Journal of Organometallic Chemistry, 116 (1976) 1—13

S,N,N'-SUBSTITUTED SULFURDIIMINES AS LIGANDS

I. COMPOUNDS OF LITHIUM, MAGNESIUM, COPPER(I), SILVER(I) AND RHODIUM(I)

J. KUYPER, P.C. KEIJZER and K. VRIEZE *

Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, Amsterdam (The Netherlands)

(Received February 16th, 1976)

Summary

Treatment of *N,N'*-substituted sulfurdiimines RN=S=NR with Grignard reagents, alkyl- or aryl-lithium compounds affords *S,N,N'*-substituted sulfurdiimine complexes of lithium and magnesium. It is shown that these reactions may be used for simple, rapid, quantitative determinations of RMgX, R_2Mg and RLi.

Reactions of *S,N,N'*-substituted sulfurdiimino compounds of lithium with suitable copper(I), silver(I) and rhodium(I) compounds afford novel complexes in which the *S,N,N'*-substituted sulfurdiimine acts as a bridging or chelating ligand. X-ray structural information on a chelate rhodium(I) compound indicates an interesting similarity to the structure of η^3-allylmetal complexes.

These complexes eliminate azoarylic compounds from the coordinated ligand in a way which is dependent upon electronic and steric factors.

I. Introduction

Sulfurdiimines RN=S=NR, which may formally be regarded as pseudo-allenes, have been shown to bond to a metal atom in monodentate or bidentate fashion depending on the metal atom and on the substituent R [1—7]: apparently both *N*- and *S*-bonded isomers may be formed.

The interesting chemical properties of allenes, such as their insertion into metal—carbon and metal—halide bonds [8,9,10], prompted us to investigate the possibility of inserting RN=S=NR into metal—carbon bonds. In a preliminary communication [11] insertions of this type, which resulted in the formation of

---

* To whom correspondence should be addressed.

S,N,N'-substituted sulfurdiimino-lithium and -magnesium complexes were reported and shown to be useful for the quantitative determination of solutions of Grignard and alkyl- and aryl-lithium compounds *.

Further studies are now reported which show that novel complexes of the S,N,N'-substituted sulfurdiimines may be formed which copper(I), silver(I) and rhodium(I). The bonding in these complexes, which are related to both azenido [12,13,14] and sulfurdiimine compounds [1—7], is discussed in connection with a very interesting reaction which involves the elimination of azo compounds.

II. Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. All solvents were dried prior to use. The N,N'-substituted sulfurdiimines were prepared according to literature procedures [1,2,15—18], and $[Cu(O_2CCF_3)]_4 \cdot 2C_6H_6$ also [12].

A. The preparation of S,N,N'-sulfurdiimino-magnesium and -lithium compounds

As an example, the preparation of [S-methyl-N,N'-di-p-tolylsulfurdiimino-lithium] is given.

A solution of MeLi in ether was added dropwise to an orange solution of pure di-p-tolylsulfurdiimine (4.0 mmol) in ether (50 ml) at —20°C. The colour almost completely disappeared immediately after addition of exactly 4.0 mmol. (As the reaction is instantaneous and proceeds quantitatively it is very useful for titration procedures). The ethereal solution was concentrated and pentane was added. Cooling to —70°C afforded an off-white precipitate which was isolated in the cold in 70% yield.

The reactions with bis(p-chlorophenyl)-di-3,5-xylyl-, and di(2,4,6-mesityl-sulfurdiimines proceeded analogously. In the case of the rather insoluble bis(p-dimethylaminophenyl)- and bis(3,5-dichlorophenyl-sulfurdiimines, suspensions were used for reactions at —20 and 0°C, respectively. Preparations with dialkyl sulfurdiimines (alkyl = Me, Et, i-Pr and t-Bu) proceeded analogously. The change in colour at the equivalence point is much less pronounced.

For reactions involving EtLi, p-tolyllithium and 2,4,6-mesityllithium temperatures of —20°C were used, while in the case of i-PrLi and t-BuLi the reactions were carried out at —40°C. Reaction temperatures of about 0—20°C were used for reactions involving MeMgX (X = Cl, Br, I), EtMgBr, i-PrMgBr, t-BuMgCl, 2-methallylmagnesium bromide, p-tolylmagnesium bromide, Me_2Mg and Et_2Mg. In the case of 2,4,6-mesitylmagnesium bromide the sulfurdiimine should be added to the Grignard reagent.

All products are soluble in ether and benzene whilst decomposition takes place in acetone and halogenated solvents. The compounds are very susceptible to hydrolysis.

B. Preparation of S,N,N'-substituted sulfurdiimino-copper(I) and -silver(I) compounds

The preparations of two representative compounds are given below.

[Cu{S-t-Bu-N,N'-di-p-tolyl-NSN}]. $[Cu(O_2CCF_3)]_4 \cdot 2C_6H_6$ (½ mol) was added in one portion to a solution of {S-t-Bu-N,N'-di-p-tolyl-NSN}Li (2 mmol)

---

* *Note added in proof:* A reaction of $(CH_3)_3SiN{=}S{=}NSi(CH_3)_3$ with methyllithium has been reported [35].

in ether (20 ml) below —20°C. A rapid reaction occurred and a white precipitate was formed. After stirring for 5 minutes at 0°C the precipitate was collected by filtration and washed several times with ether. The yield was 65%.

[Cu{S-t-Bu-N,N'Me$_2$-NSN}]. [Cu(O$_2$CCF$_3$]$_4$ · 2C$_6$H$_6$ (0.75 mol) was added in one portion to a solution of {(*S*-t-Bu-*N*,*N'*-Me$_2$-NSN}Li (3 mmol) in ether (20 ml) at —40°C. After stirring for five minutes at 0°C the ether was removed under reduced pressure. The residue was extracted with 20 ml hexane. After filtration the solution was concentrated under vacuum to 10 ml and pentane was added. After cooling to —80°C the compound was obtained as light yellow crystals in 50% yield.

