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Transition metal complexes containing hydrazine and substituted hydrazines [1]

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Contents

Abstract

This review deals with the structures, preparation and spectroscopic properties of hydrazine and substituted hydrazine metal complexes and includes examples of η^1-, η^2- and $\mu_2:\mu^2$-bonded hydrazines.

Keywords: Metal; Hydrazine; Structure; Preparation; NMR

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[1] Dedicated to Professor J. Chatt, CBE, FRS with whom BTH worked as a research student (1964–67) when Joe Chatt was just commencing his work on nitrogen fixation. During this time Paolo Chini spent 6 months in JCs laboratory, after which there was a long and fruitful collaboration on cluster chemistry between BTH and PC; it is a pleasant coincidence that recent work aimed at elucidating the nature of the hydrogenation catalyst used commercially by Hovione has resulted in the identification of a number of rhodium hydrazine and related derivatives.

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1. Introduction

Hydrazine is a powerful reducing agent [1] and was used by Chatt et al. [2] to prepare the first platinum-hydride complex, *trans*-[PtHCl(PEt$_3$)$_2$]. Subsequently, protonation of coordinated dinitrogen has been shown to give a variety of derivatives, including N_2H_4. More recently, a number of substituted and unsubstituted hydrazine transition metal complexes have been reported and these form the basis of this review[2]. Complexes containing hydrazine have not so far been reviewed specifically, and complexes containing substituted hydrazine were last reviewed in 1976 [3].

2. Hydrazine complexes

The possible modes of bonding of hydrazine to a transition metal are shown in Fig. 1. Examples of all the modes of bonding shown in Fig. 1 are now known. X-ray crystallography is important for structural characterisation but is dependent on suitable crystals being available and unfortunately only a few examples of crystallographically characterised hydrazine complexes have thus far been reported. Furthermore, the direct location of H atoms is often not possible and it is often difficult to be sure whether the complex contains hydrazine or hydrazide(−1).

Characterisation of most of the hydrazine complexes in the literature has relied heavily upon IR and ^{1}H NMR spectroscopies and, as a result, the proposed structures are still not unambiguous. It has been claimed from IR studies that the position of ν(N–N) in monodentate hydrazine complexes occurs at 928–937 cm^{-1} whereas for complexes which contain bidentate or bridging hydrazine ν(N–N) occurs at 948–980 cm^{-1}. These bands are all at higher frequency than free hydrazine (875 cm^{-1}) [4]. Nevertheless, such assignments are difficult without the benefit of IR spectra of ^{14}N/^{15}N-isotopomers, and even then the IR spectrum in the 900–1000 cm^{-1} region is often crowded due to absorption from other ligands in the complex, making identification of ν(N–N) difficult. As a result, the stereochemistry of metal hydrazine complexes based on IR measurements must be viewed with some caution.

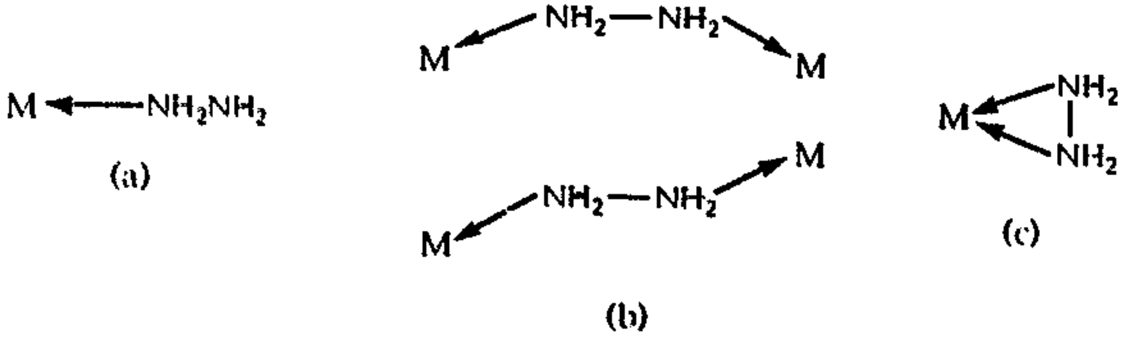

Fig. 1. Bonding modes of hydrazine: (a) monodentate; (b) bridging (μ_2:μ^2-); (c) bidentate (η^2-).

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[2] The labelling scheme throughout this review is: M–$N_\alpha H_2N_\beta H_2$, $N_\alpha H_2N_\beta HR$.

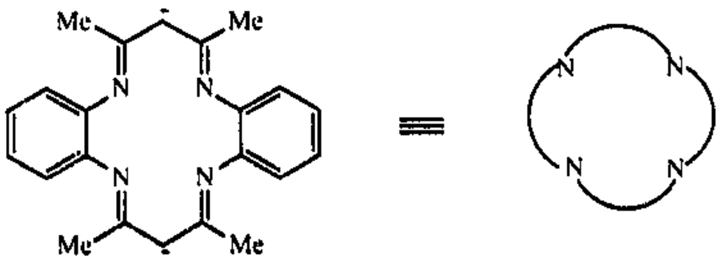
Multinuclear NMR measurements can provide much more unambiguous identification of the complex. ^{15}N NMR coupled with X-ray crystallography, when suitable crystals are available for structural characterisation, provides unambiguous structural identification of hydrazine complexes. ^{15}N NMR data[3] can be obtained directly, although this requires the complex to be isotopically enriched, or via indirect measurements, INEPT [6], which can be carried out on complexes with natural ^{15}N-abundance but these measurements depend upon there being *no* inter-exchange of N—H protons, (vide infra).

2.1. Monodentate hydrazine complexes

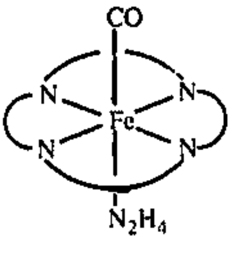
Apart from our work, there are only six examples of X-ray structurally characterised complexes containing hydrazine as a monodentate terminal ligand reported in the literature. In all cases, the hydrazine acts as a two electron donor.

The diamagnetic octahedral Fe(II) complex, $[Fe(C_{22}H_{22}N_4)(N_2H_4)(CO)]$ (**1**), contains a macrocyclic ligand $[C_{22}H_{22}N_4]^{2-}$ with trans CO and N_2H_4 groups [7,8] and was prepared by hydrazine displacement of base (e.g. CH_3CN, py) from the analogous complex under an atmosphere of CO.

A related complex $[Fe(N_2H_4)(\text{'}N_HS_4\text{'})]$ (**2**) containing a pentadentate amine–thioether–thiolate ligand, 'N_HS_4', has been reported [9] and is found to contain high spin Fe(II). This leads to high lability of hydrazine; similar behaviour is found for other analogous complexes containing σ-donor ligands (e.g. NH_3), whereas replacement of N_2H_4/NH_3 by π-acceptor ligands (e.g. CO, N_2H_2) causes the Fe(II) to



$[C_{22}H_{22}N_4]^{2-}$



(1)

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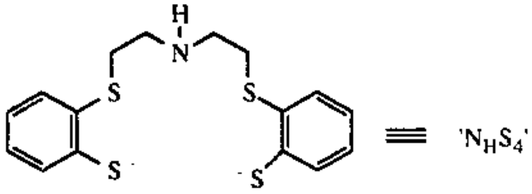
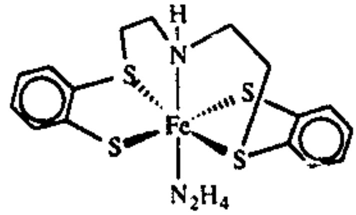
[3] Throughout this review, $\delta(^{15}N)$ is referred to external $MeNO_2$ with the appropriate conversions from other reference standards [5].





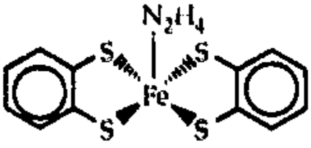
(2)

become low spin and inert. Although it has not yet been possible to coordinate N_2 to this metal complex system, this interconversion of spin states and substitution lability/inertness on changing the type of ligand provides important information about the stepwise reduction of N_2 to N_2H_2 to N_2H_4 to NH_3.

