

Recueil Review

of progress in current research

Coordination and activation of the N=S bond in sulfurdiimines RN=S=NR and sulfinylanilines RN=S=O by metal atoms

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Abstract. A survey is given of the coordination chemistry of sulfurdiimines RN=S=NR and sulfinylanilines RN=S=O towards metal atoms. It is shown that these pseudoallene ligands which are isostructural and isoelectronic with SO₂ may coordinate *via* N, S or *via* the π-N=S double bond. Nitrogen coordination is favoured by metals in the higher oxidation states *e.g.* Pt^{II}, Pd^{II}, but may also occur for Rh^I and Ir^I and even for zerovalent metals such as Cr⁰, Mo⁰ and W⁰. Sulfur coordination probably occurs for Cr⁰, Mo⁰ and W⁰, but has been observed for Rh^I and Ir^I. Finally, metal-π²-N=S bonding is clearly favoured by electron-rich metal atoms like Ni⁰, Pd⁰, Pt⁰, Rh^I and Ir^I. In the case of metal-π²-N=S coordination of the RNSNR ligands further reactions may occur which lead to NS bond rupture. Such bond rupture may result in a large number of reactions varying from simple insertion of a metal atom into an N-S bond to the formation of RNS, S and NR fragments which are captured in metal cluster complexes. Other ways of converting the RNSNR ligand involve the reactions with LiR', R'MgX and trialkylaluminium compounds. The anionic RNS(R')NR ligand so formed may behave as a bridging ligand but, more interestingly, as a pseudoallylic chelate group. It is shown that RNS(R')NR⁻ bonded as a chelate to transition metal atoms decomposes stereospecifically into azo compounds and SR⁻ fragments.

I. Introduction

Coordination of olefins to metal atoms and activation of the coordinated olefin have been dominant features in organometallic and catalytic research. Coordination of an olefin to a metal atom (η²-fashion) which is nicely illustrated by the detailed structure of Zeise's salt [KPtCl₃(η²-C₂H₄)·H₂O]¹ results in a number of changes in both the olefin skeleton and the other metal-ligand interactions. The C-C bond is slightly lengthened (0.038 Å with respect to free C₂H₄), but more importantly the four hydrogen atoms appear to bend away from the platinum atom (the angle between the normals to the CH₂ planes is 32.5°) indicating that the hybridization at the C atoms tends to sp³ and the negative charge on the olefin is increased (Figure 1). These changes on complexation of the olefin to the metal atom may be understood by the Dewar-Chatt-Duncanson bonding scheme^{2,3} which involves a σ-interaction of the filled bonding π-orbital of the olefin with relevant metal orbitals and a π-type interaction of the empty π*-orbital of

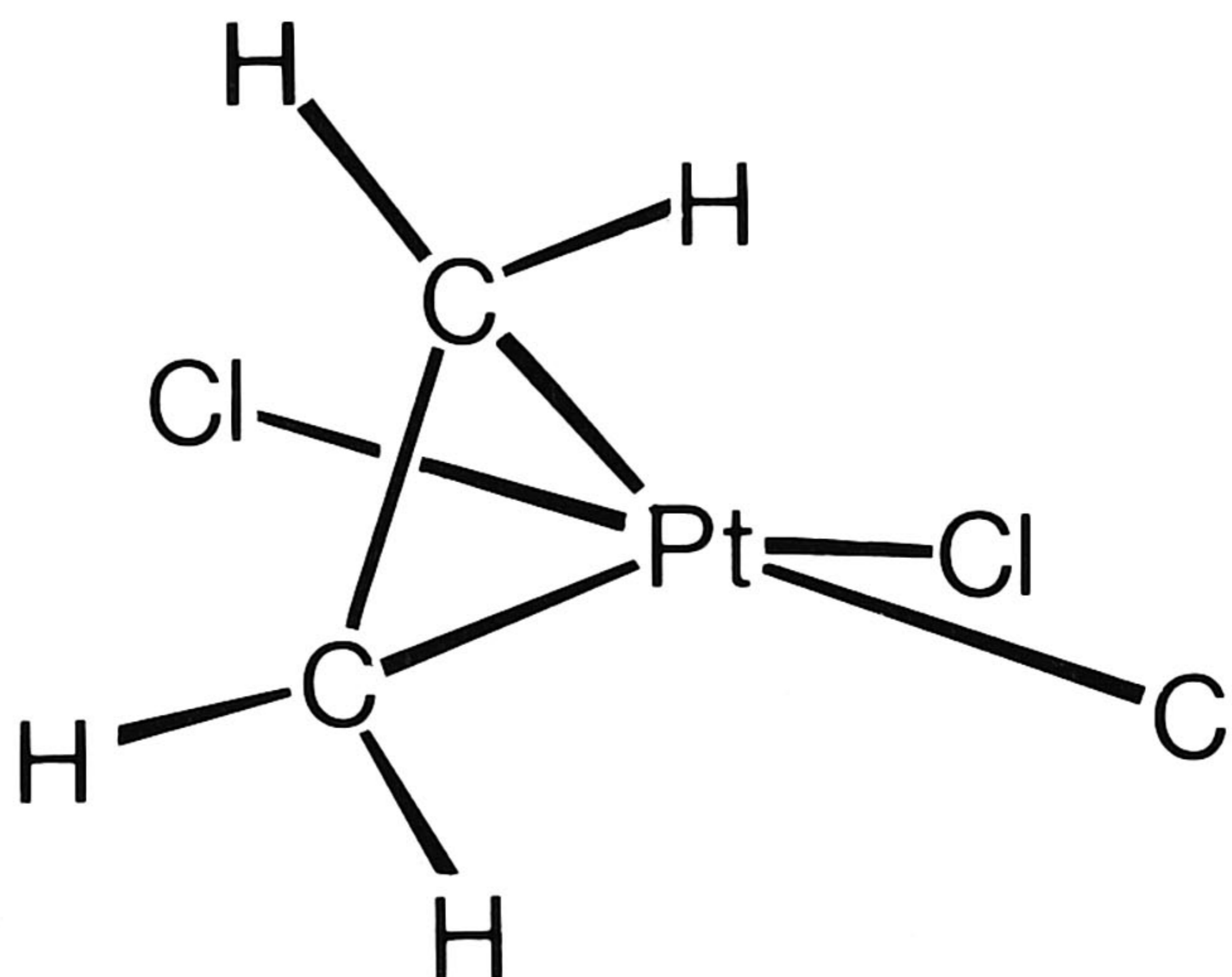


Fig. 1. Molecular geometry of the [PtCl₃(C₂H₄)]⁻ anion as determined by neutron diffraction (cf. ref. 1).

the olefin with filled *d*-orbitals of the metal atom. Chemical conversion of the η²-coordinated olefin may now occur because of the above changes. This is illustrated by the large number of stoichiometric and catalytic processes which are known in organometallic and organic synthesis. Examples are Ziegler-Natta polymerizations⁴, metathesis reactions⁵, the Wacker process⁶ and the hydroformylation process to name only a few. These processes are all based on activation of the η²-bonded olefin on metal centres.

* IUPAC name: thione oxides.

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⁶ J. K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press 113 (1978).

A challenging new aspect is the attempt to induce η^2 -type coordination of hetero-olefins i.e. compounds containing e.g., N=C, N=S, C=O groups bonded to metal atoms. On analogy with the situation for olefins more or less severe changes in the structural and bonding characteristics of these hetero-olefinic groups can then be anticipated to occur. As a consequence one might also expect that chemical conversion of these coordinated hetero-olefinic groups might possibly lead to new routes for the introduction of hetero atoms into organic compounds.

A part of our research is therefore concerned with the more general study of the relation between the mode of coordination of a hetero-olefinic group to a metal atom and the type of reaction which the coordinated ligand containing the hetero-olefinic group may undergo. As hetero-olefinic compounds we are studying sulfur diimines RN=S=NR, sulfinylanilines RN=S=O, sulfines* R(R')C=S=O and α -diimines RN=C(R')-C(R'')=NR. In this review we restrict ourselves to a discussion of the coordination chemistry of sulfur diimines and sulfinylanilines, while the metal diimine compounds will be treated in a future review⁷.

In considering these compounds it is enlightening to point out the analogy to, on the one hand, allenes R₂C=C=CR₂ and on the other hand to O=S=O. It is known that allenes may coordinate with one or both of its double bonds to either one⁸⁻¹¹ or two metal atoms¹². Sulfur dioxide, however, has more coordination possibilities i.e. *via* O, *via* S and *via* the π -S=O double bond^{13,14}. The coordination *via* S may be subdivided into complexes in which the metal atom lies in the SO₂ plane and into complexes in which the S atom has a pyramidal coordination, i.e. where the M-S vector makes an angle with the SO₂ plane. Factors influencing the various coordination modes for SO₂ have been discussed elsewhere¹³⁻²⁰. Since the compounds RN=S=NR and RN=S=O are isoelectronic and isostructural with O=S=O it is of interest to consider first their structural and spectroscopic features before reviewing their metal coordination properties. Some structural details are listed in Table I.

Table I Geometrical parameters of RN=S=NR and RN=S=O.

RN=S=NR	S=N (Å)		\angle N=S=N (°)	ref.
	<i>cis</i>	<i>trans</i>		
R				
<i>p</i> -tolylsulfonyl	1.521	1.524	115	21
<i>p</i> -tolyl	1.53	1.56	117	22
methyl	1.532	1.532	114	23
RN=S=O	S=N (Å)	S=O (Å)	\angle N=S=O	ref.
MeN=S=O	1.525	1.466	117	24
HN=S=O	1.512	1.451	120.4	25

It can be seen that the S=N double bond length is around 1.52 Å, while the S=O bond length of RNSO (1.45 Å) is similar to that (1.431 Å) of SO₂¹³. Also the N-S-O and N-S-N bond angles are close to the value of 119° of SO₂¹³. It is of interest to note that for most sulfur diimines, which are in the *cis,trans* conformation in the solid state²², two conformations (see Figure 2) are observed in the dissolved state²⁶⁻²⁸, i.e. in addition to the *cis,trans* isomer, which is generally the most abundant one, also the *trans,trans* isomer is present, as shown by low temperature ¹H-NMR spectra^{27,28}.

It is clear that steric influences are the main factors determining the equilibrium. For example, *N,N'*-di-*tert*-butylsulfur diimine occurs only in the *cis,trans* conformation, whereas *N,N'*-di-2,4,6-mesitylsulfur diimine exists in the *trans,trans* conformation*^{27,28}.

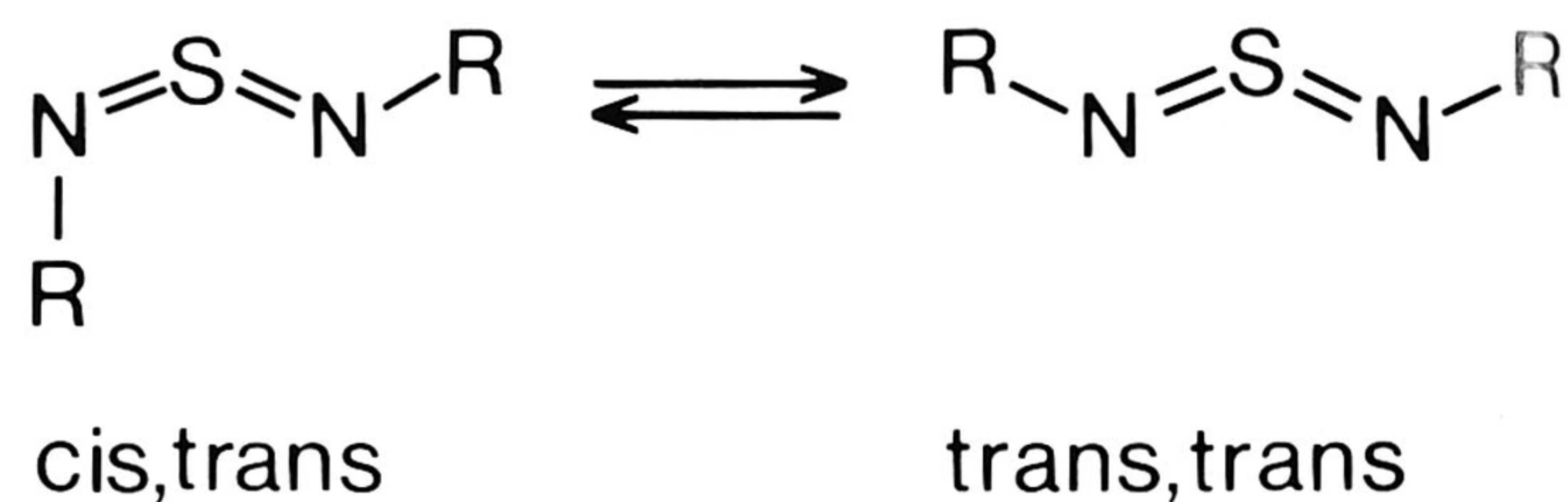


Fig. 2. The two conformations of the sulfur diimine ligand in solution.

