Coordination Chemistry Reviews, 21 (1976) 29—62

THE COORDINATION CHEMISTRY OF SUBSTITUTED HYDRAZINES

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(Received 24 March 1976)

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A. INTRODUCTION

Although an early review of the chemistry of hydrazine [1] included a number of complexes containing co-ordinated hydrazines, some of the formulations have since been shown to be incorrect, particularly with regard to the number of protons retained by the hydrazine on co-ordination. It is now known that diazene, hydrazido- and hydrazine complexes amongst others can be obtained from first-row metal ions, depending on the metal and reaction conditions. The ability of certain second- and third-row metals to form multiple bonds to nitrogen increases the potential synthetic scope of hydrazines, and reactions of hydrazines with compounds of these metals can give rise to complexes containing co-ordinated imido-, diazenido- and nitrido-ligands. Since dinitrogen complexes can also be formed from hydrazines, the reactions of the latter with transition metals have a clear relevance to nitrogen fixation, and this has provided a stimulus for recent research in this area.

The aim of this review is to survey the interactions of substituted hydrazines and related derivatives with transition metals. A recent review [2] on the reactions of hydrazines with transition metal complexes was confined to a relatively small range of substituted hydrazines, and omitted those with sulphur-containing substituents. These were partially covered in a survey of sulphur—nitrogen chelating agents [3] which appeared during the preparation of this review; the content is here restricted to complexes derived from substituted hydrazines or their metal complexes, and polynitrogen derivatives such as triazenes and tetrazenes. Hydrazones of substituted hydrazines functioning as bidentate ligands are included, but potentially polydentate ligands such as the dihydrazones of diketones are not discussed.

Alkyl or aryl substitution of hydrazine effectively prevents it behaving as a bidentate bridging ligand, and most alkyl- and aryl-substituted hydrazines function as simple monodentate ligands towards non-oxidising transition metal ions. Factors determining the stoichiometry and structures of complexes of this type are discussed in Sect. C.I.

Hydrazines with functional substituents, i.e. substituents containing potential donor atoms, frequently form stable chelated complexes. Hydrazines with substituents containing a carbonyl or thiocarbonyl group adjacent to nitrogen can complex in a neutral keto- or a deprotonated enol-form. These chelated complexes are covered in Sect. C. II and are classified according to the donor atom in the functional substituent.

First-row transition metal ions can oxidise arylhydrazines to dinitrogen and products such as benzene or phenol, depending on the reaction conditions. If, however, the metal forms stable metal—carbon bonds then σ-bonded aryl complexes can be produced. The scope of this type of reaction as a route to the preparation of alkyl or aryl complexes is discussed in Sect. D.

The ultimate products of oxidation of hydrazine itself are dependent on the conditions used, but dinitrogen and hydrogen azide can be formed either individually or as mixtures. Intermediates such as diazene, NH=NH, have been proposed but are generally too unstable to be isolated (see ref. 2). However, if the hydrazine bears substituents, then the oxidised * intermediates (diazenes) or their transition metal complexes can readily be isolated, as discussed in Sect. E. In certain cases, such as reactions with cupric ions, these reactions can be used as a preparative route to diazenes which are otherwise inaccessible. Intermediate copper diazene complexes are generally formed and the diazene may then be displaced under appropriate conditions.

The reactions of hydrazines with transition metal halido-species can be accompanied by hydrohalide elimination with formation of a diazene complex. In the case of reactions of hydrazines with metal oxo-complexes, the M=O group appears to react much as the carbonyl group of aldehydes and ketones, and metal—nitrogen multiple bonds are formed with elimination of water. Second- and third-row transition metal complexes often not only

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* In some reactions of substituted hydrazines with first-row metal ions the hydrazine is clearly oxidised and the metal reduced, as in the case of the formation of copper(I) diazene complexes. However, the products of the reactions of hydrazines with second- and third-row metals do not always have clearly defined metal oxidation states and classification as a redox reaction is not possible.

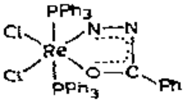
convert hydrazines to diazenes, but also promote cleavage of the nitrogen—nitrogen bond, giving metal—nitrogen multiply-bonded systems such as nitrido- or imido-complexes (see also Sect. E).

Certain complexes containing chelated substituted hydrazines (usually with sulphur-containing substituents) can be oxidised to intensely coloured complexes containing delocalised electron systems. These have redox properties analogous to those of related dithiolene complexes, and their preparation and properties are discussed in Sect. F.

Mono- and 1,1-di-substituted hydrazines can function as nucleophiles via the free NH_2 groups towards co-ordinated ligands such as isocyanides, carbon monoxide and alkyl cyanides to give a diverse range of products, discussed in Section G. Cleavage of the N—N bond frequently occurs in these reactions and provides an illustration of how the weakness of the N—N single bond tends to dominate the chemistry of hydrazine and its substituted derivatives.

B. NOMENCLATURE

The latest IUPAC proposals for the nomenclature of complexes derived from hydrazines and their oxidised forms suggest that delocalised ligands as in (A) are named as neutral molecules rather than dipoles, or if that is not possible, as ligating anions bearing the smallest possible formal negative charge. The chelated ligand of (A) is named N′-benzoyldiazenido (1-)-(N,O) in preference to N′-benzoylhydrazido(3)-(N,O). Azo-ligands containing the group R—N=N—metal are now described as diazenido-derivatives e.g. $[PtCl(-N{=}N-Ph)(PEt_3)_2]$ is named chloro-(N′-phenyldiazenido(1-)-N)-bis(triethylphosphine)platinum(II). Other more specific points of nomenclature are discussed at the relevant point in the text.



(A)

C. SIMPLE CO-ORDINATIVE BEHAVIOUR

This section comprises complexes containing hydrazines behaving as simple Lewis bases, without oxidation or deprotonation, except for bidentate hydrazines or hydrazones which can be bound in a deprotonated 'enol' form in the presence of base.

I. As monodentate ligands

Unfortunately much of the early work on transition metal hydrazine complexes is unreliable, as the possibility of oxidation or deprotonation of the hydrazine was not always recognised. The reasonably well characterised com-

TABLE 1

Complexes of monodentate substituted hydrazines

Complex	Remarks	Ref.
$[CoCl_2(H_2NNHPh)_4]$	Co(II); octahedral	
$[MX_2(H_2NNHPh)_2]$	(M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II); X = Cl, Br, I) Prep: halide + 2 $PhNHNH_2$ in alcohol. Polymeric for Ni(II), Mn(II), Co(II)	5–10
$[MX_2(H_2NNHPh)_2]$	(M = Pd(II); X = Cl, Br) Prep: PdX_2 + $PhNHNH_2$ in aq. HX	5
$[Mo(CO)_5(H_2NNHPh)]$	Prep: $[Mo(CO)_5Cl]^-$ + $PhNHNH_2$ in H_2O	25
$[(R_3P)_2RhCl_3(H_2NNHPh)]$	(R = Et, Bu^n) Prep: $[(R_3P)_3RhCl_3]$ + $PhNHNH_2HCl$ in MeOH	26
$[(Me_2PhP)_3MX_2(H_2NNHR)]$	(M = Ru, Os; X = Cl, Br; R = Me, Ph) Prep: $[(Me_2PhP)_3MX_3]$ + $RNHNH_2$ in EtOH	27
$[PtCl(PEt_3)_2(H_2NNHC_6H_4{-}p\text{F})][BF_4]$	Prep: $[(p\text{-F}{-}C_6H_4N{=}NH)PtCl(PEt_3)_2]^+BF_4^-$ + H_2 + catalyst	18
$[Pt(PEt_3)_3(H_2NNHC_6H_4{-}X)][ClO_4]_2$	(X = m- or p-F) Prep: $[(X{-}C_6H_4N{=}NH)Pt(PEt_3)_3][ClO_4]_2$ + H_2 + catalyst	22
$[Co(H_2NNHMe)_6]Cl_2$	Prep: $CoCl_2$ + anhydrous $MeNHNH_2$. On heating gives polymeric $[\{Co(H_2NNHMe)_2Cl_2\}_n]$	13
$[Co(H_2NHMe_2)_6]Cl_2$	Prep: $CoCl_2$ + anhydrous Me_2NNH_2. In water hydroxides formed	13
$[Ni(H_2NNHMe)_6]Cl_2$	Prep: $[Ni(H_2O)_6]Cl_2$ + $MeNHNH_2$ in EtOH	24
$[MCl_2(H_2NNMe_2)_2]$	[M = Co(II), Ni(II), Zn(II)]. UV suggests tetragonal structure. Co-ordination via methylated nitrogen proposed	13,14
$[HgCl_2(H_2NNHPh)_2]$	Prep: $HgCl_2$ + 2 $PhNHNH_2$ in Et_2O. Excess $PhNHNH_2$ gives Hg metal	28
$[Cu_2Cl_2(H_2NNHMe)]$	Prep: $CuCl_2$ + $MeNHNH_2$ in alcohol under dilute conditions. At higher concentrations N_2 evolved. Probably halogen bridged	29
$[W(H_2NNHPh)_6]Cl_3$	Prep: WCl_6 + $PhNHNH_2$ in CCl_4. Product probably contains $PhNHNH_3Cl$	4
$[ZrBr_4(H_2NNHPh)_4]$	Prep: $ZrBr_4$ + $PhNHNH_2$ in EtOAc. Probably contains $PhNHNH_3Cl$	30
$[TiX_4(H_2NNHPh)_2]$	(X = F, Cl, Br, I). Believed to be mixtures of $[TiCl_3(NHHPh)]$ and $PhNHNH_3Cl$ except for X = F	11,12
$[(RO)_3TiCl(H_2NNHPh)]$	(R = Et, Pr^i). Believed to be simple adducts	31
$[ZnX_2(H_2NNHAr)_2]$	(X = Cl, Br, I; Ar = C_6H_5, o-Cl-C_6H_4, o-Br-C_6H_4, p-Br-C_6H_4, o,m,p-$CH_3OC_6H_4$). Prep: ZnX_2 + $ArNHNH_2$ in EtOH	9

plexes of monodentate hydrazines are summarised in Table 1. High oxidation state transition metal halides can readily undergo hydrohalide elimination reactions with NH compounds and complexes formulated as complexes of neutral hydrazines such as $[W(H_2NNHPh)_6]Cl_3$ [4] are probably admixtures of hydrazine hydrohalides and a metal phenylhydrazido-complex. Transition metal complexes containing monodentate hydrazines have received scant attention over the last few years and there is an almost complete dearth of X-ray structural information.

Methyl- and phenylhydrazines generally give similar complexes with the non-oxidising transition metal ions Mn(II), Co(II), Ni(II), Zn(II), Cd(II), of stoichiometry $[MX_2(H_2NNHR)_2]$ [5]—[10] (R = Me or Ar; X = Cl or Br) (see Table 1). The nickel, cobalt and zinc complexes are polymeric with UV spectra characteristic of octahedral or pseudo-octahedral metal environments [5]. The mode of bridging is not known, and either halogen or hydrazine could be involved in the intermolecular linkages. The palladium and platinum complexes $[MX_2(H_2NNHPh)_2]$ (X = Cl, Br) are monomeric [5]. The titanium complexes formulated as $[TiX_4(N_2NNHPh)_2]$ [11] have since been shown to be mixtures of $PhNHNH_3Cl$ and $[TiX_3(HNNHPh)]$ [12]. The smaller methylhydrazine will also form $[M(H_2NNHMe)_6]Cl_2$ [13] [M = Co(II), Zn(II)] which are convertable to the polymeric $[\{MX_2(H_2NNHMe)_2\}_n]$ by heating in vacuo.