A related complex $[Fe(N_2H_4)(S_2C_6H_4)_2]^-$ (3) has been crystallographically characterised; in this case, the complex is approximately square pyramidal and contains high spin Fe(III) with a labile N_2H_4 [10].

The weakly bound trifluorosulphonate/(triflate) group in (4) and (5) is readily displaced by hydrazine to give (6) and (7) Eq. (1) and (7) has been characterised by X-ray crystallography [11].

The structure of $[M(N_2H_4)_2(NH_2NHCO_2)_2]$ (8, M = Co [12]; 9, M = Zn [13])



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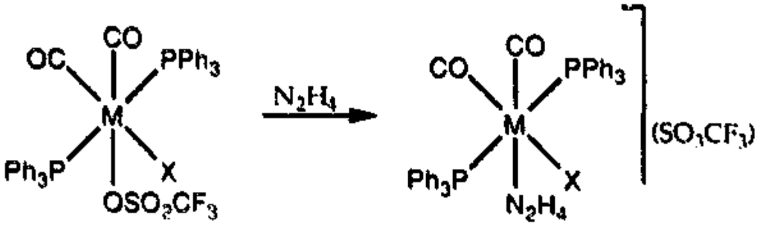
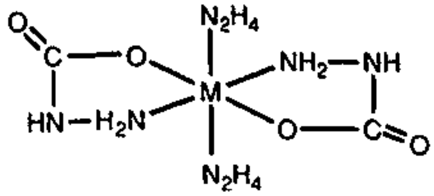


(1)

(4) M = Ru, X = Cl
(5) M = Os, X = Br

(6) M = Ru, X = Cl
(7) M = Os, X = Br

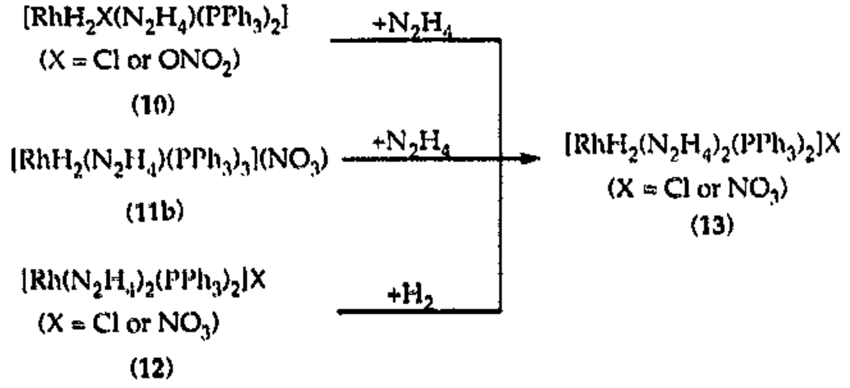


(8) M = Co (9) M = Zn

is shown above; the metal is pseudo octahedral and two monodentate hydrazine ligands are trans to each other.

Although the H atoms associated with the N_2H_4 ligands were not located in the X-ray structure of **(13b)**[4], the methods of preparation (Eq. (2)) coupled with multinuclear NMR measurements (^{1}H, ^{31}P, ^{103}Rh) on **(13)** unambiguously establish the structure [14]. Thus, the high field region of the ^{1}H NMR spectrum consists of a single resonance, $\delta(\mathrm{H})$ −17.3 ppm, which appears as a pseudo-quartet (1:4:4:1) that results from a doublet of triplets due to accidental equivalence of $^1J(\mathrm{Rh{-}H})$ and $^2J(\mathrm{P{-}H}) = 15$ Hz; the {^{1}H}-^{103}Rh INEPTRD spectrum shows a triplet, $\delta(\mathrm{Rh})$ 345.5 ppm due to coupling to two equivalent phosphorus atoms $^1J(\mathrm{Rh{-}P})$ 117 Hz, $\delta(\mathrm{P})$ 49.3 ppm.

The structural data for all the complexes containing a mono-dentate hydrazine thus far reported are shown in Table 1. There is little variation in $d(\mathrm{N{-}N})$, which



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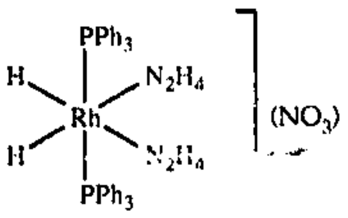

(13b)

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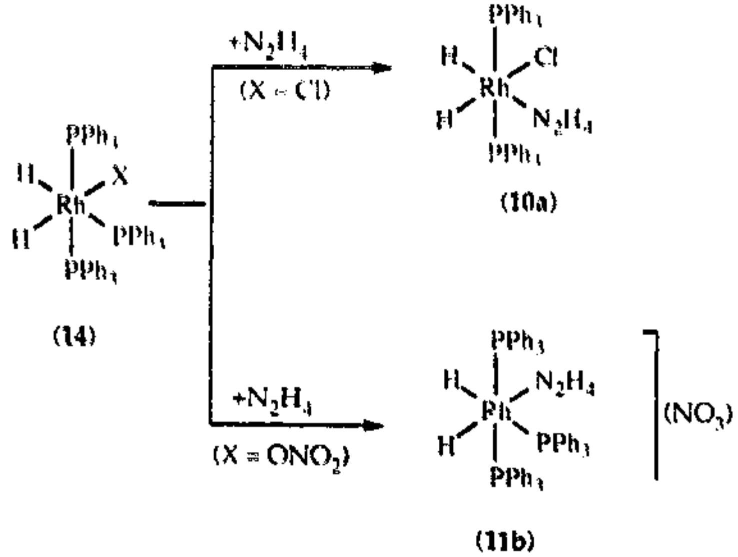
[4] Throughout this review, if a or b is appended to the numeral, then for ionic compounds, X = Cl or NO_3 respectively and, for non-ionic compounds, X = Cl or ONO_2 respectively.

Table 1
Structural data for the coordinated hydrazine in metal complexes containing a monodentate hydrazine

Complex		d(M−N) (Å)	d(N−N) (Å)	$\widehat{MNN}$ (deg)	Reference
$[Fe_2(N_2H_4)(CO)(C_{22}H_{22}N_4)]$	**(1)**	2.122(5)	1.446(6)	121.3(3)	[7,8]
$[Fe(N_2H_4)('N_HS_4')]$	**(2)**	2.192(6)	1.439(10)	118.3(1)	[9]
$[Fe(N_2H_4)(S_2C_6H_4)_2]$	**(3)**	2.178(3)	1.452(5)	115.2(2)	[10]
$[Os(N_2H_4)(CO)_2(PPh_3)_2Br](SO_3CF_3)$	**(7)**	2.181(3)	1.451(7)	119.3(3)	[11]
$[Co(N_2H_4)_2(NH_2NHCO_2)_2]$	**(8)**	2.170(2)	1.454(2)	118.1(1)	[12]
$[RhH_2(N_2H_4)_2(PPh_3)_2](NO_3)$	**(13b)**	2.291(9)	1.459(17)	118.3(35)	[14]
$[Zn(N_2H_4)_2(NH_2NHCO_2)_2]$	**(9)**	2.17(2)	1.46(4)	117.5(1)	[13]

is similar to that found for the free ligand (1.447 Å) [15], and all the values for $\widehat{MNN}$ are similar and somewhat opened from the tetrahedral value.

It is now worthwhile commenting upon the preparation and characterisation of **(10)**, **(11)** and **(12)** which have been used to prepare **(13)**. Eq. (3) shows the products resulting from the addition of hydrazine to $[RhH_2X(PPh_3)_3]$ **(14)**. **(14)** undergoes displacement of PPh_3 when X = Cl, whereas when X = ONO_2 displacement of the weakly bonded nitrato group occurs [14]. The lability of the nitrato group [16,17], which can bond as either a mono- or bi-dentate ligand, has been exploited to prepare **(10b)** and **(14b)**, Eq. (4).