¹H-NMR measurements demonstrated that these isomers may interconvert intramolecularly on the NMR time scale at temperatures higher than -45°C. The activation parameters are 10¹³ s⁻¹ for A and 46-54 kJ/mol for E_A^{27,28}. The rates decrease in the order R = aryl < *tert*-butyl < iso-propyl \lesssim ethyl \lesssim methyl i.e. the interconversion between the two conformers slows down with increasing bulkiness of R. Possible processes for the interconversion are rotation about the N=S bond, but more likely inversion at the nitrogen atoms. The electronic^{6,31} and spectroscopic properties^{32,33} have been investigated to some extent. For the case of the dialkylsulfur diimines it was shown that $\nu_{\text{as}}(\text{N}=\text{S})$, $\nu_{\text{s}}(\text{N}=\text{S})$ and $\delta(\text{NSN})$ lie in the ranges of 1190-1220, 1010-1098 and 677-807 cm⁻¹, respectively. The corresponding values for the diaryl derivatives are 1250-1300, 942-984 and 778-804 cm⁻¹, respectively.

* Compounds having the *cis,cis* conformation have not been found except for sulfur diimines in which the NSN unit is part of a ring, e.g. benzothiadiazole^{29,30}.

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Many controversial papers have appeared on the structure of RNSO. Recently, however, definite conclusions could be made on the basis of measurements of ^{15}N -enriched compounds³¹. It was shown that RNSO exists exclusively in the *cis*-conformation (Figure 3), with $\nu(\text{S}=\text{O})$ and $\nu(\text{N}=\text{S})$ (the $\text{N}=\text{S}$ and $\text{S}=\text{O}$ stretches appeared to be but lightly coupled), $\delta(\text{NSO})$ and $\delta(\text{PhNS})$ arising in the ranges of 1276–1304, 1144–1164, 720–870 and 638–652 cm^{-1} , respectively.

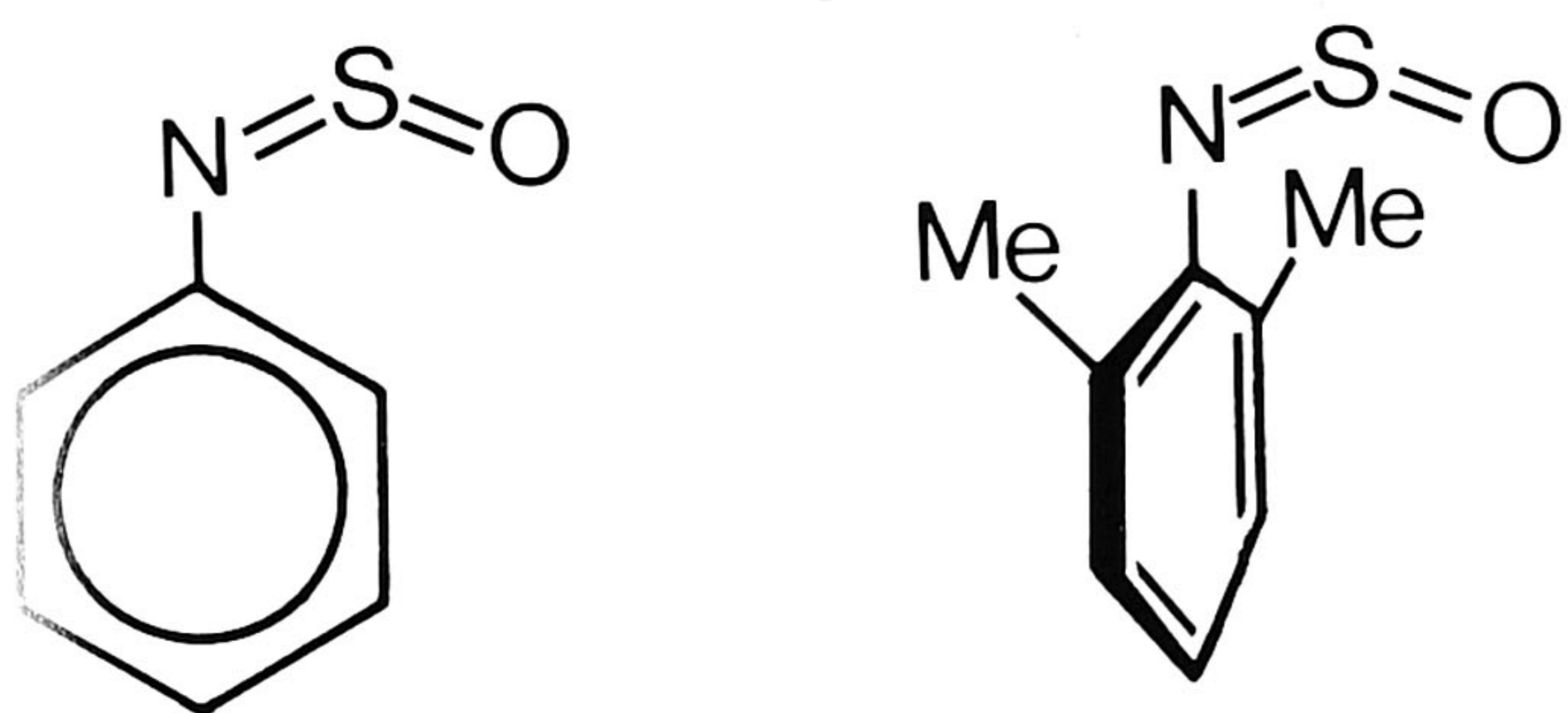


Fig. 3. The conformation of arylsulfinylaniline: a, when ortho substituents are absent; b, with methyl groups in both ortho positions.

Molecular orbital calculations are now underway to compare RNSNR, RNSO and SO_2 ³⁴. Preliminary calculations appear to indicate that (i) sulfur coordination should increase in the order $\text{RNSNR} < \text{RNSO} < \text{SO}_2$, (ii) coordination via N should occur more readily for RNSNR than for RNSO, (iii) coordination to the $\pi\text{-N}=\text{S}$ bond should be about equal for RNSNR and RNSO and (iv) coordination to the $\pi\text{-S}=\text{O}$ double bond should decrease strongly from SO_2 to RNSO. When considering the tendencies toward N, S, O or $\pi\text{-N}=\text{S}$ coordination, it is predicted that N coordination should occur for metals in the higher oxidation states and $\pi\text{-N}=\text{S}$ coordination for low valent metal atoms. The lone pair on S is more diffuse than the one on N and metal–S coordination is therefore to be expected for the larger more polarizable metal atoms. Finally, oxygen coordination to metal atoms should occur rarely and then only to small metal atoms in high oxidation states.

This knowledge concerning the structural, spectroscopic and theoretical features of the free ligands appeared to be very helpful during our studies of the interactions of these ligands with metal atoms; the more relevant results are discussed in section II.

II. Complexes of $\text{RN}=\text{S}=\text{NR}$ and $\text{RN}=\text{S}=\text{O}$

A. Metal–Nitrogen coordination

An example of nitrogen coordination was reported for $[\text{PtCl}_2(\eta^2\text{-C}_2\text{H}_4)(t\text{-BuNSN}t\text{-Bu})]^{27}$ for which a crystal structure determination showed that the bivalent Pt atom is bonded to the *cis* side of the *t*-BuNSN*t*-Bu ligand, which is in the *cis,trans* conformation³⁵. This can be ascribed to the fact that the *cis* side of this isomer is sterically more accessible than the *trans* side. The $\text{N}=\text{S}$ bond length of 1.55 Å and the NSN angle of 113° show that the molecule is scarcely perturbed by N-coordination. An analogous situation was observed for $[\text{trans-MCl}_2(t\text{-BuNSN}t\text{-Bu})\text{L}]$ ($\text{M} = \text{Pt}^{\text{II}}$ ²⁷, Pd^{II} ³⁶), where L is a phosphine PR_3 , an arsine AsR_3 or even SR_2 and SeR_2), and which were prepared from the dimers $[\text{MCl}_2\text{L}]_2$ and *t*-BuNSN*t*-Bu. However, analogous reactions with *N,N'*-diarylsulfurdiimines afforded $[\text{trans-PtCl}_2(\text{RNSNR})\text{L}]$ ($\text{R} = 3,5\text{-xylyl}$, $2,4,6\text{-mesityl}$, $4\text{-MeC}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$, $4\text{-MeOC}_6\text{H}_4$) for which a *trans,trans* configuration of the sulfurdiimine was observed²⁸. (N.B. the *cis,trans* form of the free ligand is generally the more stable one.)

Rather interesting is the situation for $[\text{trans-PtCl}_2(\text{RNSNR})\text{L}]$, where $\text{R} = \text{Me}$, Et , *i*-Pr and *n*-Pent with the ligand in the *cis,trans* configuration, since now two metal sulfurdiimine isomers in varying ratios were observed in CDCl_3 or in toluene at -60°C ²⁷. In the most abundant isomer the metal atom is linked to the N atom on the *cis* side. However, in the less abundant isomer the metal atom is bonded to the N atom on the *trans* side (Figure 4, isomers **1** and **2**, respectively). Consequently, the alkyl group on the non-coordinated (*cis*) side of the latter isomer (II) lies close to the metal atom and above the coordination plane²⁷. This is reflected by the anomalously low field $^1\text{H-NMR}$ chemical shifts of the groups in question e.g. ~ 2.7 ppm for each H atom coming close to the metal atom²⁷.

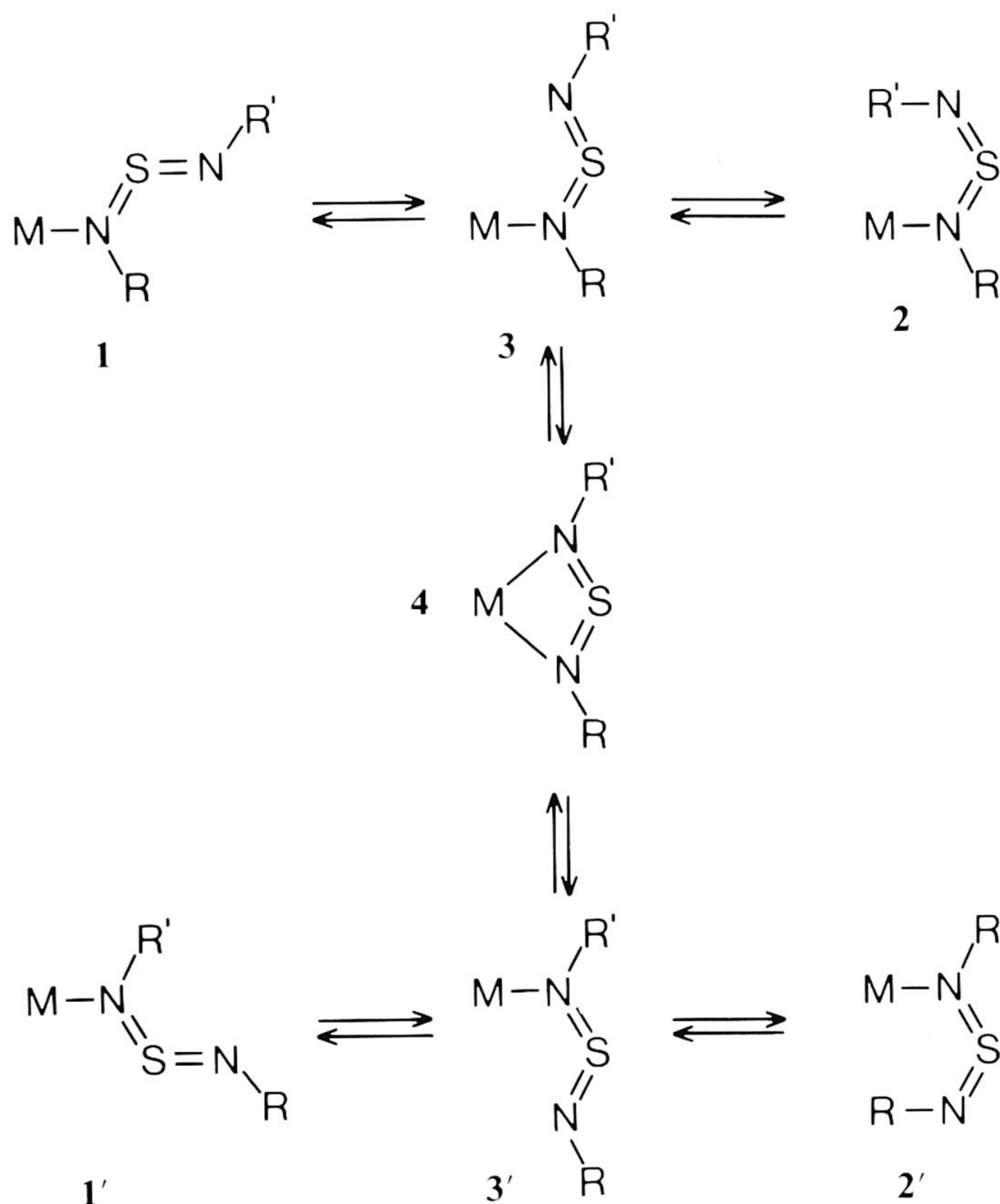


Fig. 4. Intramolecular rearrangement processes observed for metal–sulfurdiimine complexes.

