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CENTENARY LECTURE*

Catalysis and Coordination Compounds involving Electron-rich Main Group Elements

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1 Introduction

The development of transition metal catalysts for industrial organic reactions has been one of the most interesting aspects of chemical research over the past 25 years. Up to 80 per cent of all useful organic reactions are controlled by transition metal catalysts. The catalysts most commonly used for this purpose are insoluble, heterogeneous catalysts. Up to date homogeneous catalysts are applied only in twenty industrial processes. In general the catalysts are 'poisoned' by sulphur and sulphur-containing compounds.

There are only few examples known where compounds are prepared under the influence of a catalyst containing 'electron-rich' elements. Elements of Groups V and VI of the periodic table are termed 'electron-rich' when the coordination number does not exceed two ($-\overline{\underline{S}}-$, $-\overline{\underline{O}}-$, $=\overline{N}-$ *etc.*)

In contrast, biologically, transition metals like iron, manganese, molybdenum, copper, and zinc play a crucial role in oxygen-, sulphur-, and nitrogen-containing proteins. There would be no life without the essential transition metal elements. Iron and copper are used in the transport and storage of oxygen and also in electron transport. Instead of haemoglobin, haemocyanin a copper-containing protein, is the oxygen-carrying pigment in the blood of a large number of molluscs. Copper proteins, known as blue proteins, function in the plant world as one-electron transfer agents.

Molybdenum plays an important role in nitrogen fixation. It has been known since 1930 that traces of molybdenum are necessary for the growth of rhizobium bacteria which are found in nodules on the roots of leguminous plants. The metal-containing constituents of nitrogen-fixing bacteria are the enzyme nitrogenase and the electron-transfer agent ferredoxin. Nitrogenase consists of two proteins, one containing molybdenum, iron, and sulphur atoms, and the other only iron and sulphur.

Consequently, our endeavour is the investigation of reactions with electron-rich elements in the presence of transition metals as catalysts.

In the field of sulphur–nitrogen compounds we were interested in coordinating unstable intermediates at metal centres in order to study their chemistry and investigate their structure by single crystal *X*-ray analysis.

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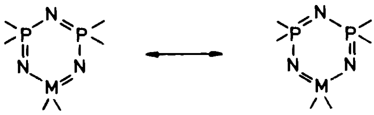
A challenging approach to new pathways between main group and transition metal elements is the preparation of metallacycles and metallapolymers. It is well known that tetrasulphur tetranitride, S_4N_4 and *cyclo*-$(NPCl_2)_3$ can be converted by heating into highly polymeric $(SN)_x$ and $(NPCl_2)_x$, respectively. We were interested in the synthesis of compounds where one of the main group elements in the precursors was replaced by a transition element of high oxidation state. In these compounds the main group unit does not function as a chelating ligand but rather forms multiple bonds towards the metal, *e.g.*



(1) (2)

The resonance forms (1) and (2) show the representations of metal-containing phosphazenes. Similar metallacycles could be obtained from 2,4-dithia-1,3,5-triazenes.

Several synthetic possibilities and precursors have been investigated. Only a few have been successful.

2 The Catalytic Approach

From the industrial point of view, heterogenous systems have great practical advantages because of the ease of separation of products. However, the homogeneous processes have been developed because they may give much higher selectivity and may be better understood reactions.

In catalytic cycles where Wilkinson's catalyst $(Ph_3P)_3RhCl$ is used the metal plays an active role. To perform as a catalyst the metal must possess the ability to change the number of electrons associated with it by two or four. Since the total number of electrons cannot exceed eighteen, most catalytic species possess fourteen or sixteen electrons. Coordination and dissociation are the types of reactions involved in most catalytic cycles in changing the oxidation state at the metal.[1]

The antibacterial and catalytic properties of Ag^+-ions have been known for a long time. In our investigations we used $AgAsF_6$. This salt has a bulky anion and is therefore easily soluble in non-coordinating solvents like sulphur dioxide. Furthermore, $AgAsF_6$ forms crystalline products with oxygen-, sulphur-, and selenium-containing ligands, which can be subjected to *X*-ray irradiation.

The reaction between $AgAsF_6$ and trimeric thioformaldehyde resulted in the formation of three products.[2] The first one (3) (H-atoms, anions, and solvent are omitted for clarity) contains two independent silver ions with coordination numbers 5 and 4, respectively, and has the following composition $[\{(CH_2S)_3\}_5Ag_2](AsF_6)_2 \cdot SO_2$.

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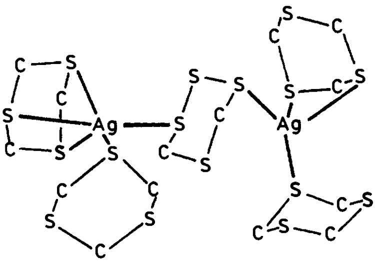
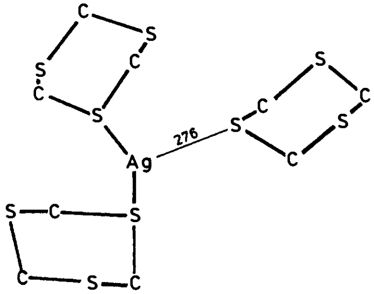
[1] Cotton and Wilkinson, 'Advanced Inorganic Chemistry', John Wiley & Sons, New York 1980.

[2] H. W. Roesky, H. Hofmann, P. G. Jones, W. Pinkert, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1215.



(3) $[\{(CH_2S)_3\}_5 Ag_2]^{2+}$

In (3) the trimeric thioformaldehyde functions as a tridentate, bidentate, and monodentate ligand. A compound of composition $[(CH_2S)_3]_2Ag(AsF_6)$ (4) is



(4) $[\{(CH_2S)_3\}_2 Ag]^+$

formed as a minor by-product,[3] or preferentially when $AgAsF_6$ is reacted with trimeric thioformaldehyde in a ratio of 1:2. In this complex the silver atom is coordinated by two sulphur atoms to form a distorted linear unit with a S–Ag–S bond angle of 153°. A further sulphur atom completes a distorted trigonal planar coordination in such a way that this Ag–S interaction is, at 276 pm, 25 pm longer than the other two. There are no other Ag–S contacts. Thus, the structure may be considered to contain $[\{(CH_2S)_3\}_2Ag]^+$ cations linked by the weak additional Ag–S interactions to form polymeric chains, with two chains per cell parallel to one of the crystallographic axes. A third product of composition $Ag(CH_2S)_3AsF_6$ has probably a polymeric structure, where two Ag^+-ions are linked by one trimeric thioformaldehyde molecule. Owing to its polymeric and non-crystalline nature, its structure is still speculative. In these complexes the ligands retain the chair conformation observed in the free ligand.

When trimeric selenoformaldehyde[3] is reacted in liquid SO_2 with $AgAsF_6$, a

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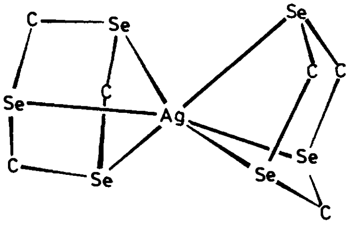
[3] H. Hofmann, P. G. Jones, M. Noltemeyer, E. Peymann, W. Pinkert, H. W. Roesky, and G. M. Sheldrick, *J. Organomet. Chem.*, 1983, **249**, 97.

product of composition $[\{(CH_2Se)_3\}_2Ag]AsF_6$ (5) is formed. The silver atom is coordinated irregularly by all six selenium atoms of the two ligands. The sulphur and selenium analogues are thus not isostructural. The Ag–Se bond lengths are observed to be in the range 278—305 pm.

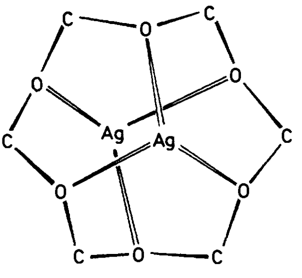


(5)$[\{(CH_2Se)_3\}_2Ag]^+$

In the described complexes with trimeric thioformaldehyde, Ag^+ can attain coordination numbers of two, three, four, and five. The different species are formed without changing the ligand. However, in contrast to Wilkinson's catalyst, the oxidation state at silver is not changed during its catalytic activity. We suppose that the different coordinated silver ions are not in an equilibrium, but the energy differences between the species of various coordination numbers should be small. Therefore, the coin metals silver and copper should be interesting metals for the catalytic reactions with sulphur and oxygen compounds. It should be mentioned that copper can change its oxidation state readily from I to II, this catalytic potential has been investigated!