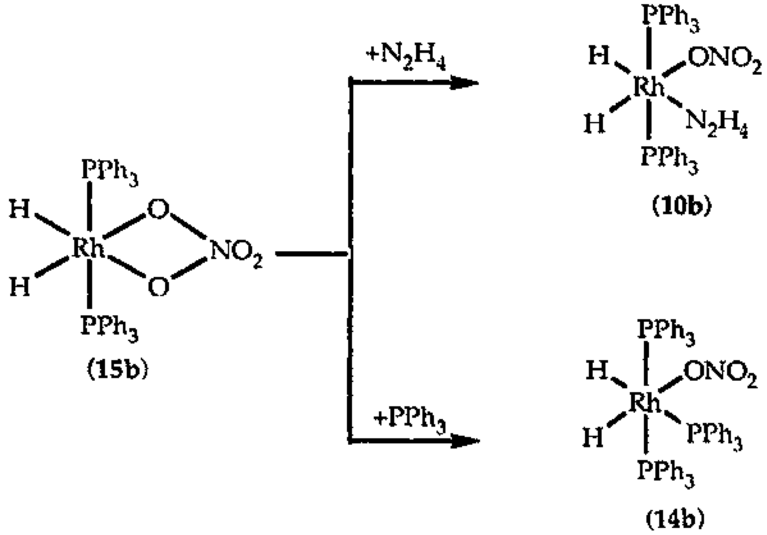
(14)

(10a)

(11b)

(3)

The preparation of $[Rh(N_2H_4)_2(PPh_3)_2]Cl$ **(12a)** is most easily accomplished by the addition of N_2H_4 to a solution of $[Rh_2Cl_2(PPh_3)_4]$ **(16a)** in CH_2Cl_2, Eq. (5). $[Rh(N_2H_4)_2(PPh_3)_2](NO_3)$ **(12b)** has also been detected spectroscopically on addition of excess hydrazine to $[Rh(ONO_2)(PPh_3)_3]$ **(17b)** [14] and careful stoichiometric addition of N_2H_4 to $[RhX(PPh_3)_3]$ **(17)** in CH_2Cl_2 + MeOH (1:1) gives $[Rh(N_2H_4)(PPh_3)_3]X$ (X = Cl, NO_3) **(18)**, Eq. (6).



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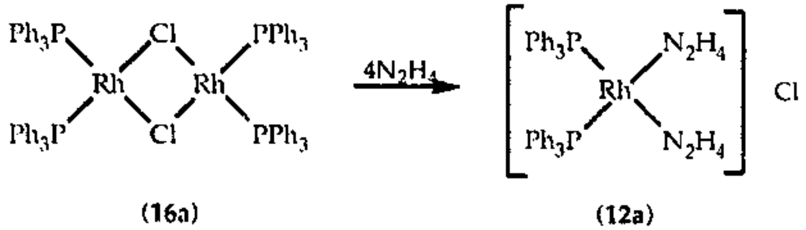

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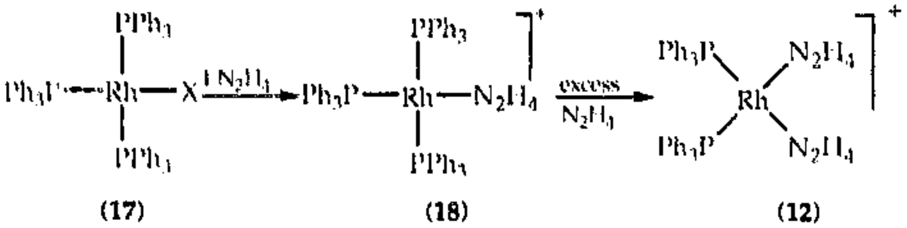


(6)

Apart from (**13b**), none of the above Rh(I) or Rh(III) hydrazine complexes have been crystallographically characterised, but the presence of many different nuclei with $I = \frac{1}{2}$, coupled with the stoichiometry of reagents and the method of preparation, allows the unambiguous structural identification of the complexes (illustrated in detail for (**10a**)).

In addition to resonances due to the starting material (**14a**) Eq. (3), the ^{31}P NMR spectrum of (**10a**) consists of a doublet at 47.7 ppm, ^1J(Rh−P) 118 Hz. From this spectrum it is difficult to establish whether one or two PPh_3s are coordinated to rhodium but the refocused and ^{1}H-decoupled Rh−{H} INEPT spectrum (Fig. 2) clearly shows a triplet at 331 ppm due to coupling to two PPh_3s.

Consistent with the formulation presented for (**10a**), there are two multiplet high field ^{1}H resonances at −16.6 and −18.8 ppm, Fig. 3. Although it is not possible to

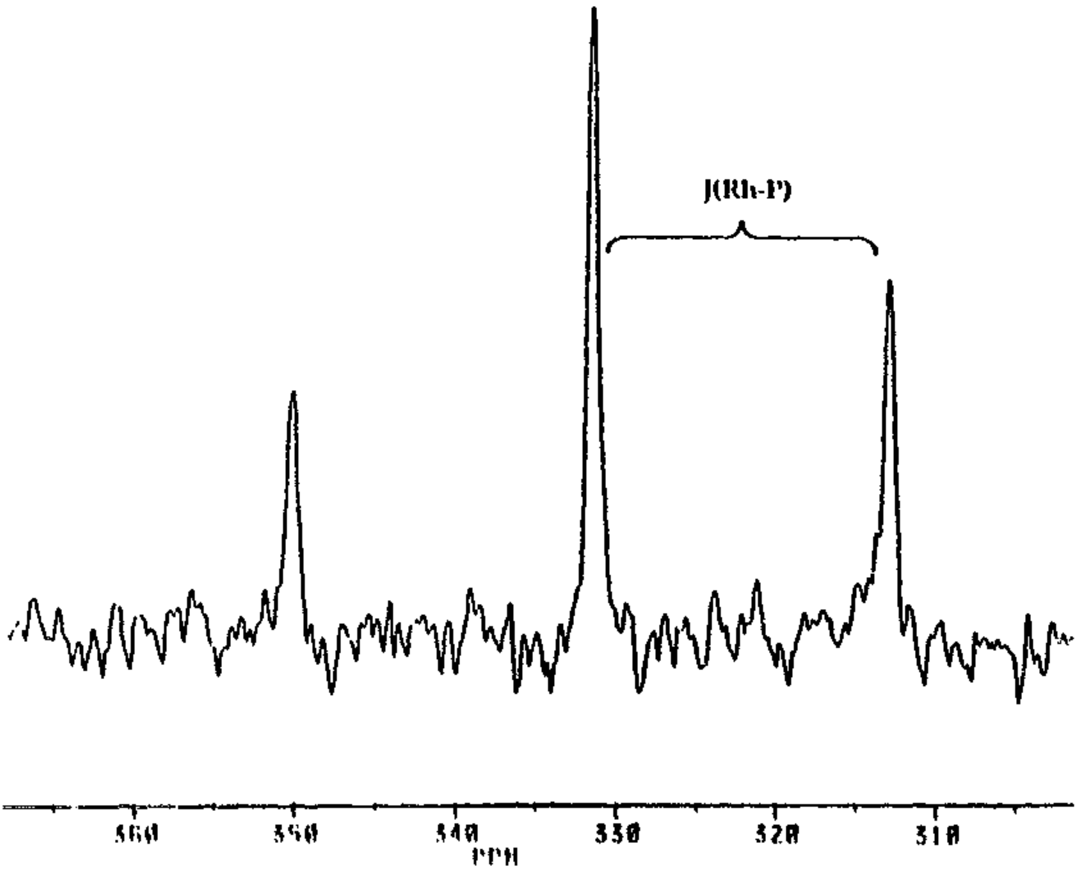


Fig. 2. ^{103}Rh-{^{1}H} INEPT spectrum of [$RhH_2Cl(PPh_3)_2(N_2H_4)$] (**10a**) at 243 K.