The existence of the two isomeric forms **1** and **2** has also been demonstrated for $[\text{trans-PdCl}_2(\text{RNSNR})\text{L}]$ ($\text{R} = \text{Me}$, Et , *i*-Pr; $\text{L} = \text{PhMe}_2\text{As}$)³⁶, for $[\text{trans}\{(\text{Ph}_3\text{P})_2(\text{CO})\text{M}(\text{MeNSNMe})\}\text{ClO}_4]$ ($\text{M} = \text{Rh}^{\text{I}}$, Ir^{I})³⁷, and for $[\text{cis-Pt}(\text{MeNSNMe})\text{L}_2\text{Cl}]\text{ClO}_4$ ($\text{L} = \text{PhMe}_2\text{P}$, PhMe_2As)³⁷. Isomer **2** for these complexes was not observed for larger R substituents on the sulfurdiimine owing to steric interactions with the bulky ligands L.

A typical observation for these monodentate bonded sulfurdiimine complexes is that intra- and inter-molecular exchange processes may occur involving the sulfurdiimine ligand. The intramolecular processes are shown in Figure 4. Isomer **3** is a complex in which the sulfurdiimine is in the *trans,trans* form, while in the intermediate **4** the sulfurdiimine is bonded as a bidentate. Such a bidentate mode of

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bonding has been found for $[M(CO)_4(RNSNR)]$ ($M = Cr^0, Mo^0, W^0$; $R = t\text{-Bu}, i\text{-Pr}$)³⁸⁻⁴⁰ for example and crystallographically confirmed for $[W(CO)_4(t\text{-BuNSN}t\text{-Bu})]$ ⁴¹. Several pathways have been observed which depend on the type of complex.

For $[trans\text{-PtCl}_2(t\text{-BuNSN}t\text{-Bu})L]$, for which only conformation **1** was found, there is an interchange of Pt between both N sites. It was concluded that for this complex the pathway $1 \rightleftharpoons 3 \rightleftharpoons 3' \rightleftharpoons 1'$ operates.

For those complexes, for which both conformations **1** and **2** were found, there are various possibilities. In the case of $[trans\text{-PtCl}_2(RNSNR)L]$ ($R = Me, Et, i\text{-Pr}, n\text{-Pent}$) one observed two processes depending on the temperature²⁷. The lower temperature process takes the pathway $1 \rightleftharpoons 3 \rightleftharpoons 2$, i.e. the sulfur diimine remains bonded by the same N atom to the Pt atom. Only N inversion ($3 \rightleftharpoons 2$) and rotation about the N=S bond ($1 \rightleftharpoons 3$) takes place. The higher temperature process involves also the pathway $3 \rightleftharpoons 4 \rightleftharpoons 3'$, i.e. the metal atom may now also jump from one N atom to the other and *vice versa* via the penta-coordinate intermediate **4**²⁷.

For $[trans\text{-PtCl}_2(\text{ArylNSNAryl})L]$ (conformation **3**) one may observe the path $3 \rightleftharpoons 4 \rightleftharpoons 3'$, i.e. the N-N jump only²⁸.

Finally for $[trans\text{-}(\text{Ph}_3\text{P})_2(\text{CO})M(\text{MeNSNMe})]\text{ClO}_4$ ($M = Rh^I, Ir^I$)³⁷, for $[cis\text{-PtCl}(\text{MeNSNMe})L_2]\text{ClO}_4$ ³⁷ and for $[trans\text{-PdCl}_2(RNSNR)L]$ ($R = Me, Et, i\text{-Pr}$)³⁶ the intramolecular pathway $2 \rightleftharpoons 3 \rightleftharpoons 4 \rightleftharpoons 3' \rightleftharpoons 2'$ was observed, while **1** remained in general rigid in the Rh^I and Ir^I complexes³⁷. In the case of the Pd^{II} complexes isomer **1** participated exclusively in intermolecular sulfur diimine exchange processes³⁶; these were extensively investigated, but they are not discussed here.

It is clear that all intramolecular processes observed (Figure 4) depend on the relative activation enthalpies of the steps $1 \rightleftharpoons 3$ (rotation about the N=S bond), $3 \rightleftharpoons 2$ (N-inversion) and $3 \rightleftharpoons 4$ (formation of a penta-coordinate intermediate). It is to be expected that N inversion and N=S bond rotation should be relatively insensitive to the metal atom and to the other ligands, while $3 \rightleftharpoons 4$ should depend very much on the metal atom and the ligands. Inversion at N should occur at around the same temperature as in the free ligand ($\sim -45^\circ\text{C}$) which is indeed observed, while N=S bond rotation appears to start at $\sim +30^\circ$ ²⁷. Which pathway occurs depends therefore almost wholly on the step $3 \rightleftharpoons 4$. If this is difficult one finds $1 \rightleftharpoons 3 \rightleftharpoons 2$, but, if this is easy, one will observe $2 \rightleftharpoons 3 \rightleftharpoons 4 \rightleftharpoons 3' \rightleftharpoons 2'$ and the step $1 \rightleftharpoons 3$ will not be found. This is indeed the case. Clearly there is a fairly large tendency for the Rh^I, Ir^I and Pd^{II} complexes to form penta-coordinate intermediates, while this is less so for Pt^{II} .

Nitrogen coordination has also been observed for $[M(CO)_4(RNSNR)]$ ($M = Cr^0, Mo^0, W^0$) in which R is a bulky group (e.g. *tert*-butyl) and which contains the sulfur diimine in the bidentate form³⁸⁻⁴¹. However, complexes $[M(CO)_5(RNSNR)]$ are formed for $R = Me, Et$ and $i\text{-Pr}$, in which the sulfur diimine is monodentate bonded *via* the N atom at the *cis* position of the ligand having the *cis,trans* conformation^{38,39}. Interestingly, in the case of $[M(CO)_5(\text{MeNSNMe})]$ ($M = Mo, W$) a second less abundant isomer was found in the solution, in which the sulfur diimine is probably S-bonded to the metal atom^{38,39}. The complexes $[M(CO)_5(RNSNR)]$ ($M = Cr, Mo, W$) appeared to be fluxional in solution and the proposed pathway which emerged from a detailed ¹H-NMR study is shown in Figure 5.

In these complexes the metal atom changes its point of coordination from one N atom to the other *via* the S atom. A process with a direct N-N jump could be excluded, the more so since an N-N jump process would involve a seven coordinate intermediate which is very unlikely for Cr^0, Mo^0

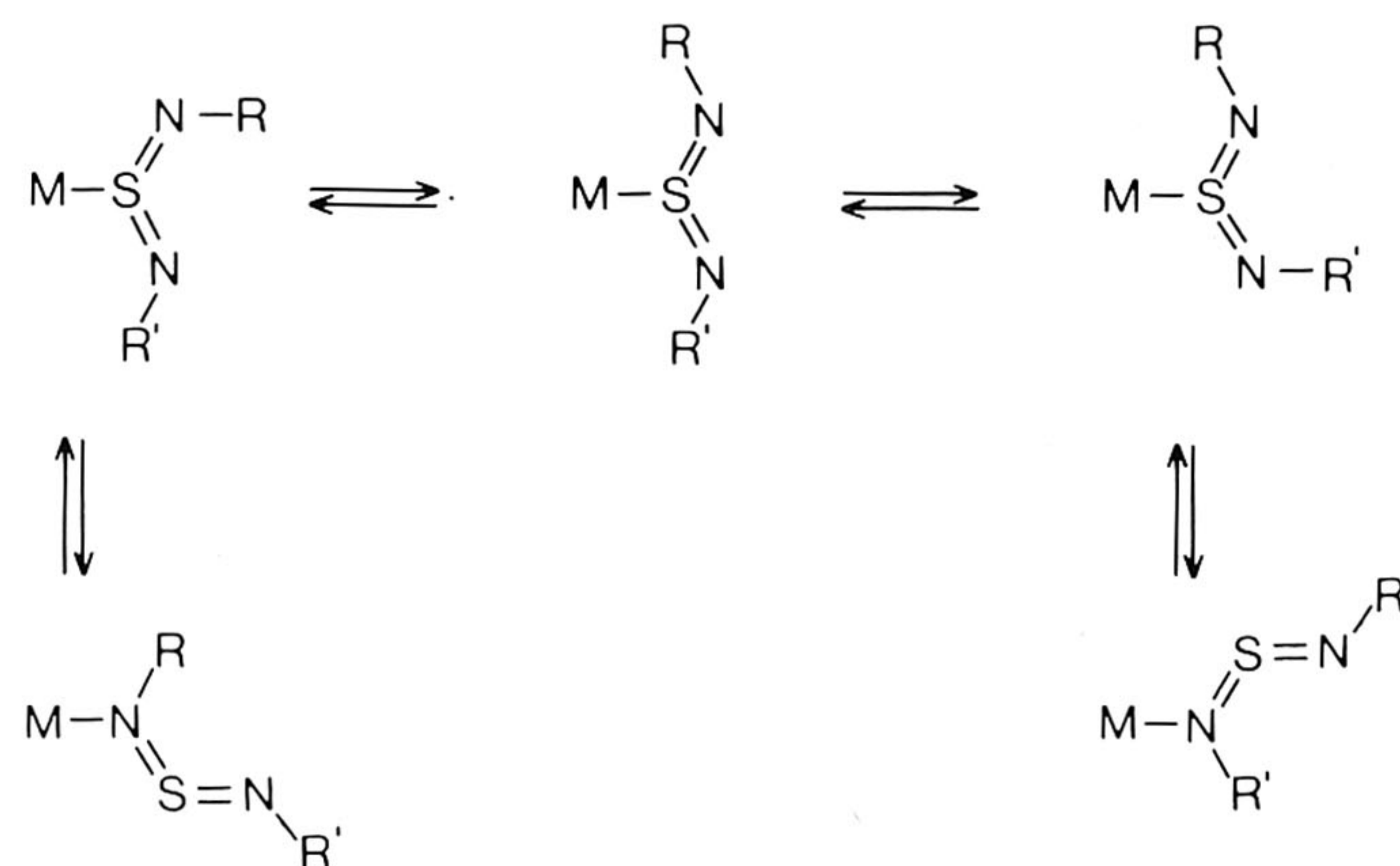


Fig. 5. The proposed mechanism for the interconversion of R and R' in $[M(CO)_5(RNSNR')]$.

and W^0 . An additional possibility is the use by the metal atom of the $\pi\text{-N}=\text{S}$ bond during the movement shown in Figure 5, but no spectroscopic support for this could be found. That, however, $M\text{-S}$ and $M\text{-}\pi\text{-N}=\text{S}$ species can be interconverted will be shown in the next section.

B. Metal-Sulfur and Metal- $\pi\text{-N}=\text{S}$ bonding

RNSO can be bonded to Rh^I and Ir^I as shown by the reactions of $[MCl(\text{cyclo-octene})_2]_2$ with RNSO in the presence of phosphines, which afforded the complexes $[trans\text{-}MCl(L)_2(RNSO)]$ ($L = P(i\text{-Pr})_3, P(c\text{-hexyl})_3$; $M = Rh^I, Ir^I$; $R = Ph, 4\text{-MeC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$)⁴². An X-ray crystallographic determination (Figure 6) showed that in contrast to the $M\text{-N}$ bonding of the sulfur diimine ligand to Rh^I and Ir^I ³⁷, the arylNSO ligand in $[trans\text{-}RhCl\{P(i\text{-Pr})_3\}_2(4\text{-MeC}_6\text{H}_4\text{NSO})]$ is S bonded to Rh^I ⁴². The Rh atom lies in the NSO plane, while the Rh-S distance is short [2.100(3) Å] analogous to $[Rh^I(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_5)(\text{SO}_2)]$ ⁴³ [$Rh\text{-S} = 2.096(2)$ Å]. The RNSO ligand is in the *cis*-conformation with a NSO bond angle of 117.2° which is similar to the angle of free RNSO ligands (see Table I). These data show that the ligand is not appreciably affected by coordination to Rh^I .