All copper compounds reported in this article were prepared similarly. The silver complexes were obtained analogously from silver trifluoroacetate in similar yields. They could also be prepared in lower yields from AgClO$_4$. In this case the products were recrystallised from CH$_2$Cl$_2$/hexane. It should be noted, in particular, that the silver compounds derived from *N*,*N'*-di-2,4,6-mesityl- and *N*,*N'*-bis(*p*-dimethylaminophenyl)sulfurdiimine are very unstable and should be kept in the cold.

The other compounds are generally fairly stable in air with the exception of compounds obtained from dialkylsulfurdiimines (alkyl ≠ t-Bu), which are susceptible to moisture.

The complexes derived from dialkylsulfurdiimines are in general very soluble in most solvents e.g. hexane, chloroform, benzene, whereas the diarylsulfurdiimine derivatives are soluble in chloroform and dichloromethane.

C. *Preparation of S,N,N'-substituted sulfurdiiminorhodium(I) compounds*

Several preparations are described as they differ in each case.

[Rh(CO)$_2${S-t-Bu-N,N'-di-2,4,6-mesityl-NSN}]. [Rh(CO)$_2$Cl]$_2$ (1 mmol) in hexane (30 ml) was added in about 1 minute to a stirred solution of {*S*-t-Bu-*N*,*N'*-*di*-2,4,6-mesityl-NSN}Li (2 mmol) in ether (20 ml) at —20°C. A rapid reaction occurred and after a few minutes a precipitate was formed. After stirring for 5 minutes at 0°C, about 20 ml of solvent was removed under vacuum, the precipitate was obtained by filtration and washed with hexane. Recrystallisation from hot benzene afforded yellow crystals of the compound in 65% yield.

[Rh(CO)$_2${S-t-Bu-N,N'-di-p-tolyl-NSN}]. [Rh(CO)$_2$Cl]$_2$ (1 mmol) in hexane (30 ml) was added in 1 minute to a stirred solution of {*S*-t-Bu-*N*,*N'*-di-*p*-tolyl-NSN}Li (2 mmol) in ether (20 ml) at —60°C. After 5 minutes the temperature was raised to —10°C and 40 ml of solvent was distilled under vacuum. Subsequently LiCl was removed by filtration and pentane (40 ml) was added to the clear dark solution. After cooling rapidly to —80°C cream yellow crystals were obtained in 70% yield. The compound slowly decomposed in the solid state while in solution decomposition occurred above 0°C.

The analogous *S*-methyl-, *S*-ethyl- and *S*-i-propyl-di-2,4,6-mesitylsulfurdiimine compounds were prepared similarly. These compounds and their solutions decomposed very slowly in air at room temperature.

[Rh(PPh$_3$)(CO){RNS(R')NR}] with R = 2,4,6-mesityl and R' = methyl, ethyl, i-propyl and t-butyl; R = p-tolyl, p-chlorophenyl and R' = t-butyl. Triphenylphosphine (2 mmol) in ether (10 ml) was added dropwise in 1 minute

to a hexane solution (20 ml) or suspension of [$Rh(CO)_2${RNS(R')NR}] (2 mmol) at −20°C. Rapid CO evolution was observed. After 5 minutes stirring the yellow precipitate was collected by filtration, washed with ether and hexane and vacuum dried for two hours. The compounds, which were observed in 80—90% yield, are air-stable and soluble in chloroform and benzene.

[Rh(PPh$_3$)(CO) {S-t-Bu-N,N'-t-Bu-NSN}]. A solution of [$Rh(CO)_2$ {*S*-t-Bu-*N,N'*-t-Bu_2-NSN{] (2 mmol) in ether (20 ml) was prepared by adding [$Rh(CO)_2$-$Cl]_2$ (1 mmol) to a solution of {*S*-t-Bu-*N,N'*-t-Bu_2-NSN}Li (2 mmol) in ether at −30°C. The solvent was removed under vacuum at 0°C and cold hexane (−20°C) was added (20 ml). LiCl was removed by filtration. PPh_3 (2 mmol) in ether (10 ml) was added dropwise at −20°C within 1 minute. Stirring was continued for another 3 minutes. Subsequently the solvent was removed at 10°C and the residue was dissolved in a minimum amount of hexane. Pentane was then added and the mixture was cooled to −70°C. The yellow compound was obtained in 70% yield. The complex is quite air-stable and is very soluble in most common solvents.

An alternative preparation of [Rh(PPh$_3$)(CO){S-t-Bu-N,N'-di-p-tolyl-NSN}]. {*S*-t-Bu-*N,N'*-di-*p*-tolyl-NSN}Li (2 mmol) in cold ether (20 ml) was added slowly to a stirred solution of [$(Ph_3P)_2(CO)Rh(ClO_4)$] (2 mmol) in benzene (30 ml) at 5°C. After 15 minutes the solution was filtered and subsequently concentrated under vacuum to a small volume. Hexane was added and the yellow precipitate was recrystallised from benzene/hexane (yield 55%). If the same procedure is used for {*S*-Me-*N,N'*-di-*p*-tolyl-NSN}Li azotoluene is mainly formed instead of the rhodium complex. Attempts to prepare iridium complexes in this way were unsuccessful, as only azotoluene was isolated in high yield.

D. Reactions of the complexes

Reactions of the magnesium and lithium compounds. Attempts were made to isolate the free *S*-alkyl-*N,N'*-diarylsulfurdiimine acids by hydrolysis, reaction with HCl or with acetic acid. Only the free amines, however, could be identified, by NMR, amongst the products. Interestingly, it was found, that reactions of the lithium compounds with CH_3I afforded azoarylic compounds.

Reactions of the copper and silver and rhodium compounds. Addition of one or more equivalents of PPh_3 to suspensions or solutions of [Cu{RNS(R')NR}$]_2$ (R = aryl, R' = alkyl) or of the analogous silver compounds in chloroform afforded, in some cases, intermediate complexes, as was observed by the appearance of new signals in the NMR spectra. These unstable complexes decompose into azoaryls and also into arylamines if moisture is present. Although the rate of the azoaryl and arylamine formations depends upon the amount of PPh_3 added, the final composition of the products is always the same. The azoaryls could be isolated and recrystallised from pentane or hexane.