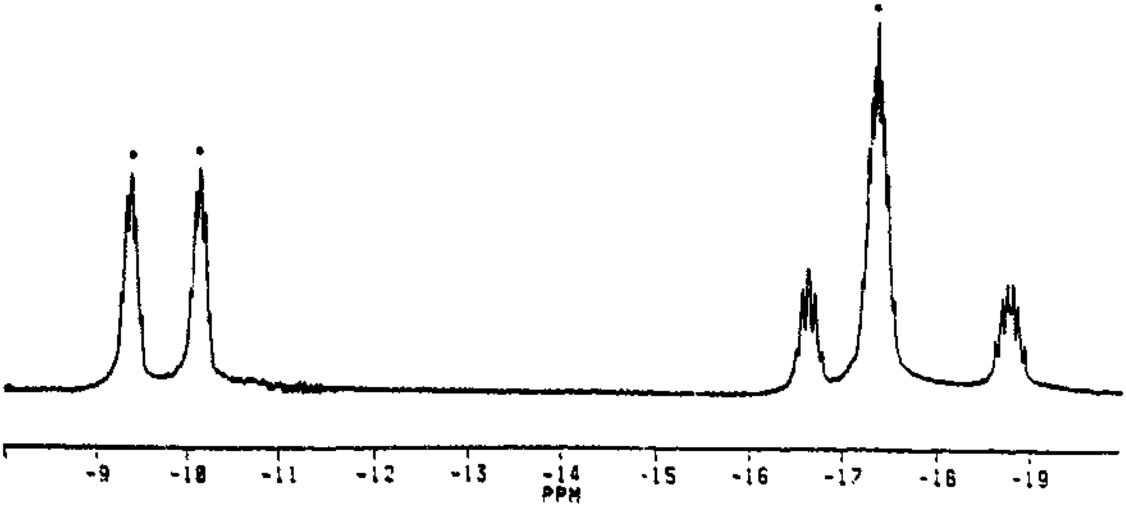


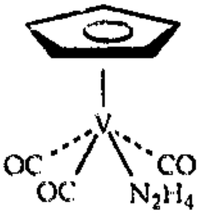
Fig. 3. ^{1}H NMR spectrum of [$RhH_2Cl(PPh_3)_2(N_2H_4)$] (**10a**) at 243 K. Asterisks denote starting material [$RhH_2Cl(PPh_3)_3$] (**14a**).

unambiguously assign which resonance is trans to Cl vs. trans to N_2H_4, specific decoupling measurements have allowed all the coupling constants to be obtained (see Table 2). The direct ^{15}N NMR spectrum of (**10a**, $^{15}N = 95\%$) is consistent with the presence of a terminal hydrazine ligand and consists of two resonances at −347.9 ppm (N_α) and −355.3 ppm (N_β); these ^{15}N, ^{31}P and ^{1}H NMR data for Rh(I)–Rh(III) complexes containing monodentate hydrazine are summarised in Tables 2 and 3.

A variety of complexes containing mono-dentate hydrazine have been formulated on the basis of analytical, IR and/or ^{1}H NMR measurements and these, together with data on the complexes described above, if appropriate, are given in Table 4; the more interesting and unambiguous aspects of their stereochemistry are described below.

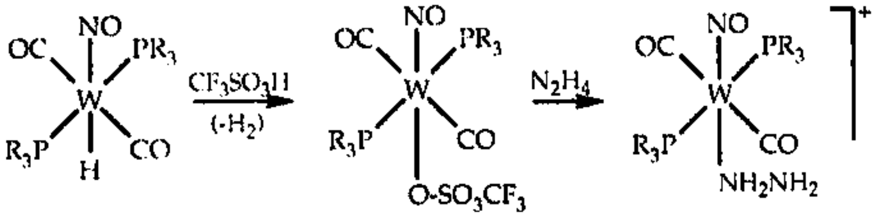
In Table 4, there appears to be quite a wide range of values for $\delta(N_\alpha H)$ and $\delta(N_\beta H)$, which are also dependent on the solvent and, where assignments have been made, then the values of $\delta(N_\alpha H)$ is always greater than $\delta(N_\beta H)$ with little difference in $^{1}J(N_\alpha H)$ and $^{1}J(N_\beta H)$.

Reaction of $[V(CO)_3(THF)Cp]$, and related molecules, with N_2H_4 results in displacement of THF to give $[V(N_2H_4)(CO)_3Cp]$ (**19**) [18]. The stereochemistry of (**19**) is based on the presence of 3 ν(CO) bands and 4 ν(N−H) bands in the IR spectrum, and the presence of two equally intense NH resonances in the NMR spectrum; this formulation with an η^1-N_2H_4 provides 18 valence electrons and precludes an η^2-N_2H_4 formulation.



(**19**)

The stereochemistry of (**24**) and (**25**) is shown below together with the method of preparation (Eq. (7)), which is similar to that described earlier and involves displacement of the weakly coordinated triflate group. It has been suggested that it is the steric bulk of the '$W(CO)_2(NO)(PR_3)_2$' fragment that dictates the η^1- rather than η^2-coordination of N_2H_4 [22].



(7)

(**24**) R=Ph
(**25**) R=Cy

Table 2
^{31}P and ^{1}H NMR data on Rh(III) and ^{31}P NMR data on rhodium(I) complexes containing a terminal hydrazine in CD_2Cl_2 solution at −30 C, except for **(18a)** and **(18b)** which were recorded in CH_2Cl_2 + MeOH (1 : 1) at −30 C[a,b]

Compound	$\delta(^{31}P_a)$	$\delta(^{31}P_b)$	$^{1}J(^{103}Rh,^{31}P_a)$	$^{1}J(^{103}Rh,^{31}P_b)$	$^{2}J(^{31}P_a,^{31}P_b)$	$\delta(^{1}H_a)$	$\delta(^{1}H_b)$	$^{1}J(^{103}Rh,^{1}H_a)$	$^{1}J(^{103}Rh,^{1}H_b)$	$^{2}J(^{31}P,^{1}H_a)$	$^{2}J(^{31}P,^{1}H_b)$	$\delta(^{103}Rh)^c$
(10a)	47.7		118			−16.6	−18.8	16[d]	22[d]	[e]	[e]	331
(11b)[a,b]	39.8	25.9	111	90	18	−10.3	−16.5	12	12	146(P_b)	12(P_a)	
(13a)	49.3		117			−17.2		16		15		358
(13b)	48.5		117			−17.3		15		15		345
(12a)	51.7		176									
(12b)	52.2		174									
(18a)[a]	44.6	32.6	165	147	40							
(18b)[a]	44.6	32.7	165	147	40							

[a] P_a is trans to P_a. [b] H_a is trans to PPh_3, H_b is trans to N_2H_4. [c] $\delta(^{103}Rh) = 0$ ppm at such a magnetic field (200 MHz) that ^{1}Hs in TMS resonate at 7.32 MHz. [d] Determined by selective ^{1}H-decoupling with simultaneous ^{31}P-decoupling. [e] These values are ca. 16–22 Hz but it was not possible to obtain them more accurately due to our inability to carry out selective ^{1}H-decoupling with simultaneous ^{103}Rh-decoupling.

Table 3
^{15}N NMR data[a] on rhodium(I)/(III) complexes containing a terminal hydrazine at −30 C except for **(12b)** which was measured at −55 °C

Compound	Solvent	$\delta(^{15}N_\alpha)$	$\delta(^{15}N_\beta)$	$^{1}J(^{1}H,^{15}N_\alpha)$	$^{1}J(^{103}Rh^{15}N_\alpha)$	$^{2}J(^{31}P_{trans},^{15}N_\alpha)$	$^{2}J(^{1}H_{trans},^{15}N_\alpha)$	$^{1}J(^{1}H,^{15}N_\beta)$	$^{1}J(^{15}N_\alpha,^{15}N_\beta)$
(10a)[b]	CH_2Cl_2	−347.9	−321.7	72	7		19	66	6
(11b)[b]	CH_2Cl_2–MeOH (1:1)	−355.3	−313.0	72	7[c]		16	66	7
(12b)[b]	CH_2Cl_2	−347.0	−322.9	72	12	30		65	
(18b)[b]	CH_2Cl_2–MeOH (1:1)	−344.6	−317.2	65	12	31		66	6

[a] δ values are in ppm relative to CH_3NO_2; *J* values are in Hz. [b] N_2H_4 was ^{15}N-enriched (ca. 99%). [c] $^{2}J(^{103}Rh,N_\beta)$ 3 Hz.