Infrared studies of solutions of ¹⁵N-enriched complexes of these compounds revealed, surprisingly, that there are two isomers in solution⁴², both of which contain two phosphine ligands situated *trans* to each other. $\nu(\text{N}=\text{S})$ and $\nu(\text{S}=\text{O})$ values of 1258 and 1108 cm^{-1} pointed to the presence of the S-bonded isomer, while $\nu(\text{N}=\text{S})$ and $\nu(\text{S}=\text{O})$ values of 948 and 1057 cm^{-1} , respectively, were assigned to a $M\text{-}\eta^2\text{-N}=\text{S}$ -bonded isomer. It must be noted that the decreases of both frequencies in the latter isomer are comparable to those of $[Pt^0(\text{PPh}_3)_2(\text{RNSO})]$ (*vide infra*), which contains an $\eta^2\text{-N}=\text{S}$ -bonded RNSO group. These results were corroborated by temperature-dependent ³¹P-NMR studies. The $M\text{-S}$ and $M\text{-}\eta^2\text{-N}=\text{S}$ -bonded isomers are in equilibrium with each other (Figure 7). This equilibrium depends on the temperature, the nature of the aryl substituent, the phosphine

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⁴² R. Meij, D. J. Stufkens, K. Vrieze, W. van Gerresheim and C. H. Stam, *J. Organomet. Chem.* **164**, 353 (1979).

⁴³ R. R. Ryan, P. G. Eller and G. J. Kubas, *Inorg. Chem.* **15**, 797 (1976).

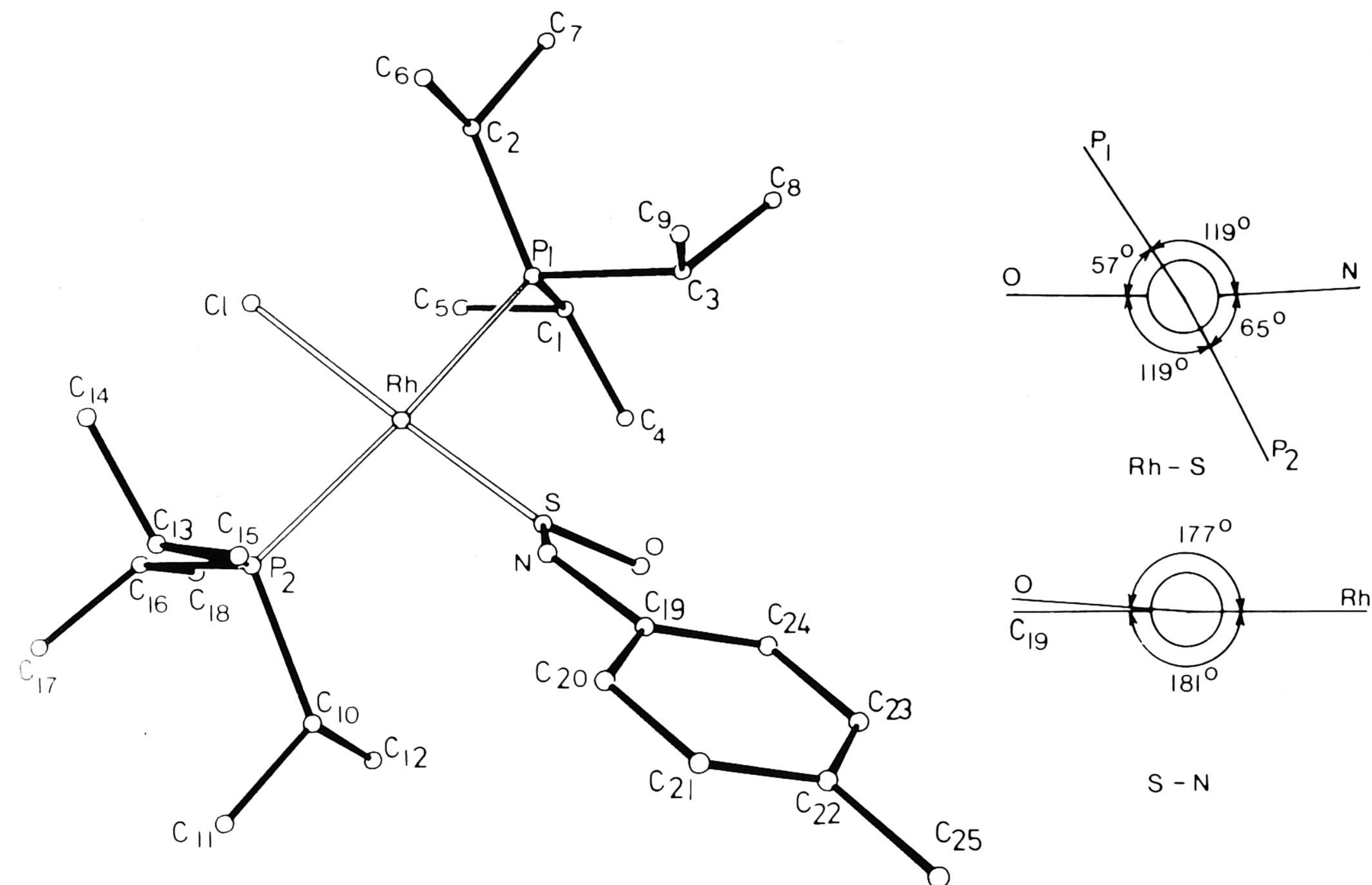


Fig. 6. The molecular structure of $[\text{trans-RhCl}\{P(\text{i-Pr})_3\}_2(4\text{-MeC}_6\text{H}_4\text{NSO})]$ and the Newman projections along the Rh-S and S-N bonds (cf. ref. 42).

and the metal atom. It was found that increasing temperature and increase of the electron releasing properties of the aryl group enhance the amount of S-bonded isomer.

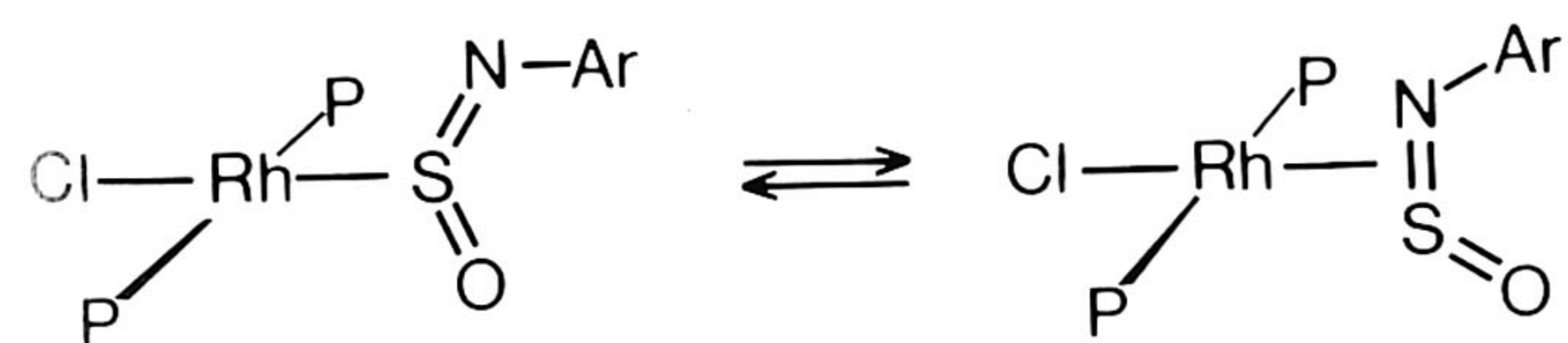


Fig. 7. The two isomers of $[\text{RhCl}(\text{PR}_3)_2(\text{ArNSO})]$ containing $\sigma^2\text{-S}$ and $\eta^2\text{-NS}$ bonded ArNSO , respectively.

Moreover, S-bonding appears to be favoured more by Ir^{I} than by Rh^{I} as well as by the use of the bulky aryl substituents and bulky phosphines.

Crystallographic proof for the occurrence of metal- $\eta^2\text{-N}=\text{S}$ -bonding was obtained for $[\text{Pt}(\text{PPh}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NSO})]$ ⁴⁴ *. The ligand, which is again in the *cis*-conformation, is side-on coordinated *via* the $\pi\text{-N}=\text{S}$ bond (Figure 8). The N=S bond length is found to be 1.63(1) Å, while the NSO bond angle is 116.4(7)°. This type ($\text{M}-\eta^2\text{-C}=\text{S}$) of coordination has also been found for sulfines $\text{R}_2\text{C}=\text{S}=\text{O}$ when coordinated to Pt^0 ⁴⁵. Although the bond angle scarcely differs from the one found for free ligands (Table I), it is clear that the NS bond length is strongly

influenced by η^2 -coordination, which is in agreement with the lengthening of olefins on coordination to a metal centre. The S=O bond distance of 1.455 Å has little changed from the value normally found for free ligands.

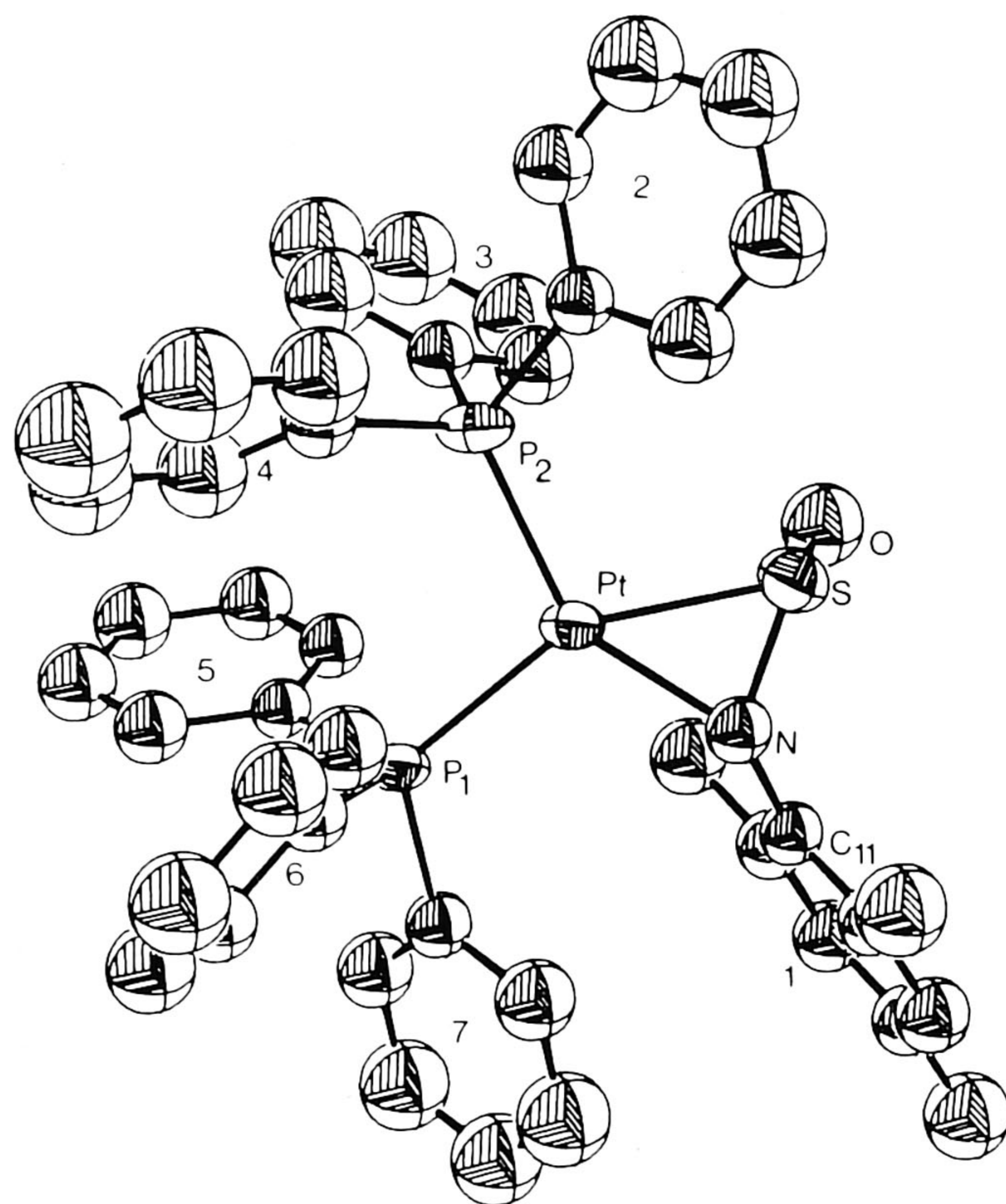


Fig. 8. The molecular structure of $[\text{Pt}^0(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{-NSO})(\text{PPh}_3)_2]$ (cf. ref. 44).

