3SiN)_2S$ and $Fe_3(CO)_{12}$.[64] No similar reaction proceeds in the case of $(PhN)_2S$, but the reaction of PhNSO with $Fe_2(CO)_9$ gives **123b**.[63]

The complex **123c** furnishes iron complexes of HNS (**123d**) and MeNS (**123e**) (Scheme 62).[65] The parent complex **123d** is obtained by hydrolysis of **123c** on silica gel and **123e** by treatment of **123d** with diazomethane.

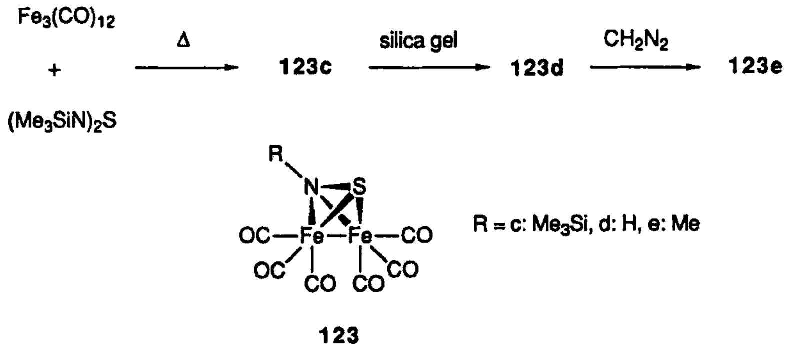
Scheme 61



123a

123b

Scheme 62



R = c: Me_3Si, d: H, e: Me

123

These complexes are stable at room temperature, indicating that the stability of thionitroso compounds increased dramatically by coordination to transition metals. The structures of these complexes have been determined as **123** from spectroscopic data. In **123**, both of the lone pairs on the nitrogen and sulfur atoms participate in coordination forming two bridges. The IR absorption ν(N—S) of **123** is 705–760 cm^{-1} corresponding to the stretching mode of N—S single bonds.

7.3. *Thionitrosyl Complexes*

Thionitrosyl complexes[66] formulated as metal-NS belong to the thionitroso compounds R—NS if the coordinated transition metal is regarded as a substituent R. The ligand NS^+ itself exists in salts like $NS^+EF_6^-$ (E = As, Sb)[67,68] and gaseous NS^+ has been characterized by photoelectron spectroscopy.[11]

Thionitrosyl complexes can be prepared from these salts.[69] The reaction of $NS^+EF_6^-$ with carbonyl and cyclopentadienyl complexes affords the thionitrosyl complexes $[C_5H_5Fe(CO)_2NS]^{2+}(AsF_6^-)_2$, $[C_5H_5Mn(CO)_2NS]^{2+}(AsF_6^-)_2$, and $[Re(CO)_5NS]^{2+}(AsF_6^-)_2$.[69] The corresponding rhenium complex was also prepared from the thiazyl iodide complex $[Re(CO)_5NSI]^+AsF_6^-$.[70]

Neutral thionitrosyl complexes have been prepared with chromium.[71,72] The thionitrosyl ligand was introduced with $S_3N_3Cl_3$ (Scheme 63).

Scheme 63

$$Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3] \; + \; {}^1\!/_3\, S_3N_3Cl_3$$

$$\longrightarrow (\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) \; + \; CO \; + \; NaCl$$

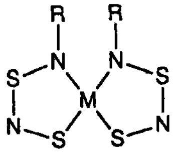
Nitrosyl ligands are considered to be coordinated at the nitrogen atom. The ν(N—S)'s change with the central metal of $[C_5H_5M(CO)_2NS]^{2+}$ (Cr(0): 1165 cm^{-1}, Mn(I): 1284 cm^{-1}, Fe(II): 1388 cm^{-1}), indicating a decrease of the π-donor ability of the central atom from Cr to Fe. The σ-donor ability of NS^+ is greater than that of NO^+, since NS^+ coordinates to $[Re(CO)_5SO_2]^{2+}$ to give $[Re(CO)_5NS]^{2+}$ while NO^+ does not react.

X-Ray structural analysis[72,73] and a study of the physical properties[72,73] of $[C_5H_5Cr(CO)_2NS]$ have been carried out. The crystal structure of $[C_5H_5Cr(CO)_2NS]$ shows a 'piano stool' configuration, the NS ligand being coordinated essentially linearly to the metal via the nitrogen atom. The Cr—N distance (1.644 Å) falls in the same range as the Cr—N distance of linear terminal nitrosyl (NO^+) ligands and is suggestive of NS^+ (an overall three-electron donor) as the character of the thionitrosyl ligand. The N—S distance is 1.551 Å, considerably longer than the gas state NS^+ equilibrium bond length (1.440 Å). This long NS bond indicates the occurrence of back donation from Cr π orbitals to NS π^* orbitals. This back donation decreases when a carbonyl group is substituted by NO.