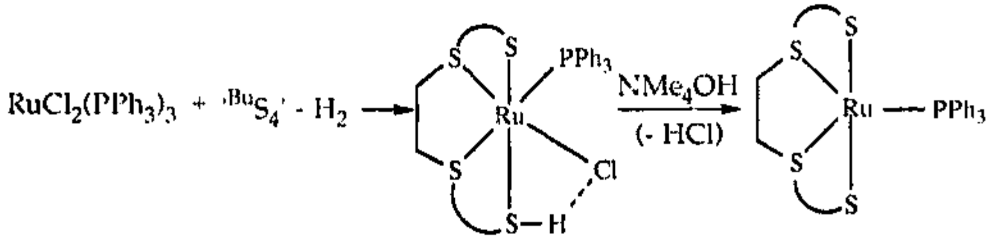
Table 4
^{1}H NMR data and IR measurements relating to N_2H_4 in complexes containing mono-dentate hydrazine

Compound		δ(H)	^1J(NH)	^3J(HH)	IR	Reference
$[V(N_2H_4)(CO)_3Cp]$	(19)	4.45^a, 2.93^b			✓	[18]
$[V(N_2H_4)(CO)_3\{\eta^5\text{-}C_5H_4(SiMe_3)\}]$	(20)	4.54^a, 3.03^b				[18]
$[Cr(N_2H_4)(CO)_5]$	(21)	4.85, 3.40			✓	[19]
$[Mo(N_2H_4)(CO)_5]$	(22)	4.6, 3.4			✓	[20]
$[W(N_2H_4)(CO)_5]$	(23)	4.8, 3.7			✓	[21]
$[W(N_2H_4)(CO)_2(NO)(PPh_3)_2]^+$	(25)	3.73, 2.27	69 63			[22]
$[W(N_2H_4)(CO)_2(NO)(PCy_3)_2]^+$	(25)	3.73, 2.27				[22]
$[Re(N_2H_4)(CO)_2Cp]$	(26)	5.05, 3.5			✓	[23]
$[Fe(N_2H_4)(CO)_2Cp]^+$	(27)				✓	[24]
$[Fe(N_2H_4)(CO)(\text{'}S_4\text{'})]^c$	(28)	4.9, 4.4			✓	[25]
$[Fe(N_2H_4)(\text{'}N_HS_4\text{'})]^c$	(2)				✓	[9]
$[Ru(N_2H_4)(PPh_3)(\text{'}S_4\text{'})]^c$	(29)	4.08, 3.22			✓	[26]
$[Ru(N_2H_4)(PPh_3)(\text{'}^{Bu}S_4\text{'})]^c$	(30)	4.01^a, 4.29^a 3.48^b		10.8^d	✓	[27]
$[Ru(N_2H_4)(CO)(\text{'}^{Bu}S_4\text{'})]^c$	(31)	4.82, 3.84			✓	[28]
$[Ru(N_2H_4)(CO)(\text{'}N_2S_2\text{'})]^c$	(32)	7.66, 5.33			✓	[29]
$[Ru(N_2H_4)(CO)_2(PPh_3)Cl]^+$	(6)	4.33^a 3.35		4.9 4.9		[11]
$[Ru(N_2H_4)_4(COD)]^{2+}$	(33)	6.04^a, 4.72^a 4.2 to 3.3^b			✓	[30]
$[Ru(N_2H_4)_3H(COD)]^+$	(34)	broad			✓	[30]
$[Ru(N_2H_4)_3(\eta^6\text{-}C_6H_6)]^+$	(35)	5.73^a, 3.31^b			✓	[31]
$[Ru(N_2H_4)_3(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)]$	(36)	5.78^a, 3.42^b			✓	[31]
$[Os(N_2H_4)(CO)_2(PPh_3)_2Br]^+$	(7)	4.35^a 3.56^b		4.5 4.5		[11]
$[Os(N_2H_4)_4(COD)]^{2+}$	(37)				✓	[32]

[a] $N_\alpha H_2$. [b] $N_\beta H_2$. [c] See text for '$^{Bu}S_4$', 'S_4', 'N_2S_2', 'N_HS_4'. [d] ^2J(HH).

Sellmann et al. have prepared a variety of hydrazine complexes. Recently, they have made use of a variety of related quadridentate ligands, which are shown below together with their abbreviations and schematic representations, and the stereochemistry of complexes containing this type of ligand and hydrazine is shown below:

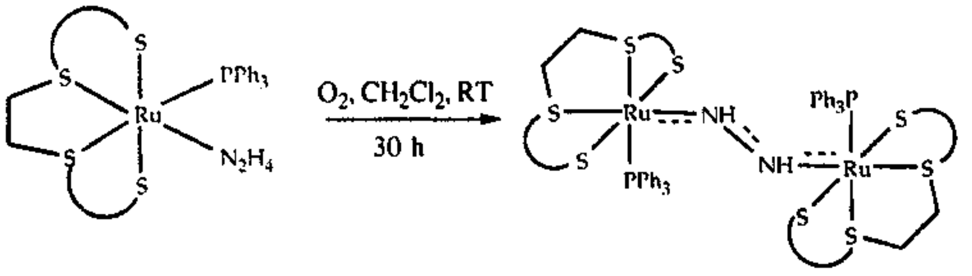
The formation of the above hydrazine complexes depends upon the generation of a five-coordinate intermediate which can then easily add a sixth ligand, e.g. N_2H_4. When L = CO, UV displacement of CO from the dicarbonyl precursor in the presence of N_2H_4 is sufficient to generate the desired complex, and, when L = PPh_3, a simple one-pot synthesis generates the precursor to the five-coordinate intermediate which can be isolated but is extremely sensitive even at −30 °C (Eq. (8)).



(8)

Owing to the asymmetry induced by the aforementioned quadridentate ligands, all four NH protons in N_2H_4 in the static structure should be magnetically inequivalent; for (**30**), two $N_\alpha H$ resonances are observed with the two $N_\beta H$s becoming equivalent because of rotation about $N_\alpha N_\beta$ (see Table 4).

Interestingly, (**30**) undergoes ready oxidation (Eq. (9)) to give the diazene complex $[\{Ru(PPh_3)('^{Bu}S_4')\}_2(\mu\text{-}N_2H_2)]$ (**38**). (**38**) has been characterised by X-ray analysis (including location of the trans N*H*s) and is centrosymmetric with the middle of the N—N unit connecting two enantiomeric '$Ru(PPh_3)('^{Bu}S_4')$' fragments. The N—N distance in (**38**) is 1.279(14) Å and corresponds to a slightly elongated N=N consistent with the presence of a 4c–6e π-bond in the Ru=N=N=Ru fragment. In solution, there is NMR evidence for the presence of other diastereoisomers of (**38**).

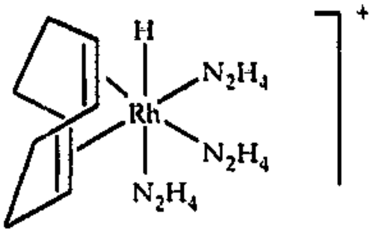


(9)

(**30**) (**38**)

There are now increasing numbers of complexes containing either monodentate or bridging diazenes; these could be important intermediates in N_2-fixation but unfortunately fall outside the scope of this review.

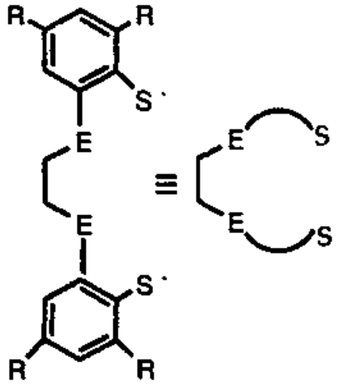
Although fac- and mer-isomers for (**34**) are possible, (**34**) has been shown to be isomorphous with the analogous complex $[Rh(NH_2NMe_2)_3H(COD)]^+$ which has been crystallographically characterised [33], vide infra.



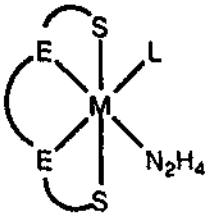
(**34**)

Other complexes that are thought to contain monodentate hydrazine, which have been formulated on the basis of other spectroscopic measurements, are described below.