The complexing behaviour of 1,1-diphenylhydrazine has not been studied, but 1,1-dimethylhydrazine forms unstable complexes with $NiCl_2$. The species $[NiCl_2(H_2NNMe_2)_4]$, $[NiCl_2(H_2NNMe_2)_2]$ and $[NiCl_2(H_2NNMe_2)]$ were identified tensimetrically [13]. $[CoCl_2(H_2NNMe_2)_2]$ is much more stable and probably has a tetrahedral structure [13]. The analogous Zn(II) and Cd(II) complexes have been prepared from $Ph_2PNHNMe_2$ (see Sect. C. II (iv)) [14]. On the basis of ^1H and IR spectra, tetrahedral structures with the hydrazine bound via the methylated nitrogen were proposed [14]. Although the protonation of Me_2NNH_2 at the methylated nitrogen [15] suggests that bonding to a metal may occur at the same site, ligation via the unsubstituted nitrogen would seem to be favoured on steric grounds. Unfortunately there are at present no X-ray crystal structures available to clarify the situation.

The simple co-ordination chemistry of N,N′-disubstituted and tetra-substituted hydrazines has been very little studied, apart from a few complexes of tetramethylhydrazine with aluminium [16] [17]. On the basis of ^1H NMR spectra it was here proposed that the hydrazine functions as a bidentate ligand. The facile rearrangement of N,N′-diphenylhydrazine (hydrazobenzene) to benzidine has complicated any studies of its behaviour as a ligand.

As indicated in Table 1, many of the hydrazine complexes are prepared from a metal salt and the appropriate hydrazine under anhydrous conditions. However, a few reductive, indirect methods of preparation have been reported. Parshall [18], showed that protonation of $[PtCl(\text{-}N{=}N\text{-}C_6H_4\text{-}p\text{-}F)(PEt_3)_2]$ (I) gave the phenyldiazene complex $[PtCl(HN{=}N\text{-}C_6H_4\text{-}p\text{-}F)(PEt_3)_2]^+$ (II) which could be hydrogenated to the phenylhydrazine complex $[PtCl(H_2NNHC_6H_4\text{-}pF)(PEt_3)_2]^+$ (III). Prolonged reduction of (III) gave $p\text{-}F\text{-}C_6H_4\text{-}$

TABLE 2

Complexes of bidentate substituted hydrazines bound via nitrogens

Complex [a]	Remarks	Ref.
$[\mathrm{M(2\text{-}H_2NNHC_5H_4N)_3}][\mathrm{ClO_4}]_2$	M = Fe(II), Co(II), Ni(II). Prep: ligand + metal perchlorate in water	35
$[\mathrm{Co(2\text{-}H_2NNHC_5H_4N)_3}][\mathrm{ClO_4}]_3$		35
$[\mathrm{Cu(2\text{-}RR'C{=}NNHC_5H_4N)Cl}]$ [a]	R = H, R′ = Me, Ph; R = R′ = Me; R = R′ = Ph. Prep: anhydrous $\mathrm{CuCl_2}$ + ligand in dry EtOH	35
$[\mathrm{M(2\text{-}RR'C{=}NNHC_5H_4N)_3}][\mathrm{ClO_4}]_2$ [a]	M = Co(II), Ni(II). Prep: metal perchlorate + 3 moles ligand in EtOH—water	35
$[\mathrm{Ag(2\text{-}RR'C{=}NNHC_5H_4N)_2}][\mathrm{ClO_4}]$	Prep: metal perchlorate + 2 moles ligand in EtOH—water	35
$[\mathrm{Co(2\text{-}RR'C{=}NNHC_5H_4N)_3}]$	Prep: cobalt(III) carbonate + 3 moles ligand in EtOH, then made alkaline	35
[Ni(6,6-dihydrazino-2,2′-dipyridyl][$\mathrm{ClO_4}$]$_2$	Prep. from ligand + nickel perchlorate in EtOH. Forms macrocycle with $\mathrm{Me_2CO}$	36
[$\mathrm{M_2}$(1,4-dihydrazinophthalazine)$_2$]$\mathrm{Cl_2}$	M = Co(II), Ni(II). X-ray crystal structure confirms dimeric formulation	37,38
$[\mathrm{M(RC(NH_2){=}NNHR')_2}]^{2+}$ [a]	R = Ph, R′ = Me; R = R′ = Ph; R = Me, R′ = Ph. M = Fe(II), Co(II), Ni(II)	40
$[\mathrm{Ni\{HN{=}C(NH_2)NHNH_2\}_2}]^{2+}$ [a]		
$[\mathrm{Ni\{HN{=}C(NHNH_2)_2\}_2}]^{2+}$ [a]	Prep. from nickel salt + hydrazino-guanidine in alcohol. Mode of bonding not known.	42
$[\mathrm{Ni\{H_2N{-}N{=}C(NHNH_2)_2\}_2}]^{2+}$ [a]		
$[\mathrm{Co(PhN_3Ph)_3}]$	X-ray structure confirms three chelating triazene ligands	46
$[\{\mathrm{M(PhN_3Ph)}\}_2]$	M = Cu(II), Ni(II). X-ray structure confirms bridging triazene with M—H bond	45,47
$[\mathrm{M(PhN_3Ph)_2(PPh_3)_2}]$	M = Ru, Os, Pt; Prep. by $\mathrm{MH_2P_4}$ + triazene	
$[\mathrm{Pt(PhN_3Ph)(P{-}P)_2}]$	P—P—ditertiary diphosphine, triazene monodentate	47,50
$[\mathrm{MX(PhN_3Ph)(CO)(PPh_3)_2}]$	M = Ru, Os, X = H, Cl. Triazene monodentate	
$[\mathrm{Rh(PhN_3Ph)_3}]$	Prep: $[\mathrm{Rh_2Cl_2(C_8H_{12})_2}]$ + triazene in benzene	
$[\mathrm{MH_2(PhN_3Ph)(PPh_3)_2}]$	M = Rh, Ir. Prep: $[\mathrm{MH_3(PPh_3)_2}]$ + triazene in benzene	
$[\mathrm{Rh(PhN_3Ph)(P{-}P)_2}]$	Ionic product containing $\mathrm{PhN_3Ph^-}$ anion	
$[\mathrm{Rh(PhN_3Ph)_2(NO)(PPh_3)_2}]$	Prep: $[\mathrm{Rh(NO)(PPh_3)_3}]$ + triazene in benzene	
$[\mathrm{PtCl(PhN_3Ph)(PPh_3)_2}]$	Prep: $[\mathrm{PtHCl(PPh_3)_2}]$ + triazene in benzene. Monodentate triazene	

$[Rh(PhN_3Ph)(C_8H_{12})]$	Prep: $[Rh_2Cl_2(C_8H_{12})_2]$ + Li$[PhN_3Ph]$ in thf. Bidentate triazene, σ—π bonded at low temp	49
$[Rh(PhN_3Ph)_2(PPh_3)_2]$	Prep: $[RuCl_2(PPh_3)_2]$ + 2 Li$[PhN_3Ph]$ in thf	
$[M(PhN_3Ph)(CO)(PPh_3)_2]$	M = Rh, Ir. Prep: $[MCl(CO)(PPh_3)_2]$ + Li$[PhN_3Ph]$ in thf. Bridging triazene ligand	
$[RuH(PhN_3Ph)(PPh_3)_3]$	Prep: $[RuHCl(PPh_3)_3]$ + Li$[PhN_3Ph]$ in thf	
$[Hg(PhN_3Ph)_2]$	Prep: $Hg(OAc)_2 + PhNHNH_2$. Triazene formed by coupling of $Ph\overset{+}{N}_2$ and excess $PhNHNH_2$	61
$[\{Cu_2(PhN_3Ph\}_2]$	Prep: $CuCl + PhN_3HPh$	63
$[Ph_2Cr(PhN_3Ph)]$	Prep: $[Ph_3Cr(thf)_3] + PhN_3HPh$	48
$[PhCr(PhN_3Ph)_2(thf)]$		
$[Cr(PhN_3Ph)_3]$		
$[\{Cu_4(MeN_3Me)\}_4]$	Prep: $CuCl + Al(MeN_3Me)_3$ in Et_2O. X-ray structure confirmed tetrameric structure	51,52
$[M(MeN_3Me)_4]$	M = Ti, Zr. Prep: $TiCl_4 + MeN_3$ + MeMgBr in Et_2O. Structure unknown	51
$[L_2(CO)MCuX(RN_3R)]$	L = $AsPh_3$, PPh_3; M = Ir, Rh; X = Cl, Br, I; R = Me, Ph. Prep: $[MX(CO)L_2]$ + $[\{Cu(RN_3R)\}_n]$ (n = 2 or 4). X-ray structure confirms M—Cu bond	53
$[R_2Zn(Me_2N{-}N{=}N{-}NMe_2)]$	R = Bu^n, Ph. Prep: $R_2Zn + Me_2N{-}N{=}N{-}NMe_2$	54
$[MX_2(Me_2N{-}N{=}N{-}NMe_2)]$	M = Cd, Mg; X = Cl, Br. Prep: MX_2 + tetrazene	55
$[(CO)_3Fe(Me{-}N_4{-}Me)]$	Prep: $Fe_2(CO)_9 + MeN_3$ in benzene. X-ray structure confirms bonding by methylated N's	56,59
$[(\pi\text{-}Cp)Co(MeN_4M)]$	Prep: $[(\pi\text{-}Cp)Co(CO)_2] + MeN_3$ in methylcyclohexane	57
$[(C_8H_8)Ni(C_6F_5N_4C_6F_5)]$	Prep: $[Ni(C_8H_8)_2] + C_6F_5N_3$	60
$[(PR_3)_2Ni(C_6F_5N_4C_6F_5)]$	Prep: $[(C_8H_8)Ni(C_6F_5N_4C_6F_5)] + PR_3(PR_3 = PPh_3, PPh_2Me, PMe_2Ph, P(OMe)_3]$	
$[M(ArSO_2N_4SO_2Ar)(NO)(PPh_3)_2]$	(M = Rh, Ir, Ar = $C_6H_5p\text{-}CH_3C_6H_4$. Prep: $[M(NO)(PPh_3)_3] + ArSO_2N_3$	57(a)
$[Pt(ArSO_2N_4SO_2Ar)(PPh_3)_2$	Prep: $[Pt(PPh_3)_3] + ArSO_2N_3$	57(b)
$[Ir(p\text{-}XC_6H_4N_4C_6H_4p\text{-}X)(PPh_3)_2]^+BF_4^-$	X = M, F, Cl, Br, CF_3, OMe. Prep: $[IrCl(CO)(PPh_3)_2] + [p\text{-}XC_6H_4N_2]BF_4$. X-ray structure confirms bidentate diaryltetrazene ligand	57(c)

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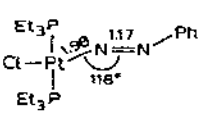
[a] The complex can be deprotonated to neutral species.



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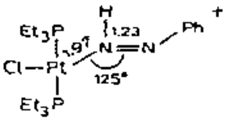

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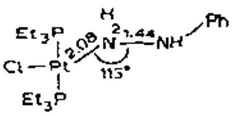


III

NH_2 and ammonia, and the system was advanced as an inorganic model for nitrogen fixation. The structures of each of the steps, I, II, and III in the above scheme have now been determined [19—21]. The N—N bond lengths increase from I to III, paralleling the expected decrease in N—N bond order. The reduction of the cationic diazenido-complexes [Pt(—N=N—Ar)$(PEt_3)_3$]-BF_4 to arylhydrazine complexes has also been effected [22]. Co-ordinated dinitrogen has not yet been converted to co-ordinated hydrazine, but it has very recently been shown [23] that the molybdenum dinitrogen complex [Mo$(N_2)_2$ (dpe)$_2$] (dpe = $Ph_2PCH_2CH_2PPh_2$) can be alkylated with methyl bromide to the N′-methylhydrazido(2-)-N complex [MoBr(NNHMe)(dpe)$_2$]Br.