In one case the intermediate phosphine complex is fairly stable and the following compound could be isolated:

[Ag(PPh$_3$)$_2${S-Me-N,N'-(3,5-Cl$_2$C$_6$H$_3$)$_2$NSN}]. PPh_3 (2.0 mmol) was added to a suspension of [Ag{*S*-Me-*N,N*-(3,5-$Cl_2C_6H_3)_2$NSN}$]_2$ (0.5 mmol) in dichloromethane (5 ml) at 0°C and a clear solution was obtained. Subsequently the solution was concentrated to a small volume (~1 ml) and cold hexane (5 ml)

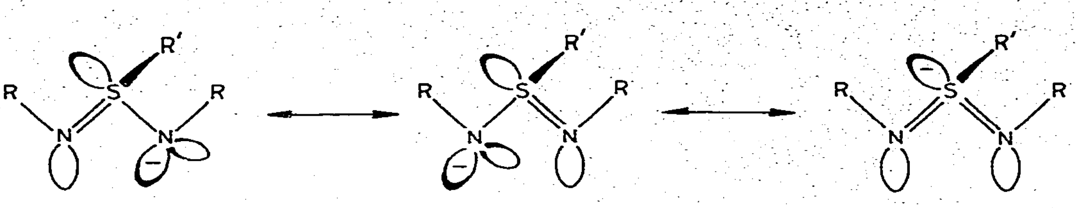
TABLE 1

ANALYTICAL DATA FOR *S,N,N'*-SUBSTITUTED SULFURDIIMINO-LITHIUM, -COPPER(I), -SILVER(I) AND -RHODIUM(I) COMPOUNDS

Compound [a]	Analysis: found (calcd. %)			
	C	H	S [b]	N
Li{*S*-t-Bu-*N,N'*-t-Bu$_2$-NSN}	59.95	11.35	12.81	12.04
	(60.46)	(11.42)	(13.45)	(11.75)
Li{*S*-t-Bu-*N,N'*-di-*p*-tolyl-NSN} · O(C$_2$H$_5$)$_2$	69.19	8.77	8.60	7.25
	(69.44)	(8.74)	(8.43)	(7.36)
Li{*S*-Ph-*N,N'*-t-Bu$_2$NSN} · $\frac{1}{2}$O(C$_2$H$_5$)$_2$	64.75	9.58	10.73	9.40
	(65.05)	(9.55)	(10.85)	(9.49)
Cu{*S*-t-Bu-*N,N'*-Me$_2$-NSN}	34.49	7.15		
	(34.18)	(7.17)		
Cu{*S*-Me-*N,N'*-i-Pr$_2$-NSN}	37.60	7.57		
	(37.39)	(7.62)		
Cu{*S*-Me-*N,N'*-di-*p*-tolyl-NSN} [c]	55.77	5.17		
	(56.14)	(5.34)		
Cu{*S*-Et-*N,N'*-di-*p*-tolyl-NSN}	57.47	5.96		
	(57.37)	(5.72)		
Cu{*S*-i-Pr-*N,N'*-di-*p*-tolyl-NSN}	58.60	6.16		
	(58.51)	(6.07)		
Cu{*S*-t-Bu-*N,N'*-di-*p*-tolyl-NSN} [c]	59.30	6.26		
	(59.56)	(6.39)		
Cu{*S*-t-Bu-*N,N'*-(4-ClC$_6$H$_4$)$_2$NSN}	48.24	4.60		
	(47.58)	(4.24)		
Cu{*S*-Me-*N,N'*-(4-CH$_3$)$_2$NC$_6$H$_4$)$_2$NSN}	53.35	6.43		
	(53.87)	(6.12)		
Cu{*S*-Me-*N,N'*-(4-CH$_3$O-C$_6$H$_4$)$_2$NSN}	50.65	4.73		
	(61.04)	(4.86)		
Ag{*S*-Me-*N,N'*-t-Bu$_2$-NSN}	36.64	7.14	10.19	
	(36.37)	(7.12)	(10.79)	
Ag{*S*-Et-*N,N'*-di-*p*-tolyl-NSN} [c]	50.52	5.31	7.70	
	(50.67)	(5.05)	(8.45)	
Ag{*S*-Me-*N,N'*-di-2,4,6-mesityl-NSN}	53.73	5.97	7.33	
	(54.16)	(5.98)	(7.61)	
Ag{*S*-Me-*N,N'*-(3,5-Cl$_2$C$_6$H$_3$)$_2$NSN}	32.96	1.86	6.65	
	(32.87)	(1.91)	(6.75)	
Ag(PPh$_3$)$_2${*S*-Me-*N,N'*-(3,5-Cl$_2$C$_6$H$_3$)$_2$NSN}	58.51	3.99	3.21	
	(58.88)	(3.91)	(3.21)	
Rh(CO)$_2${*S*-Me-*N,N'*-di-2,4,6-mesityl-NSN} [d]	53.01	5.29	6.32	
	(53.39)	(5.33)	(5.79)	
Rh(CO)$_2${*S*-t-Bu-*N,N'*-di-2,4,6-mesityl-NSN} [d]	57.08	6.09	6.06	
	(56.03)	(6.07)	(6.23)	
Rh(CO)$_2${*S*-Bu-*N,N'*-di-*p*-tolyl-NSN}	53.17	5.44	6.14	
	(52.40)	(5.06)	(6.99)	
Rh(CO)(PPh$_3$){*S*-t-Bu-*N,N'*-di-*p*-tolyl-NSN} [d]	64.06	5.36	4.69	
	(64.15)	(5.53)	(4.63)	
Rh(CO)(PPh$_3$){*S*-Bu-*N,N*-t-Bu$_2$-NSN}	59.60	6.89	5.42	
	(59.61)	(6.78)	(5.13)	

---

[a] The lithium compounds are white, the copper(I) and silver(I) compounds white or slightly yellow, the rhodium(I) compounds yellow or cream. [b] No sulfur analysis of the copper compounds could be obtained owing to the method of analysis (Schöninger). [c] Molecular weight within 10% of the calculated weight of the dimer. [d] Molecular weight within 10% of the calculated weight of the monomer.