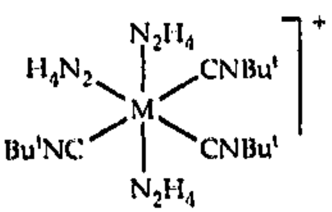
The number and relative intensities of both the ^1H and ^{13}C NMR resonances of the CN^tBu ligand, coupled with analytical data, support the stereochemistries for $[M(N_2H_4)_3(CN^tBu)_3]^+$ (M = Ru, (**39**); M = Os (**40**)) and $[M(N_2H_4)_2(CN^tBu)_4]^{2+}$ (M = Ru, (**41**); M = Os (**42**)) which are shown below [34].



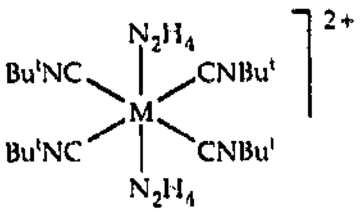
E	R	Abbreviation
S	H	'S_4'
S	Bu^t	'${}^{Bu}S_4$'
N	H	'N_2S_2'



M	L	S_2E_2	
Fe	CO	'S_4'	**(28)**
Ru	PPh_3	'S_4'	**(29)**
Ru	PPh_3	'${}^{Bu}S_4$'	**(30)**
Ru	CO	'${}^{Bu}S_4$'	**(31)**
Ru	CO	'N_2S_2'	**(32)**



(**39**) M = Ru
(**40**) M = Os

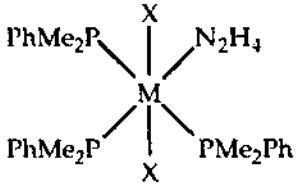


(**41**) M = Ru
(**42**) M = Os

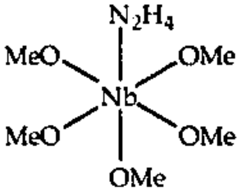
Only one $\nu(M-Cl)$ band is observed for $[M(N_2H_4)X_2(PMe_2Ph)_3]$, which is consistent with the structure shown below [35].

Low temperature ^1H NMR measurements on (**45**) show the presence of two OMe resonances of relative intensity 4:1 which suggests the formulation shown below [36].

Less well characterised complexes containing hydrazine include: $[Co(N_2H_4)_6]^{2+}$ [37], $[\{CoF_2(N_2H_4)_2\}_n]$, which is suggested to be polymeric with bridging fluorides [38], whereas $[\{CrX_2(N_2H_4)_2\}_n]$ (X = Cl, Br, I) are suggested to contain bridging



(43) M = Ru, X = Cl, Br
(44) M = Os, X = Cl.



(45)

hydrazine [39,40] with the analogous fluoro compound being unstable [41], and $[M(N_2H_4)(CN)_5]^{3-}$ (M = Fe, Ru) [42,43].

2.2. *Bridging hydrazine complexes*

As shown in Fig. 1, complexes containing a single bridging hydrazine ligand may theoretically adopt either a cis- or trans-configuration. However, X-ray data on the complexes so far reported show that the trans-configuration is always adopted when there is no other bridging ligand present (Table 5); when other bridging ligands are present, then stereochemical requirements force hydrazine to adopt a cis-zig-zag-configuration (Table 6).

The only crystallographically characterised dinuclear complexes which contain

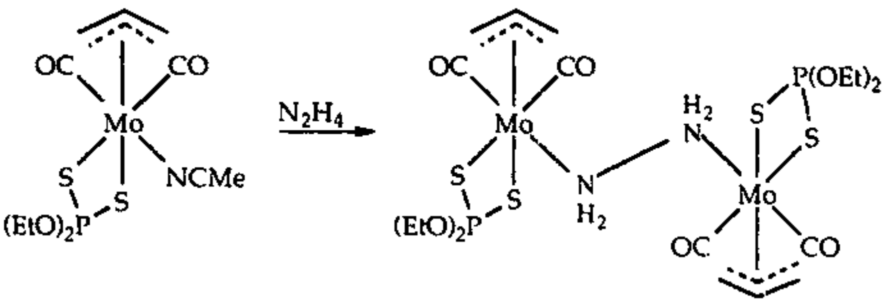
Table 5
Structural data for the coordinated hydrazine in dinuclear complexes containing a single bridging hydrazine

Complex		$d(M-N)$ (Å)	$d(N-N)$ (Å)	$\widehat{MNN}$ (deg)	Reference
$[\{Mo(\eta^5\text{-}C_3H_5)(CO)_2(S_2P(OEt)_2)\}_2(\mu\text{-}N_2H_4)]$	(46)	2.311(3)	1.462(5)	117.6(2)	[44]
$[\{Mo(CO)_2(S_2CNEt_2)_2\}_2(\mu\text{-}N_2H_4)]^a$	(47)	2.366(9)^b 2.44(2)^c	1.44(3)	124.3(7) 119(1)	[45]
$[\{MoFe_3S_4Cl_3(Cl_4cat)\}_2(\mu\text{-}N_2H_4)]^{4-}$	(48)	2.291(14)	1.47(2)		[46]
$[\{Fe(S_2C_6H_4)_2\}_2(\mu\text{-}N_2H_4)]^{2-}$	(49)	2.24(1)	1.42(2)	116.1(9)	[47]
$[\{PtCl_3\}_2(\mu\text{-}N_2H_4)]^{2-}$	(50)	2.04	1.44(2)	116.0(12)	[48]
$[\{PtCl(PBu_3)_2\}_2(\mu N_2H_4)]^{2+}$	(51)		1.41(2)		[49]

^{a} Disordered structure. ^{b} Bisects $Mo(CO)_2$ angle. ^{c} Trans to Mo−CO.

only a monobridging hydrazine ligand are shown in Table 5. In these complexes, the M—N distance is in the range of 2.04–2.44 Å and the N—N bond length is as expected for a single N—N bond; the value for $\widehat{MNN}$ is ca. 117° except in the disordered complex (**47**).

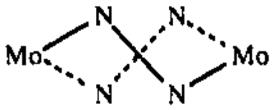
The formation of (**46**) results from displacement of acetonitrile, Eq. (10). The coordination about Mo is pseudo-octahedral: the allyl and CO groups are on one triangular face and, as has been found in other structures containing the '(η^3-allyl)Mo(CO)$_2$' fragment, the open face of the allyl is directed towards the two CO groups. There is a centre of symmetry for (**46**) at the mid-point of the N—N bond [44].

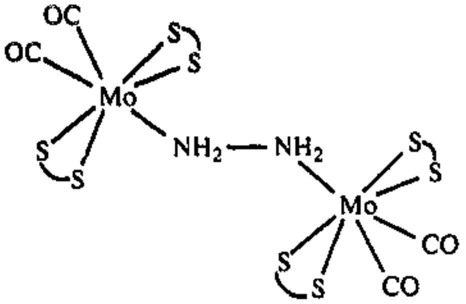


(10)

(**46**)

In (**47**), hydrazine bridges two equivalent 'Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$' fragments. Each Mo is seven-coordinate and the bridging hydrazine adopts a trans-configuration but is statistically disordered as shown below:

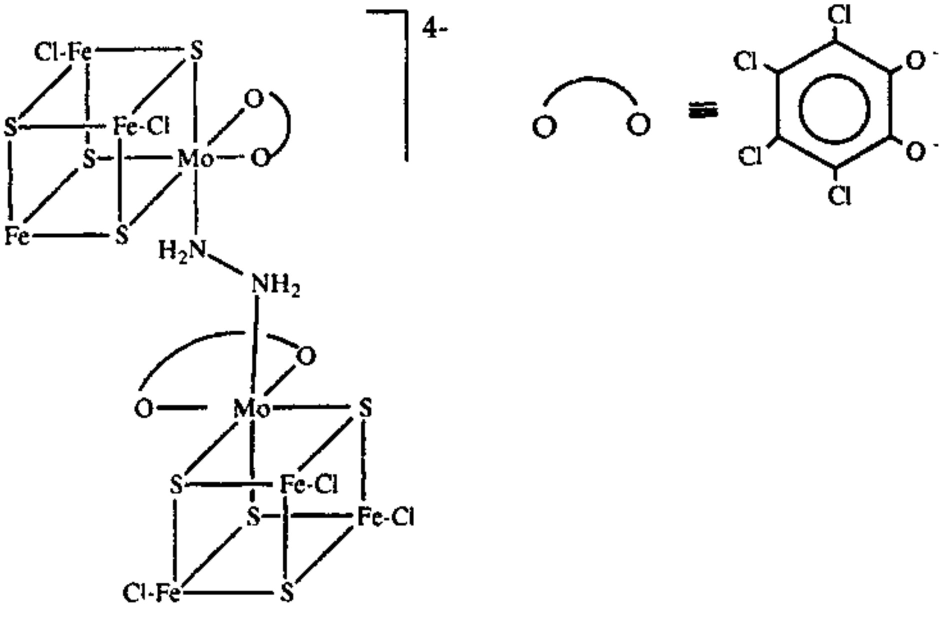




(**47**)

The structure of (**47**) shows that one Mo—N vector approximately bisects the Mo(CO)$_2$ angle whereas the other Mo—N vector is more nearly trans to a Mo—CO group and thus the value for *d*(Mo—N) is longer [45].