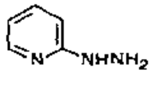
II As bidentate ligands

Attachment of functional substituents such as PhCO and H_2NCS to hydrazine generally results in the hydrazine being able to form chelated complexes with transition metal ions. These are much more stable than the monodentate type discussed above, and can frequently be deprotonated or oxidised while remaining bound to the metal. The complexes formed by these hydrazines have been classified according to the donor atoms bound to the metal, and are summarised in Tables 2, 3 and 4.

(i) Bonding via nitrogens

Included in this section (see Table 2) are complexes of triazenes, tetrazenes and other catenated polynitrogen compounds, as these can be regarded as substituted hydrazines and generally bind as chelating ligands via two nitrogens.

The observation that the addition of copper(II) salts enhanced the anti-tuberculostatic activity of isonicotinylhydrazide (2-$H_2NNHCOC_5H_4N$) stimulated research into the co-ordination chemistry of pyridine-substituted hydrazides [32,33]. The enhancement of activity was originally attributed to chelation of the copper ion, but subsequent work showed that 2-Pr^{i}NHNHCOC$_5$H$_4$N is highly active despite not forming a copper complex. Isonicotinyl hydrazide generally gives polymeric complexes with copper (II), bridging occurring through the pyridine nitrogen or carbonyl oxygen, depending on the co-ligands [34].



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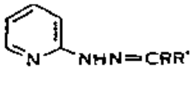
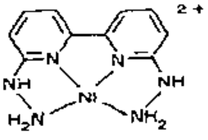


V

2-Pyridylhydrazine (IV) gives complexes of the type $[M(H_2NNHC_5H_4N)_3]$-$[ClO_4]_x$ ($x = 2$ for M = Fe(II), Co(II) or Ni(II) and $x = 3$ for M = Co(III) [35]). These complexes cannot be deprotonated, but the cationic complexes of the pyridylhydrazones(V) (see Table 2) can be readily converted to intensely-coloured neutral complexes [35].

6-6′-Dihydrazino-2,2′bipyridyl forms a monomeric nickel(II) complex(VI) which can be converted to the thirteen-membered macrocyclic derivative VII



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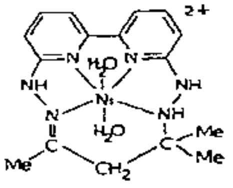

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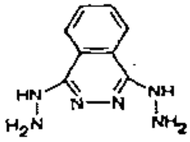
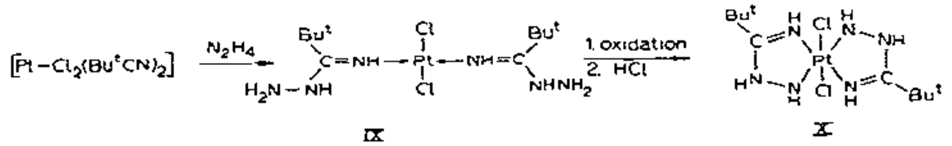


VIII

by treatment with acetone [36]. In contrast, 1,4-dihydrazinophthalazine(VIII) binds two nickel(II) ions per mole of ligand [37]. An X-ray crystal structure [38] shows each nickel to be octahedrally co-ordinated by two waters, two phthalazine nitrogens and two NH_2 groups, with an Ni—Ni distance of 3.79 Å. Magnetic measurements [39] suggest that weak antiferromagnetic exchange occurs between the nickels.

Amidrazones RC(=NH)NHNHR′ (R,R′ = alkyl, aryl, H) have been little studied as transition metal ligands, but have been reported [40] to form intensely coloured complexes with first-row divalent metal ions. More recently platinum amidrazone complexes have been produced by the hydrazinolysis of a co-ordinated nitrile ligand (reaction (1)) [41]. A species IX, containing

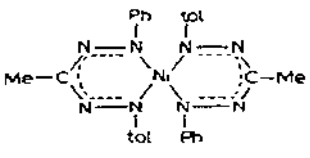


(1)

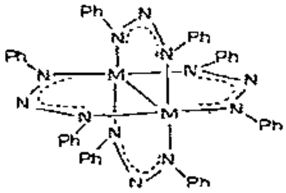
monodentate amidrazone is formed initially, which on oxidation and treatment with HCl gives the Pt(IV) complex X. Alkali converts X to an intensely coloured, highly delocalised complex considered in more detail in Sect. F.

Jensen and Miquel [42] prepared bright red cationic nickel(II) complexes $[NiL_2]^{2+}$ of the hydrazino-guanidines (L = $HN{=}C(NH_2)NHNH_2$, $HN{=}C(NHNH_2)_2$, $H_2NN{=}C(NHNH_2)_2$), but the modes of bonding were not established. Formazans such as $CH_3C({=}NNHAr')N{=}NAr$, form intensely coloured neutral complexes with nickel(II) [43], and an X-ray crystal structure of the derivative with Ar = *p*-tolyl, Ar′ = phenyl, showed square planar nickel bound by the tolyl-substituted nitrogens, giving two *trans* six-membered chelate rings(XI) [44].

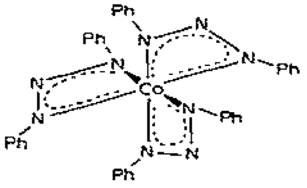
Diaryltriazenes ArNH—N=N—Ar are potentially bidentate ligands and form intensely coloured complexes with many transition metal ions. However, it



XI



XII



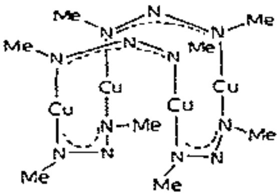
XIII

is only recently that detailed investigations of their chemistry or structures have been made. X-ray crystal structures of the complexes $[\{M(PhN_3Ph)_2\}_2]$ [45] (M = Cu(II), Ni(II), Pd(II) showed them to have the binuclear structure XII with bridging triazenido-ligands and a short metal—metal bond length.

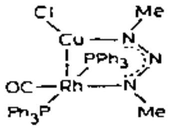
However, a crystal structure [46] of the complex $[Co(PhN_3Ph)_3]$ showed the triazenido-ligands to be bidentate as in XIII. The bond angles $Co{-}\hat{N}{-}N$ and $N{-}\hat{N}{-}N$ in the four-membered ring are 96 and 104°, respectively, indicating considerable strain. There is considerable delocalisation over the triazenido-ligand as all the N—N bond lengths are about 1.31 Å. The presumably isostructural $[Cr(PhN_3Ph)_3]$ was prepared by reaction of $[Ph_3Cr(thf)_3]$ with excess diphenyltriazene. Use of one or two equivalents of the triazene yielded $[Ph_2Cr(PhN_3Ph)]$ and $[PhCr(PhN_3Ph)_2(thf)]$, respectively [48].

Diphenyl triazenido-complexes of some of the platinum group metals have been independently studied by two groups, [47,49] and comparisons made with the isoelectronic carboxylate derivatives. Knoth [49] treated appropriate halido-complexes with the lithium salts of diaryltriazenes. The co-ordinatively unsaturated $[Rh(PhN_3Ph)(PPh_3)_2]$ adds H_2, CO, O_2 and NH_3 to give $[Rh(PhN_3Ph)(XY)(PPh_3)_2]$ (XY = H_2, CO, NH_3, O_2). Robinson and co-workers [50] prepared these and other complexes (see Table 2) by the reaction of a diaryl triazene with hydrido-complexes under reducing conditions. These complexes contain triazenide ions in a variety of bonding modes (see Table 2), and it was originally suggested that bidentate and bridging modes of co-ordination could be distinguished by IR spectroscopy. However, this was shown to be unreliable, and ^1H nmr combined with a selection of reasonable co-ordination numbers was suggested as an alternative [49].

The dimethyltriazene complex $[\{Cu(MeN_3Me)\}_4]$ was prepared from a cuprous halide and $Al(MeN_3Me)_3$ in ether [51] and an X-ray structure [52] showed the tetramer to comprise a novel sixteen-membered folded ring system (XIV). The complexes [$M(MeN_3Me)_4$] (M = Ti, Zr) were synthesised by reaction of the metal halide with the 1,3-dimethyltriazine Grignard prepared in situ from methyl azide and methylmagnesium iodide [51].



XIV



XV

Some unusual complexes containing heteronuclear metal—metal bonds bridged by a triazene ligand have recently been obtained by a form of oxidative addition of copper triazene complexes to iridium(I) or rhodium(I) derivatives [53]. An X-ray structure of the complex [$(PPh_3)_2(CO)RhCuCl(MeN_3Me)$] (XV) (from [$(PPh_3)_2RhCl(CO)$] and [{$Cu(MeN_3Me$}$_4$]) confirms the Rh—Cu bond, and shows that chloride must migrate from rhodium to copper during the reaction. The metal—metal bond is presumably stabilised by the bridging triazenido-ligand.

The tetramethyltetrazene complexes [$R_2Zn(Me_2N{-}N{=}N{-}NMe_2$] (R = Bu^n, Ph) [54] and $MX_2(Me_2N{-}N{=}N{-}NMe_2)$] (M = Mg, Cd; X = Cl, Br) [55] have been prepared from 1,1,4,4-tetramethyltetrazene and R_2Zn and MX_2, respectively. In both cases the tetrazene is believed to function as a bidentate ligand bound via the methylated nitrogens. Several complexes of 1,4-disubstituted tetrazenes are known, but all have been prepared by indirect methods, the free ligand being unstable. Thus, methyl azide reacts with [$Fe_2(CO)_9$] in benzene or [(π-Cp)$Co(CO)_2$] in methylcyclohexane to give [$(CO)_3Fe(MeN_4Me)$] [56] and [(π-Cp)$Co(MeN_4Me)$] [57], respectively.

Pentafluorophenylazide reacts analogously with bis(1,5-cyclo-octadiene) nickel to give [$Ni(C_6F_5N_4C_6F_5)(C_8H_8)$] and thence [$Ni(C_6F_5N_4C_6F_5)(PR_3)_2$] ($PR_3$ = PPh_3, PPh_2Me, PMe_2Ph, $P(OMe)_3$) by treatment with the appropriate tertiary phosphine [60]. Arylsulphonylazides $ArSO_2N_3$ (Ar = C_6H_5, p-$CH_3C_6H_4$) react with [$M(NO)(PPh_3)_3$] (M = Rh, Ir) or [$Pt(PPh_3)_3$] to give [$M(ArSO_2N_4SO_2Ar)(NO)(PPh_3)_2$] [57(a)] and [$Pt(ArSO_2N_4SO_2Ar)(PPh_3)_2$], respectively. The formation of $ArSO_2NH_2$ and $ArSO_2N_3$ on treatment of the platinum complex with mineral acid confirms the formulation as a tetrazene derivative rather than the isomeric bis(arylsulphonyldiazenido) complexes [57(b)].

Although diazonium salts usually react with transition metal complexes to give aryldiazenido or aryldiazene complexes, reaction with [$IrCl(CO)(Ph_3)_2$] gives the 1,4-diaryltetrazene complexes [Ir{p-$XCo_6H_4N_4C_6H_4$-p-X}$(CO)(PPh_3)_2$]$^+BF_4$ (X = H, F, Cl, Br, CF_3, OMe). An X-ray crystal structure of the complex with X = OMe suggested that the ligand is best considered as being bound by two σ bonds via the terminal nitrogens [57(c)].