(I) (I′) (II)

Fig. 1. Possible structures for the *S,N,N′*-substituted sulfurdiimino ligand.

was added. After filtration and crystallization at —35°C the compound was obtained as white air-stable crystals in 70% yield. It should be noted that if less than 2,0 mmol PPh_3 was added the same compound was isolated, in lower yield.

If $CHCl_3$solutions of [Rh(CO)L{RNS(R′)NR}], (L = CO, PPh_3; R = 2,4,6-mesityl; R′ = Me, Et, i-Pr, t-Bu), were kept at ambient temperature, azomesitylene was formed slowly in the case of R′ = Me, Et and i-Pr, but not with R′ = t-Bu. After two days the amounts of azomesitylene formed were ~40% (R′ = Me), ~30% (R′ = Et) and 10% (R′ = i-Pt). The rates and the amounts were somewhat higher for L = PPh_3 than for CO. C, H and S analysis were carried out in

TABLE 2

^{1}H NMR DATA FOR *S,N,N′*-SUBSTITUTED SULFURDIIMINO LITHIUM AND MAGNESIUM COMPOUNDS (in C_6D_6), δ (Cu^I) AND δ(Ag^I) (in $CDCl_3$) IN ppm RELATIVE TO TMS

Compound	*N*-Aryl or *N*-alkyl		*S*-Alkyl
Li{*S*-Me-*N,N′*-i-Pr_2-NSN}		3.43, 1.25	2.36
Li{*S*-t-Bu-*N,N′*-t-Bu_2-NSN}		1.34	1.20
Li{*S*-Ph-*N,N′*-t-Bu_2-NSN}		1.33	
Li{*S*-Me-*N,N′*-di-*p*-tolyl-NSN}	6.90, 6.85	2.16	2.60
Li{*S*-phenyl-*N,N′*-di-*p*-tolyl-NSN}	6.95	2.21	
Mg{*S*-*o*-tolyl-*N,N′*-di-3,5-xylyl-NSN} · $O(C_2H_5)_2$	6.85, 6.38	2.10	2.73 [a]
Cu{*S*-Me-*N,N′*-i-Pr_2-NSN}		3.34, 1.22, 1.05	2.71
Cu{*S*-t-Bu-*N,N′*-Me_2-NSN}		3.01	1.31
Cu{*S*-Me-*N,N′*-di-*p*-tolyl-NSN}	6.96	2.21	2.97
Cu{*S*-Et-*N,N′*-di-*p*-tolyl-NSN}	6.98	2.22	3.26, 1.30
Cu{*S*-i-Pr-*N,N′*-di-*p*-tolyl-NSN}	6.98	2.22	3.40, 1.38
Cu{*S*-t-Bu-*N,N′*-di-*p*-tolyl-NSN}	7.08, 6.93	2.22	1.40
Cu{*S*-t-Bu-*N,N′*-$(4\text{-}ClC_6H_4)_2$NSN}	7.09		1.40
Cu{*S*-t-Bu-*N,N′*-$(4\text{-}CH_3)_2NC_6H_4)_2$NSN} [b]	7.11, 6.66	2.83	1.42
Ag{*S*-Me-*N,N′*-di-*p*-tolyl-NSN}	6.93	2.21	2.78
Ag{*S*-Et-*N,N′*-di-*p*-tolyl-NSN}	6.93	2.20	2.93, 1.26
Ag{*S*-i-Pr-*N,N′*-di-*p*-tolyl-NSN}	6.93	2.20	2.78, 1.38
Ag{*S*-t-Bu-*N,N′*-di-*p*-tolyl-NSN}	7.00, 6.94	2.21	1.34
Ag{*S*-Me-*N,N′*-di-3,5-xylyl-NSN}	6.71, 6.42	2.19	2.79
Ag{*S*-Me-*N,N′*-di-2,4,6-mesityl-NSN} [b]	6.74	2.36, 2.17	3.06
Ag{*S*-Me-*N,N′*-$(4\text{-}CH_3OC_6H_4)_2$NSN}	6.93, 6.67	3.69	2.83
Ag{*S*-Me-*N,N′*-$(3,5\text{-}Cl_2C_6H_3)_2$NSN}	6.87		2.85
Ag{*S*-Me-*N,N′*-t-Bu_2-NSN}		1.26	2.43
$Ag(PPh_3)_2${*S*-Me-*N,N′*-$(3,5\text{-}Cl_2X_6H_3)_2$NSN}	6.44, 6.27		2.19

[a] Methyl resonance of the *o*-tolyl group. [b] Elimination of azoaryls in solution.

this laboratory (Table 1). ^{1}H NMR data were obtained with a Varian T60 and HA 100 spectrometer and IR data with a Beckmann 4250 spectrometer.

III. Results

A. S,N,N'-Substituted sulfurdiimino-lithium and -magnesium compounds

These compounds were obtained by a facile and quantitative reaction:

$$\mathrm{RNSNR} + \mathrm{R'M}\ (\mathrm{M} = \mathrm{Li, MgX}) \rightarrow \mathrm{M\{RNS(R')NR\}} \quad (1)$$

The exact configuration of the products is not known, however, NMR data show that the R groups are equivalent at ambient temperature. (In the case of the diarylsulfurdiimines there is a pronounced dissappearance of the colour at the equivalence point. This makes the reaction very useful for the titration of Grignard and alkyl- or aryl-lithium solutions [11]).

Two structures may, in principle, exist (Fig. 1) for the ligand which in each case may be regarded formally as a uninegative anion. Both situations are in accord with the NMR data (Table 2).

The complexes are very susceptible to hydrolysis, but it was impossible to form the *S,N,N'*-substituted sulfurdiiminic acid, even with the use of HCl (in ether) or HOAc. Of interest is the reaction of {*S*-Me-*N,N'*-di-*p*-tolylsulfurdiimino}-lithium with CH_3I, which afforded azotoluene as a product.

B. S,N,N'-Substituted sulfurdiimino-copper(I) and -silver(I)

Compounds of the general formula $[\mathrm{M\{RNS(R')NR\}}]_2$ were obtained by the reaction of $[\mathrm{M(O_2CCF_3)}]_n$ ($\mathrm{M} = \mathrm{Cu^I}, \mathrm{Ag^I}$) with $[\mathrm{Li\{RNS(R')NR\}}]$. Molecular weight (Table 1) and ^{1}H NMR data (Table 2) indicate that the ligand is bridging (Fig. 2), while the orientation of the R' group and of the free electron pair on sulfur is rigid as can be concluded from the *S*-Me-*N,N'*-di-isopropylsulfurdiiminocopper(I) compound.