3 The Cleavage of Carbon–Oxygen Bonds with Silver and Caesium

The reaction of trimeric formaldehyde $(CH_2O)_3$ with $AgAsF_6$ in liquid SO_2 leads to the formation of $[(CH_2O)_6Ag_2]Ag(AsF_6)_3$ (6). In (6) two six-membered rings are cleaved to yield the twelve-membered alternating carbon–oxygen-containing ring.[4] Structure (6) consists of two crystallographically equivalent silver atoms,



(6)$[(CH_2O)_6Ag_2]^{2+}$

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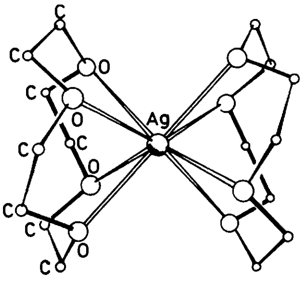
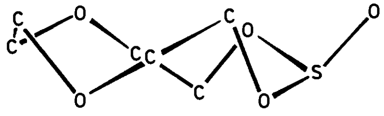
[4] H. W. Roesky, E. Peymann, J. Schimkowiak, M. Noltemeyer, W. Pinkert, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 981.

each coordinated by alternate oxygen atoms of the twelve-membered ring. This ring is isoelectronic and isostructural to the well-known S_{12}.[5] The configuration of the twelve-membered ring in (6) adopts three parallel planes. The six carbon atoms are in the central plane while three oxygen are arranged above and below this plane.

When ethylenoxide is treated with $AgAsF_6$ in liquid SO_2 the twelve-membered crown-ether complex $[(CH_2CH_2O)_8Ag](AsF_6)$ (7) is formed.[6] The yield is about 25 per cent. For the formation of one molecule of (7) eight carbon–oxygen bonds have to be cleaved. A by-product of this reaction is 1,4-dioxane. The coordination geometry around silver in (7) is cubic. However, two of the opposite planes are distorted by 30 degrees. The cleavage of the carbon–oxygen in ethylenoxide by Cs^+-ions affords an eleven-membered ring (8) of three molecules of ethylenoxide and one molecule of SO_2.[7] Compound (8) is obtained with a 20 per cent yield, it is a white solid melting at 41 °C. In the presence of Ag^+, (8) is quantitatively converted into (7) under elimination of SO_2.[8]



(7)$[(CH_2CH_2O)_8Ag]^+$



(8)

4 The Formation of Heterocycles from Elemental Sulphur

At room temperature elemental sulphur mainly contains S_8-rings, which have a crown-shaped configuration. The orthorhombic crystals of α-S_8 are obtained by recrystallization of sulphur from CS_2. Recently we reported the first coordination compound of the eight-membered sulphur ring. $[Ag(S_8)_2](AsF_6)$ (9) is prepared

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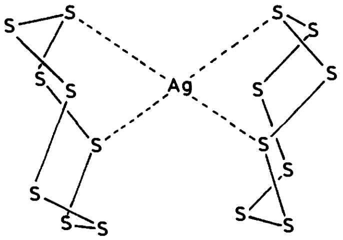
[5] J. Steidel, R. Steudel, and A. Kotoglu, *Z. Anorg. Allg. Chem.*, 1981, **476**, 171.

[6] P. G. Jones, T. Gries, H. Grützmacher, H. W. Roesky, J. Schimkowiak, and G. M. Sheldrick, *Angew. Chem.*, 1984, **96**, 357; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 376.

[7] H. W. Roesky and H. G. Schmidt, *Angew. Chem.*, 1985, **97**, 711; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 695.

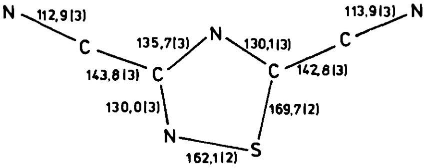
[8] H. W. Roesky and H. G. Schmidt, unpublished results.

from S_8 and $AgAsF_6$ in liquid SO_2. Compound (9) is slightly soluble in sulphur dioxide, from which we obtained single crystals for structure analysis, and the complex is sensitive to moisture and light. It may be easily distinguished by Raman spectroscopy from uncomplexed sulphur. The S_8-ring in (9) is slightly more flattened compared to that in elemental sulphur, the wider spread of bond angles and torsion angles being the main difference between the S_8-ligands and S_8 in elemental sulphur. The silver atom is 1,3-coordinated. According to Raman investigations we also observed an interaction of copper ions with elemental sulphur in liquid SO_2.



(9) $[Ag(S_8)_2]^+$

The reaction of cyanogen and elemental sulphur in the presence of copper and dimethylformamide at 125 °C affords $S(CN)_4$[9,10] (10). 1,2,4-Thiadiazole-3,5-dicarbonitrile (10) is a white solid of melting point 67 °C. It undergoes selective reactions with one or both nitrile groups to yield imidic esters, thioamides, and dicarboxamides.



(10)

It is interesting to mention that in (10) an insertion of the metal fragment $(Ph_3P)_2Pt$ into the sulphur–nitrogen bond occurs (11) when it is treated with $(Ph_3P)_2PtC_2H_4$.[11] According to Hoffmann[12] and Stone[13] the fragments

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[9] H. W. Roesky, K. Keller, and J. W. Bats, *Angew. Chem.*, 1983, **95**, 904; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 881.

[10] H. W. Roesky, H. Hofmann, K. Keller, W. Pinkert, P. G. Jones, and G. M. Sheldrick, *Chem. Ber.*, 1984, **117**, 2681.

[11] H. W. Roesky, H. Hofmann, P. G. Jones, and G. M. Sheldrick, *Angew. Chem.*, 1984, **96**, 971; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 971.

[12] R. Hoffmann, *Angew. Chem.*, 1982, **94**, 725; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

[13] F. G. A. Stone, *Angew. Chem.*, 1984, **96**, 85; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89.

$(Ph_3P)_2Pt$ and CH_2 are called isolobal if the number, symmetry properties, approximate energy, and shape of the frontier orbitals and the number of electrons in them are similar, Figure 1.

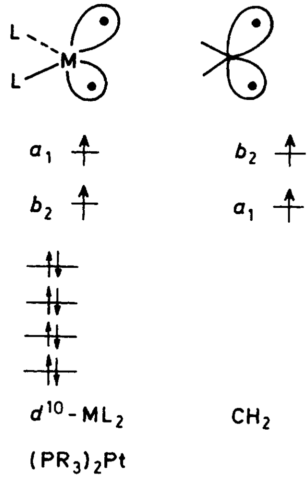
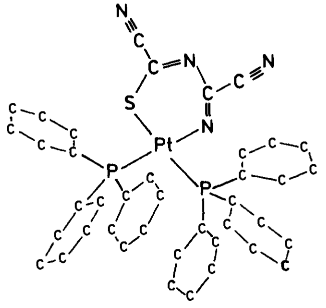


Figure 1



(11)

Compound (11) is not sensitive to oxygen or moisture.

1,2,5-Selenadiazole (12) prepared from di-iminosuccinnitrile and $SeOCl_2$ or Se_2Cl_2 reacts with $(Ph_3P)_2PtC_2H_4$ under elimination of C_2H_4 to yield the heterocycle $(Ph_3P)_2Pt(C_4N_4Se)$ (13).[14]

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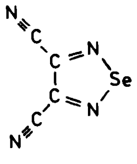
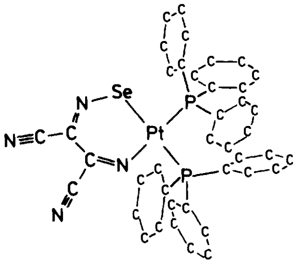
[14] H. W. Roesky, T. Gries, H. Hofmann, J. Schimkowiak, P. G. Jones, K. Meyer-Bäse, and G. M. Sheldrick, *Chem. Ber.*, 1986, **119**, 366.