There appear to be no reported examples of complexes of longer-chain

TABLE 3

Complexes of bidentate substituted hydrazines bound via nitrogen and oxygen

Complex	Remarks	Ref.
$[M(RCONHNH_2)_2]^{2+}$ [a]	M = Co(II), Ni(II), Zn(II), Mn(II), Fe(II); R = Ph, Me, Et, OEt. Prep: metal salt + hydrazine in EtOH or water	62–65
$[M(PhCONHNH_2)_3]^{2+}$	*M = Mn(II), Fe(II), Co(II), Ni(II). Ligands cannot be deprotonated*	62,65
$[M(PhCONHN{=}CMe_2)_2]X_2$ [a]	M = Co(II), Ni(II), Cu(II); X = NO_3, ClO_4	62,84
$[Cu(PhCONHNH_2)_2][Cu_3Cl_5]$	Prep: $CuCl_2$ + hydrazine in hot alcohol. X-ray crystal structure	62,68
$[\{M(RCONHNCOR)_2\}_n]$	M = Fe(II), Co(II), Ni(II), Cu(II). Polymeric structures with carbonyl oxygen bridges	66
$[TiF_4(PhNHNHCONHNHPh)]$	Prep: TiF_4 + 1 mole ligand in benzene	82
$[TiX_2(PhNHNCONNHPh)]$	X = Cl, Br. Mode of bonding not certain	82
$[MoO_2(PhN_2CONNHPh)_2]$	Prep: acidified MoO_4^{2-} + $PhN_2CONHNHPh$ in water, structure not certain	81
$[Mo_2O_3(PhN_2CONNHPh)_4]$	Prep: acidified MoO_4^{2-} + PhNHNHCONHNHPh in water. Structure not certain	81
$[M(H_2NCONHNH_2)_2]X_2$	M = Ni(II), Cu(II); 2 X = Cl_2, SO_4	
$[M(H_2NCONHNH_2)_3]SO_4$	M = Ni(II), Co(II)	
$[M(PhNHCONHNH_2)_3](NO_3)_2$	M = Ni(II), Co(II) [a]	65
$[Ni(H_2NCON(CH_3)NH_2)_2]Cl_2$		
$[Ni\{PhNHCON(CH_3)NH(CH_3)\}_2]SO_4$		
$[M(H_2NNHCOO)_3]^-$	M = Mn(II), Co(II), Ni(II), Zn(II). Prep: CO_2 bubbled through aqueous solution of metal salt and hydrazine hydrate. X-ray crystal structures of Ni(II) derivative shows pseudo-octahedral geometry	69–71, 74,75
$[M(N_2H_4)_2(H_2NNHCOO)_2]$	M = Mn(II), Co(II), Cu(II), Zn(II). Prep: metal salt + hydrazine hydrate + CO_2 from air. X-ray crystal structure for Zn(II) complex shows octahedral Zn(II)	72
$[\{Cd(H_2NNHCOO)_2\}_n]$	X-ray crystal structures show polymeric structures with bridging carbonyl oxygens	76,77
$[\{Mn(H_2NNHCOO)_2(H_2O)_2\}_n]$		
$[\{Zn(H_2NNHCOO)_2\}_n]$	X-ray crystal structure shows five-coordinate Zn(II) in polymeric carbonyl oxygen-bridged structure	78
$[M(PhNNSO)_2]$	*M = Cu, Hg. Prep: M acetate + PhNHNSO* in benzene. Cu complex square planar	83

[a] The complex can be deprotonated to a neutral species.

catenated nitrogen derivatives such as the pentazadiene Ph—N=N—N(Me)—N=N—Ph or hexa-azadiene Ph—N=N—N($COCH_3$)—N($COCH_3$)—N=N—Ph, which exist as stable crystalline solids. Attempts to prepare complexes of these with first-row metals, platinum(II) or platinum(0) were unsuccessful [58], probably as a result of delocalisation of the nitrogen lone pairs through the extended π-systems.

(ii) Bonding via nitrogen and oxygen

Although showing no anti-tuberculostatic activity analogous to the isonicotinyl hydrazides, the complexing ability of acyl- and aroylhydrazides $RCONHNH_2$ (R = alkyl or aryl) has been studied by several groups of workers [62—65], with frequent duplication of results. Acid hydrazides give bis(XVI) or tris(XVII) cationic complexes with the first row transition metals. Deprotonation of the bis-complexes XVI to the neutral complexes XVIII is a reaction common to many cationic complexes of functionally-substituted hydrazines, and IR studies have suggested that it is the amidic proton that is removed. In complexes of the hydrazones XIX this process is facilitated by formation of a conjugated ligand system. In contrast, dibenzoylhydrazine (PhCONHNHCOPh) forms polymeric complexes with most transition metal ions [66], and substituted hydrazides such as PhCONHNHPh only form relatively unstable complexes with the first-row metals [67].

$[M(H_2NNHCOR)_2]^{2+}$ XVI

$[M(H_2NNHCCR)_3]^{2+}$ XVII

$\{M(H_2NNCOR)_2]$ XVIII

$R'R''C{=}NNHCOR$ XIX

The complexes of type XVI and XVIII are usually isolated with solvent of crystallisation , and UV spectral measurements suggest octahedral co-ordination of the metal [62]. Although $[Cu(H_2NNHCOPh)_2]Cl_2$ can be prepared in the cold, hot alcoholic solutions of benzoylhydrazine and copper(II) chloride evolve dinitrogen, and a complex of stoichiometry $[Cu(H_2NNHCOPh_2]$-$[Cu_3Cl_5]$ is formed [62]. An X-ray crystal structure [68] confirmed that the hydrazide ligand is bonded via the carbonyl oxygen and hydrazinic nitrogen, and the presence of the copper(I) chloro-anion. Hot aqueous solutions of other copper(II) salts and benzoylhydrazine also evolve dinitrogen, with formation of benzoic acid and dibenzoylhydrazine [62].

Apparently prompted by their potential similarity to amino acids, hydrazine carboxylic acid ($H_2NNHCOOH$) complexes have been studied by several groups [69—71], and several X-ray crystal structures have been reported. An aqueous mixture of a divalent metal salt (Mn(II), Co(II), Cu(II), Zn(II)) and hydrazine hydrate slowly absorbs carbon dioxide from the air forming $[M(N_2H_4)_2(H_2NNHCOO)_2]$ [72]. X-ray crystal structures of the derivative with M = Zn(II) [72] and M = Co(II) [73] show that the metal ion is pseudo-octahedrally co-ordinated, the hydrazine carboxylic acid being bidentately bound via a carbonyl oxygen and a terminal nitrogen, the hydrazine carboxylic acid nitrogens being in a *trans* configuration (XX).

TABLE 4

Complexes of bidentate substituted hydrazines bound via nitrogen and sulphur

Complex	Remarks	Ref.
$[Cr(H_2'NNHCS_2)_3]2\,H_2O$	N′—S bonding. Prep: Cr salt and ligand in EtOH	87
$[M(H_2'NNHCS_2)_2]$	M = Ni(II), Pd(II), Pt(II), Zn(II), Cd(II), Pb(II). N′—S bonding, *cis* and *trans* isomers for Pt(II)	85,87, 113
$[M(H_2'NNHCSSCH_3)_2]X_2$ [a]	M = Ni(II), Pd(II), Pt(II); X = Cl, NO_3, Br. N′—S bonding	87
$[NiX_2(H_2'NNHCSSCH_3)_2]$	X = Cl, NCS; N′—S bonding. High-spin.	87
$[M(Me_2C{=}N{-}N{=}CSSMe)_2]$	M = Co(II), Ni(II), Pd(II), Pt(II). Square planar except for tetrahedral Co(II) complex	88
$[M(S_2CNHNRR')_2]$	M = Ni(II), Pd(II), Pt(II); R = H, R′ = Ph; R = R′ = Me; R = R′ = Ph; R = Me, R′ = Ph. S—S bonding	85,86
$[M(H_2'NNRCS_2)_2]$	M = Ni(II), Pd(II), Pt(II); R = Me, Et, Pr^n, Bu^n. N′—S bonding.	86
$[M(H_2NNHCSNH_2)_2]^{2+}$ [a]	M = Co(II), Cu(II), Ni(II), Pd(II), Pt(II). Cationic Pt(II) as *cis* and *trans* isomers. X-ray crystal structure for neutral and cationic Ni(II) complex	89–94, 65
$[M(PhNHNCSNR_2)_2]$	M = Ni(II), Pd(II), Pt(II); R = Me, Et	65
$[M(R_2NNCSNHR')_2]$	M = Ni(II), Pd(II), Pt(II); R = R′ = Ph; R = Ph; R′ = Bu^t	96
$[M(H_2NNHCSNHR)_2]$	M = Ni(II), Pd(II), Pt(II), Cu(II) R = Me, Et, 3(R)-menthyl	96,97
$[Ni(R_1R_2C{=}NNHCSNH_2)_2X]X$	X = Cl, Br; R_1 = R_2 = Me or heptyl; R_1 = Me, R_2 = Bu^t	115
$[\{ZnCl_2(H_2NNHCS_2NH_2)\}_n]$	X-ray crystal structure reported tetrahedral Zn	
$[\{AgCl(H_2NNHCSNH_2)\}_n]$	X-ray crystal structure shows two distinct tetrahedral atoms	98
$[\{Ag(NCS)(H_2NNHCSNH_2)\}_n]$	X-ray crystal structure shows distorted trigonal bipyramidal Ag atom	99
$[M(H_2NNHCSR)_2]^{2+}$ [a]	M = Ni(II), Pd(II), Pt(II); R = H, Ph, PhCO, $CoNH_2$, $CSNH_2$, $C({=}NH)NH_2$, OEt, OPh	100
$[Ni(H_2NNHCSCH_3)_2]$	Ligand prepared in situ from thioacetamide and hydrazine hydrate in presence nickel acetate	102
$[M(H_2NNHCSNHNH_2)_2]Cl_2$	M = Zn(II), Cd(II), Hg(II), Pb(II)	103
$[M(H_2NNHCSNHNH_2)_3]^{2+}$	M = Ni(II), Cu(II)	104,105
$[M(RNHNHCSNHNH_2)_2(NO_3)]NO_3$	M = Ni(II), Co(II); R = PhCO, MeCO, 2-hydroxybenzoyl, 2-chlorobenzoyl	106
$[M(RNHNHCSNHNH_2)Cl_2]$	M = Ni(II), Co(II). Co(II) complex pseudo-octahedral and Ni(II) complex tetrahedral	
$[Ni(PhN_2CSNN'HPh)_2(bipy)]$	X-ray crystal structure shows octahedral Ni. N′—S bonded, dithizone, *cis* sulphurs.	111
$[Hg(PhN_2CSNN'HPh)_2]\cdot 2$ py	X-ray crystal structure shows tetrahedral Hg, py not bonded. N′—S bonded dithizone	109
$[Cu(PhN_2CSNN'HPh)_2]$	X-ray crystal structure shows N′—S bonded dithizone, square planar Cu	110
$[Ni(H_2NN'HC_6H_4S(CH_2)_2SC_6H_4N'HNH_2)]^{2+}$	Ni bonded via S and N′	112
$[Ni(\overline{NN-C_6H_4S(CH_2)_2SC_6H_4NNCH})]^+$	Prep: Dihydrazine complex + formaldehyde	112
$[Ni(\overline{NHNHC_6H_4S(CH_2)_2SC_6H_4NHNHC}\text{-}(C_6H_{11})_2]$	Prep: Dihydrazine complex + cyclohexanone	112

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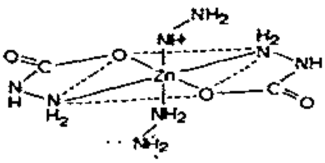
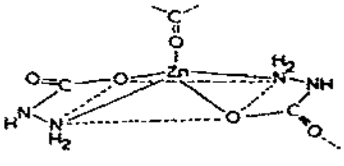
[a] The complex can be deprotonated to neutral species.