The IR data (Table 3) show that the NSN asymmetric vibration is in the range of 1180 to 1260 cm^{-1}, whereas a strong vibration in the range of 840—910 cm^{-1} can probably be ascribed to the symmetric vibration.

The stability of the compounds is clearly dependent on steric and electronic factors. Most of the compounds are quite stable in solution or as a solid, but the *p*-dimethylamino-copper and -silver compounds decompose rapidly in solution while the *p*-methoxy and 2,4,6-mesityl compounds decompose slowly in solu-

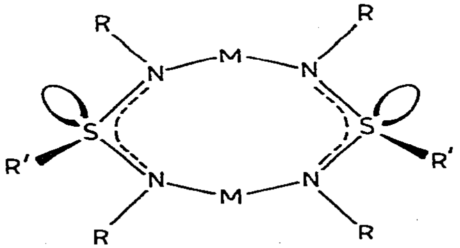


Fig. 2. Proposed structure of the copper(I) and silver(I) *S,N,N'*-substituted sulfurdiimino compounds.

TABLE 3

INFRARED DATA (Nujol, cm^{-1}) FOR *S,N,N'*-SUBSTITUTED SULFURDIIMINO COPPER(I), SILVER(I) AND RHODIUM(I) COMPOUNDS

Compound	ν(CO)	ν(NSN)[a]	
Cu{*S*-Me-*N*,*N'*-di-*p*-tolyl-NSN}		1245, 1230	902
Cu{*S*-t-Bu-*N*,*N'*-di-*p*-tolyl-NSN}		1239, 1227	918
Cu{*S*-t-Bu-*N*,*N'*-$(4\text{-ClC}_6\text{H}_4)_2$NSN}		1243, 1229	915, 900
Cu{*S*-Me-*N*,*N'*-$(4\text{-CH}_3\text{OC}_6\text{H}_4)_2$NSN}		1235, 1212	899
Cu{*S*-Bu-*N*,*N'*-$(4\text{-Me}_2\text{NC}_6\text{H}_4)_2$NSN}		1228, 1210	900
Ag{*S*-Me-*N*,*N'*-di-*p*-tolyl-NSN}		1243, 1223	918
Ag{*S*-t-Bu-*N*,*N'*-di-*p*-tolyl-NSN}		1240, 1226	906
Ag{*S*-Me-*N*,*N'*-di-2,4,6-mesityl-NSN}		1235, 1211	908
Ag{*S*-Me-*N*,*N'*-$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_2$NSN}		1255, 1232	945
Rh(CO)_2 {*S*-t-Bu-*N*,*N'*-di-*p*-tolyl-NSN}	2053, 1982	1235	901, 847
Rh(CO)_2 {*S*-Me-*N*,*N'*-di-2,4,6-mesityl-NSN}	2049, 1991	1211	891, 849
Rh(CO)_2 {*S*-Et-*N*,*N'*-di-2,4,6-mesityl-NSN}	2051, 1990	1213	855
Rh(CO)_2 {*S*-t-Bu-*N*,*N'*-di-2,4,5-mesityl-NSN}	2048, 1983	1209	854
$\text{Rh(CO)(PPh}_3)$ {*S*-t-Bu-*N*,*N'*-di-*p*-tolyl-NSN}	1966	1234	904, 842
$\text{Rh(CO)(PPh}_3)$ {*S*-t-Bu-*N*,*N'*-t-Bu_2-NSN}	1963	1180	928

[a] Frequencies characteristic for this group.

tion and the corresponding azoaryls are formed. These compounds also decompose very slowly in the solid state. In the case of R = 2,4,6-mesityl this may be due, as models indicate, to unfavourable steric interaction of the *o*-methyl groups with the metal atom, and in the other cases to the strong electron-donating substituents on the phenyl group.

Electronic factors are particularly noticeable for the systems with *p*-substituted R groups when PPh_3 is added to chloroform solutions of the copper(I) and silver(I) compounds. The rate of decomposition, which involves the formation of azoaryls and some arylamine, decreases in the order $(\text{CH}_3)_2\text{N} > \text{CH}_3\text{O} > \text{CH}_3 > \text{Cl}$ for the *p*-substituents on the R group. The amount of azoaryls formed various from 100% ($(\text{CH}_3)_2\text{N}$) to ~50% (Cl).

It should be noted that the compounds with a *p*-$(\text{CH}_3)_2$N-substituent on the R group are particularly unstable, the copper compound being the only one which could be isolated pure. Furthermore a decrease was observed in the order R = 3,5-xylyl ~ *p*-tolyl > *p*-ClC_6H_4 > 3,5-$\text{Cl}_2\text{C}_6\text{H}_3$, Ag > Cu and R′ = Me > t-Bu.

The decomposition probably proceeds via intermediate metal—phosphine complexes, which are slowly formed in the case of copper(I) and rapidly in the case of silver(I), as could be deduced from the appearance of new signals in the NMR spectra in some cases. From the reaction of [Ag{*S*-Me-*N*,*N'*-bis$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)$-NSN}]$_2$ with PPh_3 such an intermediate complex could be isolated since it is fairly stable. According to NMR and elemental analysis the composition is [$\text{Ag(PPh}_3)_2$ {*S*-Me-*N*,*N'*-bis$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)$NSN}].

C. S,N,N'-Substituted sulfurdiiminorhodium(I) compounds

The preparation of the rhodium(I) compounds proceeded via reaction 2.

$$\tfrac{1}{2}[\text{Rh(CO)}_2\text{Cl}]_2 + \text{Li}\{\text{RNS(R')NR}\} \rightarrow \text{Rh(CO)}_2\{\text{RNS(R')NR}\} + \text{LiCl} \qquad (2)$$

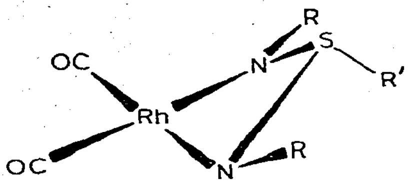


Fig. 3. Structure of $Rh(CO)_2$ {*S*-t-Bu-*N*,*N'*-di-2,4,6-mesityl-NSN}.