* The $\nu(\text{N}=\text{S})$ and $\nu(\text{S}=\text{O})$ appear at 906 and 1050 cm^{-1} , respectively⁴⁴.

⁴⁴ R. Meij, D. J. Stufkens, K. Vrieze, E. Roosendaal and H. Schenk, *J. Organomet. Chem.* **155**, 323 (1978).

⁴⁵ J. W. Gosselink, G. van Koten, K. Vrieze, B. Zwanenburg and B. H. Lammerink, *J. Organomet. Chem.* **179**, 411 (1979).

Metal- η^2 -N=S-bonding has also been proposed for $[\text{Ni}(\text{PPh}_3)_2(\text{RNSO})]^{47}$ and $[\text{Pd}(\text{PPh}_3)_2(\text{RNSO})]^{48}$. The ^{31}P and ^{195}Pt NMR spectra of ^{15}N -enriched samples of $[\text{Pt}(\text{PPh}_3)_2(\text{RNSO})]$, but also of $[\text{Pt}(\text{PPh}_3)_2(\text{RNSNR})]$ (below $+30^\circ\text{C}$)⁴⁴ show that these complexes contain η^2 -N=S-bonded ligands similar to the structure of $[\text{Pt}(\text{PPh}_3)_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{NSO})]$ in the solid state. ^{31}P -NMR for $[\text{Pt}(\text{PPh}_3)_2(3,5\text{-Me}_2\text{C}_6\text{H}_3\text{NSO})]$ as a function of temperature show that the complex is fluxional in solution as the result of a process involving rotation of the RNSO ligand about the Pt- η^2 -N=S bond axis. For $[\text{Pt}(\text{PPh}_3)_2(p\text{-MeC}_6\text{H}_4\text{NSN-}p\text{-MeC}_6\text{H}_4)]$ this movement may also occur, but ^{31}P -NMR studies revealed that in addition (between -30° to $+30^\circ\text{C}$) the Pt atom moves in an intramolecular fashion from one π -N=S bond to the other and *vice versa*⁴⁹. These processes resemble strongly the dynamic behaviour established for the olefin in Pt^{II} -olefinic compounds (rotation)¹¹ and for Pt^{II} -allene compounds (gliding movement from one π -C=C bond to the other)⁸⁻¹¹.

Although the M-NSO and M-NSN chemistry is just beginning to develop we may conclude, on the basis of the available data, that the tendencies for coordination roughly follow the theoretical predictions mentioned in the introduction. Metal- η^2 -N=S coordination is observed for zerovalent Ni^0 , Pd^0 and Pt^0 , but not for bivalent Pd^{II} and Pt^{II} , while for RNSO it appears to exist next to M-S-bonding for Rh^{I} and Ir^{I} . Nitrogen coordination is found for Pd^{II} and Pt^{II} but not for Pt^0 , while it exists for Rh^{I} and Ir^{I} in the case of RNSNR. Nitrogen coordination of RNSNR has also been found for Cr^0 , Mo^0 and W^0 in addition to M-S-bonding. However, in these complexes the other ligands are strongly π -backbonding carbonyl groups thus rendering N-coordination** more favourable, which latter type of coordination was observed to a small extent only.

Comparing the electronic differences of SO_2 , RNSO and RNSNR ligands then we do see the following trends: S-coordination ($\text{SO}_2 > \text{RNSO} > \text{RNSNR}$), N-coordination ($\text{RNSNR} > \text{RNSO}$), η^2 -N=S-coordination ($\text{RNSNR} \lesssim \text{RNSO}$) and finally η^2 -S=O-coordination ($\text{SO}_2 \gg \text{RNSO}$). However, it is also obvious from the results discussed above that steric factors become increasingly important with respect to the type of coordination in the series SO_2 , RNSO and RNSNR.

III. Activation of RNSNR by metal atoms

There are in principle various ways for activating RNSNR and RNSO, since on both molecules there are electron rich and electron poor areas, which are accessible for either electrophilic or nucleophilic attack by appropriate reagents.

We will discuss first activation of the N=S moiety in RNSNR by coordination of metals alone (RNSO has been virtually not studied). The more complicated insertion reactions involving attack of nucleophiles on the coordinated RNSNR and RNSO ligands will be discussed subsequently.

A. Activation by coordination of metal atoms

The available data indicate that the RNSNR and RNSO ligands remain unaffected when coordination occurs *via* the N atom or the S atom, although in the latter case too few examples are known with certainty. However, it has been observed that N=S bond-lengthening occurs when the metal atom, as in $[\text{Pt}(\text{PPh}_3)_2(\text{RNSO})]$, is coordinated to the π -N=S bond owing to the drift of electrons in the antibonding orbitals of the RNSO molecule⁴⁴. This bond weakening may bring about further reactions as will be demonstrated for $[\text{Pt}(\text{PPh}_3)_2(\text{RNSNR})]$ ($\text{R} = 4\text{-MeC}_6\text{H}_4$, $4\text{-ClC}_6\text{H}_4$ and $3,5\text{-Me}_2\text{C}_6\text{H}_3$). We have already discussed that the sulfur diimine is η^2 -N=S coordinated in solution. However, when these complexes are allowed to stand longer in CDCl_3 solution at $+30^\circ\text{C}$ the zerovalent platinum complexes are converted quantitatively into bivalent platinum

complexes⁴⁹. A crystal structure of $[\text{Pt}\{\text{-S-N}(2\text{-NH-}4,6\text{-Me}_2\text{C}_6\text{H}_2)(3,5\text{-Me}_2\text{C}_6\text{H}_3)\}(\text{PPh}_3)_2]$ revealed the structure shown in Figure 9.

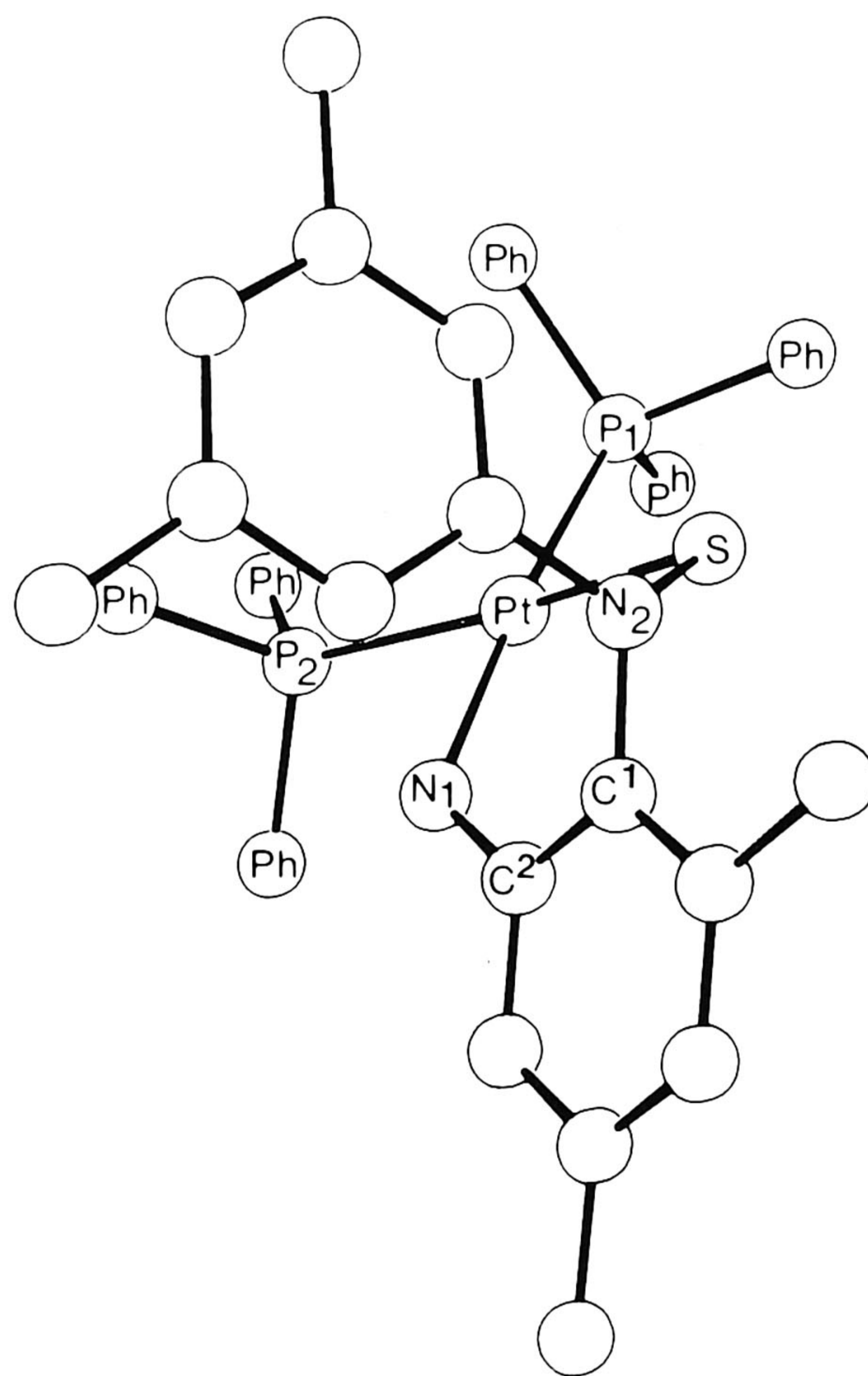


Fig. 9. The molecular structure of $[\text{Pt}\{\text{-S-N}(2\text{-NH-}4,6\text{-Me}_2\text{C}_6\text{H}_2)(3,5\text{-Me}_2\text{C}_6\text{H}_3)\}(\text{PPh}_3)_2]$. Of the phenyl groups only the positions of C(1) are shown (cf. ref. 49).

The bivalent Pt^{II} atom has a square planar coordination geometry, and it is clear that the most important features of the reaction which lead to this reaction product involve S=N bond rupture, N-C bond formation and hydrogen migration. The proposed mechanism which involves an intramolecular rearrangement process of the coordinated ligand is shown in Figure 10.

The Pt atom which at low temperatures is bonded to one π -N=S bond of the ligand in the *cis,trans* conformation, acts as a template for the process. It activates at the higher

** The RNSNR group can also act as a bidentate ligand. In this coordination mode the sulfur diimine group is a strong π -acceptor ligand^{38,30}.

⁴⁶ D. M. Blake and J. R. Reynolds, *J. Organomet. Chem.* **113**, 391 (1976).

⁴⁷ D. Walther and C. Pfützenreuter, *Z. Chem.* **17**, 426 (1977).

⁴⁸ G. la Monica, M. Pizzotti and S. Cenini, *Gazz. Chim. Ital.* **108**, 611 (1978).

⁴⁹ R. Meij, D. J. Stufkens and K. Vrieze, *J. Organomet. Chem.* **144**, 239 (1978).