XX



XXI

If carbon dioxide is bubbled through the aqueous metal salt—hydrazine mixtures the octahedral complexes $[N_2H_5][M(H_2NNHCOO)_3]$ (M = Mn(II), Cu(II), Co(II), Zn(II)) are formed [72]. Two apparently independent structure determinations of the nickel(II) derivative [74,75] confirmed that the ligands were O,N-bonded with the oxygen atoms in a *cis* configuration. The complex is racemic with both enantiomorphous forms co-existing in the crystal. The tris-hydrazine carboxylate complexes were all shown to be isostructural [72].

The hydrazine carboxylates of other transition metals are frequently polymeric, bridging occurring via carboxyl oxygens as in $[\{Mn(H_2NNHCOO)_2(H_2O)_2\}_n]$ [76] and $[\{Cd(H_2NNHCOO)_2\}_n]$ [77]. The structure [78] (XXI) of $[\{Zn(H_2NNHCOO)_2\}_n]$ is unusual in having five-co-ordinate zinc within a polymeric structure held together by carboxyl bridges.

PhNHNHCONHNHPh

XXII

PhNHNHCO—N=N—Ph

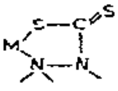
XXIII

Diphenylcarbazide(XXII) and diphenylcarbazone(XXIII) have for many years been employed as spot test reagents, intensely coloured derivatives being formed with Hg, Mg, Mo, Cr, V and Cd [79,80]. However, these derivatives have rarely been well characterised. The reactions of XXII and XXIII with molybdenum(V) and molybdenum(VI) have been studied [81], but in the absence of IR data the structural assignments are rather doubtful, as are those for complexes of copper(II) and titanium(IV) [82].

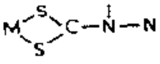
N-sulphinylhydrazine (PhNHNSO) is reported [83] to react with copper(II) acetate in benzene to give monomeric $[Cu(PhNNSO)_2]$, believed to contain square planar copper bound to the sulphonyl oxygens and phenyl-substituted nitrogens. The complex slowly decomposes in solution to give thiophenol and copper(II) oxide. Mercury(II) acetate reacts similarly to give unstable yellow $[Hg(PhNNSO)_2]$ of unknown structure [82].

(iii) Bonding via nitrogen and sulphur

The co-ordination chemistry of the sulphur analogues of the hydrazine carboxylates, the dithiocarbazates, has only relatively recently been studied in detail, although the nickel complexes were first isolated over 40 years ago [85]. Dithiocarbazates can co-ordinate in two ways, using either one sulphur and a hydrazinic nitrogen(XXIV) or the two sulphurs(XXV). The modes of co-ordination have been distinguished by IR and UV spectroscopy.



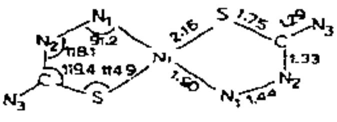
XXIV



XXV

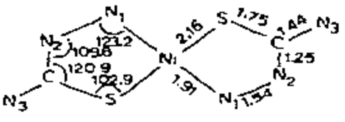
Battistoni et al. [86] showed that the co-ordination mode of a wide range of dithiocarbazic acids to Ni(II) was substituent dependent. Thus the dithiocarbazates $RR'NNHCS_2H$ (R = H, R' = Ph; R = R' = Me; R = R' = Ph; R = Me, R' = Ph) are S—S bonded, (XXV) whereas $H_2N'NRCS_2H$ (R = Me, Et, Pr^n, Bu^n) and $Me_2N'NMeCS_2H$ are N'—S bonded (XXIV). S-methyldithiocarbazate ($H_2NNHCSSMe$) with Ni(II) halides gives $[Ni(H_2NNHCSSMe)_3]^{2+}$ and $[Ni(H_2NNHCSSMe)_2X_2]$ (X = Cl, NCS). The bis-complexes $[M(H_2NNHCSSMe)_2]^{2+}$ [M = Ni(II), Pd(II), Pt(II)] can be deprotonated to give neutral $[M(H_2NN{=}CSSMe)_2]$ [87]. The Schiffs base of S-methyldithiocarbazate, $Me_2C{=}N{-}NHCSSMe$ forms stable bis complexes with Co(II), Ni(II), Pd(II), Pt(II) and Cu(II). These are square planar except for the Co(II) complex which is thought to be tetrahedral on the basis of UV and magnetic measurements [88].

The metal complexes of thiosemicarbazide ($H_2NCSNHNH_2$) were among the first functionally substituted hydrazine complexes to be studied [89,90]. Although the tris-derivatives $[M(H_2NCSNHNH_2)_3]^{2+}$ are inert to base, the complexes $[M(H_2NNHSCNH_2)_2]^{2+}$ (M = Ni, Pd, Pt) can be readily deprotonated to the neutral $[M(H_2NNCSNH_2)_2]$. X-ray crystal structures of both the protonated [91] and deprotonated [92] forms are shown below (XXVI and XXVII) with bond lengths and bond angles. Significant changes occur in the



$[Ni(H_2NNHCSNH_2)_2]SO_4$

XXVI



$[Ni(H_2NNCSNH_2)_2]$

XXVII

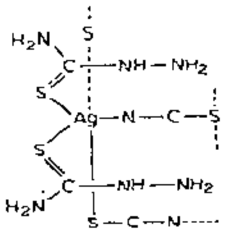
N—N and C—N_1 bond lengths on deprotonation. The contraction of the C—N_1 bond is accompanied by increases in the $Ni\hat{-N_1-}N_2$ and $C\hat{-S-}Ni$ angles. The C—N_3 bond length in the charged complex approaches that of a double bond, suggesting a large contribution from a canonical form with a C—N_3 double bond and a positive charge on N_3.

The complex $[Ni(H_2NNHCSNH_2)_2]SO_4$ exists in two forms [91,93]. One form is a co-crystallised mixture of *cis* and *trans* isomers. If the counter ion is nitrate, the complex is paramagnetic, and shown by an X-ray crystal structural determination [94] to be octahedral with two axially co-ordinated water molecules. $[Pt(H_2NNHCSNH_2)_2]^{2+}$ can be isolated as the *cis* or *trans* isomer but when deprotonated only the *trans* is stable [95].

Jensen et al. [96] carried out an extensive study of complexes of substituted thiosemicarbazides with Ni(II), Pd(II), and Pt(II). The complexes of the type such as $[Ni(Me_2NCSNHNHPh)_2]^{2+}$ can be deprotonated to a neutral species and then oxidised to the complexes $[Ni(Me_2NCSN_2Ph)_2]$ [96] which are treated in more detail in Sect. F.

Complexes of thiosemicarbazides derived from optically active amines have been prepared [97], and their circular dichroism spectra show very large Cotton effects. The relatively large asymmetry imposed on the chelated ligand by the amine group was attributed to a solvent molecule forming a hydrogen-bonded bridge between the amine nitrogen and the thioamidic nitrogen atom [97].

Silver thiosemicarbazide complexes tend to have unusual stereochemistries. $[\{AgCl(H_2NCSNHNH_2)\}_n]$ has a polymeric structure with two distinct pseudo-tetrahedral silver ions. One is bound to 2 sulphurs and 2 chlorines, the other to 1 chlorine and 3 sulphurs [98]. The co-ordination about the silver ion in $[\{Ag(NCS)(H_2NCSNHNH_2)\}_n]$(XXVIII) is a distorted trigonal bipyramid [99].

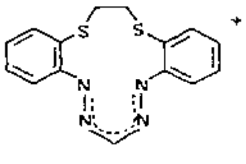


XXVIII

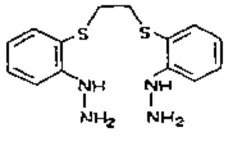
The complexing ability of thiohydrazides of the type R-CSN-HNHR′ (R = Ph, R′ = H, CH_3, Ph, PhCO, $CONH_2$, $CSNH_2$) [100] have been studied and the complexes are generally analogous to those of the thiosemicarbazides. $[Mn(CO)_4(PhCSNNHCH_3)]$ has been prepared by reaction of $[MnCl(CO)_5]$ with the thiohydrazide in the presence of base [101]. The thiohydrazide $CH_3CSNHNH_2$ is too unstable to isolate, but the complex $[Ni(CH_3CSNNH_2)_2]$ was prepared in situ from thioacetamide, hydrazine hydrate and nickel(II) [102]. A partial X-ray crystal structure showed that the ligands were in a *trans* configuration [102].

Thiocarbohydrazide ($H_2NNHCSNHNH_2$) generally acts as a neutral bidentate ligand bound via the thione sulphur and a terminal nitrogen. The complexes are of stoichiometry $[M(H_2NNHCSNHNH_2)_2]Cl_2$ [M = Zn(II), Cd(II), Hg(II), Pb(II)] [103] or $[M(H_2NNHCSNHNH_2)_3]^{2+}$ [M = Ni(II), Cu(II)] [104,105]. Substituted thiocarbohydrazides of the type $RNHNHCSNHNH_2$ (R = PhCO, MeCO, nicotinyl, 2-hydroxybenzoyl, 2-chlorobenzoyl) give the nickel and cobalt complexes $[M(RNHNHCSNHNH_2)_2(NO_3)]NO_3$ containing both ionic and bidentate nitrate [106]. IR studies suggested that the thiocarbohydrazide is not bound via the oxygen of the R substituent but via the thiocarbonyl sulphur and hydrazinic nitrogen. Although the values of the association equilibrium constants for thiocarbohydrazide with Co(II), and Ni(II) are comparable with those for carbohydrazide $(H_2NNH)_2CO$, the latter binds better to Zn(II) than its sulphur analogue [107].

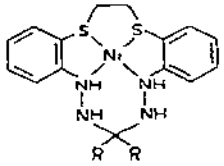
Dithizone ($PhNHNHCSN_2Ph$) has found extensive use as a colourimetric reagent for the determination of metals, and forms intense red to brown colours with 21 ions of 18 metals [108]. However, few of the complexes responsible for these intense colours have been well characterised. X-ray crystal structures of $[Hg(PhNHNCSN_2Ph)_2]$ [109] and $[Cu(PhNHNCSN_2Ph)_2]$ [110] confirmed bonding via the thione sulphur and the protonated nitrogen. The dithizone ligand in $[Ni(PhNHNCSN_2Ph)_2(bipy)]$ was shown by an X-ray crystal structure [111] to be bound in the same manner but with the thione sulphurs in a *cis* configuration.



XXIX



XXX

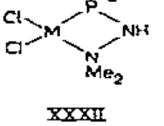


XXXI

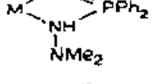
The "template" effect of a metal ion has been used to synthesise the novel macrocyclic complex XXIX by reaction of the nickel complex of the dihydrazine XXX with formaldehyde [112]. Use of cyclohexanone gives the di-cation XXXI, and the derivative with R=H was proposed as a possible intermediate in the formation of XXIX.