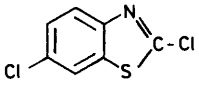
(12)



(13)

The structure of (13) was determined by an *X*-ray structure analysis which proved the insertion of platinum into the selenium–nitrogen bond. Compound (13) forms red-brown crystals which are not sensitive to moisture in air. They are stable up to 200 °C. In general we observed that insertion of a metal fragment in Se–N and S–N bonds is possible when the nitrile groups in (12) are replaced by other electron-withdrawing groups like 2,2,2-trifluoroethoxy.

Dichlorobenzothiazole (14) is prepared by reaction of 4-chlorophenylisocyanidedichloride with sulphur in the presence of metals like Zn, Al, Fe or, respectively, their halides or sulphides.[15] The reaction is conducted at about 180–190 °C to afford (14) in a yield of 72 per cent.



(14)

5 Polymers Formed by Ag^+-ions and Bridging Ligands of the Type $(CN)_2$, $(CN)_2S_3$, or $(CN)_2S_4$

It has been shown for the reaction with elemental sulphur, that coordination with metal ions occurs, or that there are good reasons for expecting that it would do so. In the reaction of $(CN)_2$ with sulphur the question arises, whether only sulphur or $(CN)_2$ coordinates towards the metal. For the preparation of 1,2,4-thiadiazole-3,5-dicarbonitrile we used copper as a catalyst but for the characterization and isolation the silver complexes proved to be better.

$AgAsF_6$ and $(CN)_2$ yield in liquid SO_2 polymeric $[Ag\{(CN)_2\}_2]_n(AsF_6)_n$ (15).[16] This complex consists of square planar silver atoms surrounded by four nitrogen atoms. The cyanogen molecules function as bridges between the silver atoms. We have not observed any cleavage of the carbon–carbon bond in cyanogen to yield

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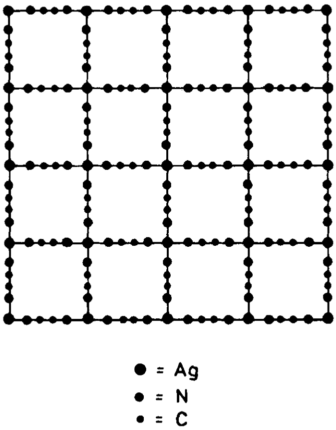
[15] H. W. Roesky, U. Kussmaul, K. Keller, and K. Kühlein; Pat. Appl. DE 3408180 (1985).

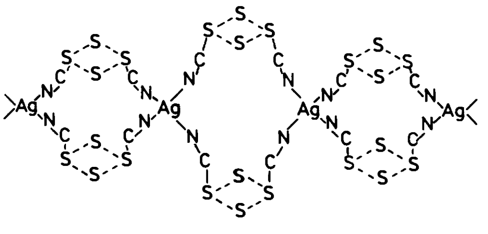
[16] H. W. Roesky, H. Hofmann, J. Schimkowiak, P. G. Jones, K. Meyer-Bäse, and G. M. Sheldrick, *Angew. Chem.*, 1985, **97**, 403; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 417.

AgCN. The structure is noticeably puckered with an Ag–N–C angle of 152.3(9)°. The two dimensional network of (15) is colourless, sensitive to moisture, and is decomposed at 176 °C. Single crystals of (15) have been exposed to u.v.-light to reduce a few of the Ag^+-ions to silver atoms. Investigations to determine whether the irradiated crystals show electronic conductivity are under way.

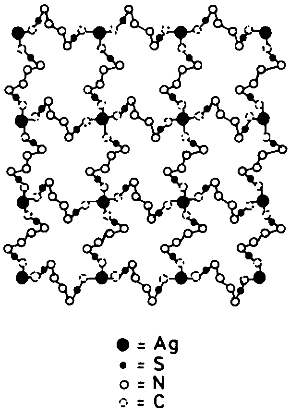


(15) $[Ag\{(CN)_2\}_2]_n^+$

Complexes with dicyanotrisulphane, $S_3(CN)_2$, or dicyanotetrasulphane, $S_4(CN)_2$, and $AgAsF_6$ can be prepared in an analogous way.[17] $S_3(CN)_2$ yields the



(16) $[Ag\{S_3(CN)_2\}_2]^+$



(17) $[Ag\{S_4(CN)_2\}_2]^+$

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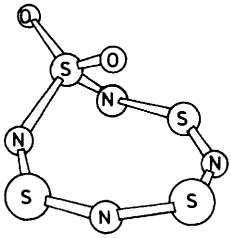
[17] H. W. Roesky, T. Gries, J. Schimkowiak, and P. G. Jones, *Angew. Chem.*, 1986, **98**, in press; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, in press.

one-dimensional (16) and $S_4(CN)_2$ the two-dimensional (17) polymer. In (16) as well as in (17) the Ag-atoms have a tetrahedral surrounding. The broken lines in (16) indicate twofold disorder of these sulphur atoms; the positions are half-occupied. The dicyanosulphanes serve in these complexes as bridging ligands and undergo coordination through their terminal nitrogen atoms.

Compound (16) forms light yellow and (17) orange-yellow crystals, respectively. $S_4(CN)_2$ is an unstable compound, which tends to undergo polymerization at room temperature within a few minutes, forming orange triazines. However, the complexes (16) and (17) are stable at room temperature but sensitive to moisture.

6 Structure–Reactivity Relationship Demonstrated with $S_4N_4O_2$

The structure–reactivity relationship is demonstrated with the eight-membered sulphur–nitrogen ring $S_4N_4O_2$ (18). This molecule is best prepared from the reaction of sulphamide with $S_3N_2Cl_2$.[18] In $S_4N_4O_2$ the sulphone sulphur atom lies 152 pm, and the two adjacent nitrogen atoms are 41 pm, above the mean plane of the five-atom S_3N_2-unit, which is co-planar within 1 pm.[19,20] In comparison to S_4N_4 (19), the electron density within the cage has been reduced, owing to the oxidation of one sulphur atom. The structural data indicate that in (18) no sulphur–sulphur interactions take place, the molecule consists of two N=S=N units linked by a sulphur atom and the SO_2 group. Electrophiles, demonstrated with Ag^+-ions,[21] coordinate towards the nitrogen atoms adjacent to the SO_2 groups of (18) to form $[Ag(S_4N_4O_2)_4]^+$ (20). Nucleophiles attack the sulphur atom opposite to the SO_2 group to yield anions with weak intramolecular sulphur–sulphur bonds.[22,23]



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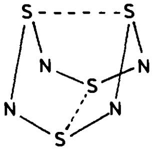

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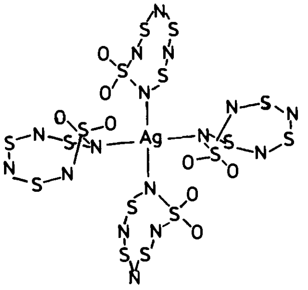

(20) $[Ag(S_4N_4O_2)_4]^+$

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[18] H. W. Roesky, W. Schaper, O. Petersen, and T. Müller, *Chem. Ber.*, 1977, **110**, 2695.

[19] H. W. Roesky, W. G. Böwing, I. Rayment, and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun.*, 1973, 735.

[20] P. G. Jones, W. Pinkert, and G. M. Sheldrick, *Acta Crystallogr., Sect. C.*, 1983, **C39**, 827.

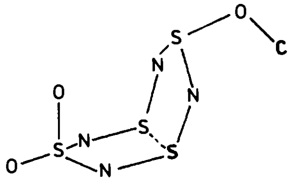
[21] H. W. Roesky, M. Thomas, H. G. Schmidt, W. Clegg, M. Noltemeyer, and G. M. Sheldrick; *J. Chem. Soc., Dalton Trans.*, 1983, 405.

[22] H. W. Roesky, M. Witt, B. Krebs, G. Henkel, and H.-J. Korte, *Chem. Ber.*, 1981, **114**, 201.

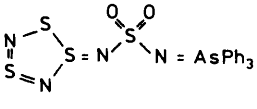
[23] H. W. Roesky, M. Witt, B. Krebs, and H.-J. Korte, *Angew. Chem.*, 1979, **91**, 444; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 415.

$Ph_4PS_4N_4O_3CH_3$ (21), the reaction product of (18) with CH_3ONa and Ph_4PCl, was investigated by *X*-ray analysis.[23] The transanular sulphur–sulphur distance was observed to be 248.2(2) pm.