Displacement of acetonitrile from the cubane [(Cl$_4$cat)MoFe$_3$S$_4$Cl$_3$(CH$_3$CN)]$^{2-}$ with anhydrous hydrazine results in the formation of (**48**) and electrochemical and



(48)

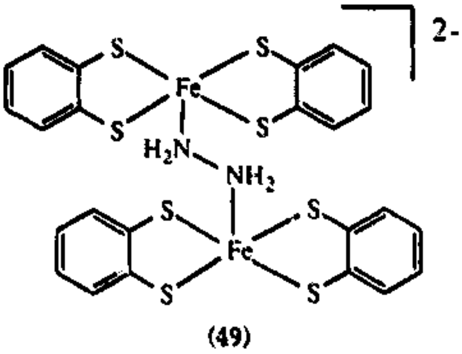
EPR studies suggest that there is no evidence for magnetic coupling between the two cluster subunits [46].

(**49**) was the first crystallographically characterised complex containing a single bridging hydrazine ligand and Fe is essentially square pyramidal with the apical sites occupied by the bridging hydrazine [47].

Simple addition of hydrazine to $[Pt_2Cl_6]^{2-}$ results in the formation of (**50**) [48] and a preliminary report of a structurally related compound (**51**) has appeared [49].

A number of singly bridged hydrazine complexes of the type $[\{M(CO)_5\}_2(\mu\text{-}N_2H_4)]$ (M = Cr [19,50]; M = Mo [19,50]; M = W [21]), $[\{W(CO)_4(PPh_3)\}_2(\mu\text{-}N_2H_4)]$ [21] and $[\{Mn(CO)_2Cp\}(\mu\text{-}N_2H_4)\{Cr(CO)_5\}]$ [51] have been reported and, consistent with their formulation, the number of expected bands due to ν(CO) is observed and only one NH_2 resonance is observed in the ^1H NMR for the symmetrical dimers whereas two resonances are found for the unsymmetrical dimer $[\{Mn(CO)_2Cp\}(\mu\text{-}N_2H_4)\{Cr(CO)_5\}]$.

Unambiguous multinuclear NMR evidence has been obtained for the formulation



(49)

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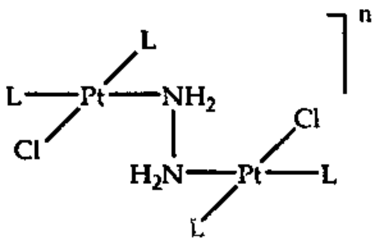
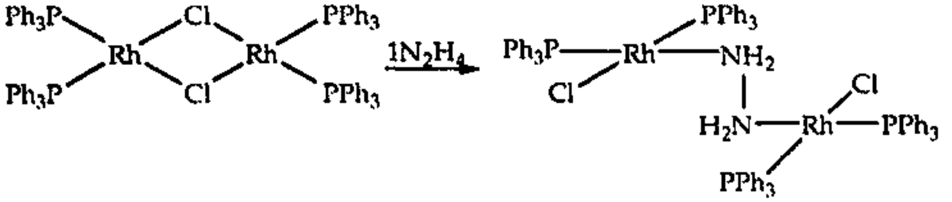


(50) L = Cl, n = 2-
(51) L = PBu^n_3, n = 2+

of (**52**), (Eq. (11)) [14]. Thus, there are two equally intense ^{31}P resonances (55.7 and 47.8 ppm), which at −30 °C both appear as doublets of doublets due to $^1J(Rh,P)$ 202, 165 Hz respectively and $^2J(P,P')$ 49 Hz, and only one ^{15}N resonance −327.5 ppm, $^1J(Rh,N)$ 11, $^1J(N,H)$ 71 and $^2J(P_{trans},N)$ 37 Hz.



(11)

(16a) (52)

There is now an increasing number of crystallographically characterised dinuclear complexes which, in addition to containing a bridging hydrazine, also contain other bridging groups (see Table 6).

Table 6
Structural data for the coordinated hydrazine in dinuclear complexes containing more than one bridging group which includes hydrazine

Complex		$d(M-N)$ (Å)	$d(N-N)^a$ (Å)	$\widehat{MNN}$ (deg)	Reference
$[\{MoFe_3S_4Cl_2(Cl_4cat)\}_2(\mu_2\text{-}S)(\mu_2\text{-}N_2H_4)]^{4-}$	(**53**)	—^{b}	—^{b}	—^{b}	[52]
$[\{MoO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}N_2H_4)]^{2-}$	(**54**)	2.490(8)	1.40(1)	126.2(6)	[53]
$[\{WO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}N_2H_4)]^{2-}$	(**55**)	2.46(11)	1.35(2)	127.5(1)	[53]
$[\{W(NPh)Me_3\}_2(\mu_2\text{-}\eta^2,\eta\text{-}NHNH)(\mu_2\text{-}N_2H_4)]$	(**56**)	2.338(11)	1.434(14)		[54]
$[\{RuCl\{P(OMe)_3\}_2\}_2(\mu_2\text{-}Cl)(\mu_2\text{-}S_2)(\mu_2\text{-}N_2H_4)]$	(**57**)	2.171(7)	1.442(1)		[55]
$[\{Ru(CH_3CN)\{P(OMe)_3\}_2\}_2(\mu_2\text{-}S_2)$ $(\mu_2\text{-}N_2H_4)_2]^{3+}$	(**58**)	2.210(9)	1.471(13)		[56]
$[\{Rh(PPh_3)_2\}_2(\mu_2\text{-}N_2H_4)_2]^{2+}$	(**59**)	2.170(13)	1.516(2)	112.0(5)	[14]
$[\{Cu(\mu_2\text{-}CN)(\mu_2\text{-}N_2H_4)\}_n]$	(**65**)	2.17(1)	1.48(2)	114.2(7)	[63]

[a] For μ_2-N_2H_4. [b] R factor is too high to give meaningful distances.

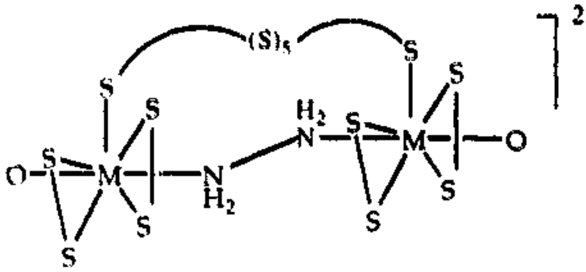
A preliminary communication has reported evidence for the heterometallic dinuclear cubane bridged by hydrazine and sulphur (**53**) [52] with the μ_2-S bridging two iron atoms in different cubanes and μ_2-N_2H_4 bridging the two Mo atoms as in (**48**). The structure is clearly related to (**48**) and contains a mirror plane bisecting the S and mid-point of the N_2H_4 but the quality of crystals prevented an accurate structural determination.