(iv) Hydrazines with phosphorus- and arsenic-containing substituents

Although the phosphorus-containing hydrazines $Ph_2P(X)NHNHR$ (R = H, Ph; X = O, S) were first prepared at the beginning of the century [116,117], their co-ordination chemistry has scarcely been investigated. Recently Petersen and co-workers [118,119] have studied some complexes of $Ph_2PNHNMe_2$ and $Ph_2PSNHNMe_2$. IR and ^1H NMR measurements suggest monodentate binding through phosphorus in $[M(Ph_2PNHNMe_2)_2Cl_2]$ (M = Pd, Pt) and the same type of bonding was postulated for $[Mn(CO)_5(Ph_2PNHNMe_2)]$ [120]. The complexes of stoichiometry $[M(Ph_2PNHNMe_2)Cl_2]$ (M = Pd, Pt) are monomeric in acetone solution and believed to contain a four-membered chelate ring (XXXII). Dimerisation occurs in dibromomethane to give a chloro-bridged species with monodentate hydrazine ligand, bound via phosphorus.



XXXII



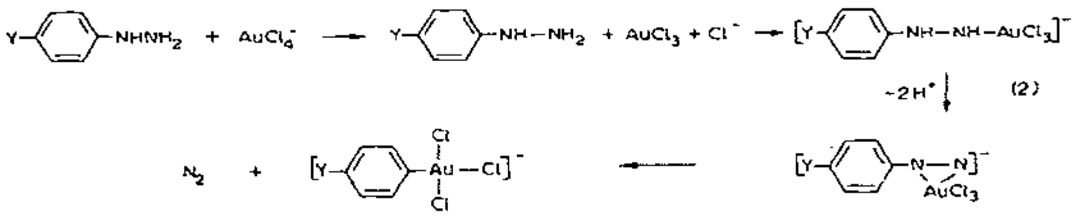
XXXIII

In the complexes $[M(Ph_2PSNHNMe_2)Cl_2]$ IR spectra show that the ligand is bound via the sulphur and the position of $\nu(N—H)$ suggested binding via the protonated nitrogen, giving four-membered chelate ring (XXXIII). Attempts to prepare zinc or cadmium complexes of $Ph_2PNHNMe_2$ resulted in loss of phosphorus and gave $[Zn(H_2NNMe_2)_2Cl_2]$ and $[Cd(H_2NNMe_2)Cl_2]$, the structures of which have been discussed in Sect. C.I.

D. REACTIONS INVOLVING ELIMINATION OF DINITROGEN

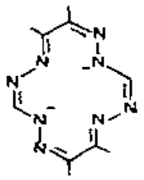
The oxidation of phenylhydrazine by ferric and cupric ions has been investigated by several workers [121—123]. In acid solution phenylhydrazine is initially oxidised by iron(III) chloride to a diazonium salt, but in the presence of an excess of the iron(III) chloride, chlorobenzene is formed in good yield [121,123]. Under acid conditions copper(II) oxidises phenylhydrazine to benzene and dinitrogen, and $[Ru(NH_3)_5Cl]Cl_2$ gives monomeric and dimeric dinitrogen complexes and benzene [129]. It was also claimed that alkylhydrazines are oxidised by copper(II) salts to dinitrogen and hydrocarbon products via a free radical pathway [124].

It was first reported over 50 years ago that aryl mercury compounds could be generated in excellent yields using phenylhydrazine; thus phenylmercuric acetate reacts with phenylhydrazine to give diphenylmercury in over 90 % yield [61]. Much more recently this has been adapted to the preparation of aryl gold complexes, by reaction of arylhydrazine hydrochlorides with tetrahalo-aurate(III) anions [125]. The mechanism outlined below (reaction 2) was proposed since a *para*-substituted arylhydrazine gave a *para*-substituted aryl gold complex, ruling out any *ortho*-metallation reaction.

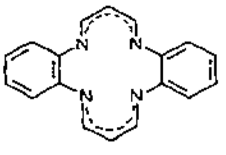


(2)

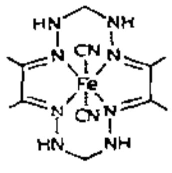
Five co-ordinate organocobalt(III) complexes of the macrocyclic ligand XXXIV $[Co(C_{10}H_{14}N_8)R]$ have been prepared by reaction of the hydrazines $RNHNH_2$ (R = Me, Et, Pr^n, Pr^i, COMe, CO_2Et, Ph, CH_2Ph) with the corresponding square planar cobalt(II) complexes of XXXIV in the presence of oxygen [126].



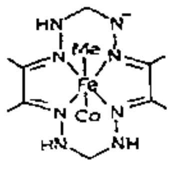
XXXIV



XXXV



XXXVI



XXXVII

Analogous reactions with cobalt(II) complexes of other macrocyclic ligands and with the five co-ordinate iron(III) thiocyanate complex of XXXV to give [Fe($C_{22}H_{22}N_4$)R] were also reported. An X-ray crystal structure of the five-coordinate iron phenyl complex of [Fe($C_{22}H_{22}N_4$)Ph] showed a rather short Fe—C bond length of 1.933 Å. More recently the preparation of an iron methyl carbonyl complex XXXVII (ν(C=O) — 2035 cm^{-1}) by reaction of the bis-(cyano) complex XXXVI with methylhydrazine and carbon monoxide in the presence of strong base has also been reported [127]. An X-ray crystal structure confirmed the presence of *trans* methyl and carbonyl ligands. The carbonyl—methylhydrazine complex $[Fe(C_{10}H_{20}N_8)(CO)(CH_3NHNH_2)]^{2+}$ can be isolated as an intermediate in the formation of the methyl—carbonyl XXXVII.

Ferrocene can be substituted at the 1 or at both the 1 and 1′ positions by reaction with the hydrazines $RNHNH_2$ (R = Ph, PhCO, Me, $PhCH_2$, *p*-Cl—C_6H_4, *p*-MeO—C_6H_4, *p*-NO_2—C_6H_4) in acetic acid in the presence of silver oxide [128]. The mechanism is not known, but free radical substitution of the ferricinium ion was proposed as a possible pathway.

E. FORMATION OF DIAZENE, DIAZENIDO- AND HYDRAZIDO-COMPLEXES

The oxidation of arylhydrazines by first-row transition metals in acid solution to diazonium salts, or their degradation products [121,122] (see Sect. D) has long been believed to proceed via the intermediate formation of unstable aryldiazenes, ArN=NH. However, it is only comparatively recently that the phenyldiazene complex [Cu_4Cl_4(PhN=NH)] was isolated from the reaction of phenylhydrazine with copper(II) chloride in aqueous solution [130]. The phenyldiazene is liberated by solution of the complex in acetonitrile and can be identified by its characteristic UV spectrum [131]. Although the analogous methyldiazene complexes cannot be prepared from methylhydrazine and copper(II) salts, [Cu_2Cl_2(MeN=NH) is isolable from the direct reaction of methyldiazene with copper(I) chloride.

Phenyldiazene complexes are now widely distributed among the transition metals, but most have been prepared by the protonation of N-phenyldiazenido-N′-complexes (e.g. eq. (3)) [132], or by reaction of diazonium salts with metal hydrido-complexes (e.g. eq. (4)) [18].

$$[RhCl_2(N_2Ar)(PPh_3)_2] + HCl \rightarrow [RhCl_3(NH{=}NAr))PPh_3)_2] \quad (3)$$

$$[PtHCl(PEt_3)_2] + PhN_2BF_4 \rightarrow [PtCl(NH{=}NPh)(PEt_3)_2]BF_4 \quad (4)$$

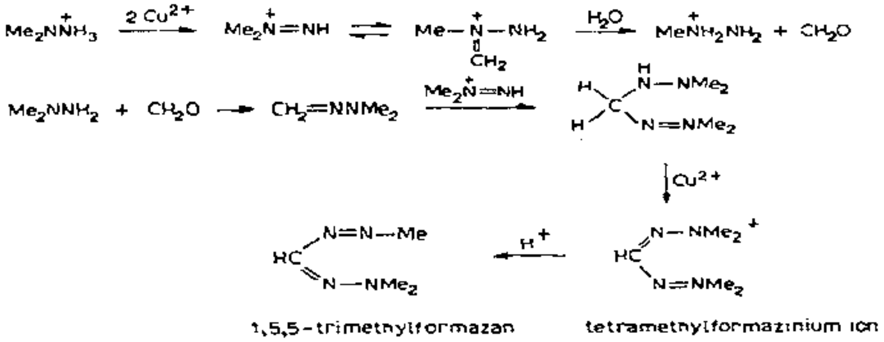
The deep red colouration produced by the addition of phenylhydrazine to acidified molybdate solutions has been attributed to the formation of a molybdenum(V) complex of 1,4-diphenyltetrazene PhNH—N=N—NHPh [133,134]. It was postulated that the tetrazene arose from the coupling of PhNHNO (from oxidation of the hydrazine) with excess phenylhydrazine, but this mechanism appears purely speculative.

1,2-Disubstituted hydrazines RNHNHR (R = alkyl) are also readily oxidised by copper(II) salts to give copper(I) complexes of 1,2-disubstituted diazenes [135]. Since the diazene is readily liberated from the complexes on treatment with base, this has been used as a preparative route to the relatively stable 1,2-disubstituted diazenes. An X-ray crystal structure of $[Cu_2Cl_2(Me—N=N—Me)]$ [136] shows approximately tetrahedrally co-ordinated coppers, each bound to three chlorides and a diazene nitrogen. The diazene has a *trans* configuration and bridges two adjacent cuprous chloride chains. A common feature of all copper diazene complexes appears to be a polymeric cuprous halide chain, but with only this crystal structure available no correlations between stoichiometry and structure can be made.

Iron(III) chlorides, mercury(II) chloride, and the permanganate ion also oxidise 1,2-disubstituted hydrazines to diazenes, but in these cases no complexes containing diazene ligands are isolable. The kinetics of the reaction of 1,2-dimethylhydrazine with manganese(III) in acid solution have been studied by stopped-flow methods [137], and the results interpreted in terms of formation of 1,2-dimethyldiazene.

Reaction of 1,1-dimethylhydrazine with copper(II) halides in dilute aqueous acid at 0° C gives the complexes $[(Me_2N=N)_2Cu_3X_3]$ (X = Cl, Br) [130], [138]. Evidence for the complex containing the so-called 1,1-dimethyldiazene ligand $(R_2\overset{+}{N}=\overset{-}{N})$* was obtained by mixing cold acidic solutions of the complex and the 1,1-diethyldiazenium ion (from the hydrazine and potassium bromate). Treatment with the base and ether extraction gave a nearly statistical distribution of $Et_2N—N=N—NEt_2$, $Et_2N—N=N—N—NMe_2$ and $Me_2N—N=N—NMe_2$.

If the reaction of copper(II) bromide and 1,1-dimethylhydrazine is carried out at 25°C, the salt $[Me_2N_2CHN_2Me_2][Cu_2Br_3]$ is formed. An X-ray crystal structure [138] confirmed the presence of the 1,1,5,5-tetramethylformazinium ion and a polymeric copper(I) anion. Acid treatment of the ionic complex gives 1,5,5-trimethylformazan in low yield. The following mechanism was advanced to explain the formation of the formazinium cation



In general, the oxidation of 1,1-disubstituted hydrazines can give rise to different products depending on the mode of decomposition of the 1,1-di-

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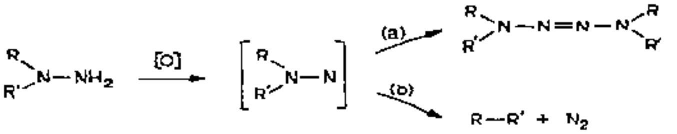
* The problem of nomenclature of complexes containing R_2NN ligands is discussed on p. 51:

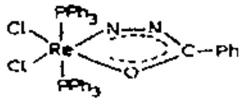
methyldiazene intermediate (eq. (5)) and on the oxidant used.