$S_3N_2{=}N{-}SO_2{-}N{=}AsPh_3$ (22) is prepared by reacting equimolar amounts of AsPh$_3$ and (18), each dissolved in benzene, and heating the mixture for a short time to boiling point. In the reaction the eight-membered ring is attacked by AsPh$_3$ (according to Scheme 1) and contracts to form the five-membered S_3N_2 ring.[24] For the convertibility of the eight-membered ring, an intermediate, where two molecules of AsPh$_3$ are involved, could be discussed (23, 23a).



(21) $[S_4N_4O_3CH_3]^-$



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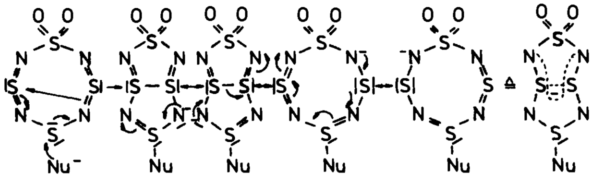
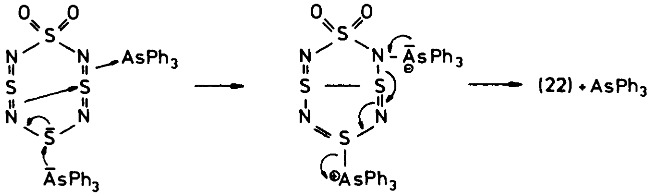


Scheme 1



(23) (23a)

In acetonitrile (22) is slowly converted into (24), an acyclic molecule containing a chain with eleven alternating sulphur and nitrogen atoms.[25] In (24) some S–N bond lengths are shorter and some longer than those in $(SN)_x$.[26,27] However, the

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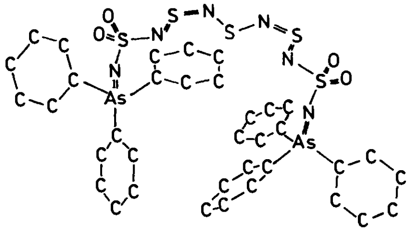
[24] H. W. Roesky, M. Witt, W. Clegg, W. Isenberg, M. Noltemeyer, and G. M. Sheldrick, *Angew. Chem.*, 1980, **92**, 959; *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 943.

[25] M. Witt, H. W. Roesky, M. Noltemeyer, W. Clegg, M. Schmidt, and G. M. Sheldrick, *Angew. Chem.*, 1981, **93**, 1017; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 974.

[26] C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito, and A. J. Heeger; *J. Am. Chem. Soc.*, 1975, **97**, 6358.

[27] C. M. Mikulski, M. S. Saran, and J. Kleppinger; *J. Am. Chem. Soc.*, 1976, **98**, 3844.

average S–N distance of 160.2 pm in (24) is in close agreement with that in $(SN)_x$ of 161.1 pm.



(24)

7 Thionitrosyl–Transition Metal Complexes

The monomeric NS molecule has only a transient existence.[28] There are no reports that it has been used directly like NO to prepare thionitrosyl–metal complexes. However, the NS molecule can be stabilized at room temperature by coordination to a transition metal. Up to now thionitrosyl complexes are known of the following metals Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, and Ir.[29] The thionitrosyl metal complexes have been prepared according to the following routes:[28]

(*a*) Reactions of nitrido complexes with elemental sulphur or with sulphur halides:[28]

$$\mathrm{MoN(S_2CNR_2)_3 + \tfrac{1}{8}S_8 \xrightarrow[\text{reflux}]{CH_3CN} Mo(NS)(S_2CNR_2)_3}$$

(*b*) Reaction of trithiazyltrichloride $N_3S_3Cl_3$ with transition metal halides or complexes:[30–33]

$$\mathrm{(Ph_3P)_3RuCl_2 + \tfrac{1}{3}N_3S_3Cl_3 \xrightarrow{THF} (Ph_3P)_2RuNSCl_3}$$

$$\mathrm{RuCl_3 + N_3S_3Cl_3 \xrightarrow{Ph_4PCl/H_2O} [Ph_4P]^+[RuNSCl_4OH_2]^-}$$

In $[RuNSCl_5]^{2-}$ the chlorine in *trans* position with respect to the NS group is easily substituted by a water molecule.

(*c*) Elimination of fluoride or chloride from NSF or NSCl metal complexes:[31,34]

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[28] H. W. Roesky and K. K. Panday, *Adv. Inorg. Chem. Radiochem.*, 1982, **26**, 337.

[29] T. Chivers and F. Edelmann, *Polyhedron Rep.*, 1986, in press.

[30] J. W. Bats, K. K. Panday, and H. W. Roesky, *J. Chem. Soc., Dalton Trans.*, 1984, 2081.

[31] R. Weber, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1983, **504**, 13.

[32] R. Weber and K. Dehnicke, *Z. Naturforsch., Teil B*, 1984, **39**, 262.

[33] K. K. Panday, H. W. Roesky, M. Noltemeyer, and G. M. Sheldrick; *Z. Naturforsch., Teil B*, 1984, **39**, 590.

[34] R. Mews and C. Lui, *Angew. Chem.*, 1983, **95**, 156; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 158.

$$[\mathrm{Re(CO)_5NSF}][\mathrm{AsF_6}] + \mathrm{AsF_5} \longrightarrow [\mathrm{Re(CO)_5NS}]^{2+}[\mathrm{AsF_6}]_2^-$$

$$\mathrm{OsCl_4(NSCl)_2} + \mathrm{Ph_4AsCl} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Ph_4As}]\mathrm{OsCl_4(NS)NSCl}$$

$$[\mathrm{Ph_4As}]\mathrm{OsCl_4(NS)NSCl} \xrightarrow[-\mathrm{Ph_4AsCl}]{\mathrm{GaCl_3}} \mathrm{OsCl_4(NS)_2}$$

(*d*) Generation of NS^+ salts and then reaction with metal complexes:[35,36]

$$[\mathrm{Re(CO)_5SO_2}][\mathrm{AsF_6}] + [\mathrm{NS}][\mathrm{AsF_6}] \longrightarrow [\mathrm{Re(CO)_5NS}][\mathrm{AsF_6}]_2 + \mathrm{SO_2}$$

(*e*) Reactions of S_4N_4 with transition metal halides or nitrides:[37]

$$\mathrm{Re_2Cl_{10}} + \mathrm{S_4N_4} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Ph_4AsCl}} [\mathrm{Ph_4As}][\mathrm{Re(NS)Cl_5}]$$

$$\mathrm{ReNCl_4} + \mathrm{S_4N_4} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Ph_4AsCl}} [\mathrm{Ph_4As}]_2[\mathrm{ReCl_4(NS)(NSCl)}]\cdot\mathrm{CH_2Cl_2}$$

X-Ray structural data are available of six thionitrosyl metal complexes. In all complexes the thionitrosyl ligand coordinates essentially linearly to the metal *via* the nitrogen atom, suggesting that the NS ligand is functioning as a three-electron donor.

So far, ourselves and others have been unable to show that cycloadditions occur at the NS-bond with olefines or acetylenes.

8 Thionitrosamine–Transition Metal Complexes

Substituted NS-ligands are thionitrosamines. The rapid decomposition of thionitrosamines by acidic materials prevents the direct reaction of hydrazines with disulphur dichloride with elimination of hydrogen chloride. In the case of 1,1-diphenylhydrazine, triethylamine was used to trap the hydrogen chloride.

$$\mathrm{Ph_2NNH_2} + \mathrm{S_2Cl_2} + 2\mathrm{NEt_3} \longrightarrow \mathrm{Ph_2NN{=}S} + 2\mathrm{NEt_3HCl} + \tfrac{1}{8}\mathrm{S_8}$$

The unstable dimethylthionitrosamine, prepared from dimethylhydrazine and elemental sulphur, reacts in THF with $\mathrm{(CO)_5Cr{\cdot}THF}$ to yield the 1:1 complex (25):[38,39]

$$\mathrm{Me_2N{-}N{=}S} + \mathrm{(CO)_5CrTHF} \longrightarrow \underset{(25)}{\mathrm{Me_2N_2SCr(CO)_5}} + \mathrm{THF}$$

The structures of (25) and of $\mathrm{Ph_2N_2SCr(CO)_5}$ were investigated by *X*-ray analysis. The dimethylthionitrosamine or diphenylthionitrosamine ligands coordinate *via* the sulphur atom to the metal. The two molecular structures are

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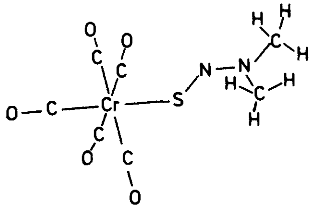
[35] G. Hartmann and R. Mews, *Angew. Chem.*, 1985, **97**, 218; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 202.