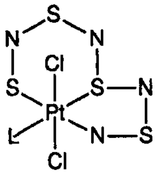
As judged by the results of electron impact mass spectroscopy the Cr—CO bond is apparently weaker in the thionitrosyl complex than in the nitrosyl complex and the Cr—N bond stronger in the thionitrosyl complex than in the nitrosyl complex. The stronger π-acceptor ability of NS^+ compared to that of NO^+ was explained by the relatively lower π^* orbitals and higher π orbital of NS^+ compared to NO^+ as evident from the photoelectron spectra of $[C_5H_5Cr(CO)_2NS]$ and $[C_5H_5Cr(CO)_2NO]$.[74]

7.4. *Other Complexes*

As more exotic types of thionitrosyl complexes, transition metal complexes of the bidentate ligand RN_2S_2 and the tridentate ligand $N_4S_4^{2-}$ have been reported. For the bidentate ligand RN_2S_2, complexes **124** are known with Co, Ni and Pd as central atoms.[75–82] Also Pt complexes of $N_4S_4^{2-}$ **125** are known.[83,84] We will not describe these complexes in detail here because they cannot be regarded as 'thionitroso compounds.'



124
M = Co, Ni, Pd.



125

8. CONCLUSIONS

Thionitroso compounds are generally thermodynamically unstable. This is due to the polarization of the NS bond and to their biradical character which enhance the reactivity of thionitroso compounds. The biradical character of thionitroso compounds has been pointed out by theoretical studies; the lowest triplet excited state T_1 lies very close to the singlet ground state S_0.

Many approaches to *C*-thionitroso compounds have been reported. Spectroscopic detection of thionitroso compounds has been carried out and the experimental observations compared with the predictions of theoretical calculations.

Thionitroso compounds can be stabilized by the introduction of an electron-donating group such as an amino group. Although *C*-thionitroso compounds have not been isolated so far, *N*-thionitrosoamines with a resonance structure $R_2N^+{=}N{-}S^-$ are isolable. Coordination to transition metals also stabilizes thionitroso compounds and several types of complexes have been studied.

Although their high reactivity prevents the isolation of thionitroso compounds, various types of reactions have been studied with transient thionitroso compounds, generated *in situ* in low concentration, and thus interesting reactivities of thionitroso compounds could be revealed.

Although thionitroso compounds have been investigated for about 25 years from various angles as described here, additional new and fascinating chemistry of thionitroso compounds still remains unexplored.