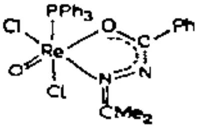
(5)

Path (b) is followed if R= R' = benzyl, or with other alkyl groups if a heterogeneous oxidising system such as mercuric oxide—ethanol is used. The solid surface presumably serves to keep the 1,1-dimethyldiazene fragments apart, facilitating dinitrogen evolution and preventing tetrazene formation. The use of homogenous oxidants such as iron(III) chloride gives tetrazenes via path (a) [139].

The reaction of transition metal complexes containing oxo-groups with substituted hydrazines, provides a preparative route to a range of diazene and hydrazido-complexes. Thus, the rhenium(V) oxo-complex [$ReOCl_3(PPh_3)_2$] reacts with benzoylhydrazine hydrochloride in refluxing ethanol to give complex XXXVIII, and in refluxing acetone complex XXXIX [140].



XXXVIII

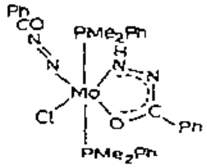


XXXIX

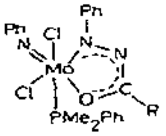
X-ray structural information shows that the C—O and C—N bonds of complexes such as XXXIX [141] have bond orders intermediate between single and double bonds. It is therefore clear that no one of the several possible canonical forms represents the true structure, and in this section this is indicated by the use of dotted bonds to denote delocalisation. As mentioned in the introduction, for the purpose of nomenclature the ligand is arbitrarily assigned the lowest possible charge. Thus complex XXXVIII is named as a rhenium(III) derivative with the chelated ligand bearing a uninegative charge. Complex XXXVIII reacts with certain tertiary and ditertiary phosphines in refluxing methanol to give methyl benzoate and rhenium(I) dinitrogen complexes [142] via an intermediate, isolable benzoyldiazenido-complex [142] (eq. (6)).

$$\mathrm{XXXVIII} \xrightarrow[\mathrm{MeOH}]{PR_3} [ReCl_2(N_2COPh)(PR_3)_3] \xrightarrow[\mathrm{MeOH}]{PR_3} [ReCl(N_2)(PR_3)_4] + PhCO_2Me \qquad (6)$$

Just as hydrazine itself is cleaved at the N—N bond phenyl- or acetylhydrazine reacts with [$ReOCl_3(PPh_3)_2$] to give [$ReNCl_2(PPh_3)_2$] [143]. The hydrazines RNHNHR' (R = R' = Me; R = Ph, R' = PhCO or MeCO) are also cleaved to give the imido-complexes [$ReCl_3(NR)(PPh_3)_2$]. When R = R' = Et or Pr^n, then an alkyl group is lost, giving the nitrido-complex, and in the case of R = R' = CH_2Ph, the amido-complex [$ReCl_3(NHCH_2Ph)(PPh_3)_2$] is the main product [144].



XL

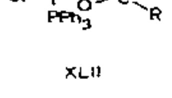


XLI

The oxo-complex [$\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$] reacts with benzoylhydrazine in refluxing methanol to give complex XL [145] and the structure was confirmed by X-ray crystallography [141]. The presence of the proton appears to prevent degradation of the chelated diazene to co-ordinated dinitrogen as observed for the rhenium complex XXXVIII. As with rhenium, the hydrazines RCONHNHPh (R = CH_3, Ph) undergo N—N bond fission on reaction with [$\text{MoOCl}_2(\text{PMe}_2\text{Ph})_3$] to give complexes of structure XLI [145]. The Mo(V) oxo-complex [$\text{MoOCl}_3(\text{dpe})$] (dpe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) reacts with the hydrazines RCONHNHR′ to give the novel ionic species [$\text{MoOCl}(\text{dpe})_2$] [$\text{MoOCl}_3(\text{RCON}_2\text{R}')$] [146], the structure having been established by X-ray crystallography [147].

Only one of the oxo-groups of the bis-oxo-molybdenum(VI) complexes [$\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$] (R = Me, Et, Ph) is removed on reaction with the 1,1-disubstituted hydrazines $\text{R}'\text{R}'\text{NNH}_2$ (R′ = Me, Et), to give the complexes [$\text{MoO}(\text{NNR}'\text{R}')(\text{S}_2\text{CNR}_2)_2$] [148]. Only when R = Me and R′ = Ph can the bis-derivative [$\text{Mo}(\text{N}_2\text{Ph}_2)_2(\text{S}_2\text{CNMe}_2)_2$] be prepared. Complexes of analogous ligands have also recently been prepared by the alkylation of co-ordinated dinitrogen in the complexes [$\text{M}(\text{N}_2)_2(\text{dpe})_2$] [23] (M = Mo or W; dpe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$). In addition certain alkyl- or aryl-diazenido-complexes of molybdenum [148] can be protonated at the terminal substituted nitrogen to give derivatives containing the N—NHR group (R = Me, Ph). An X-ray crystal structure of [$\text{MoO}(\text{NNMe}_2)(\text{S}_2\text{CNMe}_2)_2$] [147] shows the Mo—N—NR_2 system to be essentially linear with Mo—N and N—N distances of 1.85 and 1.24 Å, respectively. These bond lengths suggest that there is considerable delocalisation along the ligand, and that the true structure lies between the two forms $\text{Mo}\leftarrow\ddot{\text{N}}=\overset{+}{\text{N}}\text{Me}_2$ and $\text{Mo}=\text{N—NMe}_2$. However, for nomenclature purposes the complexes as those of copper discussed earlier, are named as hydrazido(2-)-derivatives

Mono-substituted hydrazines $\text{R}'\text{NHNH}_2$ (R′ = Me, Ph, PhCO) react with oxo-complexes [$\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$] in the presence of an excess of sodium dithiocarbamate to give the diazenato-complexes [$\text{Mo}(\text{N}_2\text{R}')(\text{S}_2\text{CNR}_2)_3$] [148] which can be protonated or alkylated to give the cationic hydrazido-(2-)-complexes [$\text{Mo}(\text{N-NR}'\text{R}'')$—$(\text{S}_2\text{CNR}_2)_3]^+$(R″ = H, Me, Et) [148].



XLII

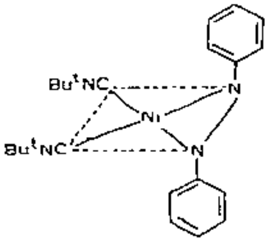
Osmium complexes containing a chelated diazene ligand are obtained from $[OsOCl_3(PPh_3)_2]$ and the hydrazines RCONHNHAr (R = Me, Et, Pr^i, Pr^n; Ar = C_6H_5, p-Cl-C_6H_4, p-O_2N-C_6H_4, p-CH_3-C_6H_4, p-CH_3O-C_6H_4) [149]. Structure XLII was confirmed by X-ray crystallography for the derivative with R = CH_3; Ar = p-CH_3—C_6H_4 [147]. An unusual feature of these complexes is the large ^1H and ^{13}C NMR shifts that are observed despite the apparent diamagnetism of the complexes. The anomalous shifts are proportional to temperature, restricted to the diazene ligand, and highly dependent on the substituents in the diazene aryl group. They have been attributed to the mixing of a thermally inaccessible paramagnetic state localised on the diazene ligand with an essentially diamagnetic ground state.

The intensely coloured complexes $[Mo(PhCSN_2R)_3]$ (M = Re, Mo; R = Ar, Me) are precipitated in high yield by addition of the thiohydrazides PhCSNHNHR to acidified molybdate or perrhenate [145]. The complexes show similar redox properties to the related dithiolene complexes, although the reduced products are rather unstable. One of the diazene ligands of $[Mo(PhCSNNH)_3]$ reacts with acetone in the presence of acid to give $[Mo(PhCSNHN{=}CMe_2)(PhCSNNH)_2]$. The oxidation necessary for the formation of the tris-diazene complex originates from the metal oxo-anion which contrasts with the formation of related complexes of the platinum metals, discussed in Sect. E, where an external oxidant such as iodine is required.

Diazene or hydrazido-complexes can also be prepared by the reaction of certain halido-complexes of second- and third-row transition metals with substituted hydrazines by elimination of hydrogen halide. This can be represented by the general equation

$$[L_nMX_{6-n}] + RNHNHR \rightarrow [MX_{4-n}(RN_2R)L_n] + 2HX$$

Lithiated hydrazines react analogously with elimination of lithium halide (eq. (7)) [150]. Analogous complexes can also be prepared by reaction of azobenzene with Ni(O) species [151] or by displacement of a π-bonded olefin with azobenzene [152]. An X-ray crystal structure of $[Ni(PhN_2Ph)(Bu^tNC)_2]$ [153] (XLIII) shows that the N—N bond length (1.39 Å) is considerably longer than in azobenzene (~1.20 Å) and lies close to the value for a N—N single bond. The nitrogen lone pairs are probably not involved in the bonding which is analogous to that in olefin complexes. By contrast, reaction of azoben-



XLIII

zene with $[(\pi\text{-Cp})_2Ni]$ gives an *ortho*-metallated azobenzene complex [154], which represents the more common mode of bonding of azobenzene.

$$[MX_2L_2] + PhN(Li)N(Li)Ph \rightarrow [M(PhN_2Ph)L_2] + 2LiX \qquad (7)$$

M = Ni, Pd, Pt; $L = PPh_3$, Bu^nNC

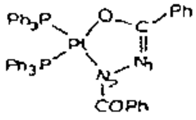
However, the diazene or hydrazido-complexes of palladium and platinum can be prepared more directly by treatment of an halido-complex with the hydrazine in the presence of base (eq. 8) [155,156].

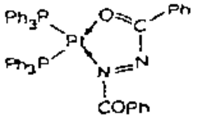
$$[MCl_2(PR_3)_2] + RCYNHNHR' \xrightarrow[Na_2CO_3]{EtOH} [M(RCYN_2R')(PR_3)_2] \qquad (8)$$

$PR_3 = PPh_3, PMe_2Ph$; M = Pd, Pt; Y = S, R = Ph, R′ = Me;

Y = O, R = CH_3, R′ = CH_3CO; Y = O, R = Ph, R = PhCO

Crystal structures of the derivatives with Y = O, R = CH_3, R′ = CH_3CO [141] and Y = O, R = Ph, R′ = PhCO [157] have shown the platinum to be square planar, bound to one oxygen and a nitrogen to give a five-membered chelate ring. The square planar geometry shows unequivocally that the platinum is in the divalent oxidation state and the ligand must be dianionic XLIV rather than the neutral diazene XLV. This is also borne out by the

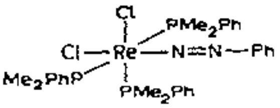

XLIV


XLV

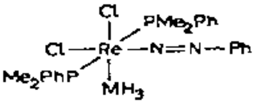
observed bond lengths of 1.29 Å for C—N_1 and 1.41 Å for N_1—N_2 which correspond closely to the values expected for a C=N double bond and N—N single bond, respectively. The complexes are accordingly named as derivatives of the N—N′-dibenzoylhydrazido(2-)N—O ligand. The same complexes can be prepared by the oxidative addition of N,N′-diaryl or N,N′-diacyldiazenes to zerovalent platinum complexes.