[36] M. Herberhold and L. Haumaier, *Z. Naturforsch., Teil B*, 1980, **35**, 1277.

[37] J. Anhaus, Z. A. Siddiqi, H. W. Roesky, J. W. Bats, and Y. Elerman, *Z. Naturforsch., Teil B*, 1985, **40**, 740.

[38] H. W. Roesky, R. Emmert, W. Clegg, W. Isenberg, and G. M. Sheldrick, *Angew. Chem.*, 1981, **93**, 623; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 591.

[39] H. W. Roesky, R. Emmert, W. Isenberg, M. Schmidt, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 183.

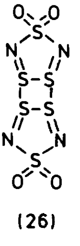


(25)

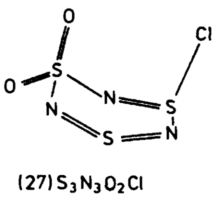
similar. In both cases the $CrSNNC_2$ units are effectively planar, and these planes lie approximately eclipsed to the carbonyl groups. The mean S–Cr–C (*cis*) angles are very close to 90°, indicating π-backbonding with the ligand to the same extent as with the carbonyls.

However, there is also a marked *trans* effect on the Cr–C bond lengths. In (25) the Cr–C bond distance [184.6(2) pm] of the CO group in the *trans* position to the sulphur atom is shortened in comparison to the average value of the remaining CO ligands (190.3 pm).

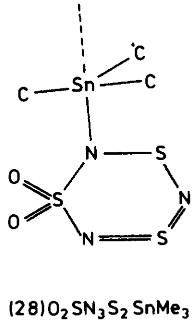
Attempts to prepare monomeric S=N–X compounds by reaction of $(Me_3Si)_2N\text{-}SO_2\text{-}N(SiMe_3)_2$ with SCl_2 in a molar ratio of 1:2 resulted in the formation of $S_6N_4O_4$ (26).[40] We assume that first $S{=}N\text{-}SO_2\text{-}N{=}S$ is formed which dimerizes to yield (26). It is the first compound containing an uncharged four-membered sulphur ring. Compound (26) forms with $TiCl_4$ a 1:2 and with $AgAsF_6$ a 1:1 complex, and it reacts readily with chlorine to give $S_3N_2O_2Cl_2$ which decomposes slowly at −30 °C to yield $S_3N_3O_2Cl$ (27).[41] Derivatives of (27) have been obtained by treating $S_4N_4O_2$ (18) with $N(SnMe_3)_3$ or $N(SiMe_3)_3$, the



(26)



(27) $S_3N_3O_2Cl$



(28) $O_2SN_3S_2SnMe_3$

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[40] H. W. Roesky, R. Emmert, and T. Gries, *Chem. Ber.*, 1984, **117**, 404.

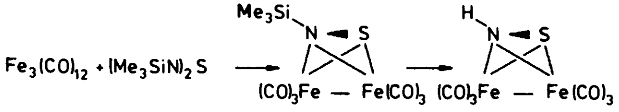
[41] H. W. Roesky, R. Emmert, M. Noltemeyer, and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1984, **39**, 701.

resulting products (28) have the same ring skeleton except that the $SiMe_3$ and $SnMe_3$ groups are bonded to nitrogen adjacent to the SO_2 groups.[42]

N,*N*-Dialkylthiazylamides have been prepared by reaction of Me_3SiNMe_2[43] with $[Re(CO)_5NSF][AsF_6]$ to yield $[Re(CO)_5NSNMe_2][AsF_6]$ (29).

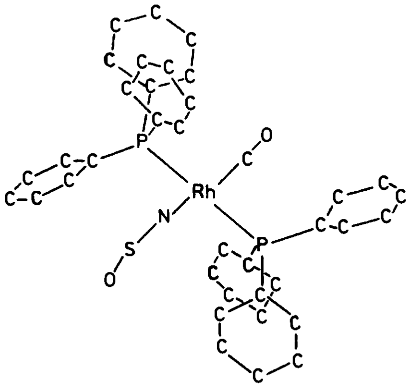
$$[Re(CO)_5NSF][AsF_6] + Me_3SiNMe_2 \xrightarrow[-30\,^{\circ}C]{SO_2} [Re(CO)_5NSNMe_2][AsF_6] + Me_3SiF \qquad (29)$$

$NSNMe_2$ is an isomer of the above mentioned dimethylthionitrosamine. HNS is stabilized by coordination to two iron centres.[44] The reaction of $Fe_3(CO)_{12}$ with $(Me_3SiN)_2S$ affords $(Me_3SiNS)Fe_2(CO)_6$ (30), which was converted quantitatively into $(HNS)Fe_2(CO)_6$ (31) by chromatography on silica gel.



(30) (31)

Compound (31) is converted into $(CH_3NS)Fe_2(CO)_6$ by means of diazomethane. $(RNS)Fe_2(CO)_6$ compounds have been known since 1968.[45,46]



(32)

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[42] H. W. Roesky, M. Witt, M. Diehl, J. W. Bats, and H. Fuess, *Chem. Ber.*, 1979, **112**, 1372.

[43] G. Hartmann, R. Mews, and G. M. Sheldrick, *Angew. Chem.*, 1983, **95**, 753; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 723.

[44] M. Herberhold and W. Bühlmeyer, *Angew. Chem.*, 1984, **96**, 64; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 80.

[45] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1968, **7**, 1833.

[46] R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers, J. D. Schagen, J. J. Zwinselman, A. R. Overbeck, and C. H. Stam; *J. Organomet. Chem.*, 1979, **170**, 337.

9 Complexes with the Sulphinylnitrilo Group, NSO^-, and HNSO

The reports on NSF and NSCl[29] transition metal complexes are numerous, but examples for the isoelectronic NSO^- group are rare. We were able to show[47] that the reaction of $CsNSO_2$ with $[RhH(CO)(PPh_3)_3]$ in acetonitrile yields *trans*-$[Rh(CO)(NSO)(PPh_3)_2]$ (32) under elimination of Ph_3PO.

$$[RhH(CO)(PPh_3)_3] + CsNSO_2 \longrightarrow \underset{(32)}{[Rh(CO)(NSO)(PPh_3)_2]} + Ph_3PO + CsH$$

Compound (32) is a yellow crystalline solid that melts at 190 °C with decomposition. The crystal structure contains an arrangement of mononuclear square-planar molecules with a *trans* configuration of the triphenylphosphine ligands. The NSO ligand shows bond lengths which can be considered close to double bonds. The Rh–N distance (198.9 pm) is significantly longer than the Rh–C value (184.3) in the *trans* position, indicating an absence of bond strengthening by back bonding. The N–S–O bond angle in the ligand (122.5°) is consistent with the double bond valence structure, whereas the relatively large Rh–N–S bond angle (135.1°) is probably influenced by interligand and intermolecular forces.