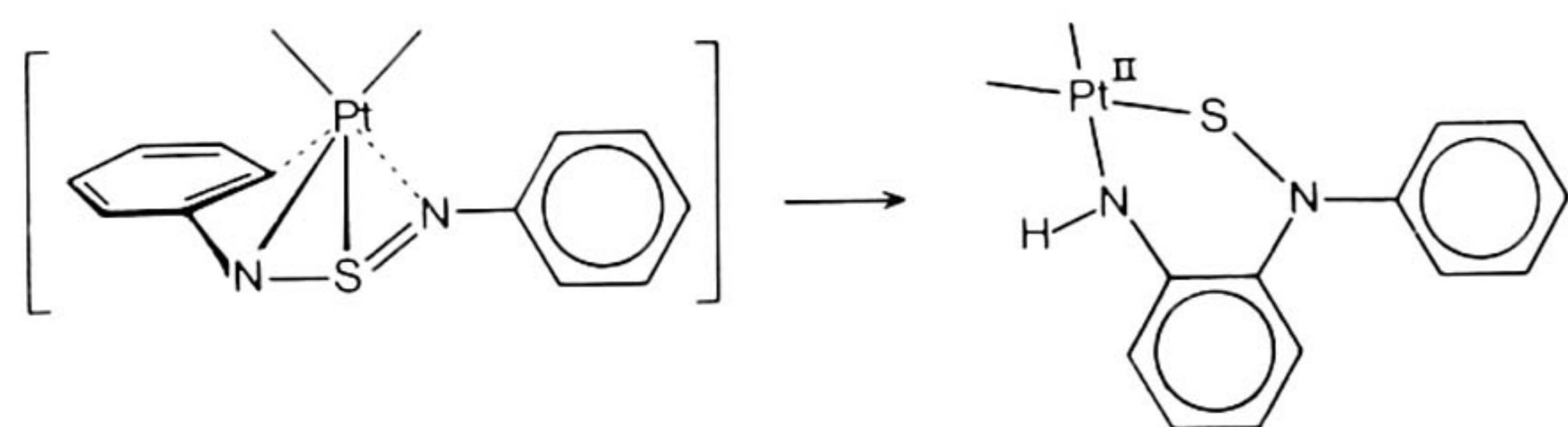


Fig. 10. The proposed transition state or intermediate in which the intramolecular irreversible rearrangement to $[Pt^{II}\{SN(1-NHR')(R)\}(PPh_3)_2]$ occurs.

temperatures the *ortho*-C-H bond which is close to the N atom on the other side of the ligand and assists nucleophilic attack of this N atom on the *ortho*-C atom. Concomitant oxidation of Pt^0 to Pt^{II} , S=N bond breaking of the coordinated η^2 -N=S bond and hydrogen migration then affords the final product. The almost quantitative yield of this product illustrates the specificity of this intramolecular rearrangement process. N=S bond breaking by Pt^0 accompanied by a series of other, less specific rearrangements, occurred in the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with 5,6-dimethyl-2,1,3-benzothiadiazole which yielded the dimeric

complex $[Pt_2S\{N(6-\mu-N-4,5-Me_2C_6H_2)\}(\mu-PPh_2)(PPh_3)_2-Ph]^{50}$ (Figure 11).

Also, in this reaction the platinum atom is oxidized from Pt^0 to Pt^{II} , while one of the Pt atoms is inserted into one of the N=S bonds probably *via* initial $Pt^0-\eta^2$ -N=S coordination. The subsequent steps in the formation of the dimer are unknown. Interesting features are the P-C bond cleavage which leads to a phenyl and a PPh_2 fragment both captured in the dimer.

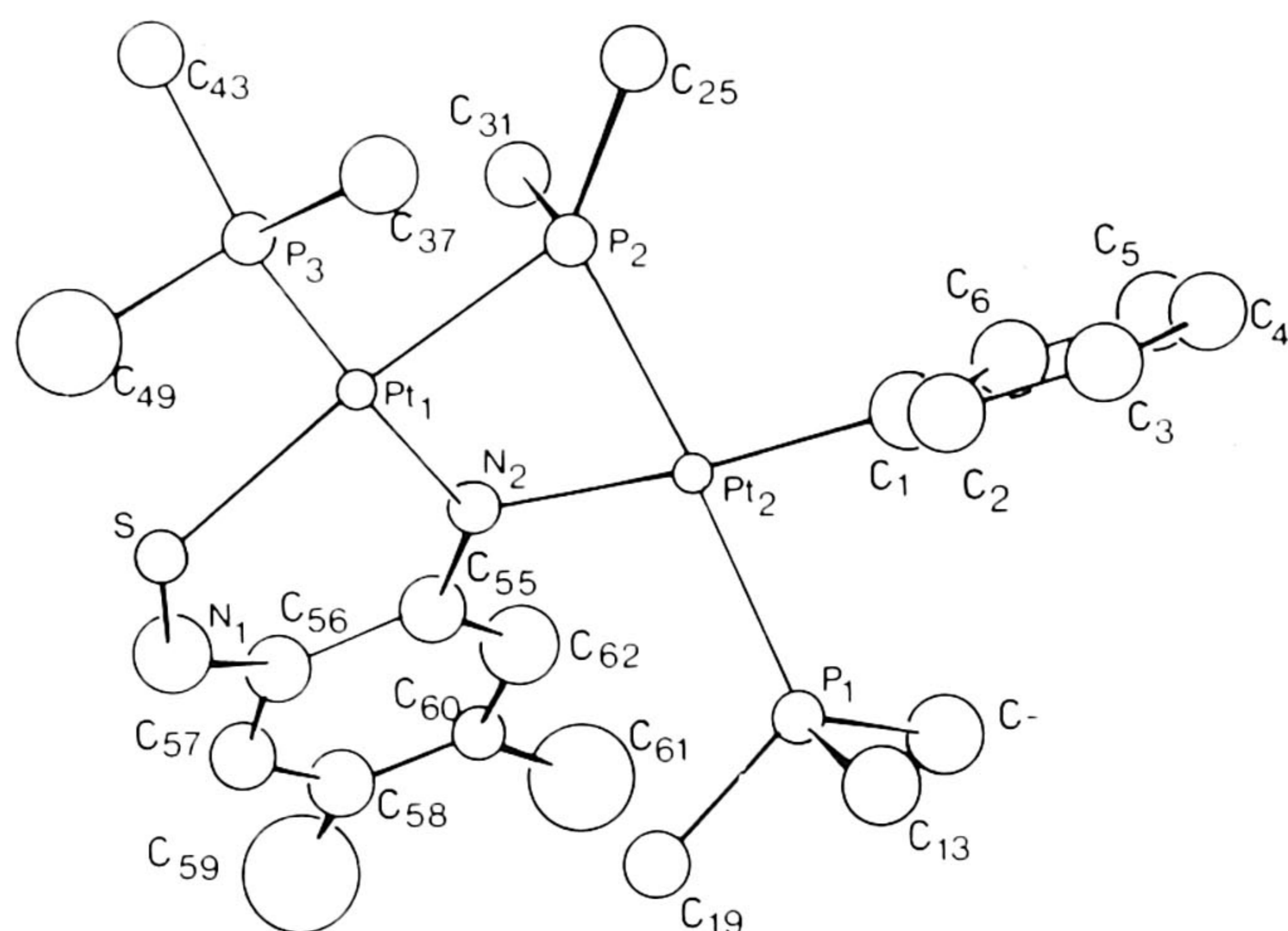


Fig. 11. The molecular structure of $[Pt_2S\{N(6-\mu-N-4,5-Me_2C_6H_2)\}(\mu-PPh_2)(Ph_3P)_2Ph]$. Of the phenyl groups only the positions of C(1) are shown (cf. ref. 50).

More drastic bond rupture reactions have been observed for the reactions of $[Fe_2(CO)_9]$ with $RNSNR$ ($R = t-C_4H_9$ and $p-MeC_6H_4$) which were studied in fairly great detail⁵¹. The isolated products reflected the fact that the sulfur-dimine skeleton during the interaction with the dinuclear iron cluster underwent exclusively N=S bond rupture reactions which were strongly dependent on the nature of R. The proposed reaction is shown in Figure 12.

⁵⁰ R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers and A. R. Overbeek, *J. Organomet. Chem.* **155**, 123 (1978).

⁵¹ R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers, J. D. Schagen, J. J. Zwinselman, A. R. Overbeek and C. H. Stam, *J. Organomet. Chem.* **170**, 337 (1979).

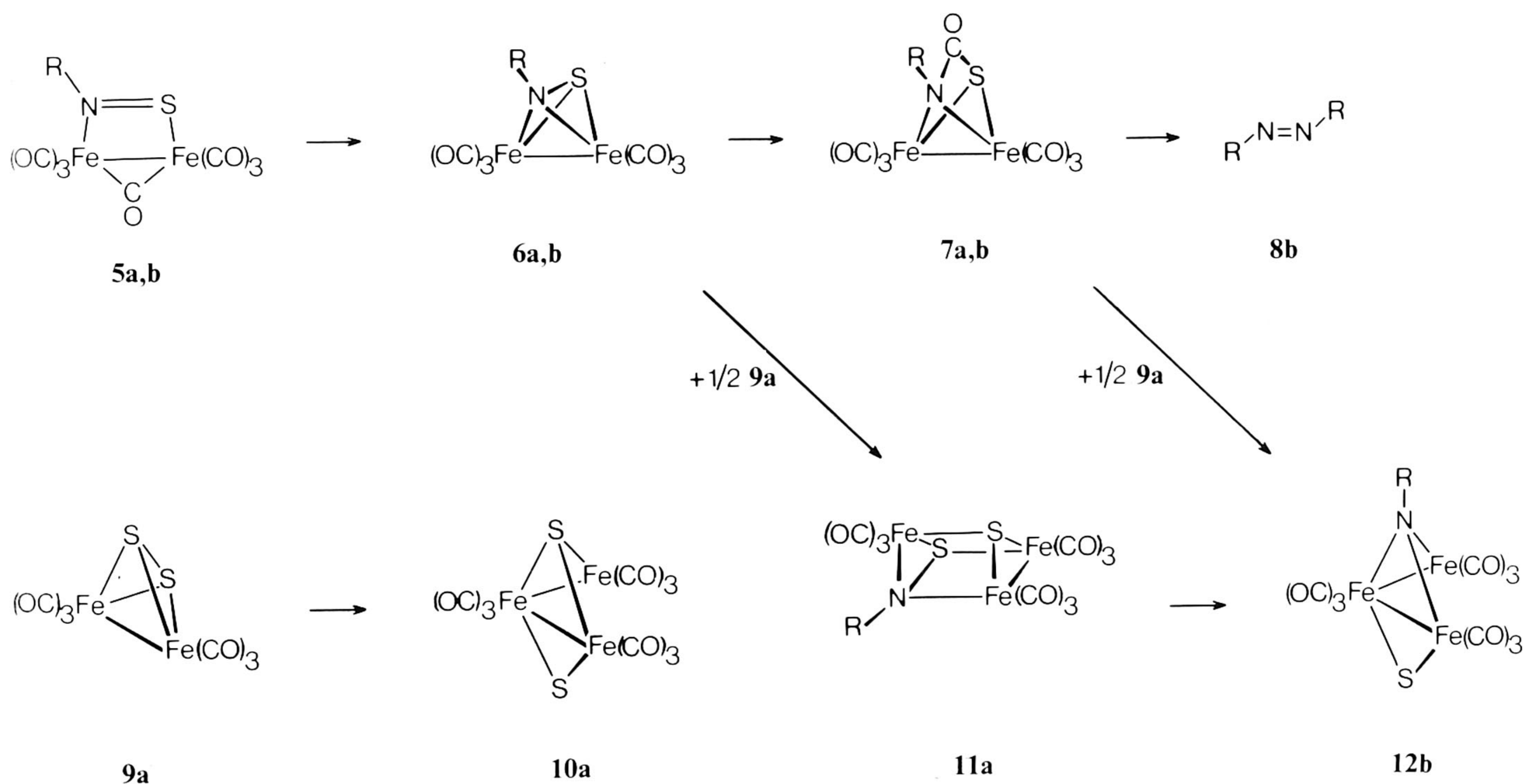
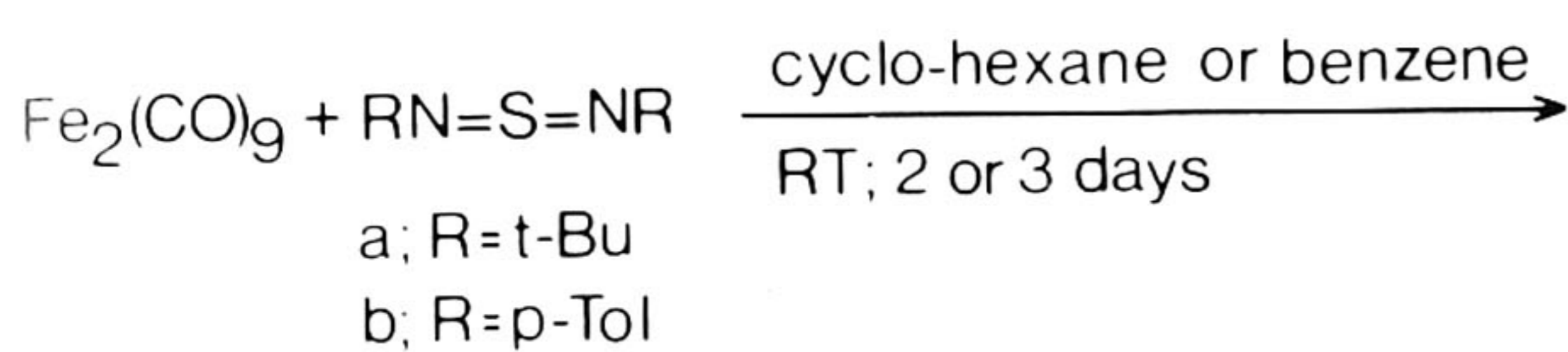


Fig. 12. The various reaction products and possible routes for their formation in the reaction of $RN=S=NR$ ($R = t\text{-Bu}$ or $p\text{-Tol}$) with $[Fe_2(CO)_9]$.