The analogous nickel complex $[Ni(p\text{-}CH_3C_6H_4CON_2COC_6H_4\text{-}p\text{-}CH_3)\{P(p\text{-}CH_3\text{-}C_6H_4)_3\}_2]$ has recently been prepared from $[Ni(\text{cyclooctadiene})_2]$, tritolylphosphine and the ditolyldiazene in pentane [158]. The ^1H NMR spectrum revealed that there is an equilibrium between a square planar diamagnetic and a tetrahedral paramagnetic species. This equilibrium is solvent dependent, and the diamagnetic species is favoured by solvents such as carbon disulphide. At elevated temperature there is a further dynamic process which renders the two tolyl groups of the tetrahedral form equivalent [158].

The complexes $[Rh_2(PhCON_2COPh)(CO)_2(PMe_2Ph)_2]$ formulated as containing a bridging dibenzoyldiazene ligand was prepared by the reaction of dibenzoylhydrazine with $[RhCl_3(PMe_2Ph)_3]$ in the presence of base [156]. The mode of bridging of the diazene ligand is not known. The reaction probably proceeds via $[RhCl(CO)(PMe_2Ph)_2]$ as this gives the same dimeric product on reaction with the hydrazine. Phenylhydrazine reacts with *mer*-[$ReCl_3$-($PMe_2Ph)_3$] in ethanol under reflux to give predominantly [$ReCl_2(NH_3)(N_2Ph)$-($PMe_2Ph)_2$] (XLVI) together with a small amount of [$ReCl_2(N_2Ph)(PMe_2Ph)_3$]-(XLVII) [159]. The appearance of ammonia in the co-ordination sphere of



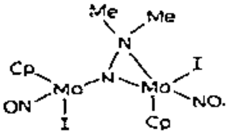
XLVI



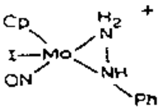
XLVII

XLVI suggests that a complex redox reaction involving N—N bond cleavage has occurred. Although complex XLVII is inert to hydrohalic acids, complex XLVI is readily protonated, and an X-ray crystal structure [160] has confirmed that the phenyldiazenato-ligand is protonated at the nitrogen adjacent to the phenyl group. The reasons for the subtle dependence of the reactivity of the diazene ligand on the other ligands in the co-ordination sphere are not all clear.

Complexes containing bridging hydrazido or diazene ligands are relatively rare, but it was recently reported [161] that the dimers [{(π-Cp)Mo(NO)X_2}$_2$] (X = Cl, Br, I) react with the hydrazines $RR'NNH_2$ (R = R′ = Me, Et; R = Me, R′ = Ph) to give dimers bridged by the RR′NN group. An X-ray crystal structure XLVIII (X = I, R = R′ = Me) confirmed the presence of a novel asym-



XLVIII



XLIX

metric bridging hydrazido(2-) ligand. Under similar conditions, phenylhydrazine initially gives [(π-Cp)Mo(NO)I_2(H_2NNHPh)] which then reacts further with phenylhydrazine to give [(π-Cp)Mo(NO)I (HNNHPh)]. The latter can be protonated to give [(π-Cp)Mo(NO)I(H_2NNHPh)]$^+$; shown by an X-ray crystal structure (XLIX) to contain a dihapto phenylhydrazine ligand [161 (a)], which is the first well-established example of a hydrazine bound in this manner. [(π-Cp)Mo(NO)I(HNNHPh)] also reacts with [{(π-Cp)Mo-(NO)I_2}$_2$] to give [{(π-Cp)Mo(NO)I}$_2$NNHPh], a structural analogue of XLVIII. The only other complex containing bridging hydrazine-derived ligands is [{($PPh_3)_2Pt(N_2H)$}$_2$] [162] where the bridging N_2H group was confirmed by an X-ray structure [163].

F. FORMATION OF DITHIOLENE-LIKE COMPLEXES

As indicated in Sect. C. II (iii) [$Ni(PhCSNHNH_2)_2$]$^{2+}$ can readily be deprotonated to neutral [$Ni(PhCSNNH_2)_2$]. Aerial or iodine oxidation then gives bright blue [$Ni(PhCSNNH)_2$] [100,164] which can be reversibly electrochemically reduced to mono and dianionic species (Table 5). The platinum

TABLE 5

Electrochemical data for dithiolene-like complexes

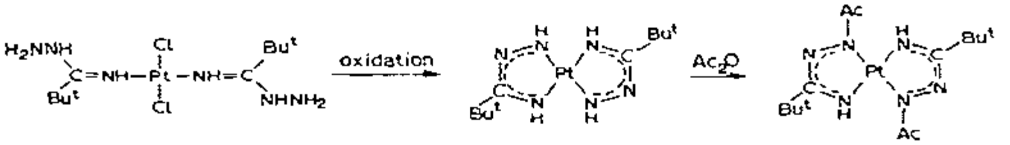
Process	$E_{1/2}$ (V) vs. S.C.E.			
	$[Pt(Me_2NCSN_2Ph)_2]$ [a]	$[Ni(Et_2NCSN_2Ph)_2]$ [b]	$[Pt(PhCSNNH)_2]$ [c]	$[Ni(PhCSNNH)_2]$ [d]
$1^+ \rightleftharpoons 2^+$	+0.80	+0.70	—	—
$0 \rightleftharpoons 1^+$	+0.44	+0.51	—	—
$1^- \rightleftharpoons 0$	−0.76	−0.72	−0.42	−0.14
$2^- \rightleftharpoons 1^-$	−1.19	−1.05	−1.27	−1.13

[a] In CH_3CN Pr_4^n $NClO_4$ support electrolyte (S.E.).
[b] In CH_2Cl_2 Bu_4^n NBF_4 S.E.
[c] In DMF Bu_4^n NBF_4 S.E.
[d] In DMSO Pr_4^n $NClO_4$ S.E.

analogue [Pt(PhCSNNH)$_2$] has been prepared by the hydrogen peroxide oxidation of [Pt(PhCSNHNH$_2$)$_2$] in alcohol and also undergoes reversible electrochemical reduction [165] (Table 5).

The related complexes [Pt(RR'NCSN$_2$Ph)$_2$] (R = R' = Me; R = H, R' = Bu^t; R = H, R' = Ph), derived from substituted semicarbazides, were initially prepared by Podchainova et al. [166] by aerial oxidation of alkaline solutions of the complexes [Pt(RR'NCSNHNHPh)$_2$], but were incorrectly formulated. Further investigations established the correct stoichiometry, and their redox properties were also studied [164] (Table 5), and the neutral complexes shown to be the central members of a five-membered electron transfer series. The cyclovoltammetric electrochemical data, although not strictly comparable as different solvents are used, shows that the platinum complexes are generally harder to reduce than their nickel anlogues. In contrast to the substituted thiosemicarbazide complexes, the thiohydrazide derivatives only show irreversible oxidation waves, reflecting the instability of the oxidised species.

More recently Bechgaard reported [167] the related five-membered electron-transfer series of nickel complexes [Ni(Et$_2$NCSN$_2$Ph)$_2$]^Z ($Z = 2^+, 1^+, 0, 1^-, 2^-$, Table 5). The complex with $Z = 0$ is interesting in that an X-ray crystal structure [168] has shown the nickel is in a tetrahedral environment with a dihedral angle of 78° between the planes of the chelate rings. All the related palladium and platinum complexes are assumed, or have been shown to be, square planar. The deviation from planarity for the nickel complex was attributed to steric interactions of the phenyl groups. The complex with $Z = 0$ and analogous compounds, also show small temperature independent contact shifts in their ^{1}H NMR spectra, attributed to unpaired spin density arising from thermal population of low-lying excited states.



IX L LI

(9)

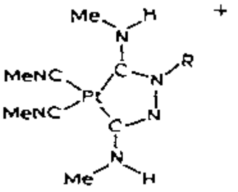
The related complexes L have been prepared by the oxidation of the amidrazone-derived complexes IX generated by the reaction of hydrazine with platinum(II) *t*-butyl cyano-complexes [41]. The first part of the reaction has already been discussed in Sect. C. II (i).

The red neutral complex is converted to the green acetato-complex LI by acetic anhydride (eq. (9)). An X-ray crystal structure [41] of LI showed square planar co-ordination about the platinum. Polarographic reduction of L showed two waves at $E_{1/2}$ − 0.25 and −0.56 V vs. S.C.E. Controlled potential reduction experiments [41] revealed that the species with $E_{1/2}$ − 0.56 V was a binuclear mono-anion. Reduction of the formally platinum(II) derivative LI proceeds with formation of a mixed-valence dimer probably bridged via the acetate groups.

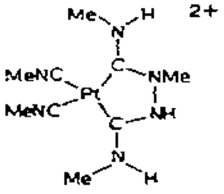
In the above complexes there is a real problem in assigning a formal oxidation state to the metal and providing an adequate nomenclature system. Jensen et al. [96] showed that the zinc complex [$Zn(Et_2NCSN_2Ph)_2$] was paramagnetic with a magnetic moment of 2.4 B.M., suggesting that this and the Ni, Pd and Pt complexes should be formulated as the divalent metal co-ordinated by anionic radical ligands. To circumvent the difficulty of naming this type of ligand and to avoid trying to name canonical forms, it has now been proposed that the complexes should be named on the basis of defining the stereochemistry by a prefix (e.g. T-tetrahedral: S-P, square-planar), and naming the ligand as a neutral species. Thus the complex [$Ni(Et_2NCSN_2Ph)_2$] is now named T-[N-diethylaminothiocarbonyl,N′-phenyldiazene(N′-S)nickel].

G. REACTIONS WITH CO-ORDINATED LIGANDS

The bright red complexes resulting from the reaction of hydrazine with platinum(II) isocyanide complexes were originally [168] formulated as hydrazine-bridged dimers, but subsequent investigation [169,170] showed that these should be reformulated as the chelated carbene complex LII (R = H). An analogous complex is formed with methylhydrazine (LII, R = Me) and its structure has been confirmed by X-ray crystallography [169]. It can be protonated with HCl to the di-cation LIII whereas protonation of complex LII with R = H under similar conditions results in loss of the isocyanide ligands and formation of [$CH_3NHCNHNHCNHCH_3)PtCl_2$]. The methyl group presumably functions as a blocking group and prevents complete protonation of the chelated dicarbene ligand.



LII



LIII

Fischer and Aumann have reported [171] the formation of cyano-complexes from reaction of chromium and tungsten carbene derivatives with 1,1-dimethylhydrazine. The mechanism proposed (eq. (10)) involved nucleophilic attack at the carbene carbon, with methanol and dimethylamine formed as by-products.

$$[(CO)_5CrC(OMe)Me] \xrightarrow{Me_2NNH_2} [(CO)_5CrC(NHNMe_2)Me] \rightarrow [(CO)_5Cr(NCMe)] + Me_2NH \qquad (10)$$

The carbon of certain metal carbonyls is also susceptible to nucleophilic attack by hydrazines and isocyanates are the ultimate products (eq. (11)) [172].

$$[\pi\text{-CpFe(CO)}_3]^+ + \text{H}_2\text{NNR'R} \rightarrow \underset{\text{LIV}}{[\pi\text{CpFe(CO)}_2(\text{CONHNRR'})]} \rightarrow [\pi\text{-CpFe(CO)}_2\text{NCO}] + \text{NHRR'} \qquad (11)$$

The intermediate LIV can only be isolated when a 1,1-disubstituted hydrazine is used.

ACKNOWLEDGEMENTS

I should like to thank Professor Chatt and my colleagues at the Unit of Nitrogen Fixation for their helpful comments and advice during the preparation of this manuscript.

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