Stable products were obtained for R = mesityl and R' = alkyl, while an unstable product was isolated in the case of R = *p*-tolyl and R' = t-Bu. The complex [$Rh(CO)_2$ {t-BuNS(t-Bu)B-t-Bu}] was clearly formed in solution, but its extreme solubility made its isolation impossible.

Molecular weight (Table 1) and ^1H NMR measurements (Table 4) indicated the structure shown in Fig. 3. A sterically-hindered rotation was observed for R = 2,4,6-mesityl, if R' = Me, Et and much slower for i-Pr, at ambient temperature, while there is no rotation if R' = t-Bu. Only in the last case is the compound indefinitely stable at room temperature, whereas the other compounds decompose slowly in solution and azomesitylene is formed.

Preliminary single crystal X-ray data on [$Rh(CO)_2$ {*S*-t-Bu-*N*,*N'*-di-2,4,6-mesityl-NSN}] [19] have confirmed the proposed structure. In addition it has been shown that the S atom is not in the RhN_2 plane, while the R groups are also outside the RhN_2 plane (Fig. 3).

Of interest is that addition of PPh_3 to solutions of the complexes resulted in the formation of stable species, [$Rh(PPh_3)(CO)$ {RNS(R')NR}] (eq. 3). The

$$Rh(CO)_2\{RNS(R')NR\} + PPh_3 \rightarrow Rh(PPh_3)(CO)\{RNS(R')NR\} + CO \qquad (3)$$

yields were nearly quantitative. Addition of another equivalent of PPh_3 did not give further substitution, although decomposition occurred in a few cases.

Only the phosphine-substituted compounds of the *S*-t-Bu-sulfurdiimines are stabler than the $Rh(CO)_2$ compounds. Except for rotation of only one of the mesityl rings in the corresponding *S*-substituted Me, Et and i-Pr compounds, the structure is rigid in solution at ambient temperature, as shown by the inequivalency of the R groups; the rotation is similar in behaviour but more rapid than in the case of the dicarbonyl analogues. Also in the case of the *S*-substituted Me, Et and i-Pr compounds slow decomposition of the compounds and the formation of azomesitylene occur in solution. An important observation is that these compounds may also be prepared according to eq. 4. This indicates that the sulfur-

$$Rh(PPh_3)_2(CO)ClO_4 + Li\{RNS(R')NR\} \rightarrow Rh(PPh_3)(CO)\{RNS(R')NR\} + PPh_3 \qquad (4)$$

diimino ligand has a strong chelating tendency, since one of the PPh_3 groups is replaced. The analogous reaction with the iridium analogue, however, resulted in the formation of azo compounds.

IV. Discussion

The experimental results obtained for the metal compounds of the previously-unknown *S*,*N*,*N'*-substituted sulfurdiimino ligands show several interesting

TABLE 4

^{1}H NMR DATA FOR *S,N,N′*-SUBSTITUTED SULFURDIIMINORHODIUM COMPOUNDS

Compound	Solvent	*N*-Aryl [a] or *N*-alkyl [a]	CH_3(aryl) [b]	*S*-Alkyl
Rh(CO)$_2$ {*S*-t-Bu-*N,N′*-di-*p*-tolyl-NSN}	C_6D_6	7,05, 6,87	2,09	0,94
Rh(CO)$_2$ {*S*-Me-*N,N′*-di-2,4,6-mesityl-NSN}	$CDCl_3$	6,81	2,61(br), 2,21	2,38
Rh(CO)$_2$ {*S*-Et-*N,N′*-di-2,4,6-mesityl-NSN}	$CDCl_3$	6,82	2,62(br), 2,20	2,65, 0,86
Rh(CO)$_2$ {*S*-i-Pr-*N,N′*-di-2,4,6-mesityl-NSN}	$CDCl_3$	6,77	2,73(br), 2,57(br), 2,20	0,88
Rh(CO)$_2$ {*S*-t-Bu-*N,N′*-di-2,4,6-mesityl-NSN}	$CDCl_3$	6,74	2,85, 2,53, 2,18	0,92
Rh(CO)$_2$ {*S*-t-Bu-*N,N′*-di-2,4,6-mesityl-NSN}		6,75	2,94, 2,65, 2,09	0,70
Rh(CO)(PPh$_3$) {*S*-t-Bu-*N,N′*-t-Bu$_2$-NSN}	$CDCl_3$	1,47		0,91
		1,30		
Rh(CO)(PPh$_3$) {*S*-t-Bu-*N,N′*-di-*p*-tolyl-NSN}	$CDCl_3$	6,37	2,01	1,31
		7,00, 6,92	2,20	
Rh(CO)(PPh$_3$) {*S*-t-Bu-*N,N′*-(4-ClC$_6$H$_4$)$_2$NSN}	$CDCl_3$	6,48, 6,33		1,29
		7,00		
Rh(CO)(PPh$_3$) {*S*-Me-*N,N′*-di-2,4,6-mesityl-NSN}	C_6D_6	6,47, 6,34	2,56, 2,05, 1.90	2,16
			3,04(br) , 2,05	
Rh(CO)(PPh$_3$) {*S*-Et-*N,N′*-di-2,4,6-mesityl-NSN}	$CDCl_3$	6,45, 6,28	2,83(2x) , 2,20	2,57, 0.79
		6,84	2,38, 2,09, 1,95	
Rh(CO)(PPh$_3$) {*S*-t-Bu-*N,N′*-di-2,4,6-mesityl-NSN}	C_6D_6	6,46, 6,13	2,72, 2,13, 2,02	0.82
			3,36, 2,97, 2,13	

---

[a] In the case of inequivalent aryl or alkyl groups the data are put on consecutive lines. [b] The CH_3 groups substituted on the aryl ring. (br) broadened by rotation of one or both mesityl groups.

structural and chemical features.