REFERENCES

1. F. Duus, In *Comprehensive Organic Chemistry*; D. H. R. Barton and W. D. Ollins, Eds.; Pergamon Press: Oxford, 1979; Vol. 3, pp. 373–487.
2. Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 1 (1978).
3. Y. Inagaki and R. Okazaki, *Sulfur Rep.*, **2**, 137 (1982).
4. R. Bussas, G. Kresze, H. Münsterer and A. Schwöbel, *Sulfur Rep.*, **2**, 215 (1983).
5. S. Motoki and T. Saito, *Sulfur Rep.*, **4**, 33 (1984).
6. G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla and A. Trede, *Angew. Chem., Int. Ed. Engl.*, **1** 89 (1962).
7. G. W. Kutney and K. Turnbull, *Chem. Rev.*, **82**, 333 (1982).
8. C. Wentrup and P. Kambouris, *Chem. Rev.*, **91**, 363 (1991).
9. R. S. Atkinson and B. D. Judkins, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2615.
10. D. J. Little, A. Dalgleish and R. J. Donovan, *Faraday Discuss. Chem. Soc.*, **53**, 211 (1972).
11. J. M. Dyke, A. Morris and I. R. Trickle, *J. Chem. Soc., Faraday Trans. 2*, **73**, 147 (1977).
12. W. H. Kirchhoff and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **85**, 1726 (1963).
13. O. Glemser and R. Mews, *Angew. Chem., Int. Ed. Engl.*, **19**, 883 (1980).
14. W. J. Middleton, *J. Am. Chem. Soc.*, **88**, 3842 (1966).
15. M. P. S. Collins and B. J. Duke, *J. Chem. Soc., Dalton Trans.*, **1978**, 277.
16. A. Mehlhorn, J. Sauer, J. Fabian and R. Mayer, *Phosphorus Sulfur*, **11**, 325 (1981).
17. J. Wasilewski and V. Staemmler, *Inorg. Chem.*, **25**, 4221 (1986).
18. B. A. Hess, L. J. Schaad and R. Zahradnik, cited in reference 17.
19. M. W. Schmidt, P. N. Truong and M. S. Gordon, *J. Am. Chem. Soc.*, **109**, 5217 (1987).
20. R. Vetter and A. Mehlhorn, *J. Mol. Struct. (Theochem)*, **206**, 11 (1990).
21. J. Fabian and A. Mehlhorn, *Z. Chem.*, **27**, 30 (1987).
22. A. Mehlhorn, *Collect. Czech. Chem. Commun.*, **53**, 2116 (1988).
23. P. Redondo, J. R. Flores and J. Largo-Cabrerizo, *J. Comput. Chem.*, **10**, 295 (1989).
24. P. Tavs, *Angew. Chem.*, **78**, 1057 (1966).
25. T. Minami, K. Yamataka, Y. Ohshiro, T. Agawa, N. Yasuoka, and N. Kasai, *J. Org. Chem.*, **37**, 3810 (1972).
26. F. A. Davis and E. B. Skibo, *J. Org. Chem.*, **41**, 1333 (1976).
27. G. Domschke, R. Mayer, S. Bleisch, A. Bartl and A. Stasko, *Magn. Reson. Chem.*, **28**, 797 (1990).
28. R. Mayer, *Phosphorus Sulfur*, **23**, 277 (1985).
29. D. H. R. Barton and M. J. Robson, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1245.
30. R. Mayer, G. Domschke, S. Bleisch and A. Bartl, *Tetrahedron Lett.*, **1978**, 4003.
31. L. N. Markovskii, A. V. Solov'ev, E. I. Kaminskaya, A. B. Borodin and Y. G. Shermolovich, *Zh. Org. Khim.*, **26**, 2083 (1990).
32. M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 2591.
33. Y. Hata and M. Watanabe, *J. Org. Chem.*, **45**, 1691 (1980).
34. O. Meth-Cohn and G. van Vuuren, *J. Chem. Soc., Chem. Commun.*, **1984**, 1144.
35. O. Meth-Cohn and G. van Vuuren, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 245.
36. C. L. Pedersen, C. Lohse and M. Poliakoff, *Acta Chem. Scand.*, **B32**, 625 (1978).
37. M. F. Joucla and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, **1984**, 374.
38. M. R. Bryce and J. N. Heaton, *Tetrahedron Lett.*, **32**, 7459 (1991).
39. M. Takahashi, R. Okazaki and N. Inamoto, *Chem. Lett.*, **1989**, 2087.
40. Y. Inagaki, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **52**, 2002 (1979).
41. Y. Inagaki, T. Hosogai, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **53**, 205 (1980).
42. R. Okazaki, M. Unno and N. Inamoto, *Chem. Lett.*, **1987**, 2293.
43. M. R. Bryce and P. C. Taylor, *J. Chem. Soc., Chem. Commun.*, **1988**, 950.
44. M. R. Bryce and P. C. Taylor, *Tetrahedron Lett.*, **30**, 3835 (1989).
45. M. R. Bryce and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 3225.
46. R. Okazaki, M. Takahashi, N. Inamoto, T. Sugawara and H. Iwamura, *Chem. Lett.*, **1989**, 2083.
47. M. Takahashi, R. Okazaki, N. Inamoto, T. Sugawara and H. Iwamura, *J. Am. Chem. Soc.*, **114**, 1830 (1992).