Complexes containing the HNSO ligand were prepared by the following routes:
(*a*) Displacement of coordinated SO_2 by HNSO:[48]

$$[Re(CO)_5SO_2][AsF_6] + HNSO \xrightarrow[-50\,^{\circ}C]{-SO_2} [Re(CO)_5HNSO][AsF_6]$$

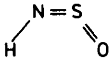
(*b*) Displacement of fluoride[48] ion from coordinated NSF by OH^-. Me_3SnOH was used as the reagent.

$$[Re(CO)_5NSF][AsF_6] + Me_3SnOH \longrightarrow [Re(CO)_5HNSO][AsF_6] + Me_3SnF$$

(*c*) Reaction of metal complexes with $S_4N_4H_4$:[49–51]

$$(Ph_3P)_4Pt + S_4N_4H_4 \longrightarrow \underset{(33)}{(Ph_3P)_2Pt(HNSO)_2}$$

The *X*-ray structure of (33) is reported,[49] HNSO is probably bonded through oxygen to the platinum. Two isomers, (34) and (35), of HNSO are possible, according to *ab initio* MO calculations the *cis* thionylimide structure (34) is lower in energy than the thiazyl-*S*-hydroxide form (35).[52]



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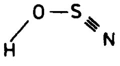

(35)

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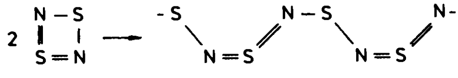
[47] H. W. Roesky, K. K. Pandey, B. Krebs, and M. Dartmann; *J. Chem. Soc., Dalton Trans.*, 1984, 2271.
[48] G. Hartmann, R. Hoppenheit, and R. Mews, *Inorg. Chim. Acta*, 1981, **76**, L201.
[49] E. M. Holt, N. W. Alcock, A. A. Bhattacharyya, and A. G. Turner, *Inorg. Chim. Acta*, 1981, **47**, L255.
[50] A. A. Bhattacharyya, A. G. Turner, E. M. Holt, and N. W. Alcock, *Inorg. Chim. Acta*, 1980, **44**, L185.
[51] A. A. Bhattacharyya and A. G. Turner, *Inorg. Chim. Acta*, 1981, **53**, L89.
[52] A. G. Turner, *Inorg. Chim. Acta*, 1984, **84**, 85.

10 Complexes of Disulphur Dinitride, S_2N_2

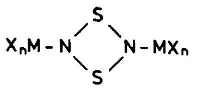
S_2N_2 (36) is generated by pyrolysis from S_4N_4 in the presence of silver metal.[26] It is the smallest S–N-heterocycle so far known and it was shown by *X*-ray analysis that the molecule has a square-planar configuration with nearly equal S–N bond lengths.

S_2N_2 polymerizes easily to $(SN)_x$ (37) in the solid state at room temperature, this is the most exciting reaction of S_2N_2. Alternative high-yield syntheses have recently been devised.[53–56] S_2N_2 decomposes explosively when struck or when warmed above 30 °C. Its chemistry has therefore not been extensively studied. It forms adducts with Lewis acids. In these adducts the S–N-heterocycle remains planar and the S–N distances are almost the same as in the free S_2N_2 molecule. Although S_2N_2 has attracted attention as the precursor for $(SN)_x$, there are no reports of insertion reactions of metal fragments into the S–N bond of S_2N_2.



(36) (37)

In general S_2N_2 forms 1:2 adducts with transition metal compounds with the nitrogen atoms as the donor sites (38). One exception is known,[57] which we obtained by reacting $(Ph_3P)_2(CO)_2RuCl_2$ with $S_2N_2{\cdot}(AlCl_3)_2$. The ligand exchange results in the formation of $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl][AlCl_4]$ (39), the structure of which was determined by single crystal *X*-ray structure analysis. The coordination geometry about the Ru atom may be described as a highly distorted octahedron. In contrast to free S_2N_2, and all these complexes that have been structurally characterized, a marked degree of bond fixation is observed for the S_2N_2 ring in the Ru complex. There are significant differences in the S–N bond



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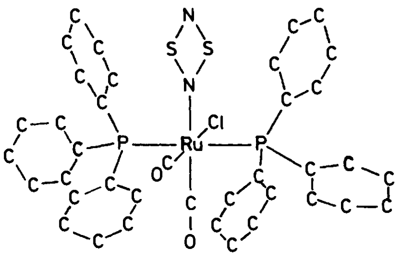

(39) $[(Ph_3P)_2(CO)_2(S_2N_2)RuCl]^+$

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[53] F. A. Kennett, G. K. MacLean, J. Passmore, and M. N. S. Rao, *J. Chem. Soc., Dalton Trans.*, 1982, 851.
[54] H. W. Roesky and J. Anhaus, *Chem. Ber.*, 1982, **115**, 3682.
[55] A. J. Banister and Z. V. Hauptmann, *J. Chem. Soc., Dalton Trans.*, 1980, 731.
[56] T. Chivers, A. W. Cordes, R. T. Oakley, and P. N. Swepston, *Inorg. Chem.*, 1981, **20**, 2376.
[57] H. W. Roesky, J. Anhaus, and W. S. Sheldrick, *Inorg. Chem.*, 1984, **23**, 75.

lengths, probably due to an intramolecular S•••Cl contact of 291.8(4) pm. In comparison, the sum of van der Waals radii is 375 pm.

The known methods for the preparation of 1:2 adducts with S_2N_2 are given in the following examples:

(*a*) Direct reaction of S_2N_2:[57,58]

$$2SbCl_5 + S_2N_2 \longrightarrow S_2N_2(SbCl_5)_2$$

(*b*) S_4N_4 route:[57,59–62]

$$2TiCl_4{\cdot}S_4N_4 \longrightarrow 2TiCl_4{\cdot}S_2N_2 + S_4N_4$$

(*c*) From $S(NSO)_2$ under elimination of SO_2:[57]

$$S(NSO)_2 + TiCl_4 \xrightarrow{CH_2Cl_2} TiCl_4{\cdot}S_2N_2 + SO_2$$

(*d*) Reduction of NSCl compounds:[63,64]

$$2NbCl_5(NSCl) \longrightarrow (\mu\text{-}S_2N_2)(NbCl_5)_2 + Cl_2$$

$$[Ph_4As][VCl_5] + N_3S_3Cl_3 \longrightarrow [Ph_4As]_2[\mu\text{-}S_2N_2)(VCl_5)_2]$$

11 Five-membered Metal-containing Sulphur–Nitrogen Rings

A direct insertion of a metal fragment into S_2N_2 has not been observed. However, the reactions of Sn–N compounds produce the five-membered $Me_2SnN_2S_2$ (40) ring:[65,66]

$$4S_2Cl_2 + 4N(SnMe_3)_3 \longrightarrow \underset{(40)}{\tfrac{1}{2}(Me_2SnN_2S_2)_2} + 2Me_4Sn + \tfrac{1}{2}S_8 + 8Me_3SnCl$$

Compound (40) is also formed when S_4N_4 and $N(SnMe_3)_3$ are allowed to react at elevated temperatures; at lower temperatures a sulphur di-imide can be isolated as an intermediate:

$$S_4N_4 + 2N(SnMe_3)_3 \longrightarrow 3Me_3Sn\text{–}N{=}S{=}N\text{–}SnMe_3 + \tfrac{1}{8}S_8$$

$$2Me_3Sn\text{–}N{=}S{=}N\text{–}SnMe_3 + \tfrac{1}{4}S_8 \longrightarrow \underset{(40)}{(Me_2SnN_2S_2)_2} + 2Me_4Sn$$

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[58] H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 239.

[59] U. Thewalt and B. Müller, *Z. Anorg. Allg. Chem.*, 1980, **462**, 214.

[60] U. Thewalt and M. Burger, *Angew. Chem.*, 1982, **94**, 646; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 634.

[61] U. Thewalt and K. Holl, *Z. Naturforsch., Teil B*, 1984, **39**, 145.

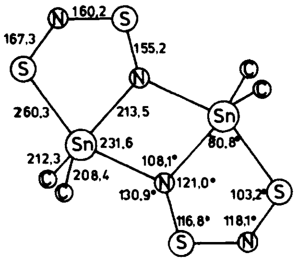
[62] H. W. Roesky, J. Anhaus, H. G. Schmidt, G. M. Sheldrick, and M. Noltemeyer, *J. Chem. Soc., Dalton Trans.*, 1983, 1207.

[63] J. Eicher, P. Klingelhöfer, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1984, **514**, 79; J. Hanich and K. Dehnicke, *Z. Naturforsch., Teil B*, 1984, **39**, 1467.

[64] J. Hanich, M. Krestel, U. Müller, and K. Dehnicke; *Z. Anorg. Allg. Chem.*, 1985, **522**, 92.

[65] H. W. Roesky and H. Wiezer, *Angew. Chem.*, 1973, **85**, 722; *Angew. Chem., Int. Ed. Engl.*, 1975, **12**, 674.