The first point of interest is the structure of $[Rh(CO)_2\{S$-t-Bu-N,N'-di-2,4,6-mesitylene-NSN$\}]$ (Fig. 3) which shows an interesting resemblance to the structure of the η^3-allyl palladium complexes [20,21], since the NSN plane is not coplanar with the RhN_2 plane. The sulfur atom is about 0.5 Å out of the plane. This is different from the structures of $W(CO)_4$(t-BuN=S=N-t-Bu) [5], of $(\eta^5$-$C_5H_5)(CO)_2Mo\{(3,5$-$(CF_3)_2C_6H_3)_2N_3\}$ [22] and of $Co(Ph_2N_3)_3$ [23], in which the metal atom lies in the plane of the NSN- and NNN-units, respectively. Furthermore, the preliminary structural data seem to indicate, that the N—S bonds (~1.65 Å) are longer than in e.g. MeN=S=NMe (1.53 Å; from electron diffraction data [27]) while the Rh—N bonds appear to be rather short (~2.05 Å) (cf. Rh—N 2.12 Å in $[(Ph_3P)_2(CO)RhCu(Me_2N_3)Cl]$ [25], which would indicate delocalization of the bonding electrons in the RhNSN unit. The short Rh···S distance of about 2.70 Å is also remarkable.

The dimeric structure of the copper(I) and the silver(I) complexes $[M\{RNS(R')NR\}]_2$ shows that, by analogy with the triazenido complexes of a number of metal atoms (e.g. copper(I), silver(I) and palladium(II) [12,13,26—29]), the S,N,N'-sulfurdiimine ligand may also acts as a bridging ligand (Fig. 2). No structural conclusions can be drawn from the data for the lithium(I) and magnesium(I) complexes, but it seems likely that bridging or chelating ligands are present, in view of the preference of these metal atoms for four-coordination.

It is important to note that no monodentate S,N,N'-substituted sulfurdiimines have as yet been found, whereas monodentate triazenido groups are known as e.g. in $[(Ph_3P)_2(CO)Ir\{(p$-tolyl$)_2N_3\}]$ [13,27,30]. Indeed, reaction 4 clearly seems to indicate that the ligand, rather than staying in the monodentate form, prefers to substitute one PPh_3 group so that it may act as a chelate. When this reaction was carried out with iridium instead of rhodium the analogous complex was not formed but formation of an azo compound was observed. The Ir—PPh_3 bond is probably too strong for substitution to occur. The intermediate monodentate S,N,N'-sulfurdiiminoiridium complex, which is probably formed, is clearly unstable in view of the observed decomposition.

Further investigations of the elimination of the azo compounds from the complexes reported here have revealed the influence of steric and electronic factors and the probable importance of monodentate S,N,N'-sulfurdiimines as intermediates in the elimination reactions. For example, strong electron-donating substituents in the *para* position of the R groups appear to promote formation of the azoaryls, as do bulky * 2,4,6-mesityl groups R in the case of the dimeric copper(I) and silver(I) complexes. It is important to note that the rate of this elimination increases when PPh_3 is added to solutions of the dimeric copper(I) and silver(I) complexes. The addition of PPh_3 probably causes Cu—N or Ag—N bond rupture and the formation of monodentate S,N,N'-sulfurdiimino groups, which then rapidly decompose into azo compounds. Very interesting also is the elimination of azomesitylene from the corresponding rhodium complexes. This process might start with the formation of a Rh—S bond, which is reasonable in view of the short Rh···S distance (~2.70 Å), probably via an inter-

---

* In the case of the complexes of rhodium(I) bulky R groups stabilize the chelate situation. This has been noted previously [4,5].

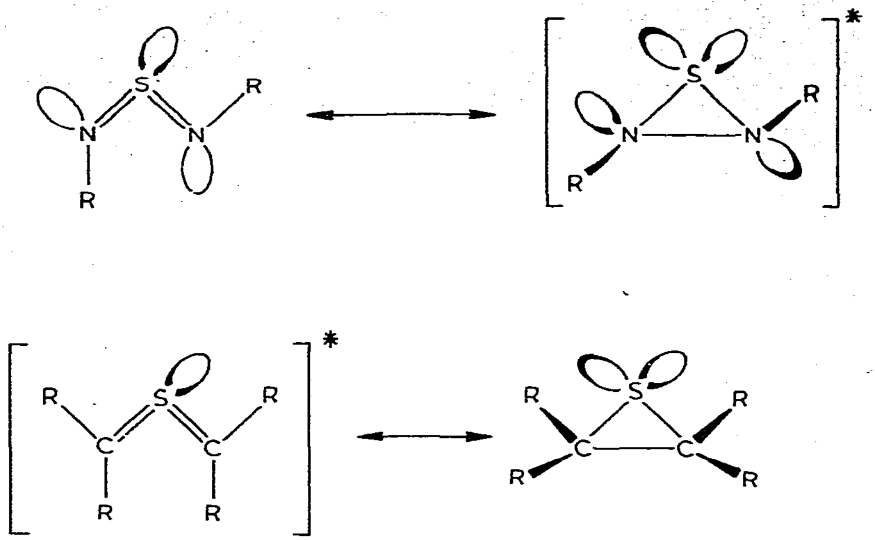


Fig. 4. Relationship between episulfides and *N,N'*-substituted sulfurdiimines.

mediate π-allyl type coordination and subsequent rupture of the Rh—N bonds. The order of stability of these compounds is *S*-t-Bu(stable) > *S*-i-Pr > *S*-Et > *S*-Me. This agrees with the above picture as the formation of an Rh—S bond is not possible in the case of the *S*-t-Bu compound, since this is prevented by the *o*-methyls of the mesityl groups, which do not rotate in this compound, but is possible in the other cases where the mesityl group rotates and the azomesitylene formation is also faster and greater if the rotation is faster.

Although, as is clear from the above discussion, it is not possible to deduce with any certainty the mechanism of the decomposition reaction, it seems profitable to refer to the reaction of episulfides with LiR, which results in removal of sulfur and stereoselective formation of *cis*, or *trans* olefins depending on the configuration of the starting product [31]. In Fig. 4 the structural relationship between the episulfides and *N,N'*-substituted sulfurdiimines is shown.