It appears that in the first instance $[\text{Fe}_2(\text{CO})_7(\text{RNS})]$ (**5**) is formed. This complex contains six terminal and one bridging carbonyl groups. A simple electron count reveals that each Fe atom has the eighteen electron configuration if the RNS moiety functions as a four-electron donor ligand which requires that the double N=S bond is positioned parallel to the Fe-Fe bond. Conversion of (**5**) into $[\text{Fe}_2(\text{CO})_6(\text{RNS})]$ (**6**), already isolated by Otsuka et al.⁵² for R = *t*-Bu, involves the loss of the bridging carbonyl group, while the RNS unit, now necessarily acting as a six-electron donor group, lies perpendicular to the Fe-Fe bond. The enhanced electron donation by the RNS groups causes a reduction of the NS bond order from two in (**5**) to one in (**6**) and thus a weakening of the NS bond. This makes the NS bond susceptible for reaction, as is shown by the isolation of $[\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{O})\text{S}\}]$ (**7**), for which a crystal structure determination⁵¹ was carried out for the case of R = 4-MeC₆H₄. Compound (**7**) is most probably formed by insertion of a CO group into the NS bond. Heating of (**7**) yielded azotoluene (**8**) indicating the loss of COS and the involvement of nitrene (NR) fragments in the decomposition reaction. Other compounds formed are $[\text{Fe}_2(\text{CO})_6\text{S}_2]$ (**9**) and $[\text{Fe}_3(\text{CO})_9\text{S}_2]$ (**10**) which have been prepared also by other routes^{53,54}, and which indicate the formation of S atoms. Finally, we were able to isolate the complexes $[\text{Fe}_3(\text{CO})_9(\text{RNS})\text{S}]$ (**11**) and $[\text{Fe}_3(\text{CO})_9(\text{RN})\text{S}]$ (**12**). The determination of the crystal structure of (**11**) (for R = *t*-Bu) showed a prismane-type structure containing a four electron donor S atom and a six electron donor RNS fragment, as evidenced by the NS bond length of 1.70 Å which is in accordance with a single bond⁵¹. The crystal structure of (**12**), for R = 4-MeC₆H₄, shows the presence of a bent trinuclear Fe₃ chain which is bridged on both sides by a triply bridging four electron donor nitrene NR fragment and a triply bridging four electron donor S atom⁵¹.

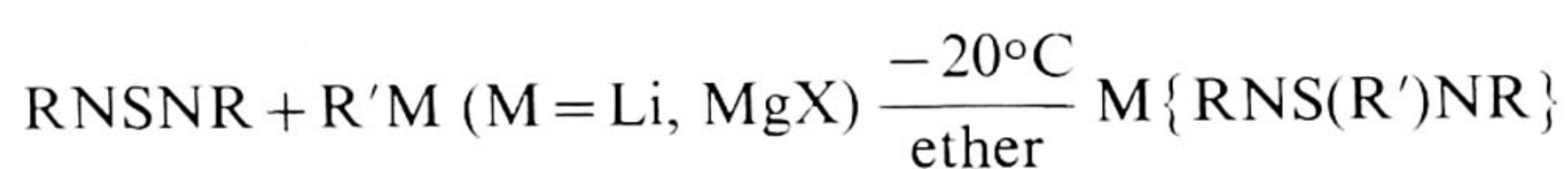
The formation of these trinuclear species is rather puzzling, but the product distribution in dependence of R indicates that (**11**) and (**12**) are formed from (**6**) and (**7**) respectively by reaction with Fe(CO)₃S groups, which have to be formed from Fe₂(CO)₆S₂ or Fe₃(CO)₉(S)₂. The proposed reaction scheme and the structural details of the isolated products serve to illustrate that electron-rich atoms such as Fe⁰ are able to break up the RN=S=NR molecule, probably *via* initial Fe⁰-π-N=S coordination, into RNS, S and NR fragments which are captured and stabilized in the cluster complexes. Also, it appears that the dinuclear Fe-Fe unit has a function in activating bonds by acting as an electron sink *i.e.* in weakening NS bonds, as illustrated by the above-discussed reaction sequence **5** → **6** → **7** (see Fig. 12).

The N=S bond rupture reactions are not restricted to Fe⁰, but have also been observed for Ni^I and Fe⁻¹ in the reactions of sulfurdiimines with $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ and $[\text{Hg}\{\text{Fe}(\text{CO})_3\text{NO}\}_2]$. No detailed studies were carried out, but the crystal structures of $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Ni}\}_3(\text{N-}t\text{-Bu})]$ ^{55,56} and $[\text{Fe}_4(\text{NO})_4(\text{N-}t\text{-Bu})_2\text{S}_2]$ ⁵⁷, respectively, have been reported indicating the formation of NR and S fragments resulting from NS bond rupture.

RNSO also is broken up by Fe₂(CO)₉⁵² but no detailed studies have been carried out.

B. Conversion of RNSNR and RNSO by addition reactions with LiR, MgRX and AlR₃

It has been shown for RNSNR and RNSO that the S atom carries less negative charge than the N atom (or O atom)³⁴. It is therefore not surprising that reactive species such as LiR', -MgR' and >AlR' add over the double bonded system of the hetero-olefin RNSNR^{58,59} and RNSO^{60,61}. In the case of alkyllithium, aryllithium and Grignard reagents the following reactions were observed, and proved to proceed quantitatively:



Owing to the very distinctive colour changes at the equivalence point and to the fact that RNSNR does not react with impurities, *e.g.* alkoxides, metallic impurities, which may be present in these reagents, this reaction is an excellent method for the quantitative determination of Grignard and alkyl- and aryl-lithium reagents^{58,59} [ArylNSO also is suitable for this purpose and is used as such in our laboratory⁶⁰]. The products of the reaction with RNSNR have been shown to be of the type M{RNS(R')NR}, but the structural features have not been studied.

More information was obtained for the reaction of $[\text{AlMe}_3]_2$ with RNSNR⁶¹ and with RNSO⁶², which afforded $[\text{Me}_2\text{Al}\{\text{RNSMeNR}\}]_2$ and $[\text{Me}_2\text{Al}\{\text{RNS}[\text{Me}]\text{O}\}]_2$, respectively. Both products were shown to be dimeric and to contain RNSMeNR and RNS(Me)O as ligands bridging the aluminium atoms.

These novel (*S*-substituted) sulfurdiimino-lithium, -magnesium, and -aluminium compounds appear to be excellent starting materials for the preparation of other sulfurdiimino metal complexes. Although the research in this field is still in progress, it is possible to mention here some interesting findings.

Reaction of $[\text{M}\{\text{RNS}(\text{R}')\text{NR}\}]$ (M' = Li, MgX) with $[\text{M}'\{\text{O}_2\text{C}(\text{CF}_3)\}_n]$ (M' = Cu^I, Ag^I) gave smoothly the dimeric complexes $[\text{M}'\{\text{RNS}(\text{R}')\text{NR}\}]_2$ which contain RNS(R')NR anionic groups bridging two metal atoms, as in the case of the aluminium compounds. However, reactions of $[\text{M}\{\text{RNS}(\text{R}')\text{NR}\}]$ with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and the π-allyl complexes $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{PdCl}]_2$ (R'' = H, Me) afforded $[\text{Rh}(\text{CO})_2\{\text{RNS}(\text{R}')\text{NR}\}]$ ⁵⁹ and $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{Pd}\{\text{RNS}(\text{R}')\text{NR}\}]$ ⁶³, respectively, in quantitative yields. In the Rh and Pd compounds the RNS(R')NR ligand acts as a chelate, as demonstrated by the crystal structure of $[\text{Rh}(\text{CO})_2\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NS-}t\text{-BuN}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\}]$ ⁶⁴ (Figure 13).

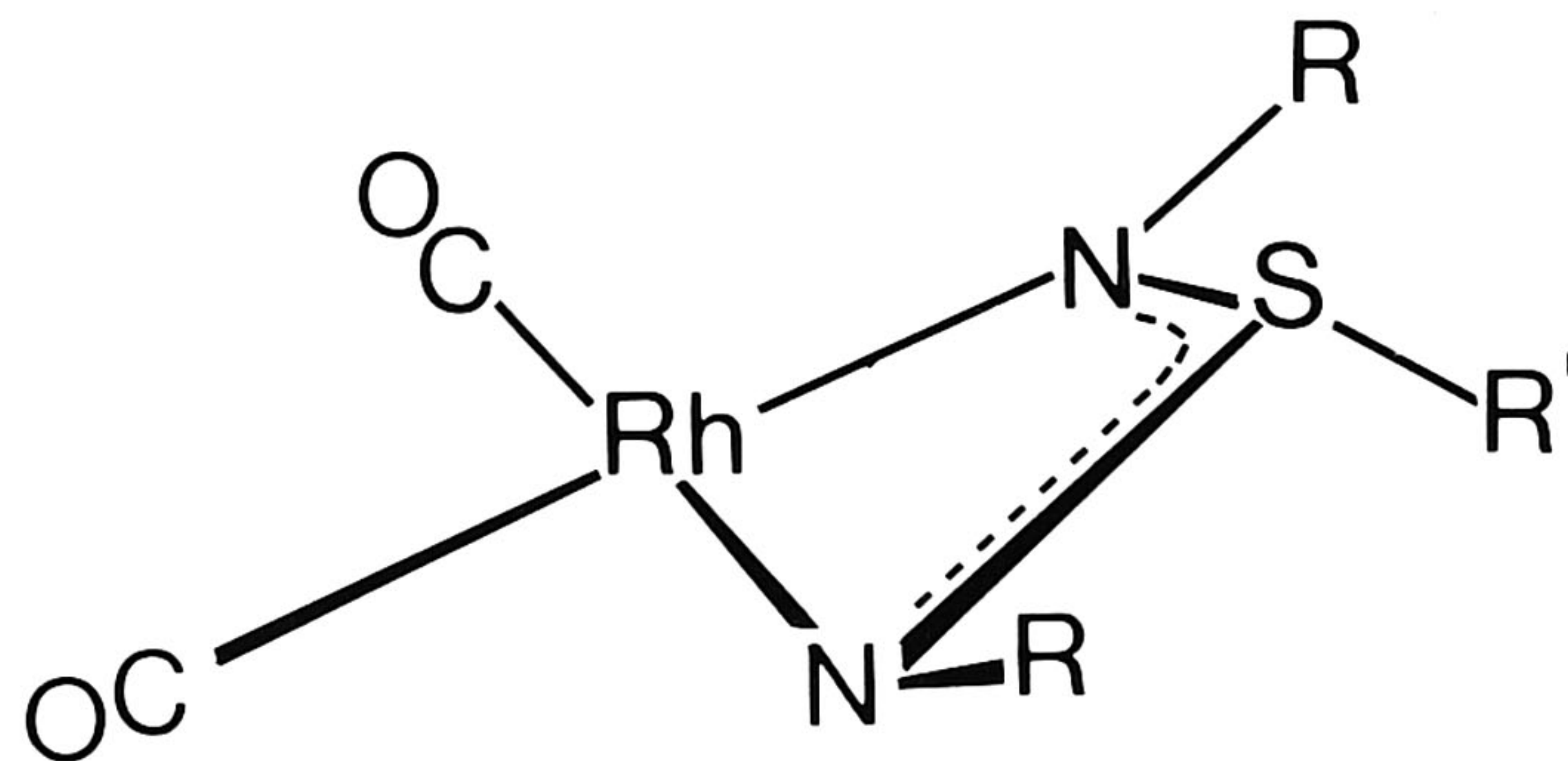


Fig. 13. Structure of $\text{Rh}(\text{CO})_2\{\text{S-}t\text{-Bu-N,N}'\text{-dimesityl-NSN}\}$ (*cf. ref. 64*).

⁵² S. Otsuka, T. Yoshida and A. Nakamura, *Inorg. Chem.* **7**, 1833 (1978).

⁵³ C. H. Wei and L. F. Dahl, *Inorg. Chem.* **4**, 1 (1965).

⁵⁴ C. H. Wei and L. F. Dahl, *Inorg. Chem.* **4**, 493 (1965).

⁵⁵ S. Otsuka, A. Nakamura and T. Yoshida, *Inorg. Chem.* **7**, 276 (1968).

⁵⁶ S. Otsuka, A. Nakamura and T. Yoshida, *Ann. Chem.* **719**, 54 (1968).

⁵⁷ R. S. Gall, T. W. Chu and L. F. Dahl, *J. Am. Chem. Soc.* **96**, 4019 (1974).