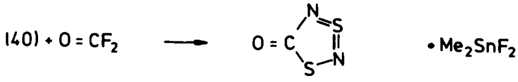
[66] H. W. Roesky and H. Wiezer, *Chem. Ber.*, 1974, **107**, 3186.



(40) dimer in solid state

Structural investigations of (40) show that the molecule in the solid state consists of dimers with two five-membered and one four-membered ring. The tin atoms have coordination number five. It is nearly a planar molecule.

Compound (40) is an interesting precursor for the preparation of $O{=}CN_2S_2$ (41) and $O{=}SN_2S_2$ (42):[67,68]



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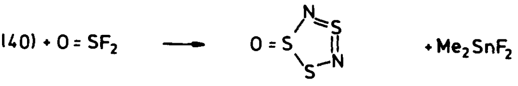
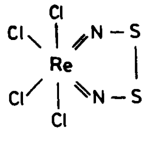


(42)

The reduction of $ReCl_3(NSCl)_2POCl_3$ with Ph_3P leads to a five-membered ring of composition $[Ph_3PCl][Cl_4ReN_2S_2]$ (43).[69]



(43) $[ReCl_4N_2S_2]^+$

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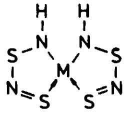
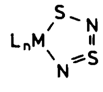
[67] H. W. Roesky and E. Wehner, *Angew. Chem.*, 1975, **87**, 521; *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 498.

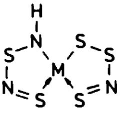
[68] H. W. Roesky, E. Wehner, E. J. Zehnder, H.-J. Deiseroth, and A. Simon, *Chem. Ber.*, 1978, **111**, 1670.

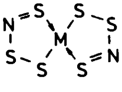
[69] W. Hiller, J. Mohy la, J. Strähle, H. G. Hauck, and K. Dehnicke; *Z. Anorg. Allg. Chem.*, 1984, **514**, 72.

The reaction of S_4N_4 with PbI_2 and HgI_2 in liquid NH_3 leads to the formation of metal–sulphur–nitrogen compounds; this was first observed in 1904 by Ruff and Geisel.[70] Extensive studies[71,72] with anhydrous metal halides of Ni, Co, Pd, Pt, Pb, and S_4N_4 yield the following five-membered rings with the general formulas: $M(S_2N_2H)_2$ (44), $L_nM(S_2N_2)$ (45), $M(S_2N_2H)(S_3N)$ (46), and $M(S_3N)_2$ (47).

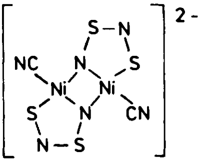

(44)

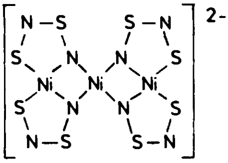

(45)


(46)


(47)

The greater stability of the *cis*-isomer (44) is in agreement with CNDO-MO calculations[73] carried out for $Ni(S_2N_2H)_2$ and $Pd(S_2N_2H)_2$. The hydrogen atoms in (44) and (46) can be easily replaced to form the anions or can be substituted by organic residues. Treatment of $Ni(S_2N_2H)_2$ with KCN in methanol yields the anion $[Ni_2(S_2N_2)_2(CN)_2]^{2-}$ (48).[74]


(48)


(49)

A trinuclear anion of composition $[Ni_3(S_2N_2)_4]^{2-}$ (49) was obtained, when $NiCl_2 \cdot 6H_2O$ was reacted in methanol in the presence of Ph_4POH.[75]

A characteristic of all the above mentioned metal-containing five-membered sulphur–nitrogen rings is the fact that, using the Lewis description, only one uncharged resonance structure is possible in each case. In (44), (46), and (47) the S–N parts of the molecules function as chelating ligands. The metals which are known to form these particular chelating rings are in low oxidation states. It seems reasonable to conclude that with these ligands also metal organic derivatives should be easy available. $C_5H_5Co(CO)_2$ reacts in benzene to yield black, air stable

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[70] O. Ruff and E. Geisel, *Ber. Deut. Chem. Ges.*, 1904, **37**, 1573.

[71] J. Weiss; *Fortschr. Chem. Forsch.*, 1965, **5**, 635.

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[73] S. Millefiori, A. Millefiori, and G. Granozzi, *Inorg. Chim. Acta*, 1981, **48**, 233.

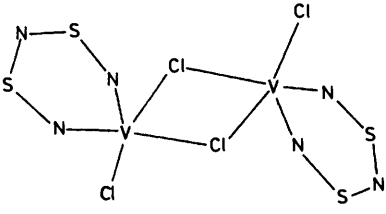
[74] K. Hornemann and J. Weiss, *Angew. Chem.*, 1982, **94**, 645; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 633.

[75] J. Weiss, *Angew. Chem.*, 1984, **96**, 232; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 225.

crystals of $C_5H_5CoS_2N_2$.[76] Metal organic coordination compounds with sulphur–nitrogen ligands is still an unturned field of research. Finally, it can be predicted that structures (43) and (45) should be favoured by metals of high oxidation states.

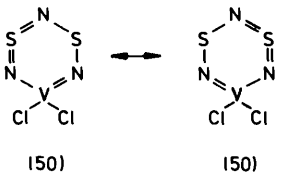
12 Cyclo-metalla-dithiatriazenes

The complexes mentioned in Sections 8 to 11 are particularly interesting starting materials for the preparation of cyclo-metalla-dithiatriazenes. In 1983 we reported for the first time the synthesis of $[Cl_2VS_2N_3]_n$ (50) by reaction of S_4N_4 with VCl_4.[62] The structure of (50) consists of centrosymmetric dimers, in which the vanadium atoms are each coordinated by two bridging chlorines, one terminal chlorine, and the two terminal nitrogen atoms of an NSNSN-chain. The four S–N bond lengths in the six-membered VS_2N_3 ring are approximately equal, and the ring is effectively planar. The bridging V–Cl distances [244.5(1) and 246.9(1) pm] are longer than the terminal V–Cl distance [226.6(1) pm]. If an additional V–N interaction of 231.2(3) pm is considered [the other two V–N bonds 171.4(3) and 184.1(3) pm], then the coordination of vanadium becomes octahedral, and the dimers link together to form polymeric chains. This additional interaction of one of the two terminal N atoms accounts for the difference in V–N bond lengths. Finally, it should be mentioned that crystalline (50) is a semi-conductor at room temperature ($\alpha = 10^{-4}\Omega^{-1}\ \mathrm{cm}^{-1}$). The NSNSN part of the molecule can be considered as a donor and the vanadium as the acceptor part. In addition the intermolecular interactions lead to stack formation, and, as such, (50) would represent a new type of semi-conductor.



(50)

The bonding properties of (50) can be described by the following resonance structures, they indicate multiple bonding between the nitrogen and vanadium (bond order of 2.5) and equal lengths of bonding for the four S–N bonds.



(50) (50)

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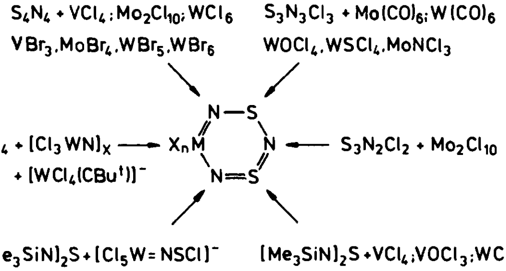
[76] F. Edelmann, *J. Organomet. Chem.*, 1982, **228**, C47.

Compound (50) melts at 157 °C without decomposition. This surprising high kinetic stability of (50) is supported by the electronic spectra. A solution of (50) in toluene exhibits a band at 378 nm, in comparison to phospha-dithiatriazenes[77] we assign this band to a $\pi^* \longrightarrow \pi^*$ transition. The corresponding energy for this HOMO–LUMO transition is about 9 000 cm^{-1} higher than in the comparable phosphorus compounds.