If this formal analogy is extended to the decomposition reaction, the mecha-

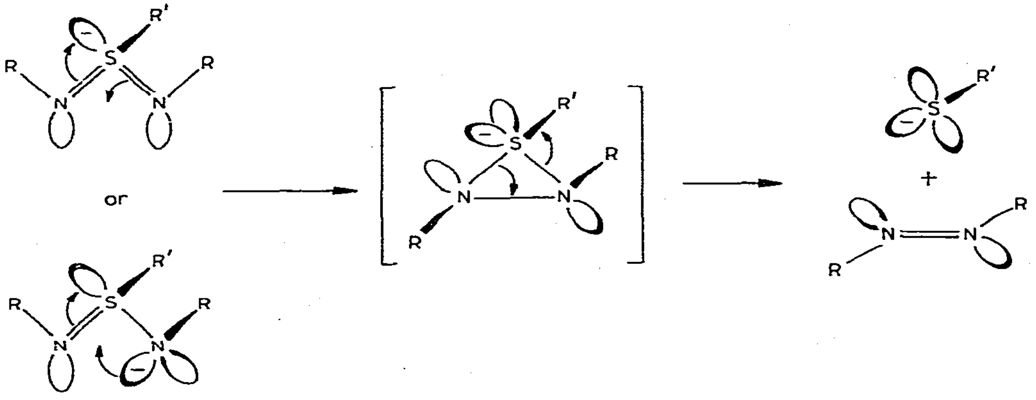


Fig. 5. Proposed reaction mechanism for the elimination of azoarylic compounds.

nism of Fig. 5 may rationalize the phenomena observed. The metal atom is not included in Fig. 5, although it is most probably linked to the sulfur atom in the intermediate situation (compare also the known conversion from *O*-sulfinato- to *S*-sulfinato-metal compounds [32,33]). This, however, makes no essential difference to the mechanism, which involves ring closure, and subsequent extrusion of the SR$^-$ group with concomitant stereoselective formation of a *trans*-azo compound. It is easily understood that stronger electron-donating *para*-substituents will promote the extrusion of the RS$^-$ group and also the ring closure, this becomes clear if one considers the related case of O=S=O in which both the S—O bond length increases and the O—S—O bond angle decreases as the charge on SO_2 is increased [34]. The reason for this is that extra electrons will occupy an orbital with O—O bonding and S—O anti-bonding character. Since, in the supposedly intermediate monodentate situation of the sulfurdiimino ligand, electronic rearrangements and rotations of groups will be facilitated, it seems reasonable in this mechanism, that in the case of the copper(I) and silver(I) compounds, bulky R groups and addition of PPh_3 have a rate-increasing effect.

Finally, we wish to draw attention to the observation that the alkylation of RN=S=NR provides a very simple and direct method for the titration of Grignard and alkyl- or aryl-lithium reagents without the disadvantages of the more complicated titrations [11].

References

1 J. Kuyper and K. Vrieze, J. Organometal. Chem., 74 (1974) 289.
2 J. Kuyper and K. Vrieze, J. Organometal. Chem., 86 (1975) 127.
3 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 108 (1976) 257.
4 J. Kuyper, L.G. Hubert-Pfalzgraf, P.C. Keijzer and K. Vrieze, J. Organometal. Chem., 108 (1976) 271.
5 R. Meij, J. Kuyper, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 110 (1976) 219.
6 W.E. Lindsell and R. Faulds, J. Chem. Soc., Dalton, (1975) 40.
7 R. Meij and K. Olie, Cryst. Struct. Commun., 4 (1975) 515.
8 R.G. Schultz, Tetrahedron, 20 (1964) 2809.
9 M.S. Lupin and B.L. Shaw, Tetrahedron Lett., (1964) 883.
10 J. Tsuji and T. Susuki, Tetrahedron Lett., (1965) 3027.
11 J. Kuyper and K. Vrieze, J. Chem. Soc., Chem. Commun., (1976) 64.
12 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 96 (1975) 289.
13 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 105 (1976) 379.
14 J. Kuyper and K. Vrieze, J. Organometal. Chem., 101 (1976) 129.
15 B. Cohen and A.S. McDiarmid, J. Chem. Soc. A, (1966) 1780.
16 D.H. Clemens, A.J. Bell and J.L. O'Brien, Tetrahedron Lett., 20 (1965) 1487.
17 R. Appel and J. Kohnke, Chem. Ber., 103 (1970) 2152.
18 R. Cramer, J. Organometal. Chem., 26 (1961) 3476.
19 H. van der Meer, to be published.
20 A.E. Smith, Acta Cryst., 18 (1965) 331.
21 W.E. Oberhansli and L.F. Dahl, J. Organometal. Chem., 3 (1965) 43.
22 E. Pfeiffer and K. Olie, Cryst. Struct. Commun., 4 (1975) 605.
23 M. Corbett and B.F. Hoskins, J. Amer. Chem. Soc., 89 (1967) 1530.
24 J. Kuyper, P.H. Isselman, F.C. Mijlhoff, A. Spelbos and G. Renes, J. Mol. Struct., 29 (1975) 247.
25 R.T. Kops, A.R. Overbeek and H. Schenk, to be published.
26 S. Candeloro de Scantis, L. Toniolo, T. Boschi and G. Deganello, Inorg. Chim. Acta, 12 (1975) 251.
27 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc., Dalton, (1974) 1206.
28 P. Hendriks, K. Olie and K. Vrieze, Cryst. Struct. Commun., 4 (1975) 621.
29 S. Candeloro de Sanctis and N.V. Pavel, J. Amer. Chem. Soc., in press.
30 W. Knoth, Inorg. Chem., 12 (1973) 38.
31 N.P. Neureiter and F.G. Bordwell, J. Amer. Chem. Soc., 81 (1959) 578.
32 S.E. Jacobson, P. Reich-Rohrwig and A. Woicicki, Chem. Commun., (1971) 1526.
33 C.A. Reed and W.R. Roper, Chem. Commun., (1971) 1556.
34 P.D. Dacre and M. Elder, Theor. Chim. Acta, 25 (1972) 254.
35 O.J. Scherer and R. Schmidt, J. Organometal. Chem., 16 (1969) P11.