⁵⁸ J. Kuyper and K. Vrieze, *J.C.S. Chem. Commun.* 64 (1976).

⁵⁹ J. Kuyper, P. C. Keijzer and K. Vrieze, *J. Organomet. Chem.* **116**, 1 (1976).

⁶⁰ J. Kuyper and K. Vrieze, unpublished work.

⁶¹ H. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, to be published.

⁶² H. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, to be published.

⁶³ P. Hendriks, J. Kuyper and K. Vrieze, *J. Organomet. Chem.* **120**, 285 (1976).

⁶⁴ H. van der Meer and D. Heijdenrijk, *Cryst. Struct. Comm.* **5**, 401 (1976).

An interesting feature of this structure is that the $\text{Rh}(\text{CO})_2$ group and the NSN group are not coplanar. Instead, the NSN ligand is bonded in a pseudo-allylic fashion to the Rh atom with a $\text{Rh} \dots \text{S}$ distance of $\sim 2.70 \text{ \AA}$. The S–N bond length is 1.65 \AA which is closer to the single bond value of 1.70 \AA than to the double bond value of 1.52 \AA .

In Figure 14 it is shown that in the case of the π -allylic palladium compounds the pseudo π -allylic bonding of $\text{RNS}(\text{R}')\text{NR}$ gives rise to two isomers which interconvert at room temperature on the $^1\text{H-NMR}$ scale⁶³.

The $\text{RNS}(\text{R}')\text{NR}$ ligand when bonded to a transition metal atom is in general not particularly stable. Rather interesting results were obtained for the Rh and Pd compounds in which the $\text{RNS}(\text{R}')\text{NR}$ group acts as a bidentate. It was found that this ligand may be converted slowly into azo compounds and SR' . In Figure 15 such a selective decomposition is shown for the case of $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{Pd}\{\text{RNS}(\text{R}')\text{NR}\}]$. In this case it could be demonstrated that the SR' group is captured as a ligand bridging the two Pd atoms in $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{Pd}(\text{SR}')_2]$ ⁶³. The decomposition reaction is dependent on both electronic and steric factors. The complexes are most stable when R and R' are bulky *e.g.* for R = 2,4,6-mesityl and for R' = *tert*-butyl. The decomposition goes faster when R is phenyl and for R' = methyl.

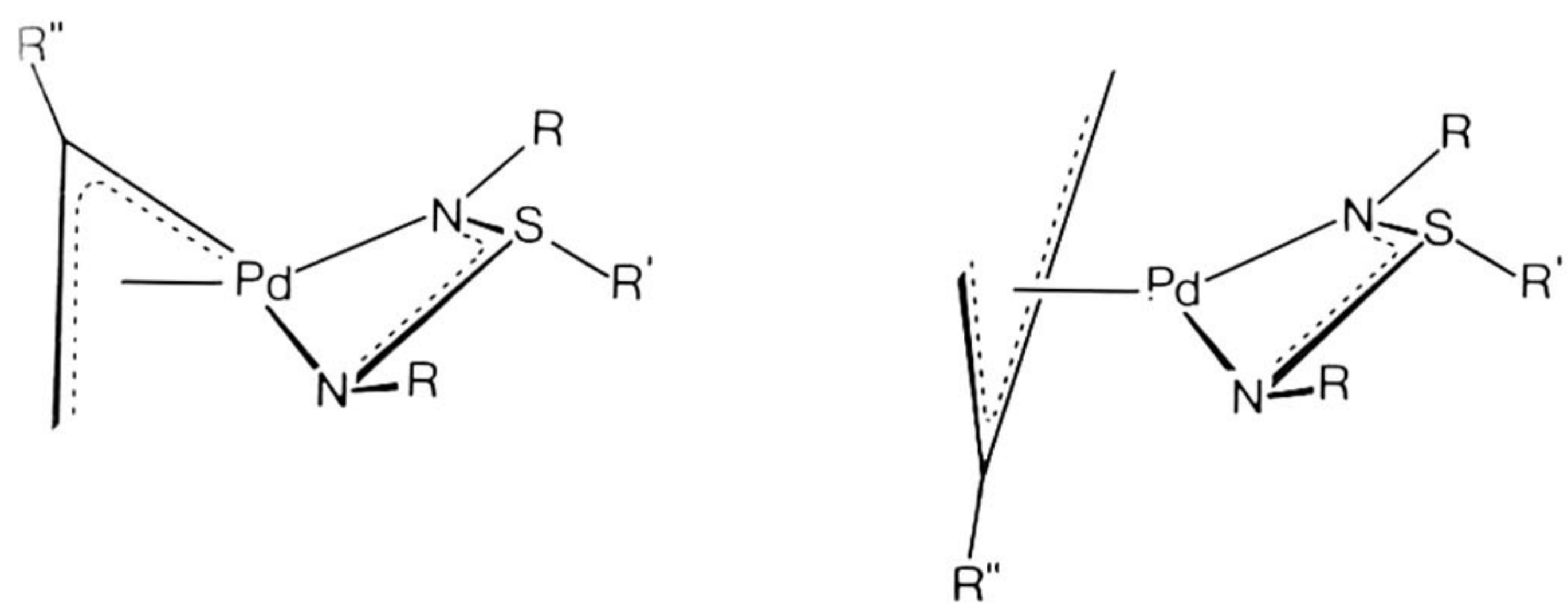


Fig. 14. Two stereoisomers of $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{Pd}\{\text{RNS}(\text{R}')\text{NR}\}]$.

Electron donating R substituents enhance the rate of decomposition, as shown by the observation that the rate increases in the order $3,5\text{-Cl}_2\text{C}_6\text{H}_3 < 4\text{-ClC}_6\text{H}_4 < 4\text{-MeC}_6\text{H}_4$.

In order to try to understand these phenomena it is useful to look at the structure of the rhodium complex^{59,64}. The structural details show that the mesityl groups are positioned in such a way that they are wedged with the *ortho*-methyl groups between the Rh and S atoms and that as a result rotation of the mesityl groups around the N–C bond is strongly hindered. This is indeed confirmed by the NMR spectra of solutions of this complex which show that at ambient temperatures the mesityl groups do not rotate, while at higher temperatures a slow rotation is observed. However, for smaller R' groups and/or smaller R groups the R substituents do rotate at ambient temperatures. It is interesting that there is a clear correlation between the ease of rotation of the R group and the rate of decomposition into azo compounds.

In view of these results, it was therefore assumed that the first step in the decomposition process involves a movement of the $\text{RNS}(\text{R}')\text{NR}$ group to the effect that the S atom approaches the metal atom and possibly binds to the metal resulting in the formation of a metal–S-bonded intermediate. Such a movement is possible only when the steric hindrance along the NSN skeleton is small *i.e.* with the smaller R and R' groups. For the subsequent elimination of the SR' anion and formation of the N=N bond electronic factors become important, which can be deduced from results relating to complexes containing coordinated SO_2 ⁶⁵. It has been argued on the basis of molecular orbital arguments that the OSO angle decreases and the S–O bond length increases with increasing negative charge, since extra

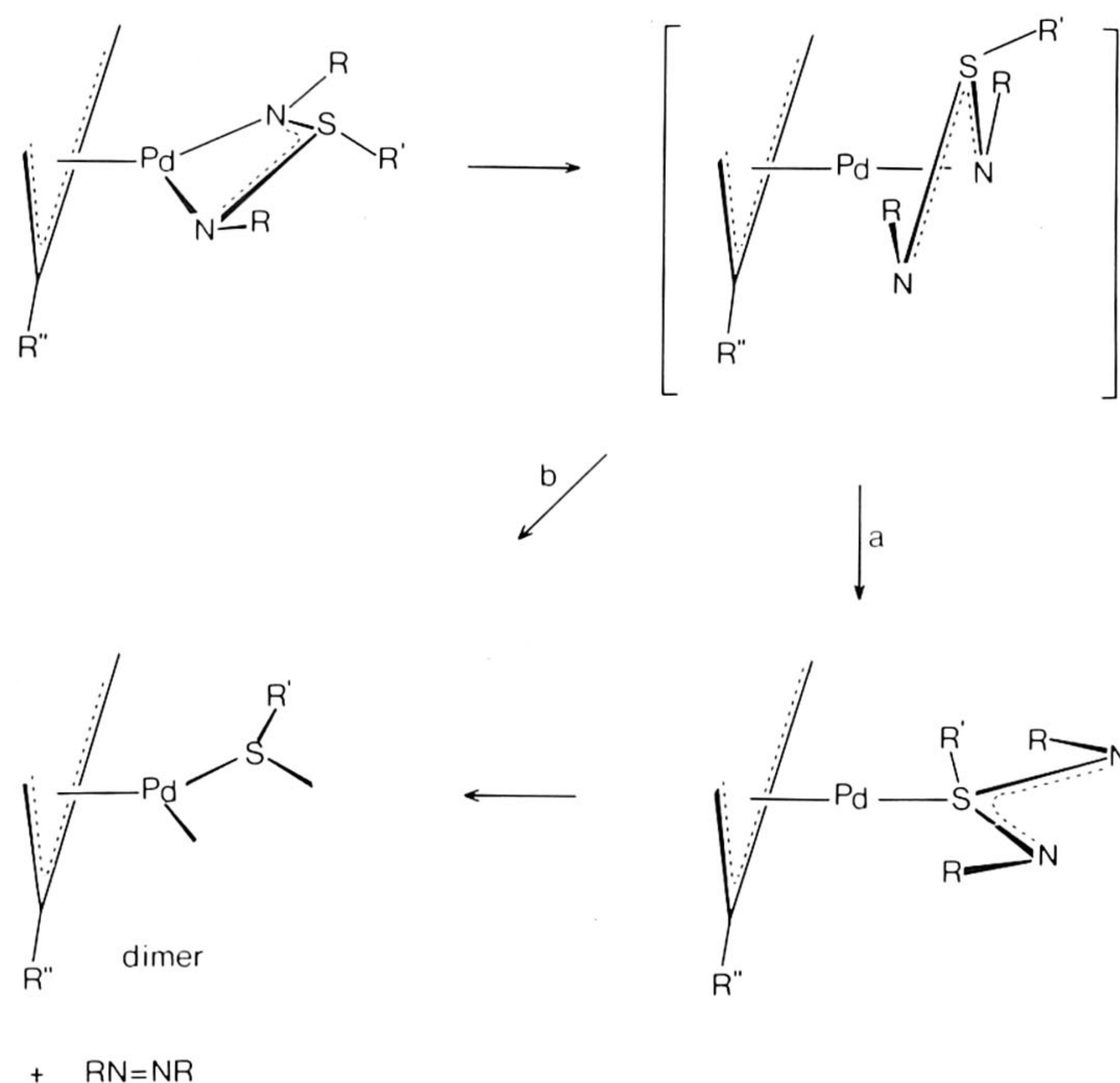


Fig. 15. Proposed mechanism for the formation of azoarenes and $[(\eta^3\text{-R}''\text{C}_3\text{H}_4)\text{Pd}(\text{SR}')_2]$.

electronic charge will go into an orbital with S–O antibonding and O–O bonding character⁶⁵. It should be noted that it is not strictly necessary for the $\text{RNS}(\text{R}')\text{NR}$ group to go completely to the metal–S-bonded species shown in Figure 15. Also in the pseudo π -allylic type in which the metal is bonded to both the S and N atoms the electronic arguments outlined above are likewise applicable to explain the elimination taking place for the Rh and Pd complexes.

IV. Concluding remarks

In this review we have attempted to give a survey of part of our research together with a discussion of the relevant RNSO and RNSNR complexes reported in the literature. Emphasis has been placed on the discussion of the possible coordination modes of ligands containing N=S groups and of the relation between the mode of coordination and the type of reaction of the coordinated ligand. It is important that N=S bonds, in suitable circumstances, bind like ethylene to metal atoms and may then also be activated for further reaction. A recent example is the catalytic synthesis of $\text{PhN}=\text{S}=\text{NPh}$ from $\text{PhN}=\text{S}=\text{O}$ with a Ni^0 catalyst⁶⁶, demonstrating the possible use of such catalysts to incorporate N=S bonds into organic substrates. In a future review on the coordination and activation of N=C bonds we will show that such coupling reactions of imine groups with organic substrates are likewise possible and most probably will appear to provide a versatile synthetic route.

In short, it seems that the field of study of hetero-olefinic metal compounds, is a very promising one with a great potential in catalysis and organic chemistry.

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⁶⁵ P. D. Dacre and M. Elder, *Theor. Chim. Acta* **25**, 254 (1972).

⁶⁶ D. Walther, E. Dinjus and H. Wolf, *Z. Chem.* **19**, 381 (1979).