Cyclo-metalla-dithiatriazenes are known from vanadium, molybdenum, and tungsten. The various synthetic routes for this class of compounds are summarized in Scheme 2.[62,78–85]



Scheme 2

Anionic crystalline complexes can be prepared by adding a bulky phosphonium or arsonium salt; CH_3CN also coordinates to the metal to yield crystalline products.[86] The reaction of $[Ph_4As][WCl_4(CBu^t)]$ with S_4N_4 in dichloromethane leads to $[Ph_4As][WCl_4(S_2N_3)]$ and, if traces of water are present, to the salt $[Ph_4As][WCl_3O(OS_2N_2)]$ (51).[85] The structure consists of tetraphenylarsonium cations and $[WCl_3O(OS_2N_2)]^-$ anions. The coordination geometry around the metal may be regarded as distorted octahedral. A weak *trans*-effect of the =NSNSO ligand is indicated by the different axial and equatorial metal–chlorine bond lengths. The metal atom and the =NSNSO ligand form a six-membered ring, in which the NSNSO is planar within experimental error.

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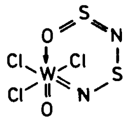
[84] H. W. Roesky, J. Schimkowiak, M. Noltemeyer, and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1986, **41**, 175.

[85] J. Anhaus, Z. A. Siddiqi, H. W. Roesky, and J. W. Bats, *J. Chem. Soc., Dalton Trans.*, 1985, 2453.

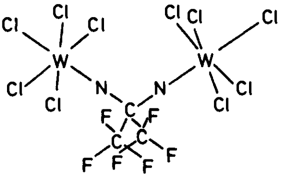
[86] J. Anhaus, P. G. Jones, M. Noltemeyer, W. Pinkert, H. W. Roesky, and G. M. Sheldrick, *Inorg. Chim. Acta*, 1985, **97**, L7.



(51) $[Cl_3WO(OS_2N_2)]^-$

13 Attempted Preparations of Metal–Carbon–Nitrogen Heterocycles

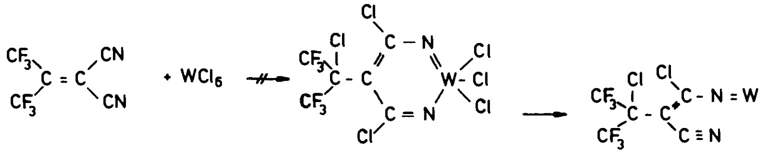
Hexafluoroacetone usually undergoes cycloaddition with unsaturated ligands. Accordingly, reactions of hexafluoroacetone with $Cl_3W{\equiv}N$ have been carried out. The reaction takes a different course and, by the addition of tetraphenylarsonium chloride, $[Ph_4As]_2[WCl_5)\{\mu\text{-}NC(CF_3)_2N\}(WCl_5)]$ (52) was isolated. The anion of (52) lies on a twofold axis passing through the central carbon atom, which is tetrahedrally coordinated. Since the geometry at nitrogen is almost linear, a triply bonded resonance extreme with a positive formal charge on nitrogen may make a significant contribution.[87]



(52) $[(WCl_5)\{\mu\text{-}NC(CF_3)_2N\}(WCl_5)]^{2-}$

Reactions of (52) with $(Me_3SiN)_2S$ to yield heterocycles are under way.

Attempts to use bis-nitriles (53) as starting materials for the preparation of carbon-containing metallacycles (54) were not successful. It was shown that only one nitrile group was able to react with WCl_6 to form (55).[88]



(53) (54) (55)

The experiments follow the same route with $CCl_2(CN)_2$.

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[87] N. K. Homsy, H. W. Roesky, M. Noltemeyer, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1985, 2205.

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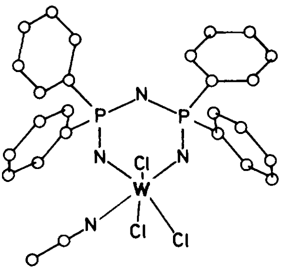
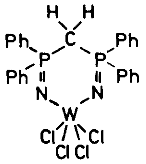
14 Cyclo-metalla-phosphazenes

Polymeric phosphazenes have been prepared from cyclic phosphazenes by pyrolysis. These polymers have interesting properties.[89–91] Metal-containing polymeric phosphazenes would have a broad application for batteries, electrodes, catalysts, surface coating, and many other purposes. Recently we have discovered an easy way to prepare cyclo-metalla-phosphazenes. The reaction of $[H_2NPPh_2NPPh_2NH_2]Cl$ with WCl_6 yields the six-membered ring (56).[92]



(56) $Cl_3WN_3P_2Ph_4 \cdot CH_3CN$



(57)

Single crystals of (56) for an *X*-ray structural analysis were obtained by recrystallization from acetonitrile. Compound (56) crystallizes with two molecules of CH_3CN; one of these is weakly coordinated to tungsten. The structure of (56) consists of a six-membered ring, in which the bond lengths two by two are equal, and the ring is effectively planar.

Another route[93] for carbon-containing unsaturated metalla–phosphorus–nitrogen heterocycles is the reaction of $(Me_3SiNPPh_2)_2CH_2$ with WCl_6 or other metal halides to form (57) under elimination of Me_3SiCl.

The kinetic stability of (56) was surprising, and it seemed worthwhile to attempt to extend this reaction to acyclic $Ph_3P{=}NSiMe_3$ (58). WF_6 reacts with (58) to give, depending on molar ratio, temperature, and solvent, triphenylphosphineiminatotungsten(VI)pentafluoride (59) and bis(triphenylphosphineiminato)tungsten(VI)-tetrafluoride (60).[94] Their kinetic stability is remarkable. Compound (59) hydrolyses only slowly in moist air, while (60) is not noticeably affected by boiling water. The redox behaviour of (60) and its utility for a rechargeable battery is under study.

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[90] H. R. Allcock, in 'Rings, Clusters and Polymers of the Main Group Elements', ed. A. H. Cowley, ACS Symposium Series No. 232, American Chemical Society, Washington DC, 1983, p. 49.

[91] H. R. Allcock, N. M. Tollefson, R. A. Arcus, and R. R. Whittle, *J. Am. Chem. Soc.*, 1985, **107**, 5167.

[92] H. W. Roesky, K. V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst, and G. M. Sheldrick, *Angew. Chem.*, 1986, **98**, 447; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 477.

[93] H. W. Roesky, K. V. Katti, and U. Seseke, *Inorg. Chem.*, 1986, in press.

[94] H. W. Roesky, U. Seseke, M. Noltemeyer, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1986, 1309.

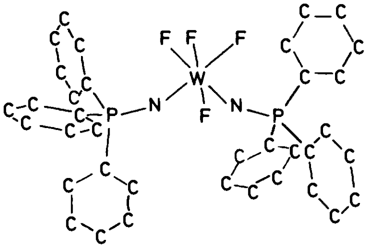
$$\mathrm{Ph_3P{=}NSiMe_3 + WF_6 \xrightarrow[-78^\circ C]{CH_2Cl_2} Ph_3P{=}NWF_5 + Me_3SiF}$$

(58) (59)

$$\mathrm{(58) + (59) \xrightarrow[R.T]{CH_3CN} (Ph_3P{=}N)_2WF_4}$$

(60)

Phosphineiminato complexes generally show linear MNP units, which are described as $M{=}\overset{+}{N}{=}PR_3$ with *sp*-hydridized nitrogen. However, bent geometry is also observed and has been ascribed to overlaps of an occupied *p* orbital with a vacant *d* orbital of phosphorus. The structure of (60) lies between these two extreme forms (W–N–P 157.2°). The W–N bond length of 182.5 pm corresponds to some multiple bonding character and the consequent neutralization of the high nuclear charge of tungsten may explain the high kinetic stability.



(60)

15 Summary and Conclusions

The information presented here is intended to demonstrate our approach to new pathways between main group and transition metal elements. Catalytic reactions as demonstrated with electron-rich elements will play an important role in the future. In particular, the syntheses of sulphur-containing heterocycles from elemental sulphur without using sulphur chlorides will lead to interesting new compounds and will improve our understanding of natural products formation. We can assume that the biologically essential elements will be preferentially investigated for this purpose. The current interest in the role of coordination complexes with sulphur ligands in bioinorganic chemistry provides an additional incentive for such studies.

The fixation of unstable intermediates in metal complexes will improve our understanding of mechanisms and facilitate their chemical reactions. Although considerable progress has been made the field is still at an early stage of development.

Metallacycles with various elements including carbon will be synthesized and this class of compounds will rapidly be developed because of their potentially outstanding properties for electric and ceramic devices.

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