48. M. Takahashi, Ph.D. Thesis, The University of Tokyo, 1990.
49. R. Mayer, S. Bleisch and G. Domschke, *Z. Chem.*, **18**, 323 (1978).
50. J. L. M. Dillen, O. Meth-Cohn, C. Moore and P. H. van Rooyen, *Tetrahedron*, **44**, 3127 (1988).
51. Y. Sawaki, S. Ishikawa and H. Iwamura, *J. Am. Chem. Soc.*, **109**, 584 (1987).
52. S. Ishikawa, S. Tsuji and Y. Sawaki, *J. Am. Chem. Soc.*, **113**, 4282 (1991).
53. W. J. Middleton, **U.S. US 3,344,135** (1967); *Chem. Abstr.*, **67**, 116823 (1967).
54. H. W. Roesky, R. Emmert, W. Isenberg, M. Schmidt and G. M. Scheldrick, *J. Chem. Soc., Dalton Trans.*, **1983**, 183.
55. G. Seitz and W. Overheu, *Chem.-Ztg.*, **103**, 230 (1979).
56. H. W. Roesky, R. Emmert, W. Clegg, W. Isenberg and G. M. Scheldrick, *Angew. Chem., Int. Ed. Engl.*, **20**, 591 (1981).
57. G. Tresoldi, G. Bruno, F. Crucitti and P. Piraino, *J. Organomet. Chem.*, **252**, 381 (1983).
58. G. Tresoldi, G. Bruno, P. Piraino, G. Faraone and G. Bombieri, *J. Organomet. Chem.*, **265**, 311 (1984).
59. G. Tresoldi, S. Sergi, S. L. Schiavo and P. Piraino, *J. Organomet. Chem.*, **322**, 369 (1987).
60. G. Tresoldi, S. Sergi, S. L. Schiavo and P. Piraino, *J. Organomet. Chem.*, **328**, 387 (1987).
61. M. Herberhold and A. F. Hill, *J. Organomet. Chem.*, **315**, 105 (1986).
62. A. Gieren, C. Ruiz-Pérez, T. Hübner, M. Herberhold and A. F. Hill, *J. Chem. Soc., Dalton Trans.*, **1988**, 1693.
63. S. Otsuka, T. Yoshida and A. Nakamura, *Inorg. Chem.*, **7**, 1833 (1968).
64. M. Herberhold and W. Bühlmeyer, *Angew. Chem., Int. Ed. Engl.*, **23**, 80 (1984).
65. R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers, J. D. Schagen, J. J. Zwinselman, A. R. Overbeek and C. H. Stan, *J. Organomet. Chem.*, **170**, 337 (1979).
66. For a review, M. Herberhold, *Nachr. Chem. Tech. Lab.*, **29**, 365-6, 368-9; *Chem. Abstr.*, **95**, 115630 (1981).
67. O. Glemser and W. Koch, *Angew. Chem., Int. Ed. Engl.*, **10**, 127 (1971).
68. R. Mews, *Angew. Chem., Int. Ed. Engl.*, **15**, 691 (1976).
69. G. Hartmann and R. Mews, *Angew. Chem., Int. Ed. Engl.*, **24**, 202 (1985).
70. G. Hartmann and R. Mews, *Z. Naturforsch.*, **40b**, 343 (1985).
71. B. W. S. Kolthammer and P. Legzdins, *J. Am. Chem. Soc.*, **100**, 2247 (1978).
72. T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins and J. Trotter, *Inorg. Chem.*, **18**, 3548 (1979).
73. T. J. Greenhough, B. W. S. Kolthammer, P. Legzdins and J. Trotter, *J. Chem. Soc., Chem. Commun.*, **1978**, 1036.
74. J. L. Hubbard and D. L. Lichtenberger, *Inorg. Chem.*, **19**, 1388 (1980).
75. J. Weiss and M. Ziegler, *Z. Naturforsch.*, **21b**, 891 (1966).
76. U. Thewalt and J. Weiss, *Z. Anorg. Allg. Chem.*, **348**, 238 (1966).
77. U. Thewalt and J. Weiss, *Z. Anorg. Allg. Chem.*, **352**, 225 (1967).
78. J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, **355**, 271 (1967).
79. U. Thewalt and J. Weiss, *Z. Naturforsch.*, **23b**, 1265 (1968).
80. J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, **363**, 159 (1968).
81. U. Thewalt, *Z. Naturforsch.*, **29b**, 308 (1974).
82. U. Thewalt, *Z. Anorg. Allg. Chem.*, **451**, 123 (1979).
83. M. B. Hursthouse, M. Motevalli, P. F. Kelly and J. D. Woollins, *Polyhedron*, **8**, 997 (1989).
84. P. F. Kelly and J. D. Woollins, *Polyhedron*, **8**, 2907 (1989).

NOTE ADDED DURING THE PROCESS OF PUBLICATION

A review on the generation of double bonded chalcogen compounds and their reactions for the synthesis of heterocyclic compounds was published during the preparation of this review.* Thionitroso compounds are described there as one of the heterodienophiles. The only report concerning a selenonitroso compound (RN=Se)** was also cited in the review.

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*M. R. Bryce, J. Becher, and B. Fält-Hansen, *Adv. Heterocycle. Chem.*, **55**, 1 (1992).

**C. L. Pedersen, *Tetrahedron Lett.* 745 (1979).