The structures of (**54**) and (**55**) are shown schematically below. The metal ions are pseudo pentagonal bipyramidal with N_2H_4 and oxygen occupying the axial sites. However, there is a possibility that this compound could be formulated as a bridging diazene (μ-N_2H_2) complex since: (a) the NH groups were not located in the ^1H NMR; (b) Eq. (12) better fits with the formation of a bridging diazene rather than a bridging hydrazine complex when it becomes impossible to balance both sides of the equation

$$\begin{aligned}&2(NH_4)_2[MO_2S_2] + 11S + N_2H_4 + 2HCl + 2(Et_4N)Br \rightarrow\\&\quad (Et_4N)_2[\{MO(S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}N_2H_2)]\\&\qquad + 2H_2O + 2(NH_4)Br + 2(NH_4)Cl \qquad (12)\end{aligned}$$

(c) the MN_2M unit is almost trans planar, as found for other bridging diazene complexes, but the N—N bond lengths in (**54**) and (**55**) are significantly longer (see Table 6) than in other bridged diazene complexes, e.g. $[\{Cr(CO)_5\}_2(\mu_2\text{-}N_2H_2)]$ 1.25 Å [57], $[\{Ru('S_4')(PPh_3)\}_2(\mu_2\text{-}N_2H_2)]$ 1.279 Å [27].

The alternative formation as a 1,2 hydrazido(−II) ligand, which would have a d(N—N) value in the range observed, is precluded both from charge considerations and the observed value of d(M—N) which is much longer than that found in examples of complexes exhibiting this type of behaviour.

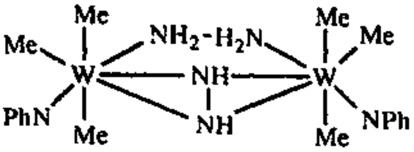


(**54**) M = Mo
(**55**) M = W

Complex (**56**) has been obtained by the reaction of hydrazine with $[W(NPh)Me_4]$. The structure consists of pseudo-octahedral metals and, in this case, unambiguous evidence has been obtained for the formulation of the bridging ligands from both ^1H and ^{15}N NMR measurements [54].

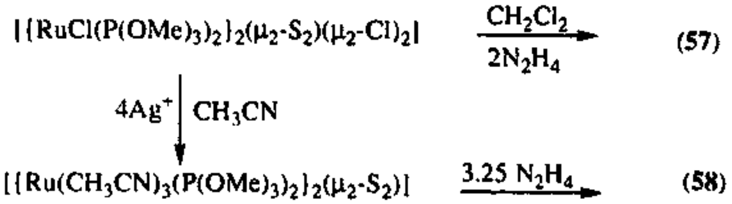
The structures of (**57**) and (**58**) are closely related; both are based on pseudo-octahedral metals with, in each case, hydrazine trans to $P(OMe)_3$ [55,56].

The preparations of (**57**) and (**58**) are shown in Eqs. (13) and (14); both reactants



(56)

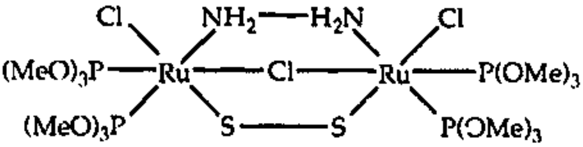
are Ru(III), Ru(III) dimers but each product is a Ru(II), Ru(III) dimer which has only 35 valence electrons yet there is no evidence for any Ru—Ru bonding.



$$[\{RuCl(P(OMe)_3)_2\}_2(\mu_2\text{-}S_2)(\mu_2\text{-}Cl)_2] \xrightarrow[2N_2H_4]{CH_2Cl_2} \textbf{(57)} \qquad (13)$$

$$\downarrow 4Ag^+ \; CH_3CN$$

$$[\{Ru(CH_3CN)_3(P(OMe)_3)_2\}_2(\mu_2\text{-}S_2)] \xrightarrow{3.25\ N_2H_4} \textbf{(58)} \qquad (14)$$



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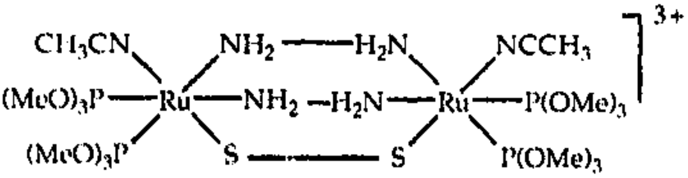


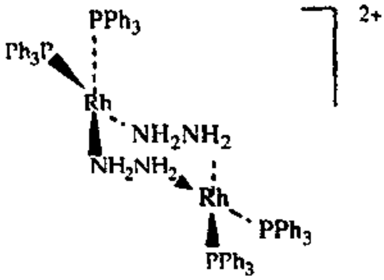
(58)

The formation of **(59)** is best achieved according to Eq. (15)

$$[Rh_2Cl_2(PPh_3)_4] \xrightarrow[CH_2Cl_2]{2N_2H_4} \underset{\textbf{(59)}}{[\{Rh(PPh_3)_2\}_2(\mu_2\text{-}N_2H_4)_2]^{2+}} \qquad (15)$$

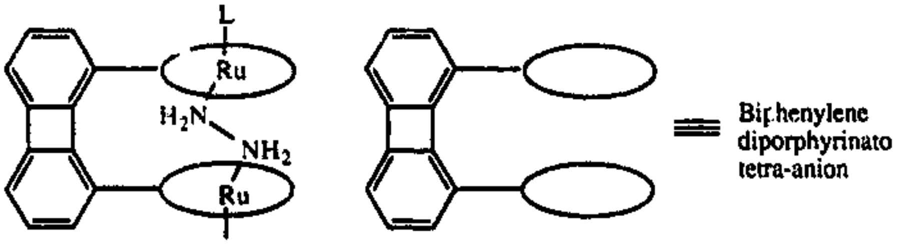
The structure of **(59)** consists of square-planar rhodium atoms with two bridging hydrazines. The formulation of **(59)** is fully confirmed by multinuclear NMR measurements in solution [14]. Thus, consistent with the presence of bridging hydrazines there is only one ^{15}N resonance at -340.3 ppm, which clearly becomes a triplet at -30 °C without ^{1}H-decoupling $^{1}J(N,H)$ 72, $^{1}J(N,Rh)$ 10, $^{2}J(P_{trans},N)$ 10, $^{3}J(P_{trans},N)$ 10 Hz (see Fig. 4) and $\delta(P)$ 51.5 ppm, $^{1}J(Rh,P)$ 176 Hz.

The two metals in the cofacial diporphyrin complex **(60)** are ideally aligned to accommodate small bridging ligands, e.g. N_2, N_2H_4, N_2H_2 [58,59], and, in addition to the other ^{1}H NMR resonances, there is a single high field (-10.75 ppm) resonance



(59)

due to the NH_2 groups; this assignment has been confirmed by ^{15}N-enrichment and the high field shift arises from the ring currents of both the porphyrin rings.

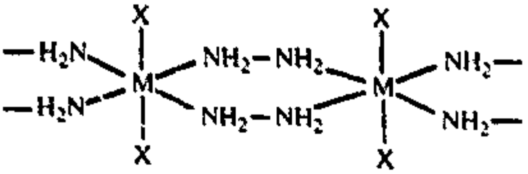


L = 1-*tert* butylphenylimidazole, or PPh_3

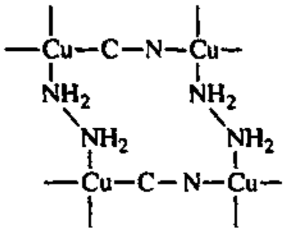
(60)

$[\{Ru(PPh_3)_2Cl_2\}_2(\mu_2\text{-}N_2H_4)_2]$ (**61**) is converted into $[\{Ru(PPh_3)(CO)Cl_2\}_2(\mu_2\text{-}NH_2NH_2)_2]$ (**62**) on addition of CO and have both been formulated on the basis of molecular weight, elemental analysis and the number of ν(M–Cl)/ν(CO) bands in the IR spectrum [60]. Related structures with bridging hydrazines have been found for $[\{MX_2\}(\mu_2\text{-}N_2H_4)_2]_n$ but in this case they are polymeric (**63**, X = Cl, M = Mn [61], Zn [62]; **64**, X = CH_3CO_2, M = Zn [62]).

Complex (**65**) is also polymeric and contains infinite chains of bridging hydrazine and cyano groups [63].



(**63**) X = Cl M = Mn, Zn
(**64**) X = CH_3CO_2, M = Zn



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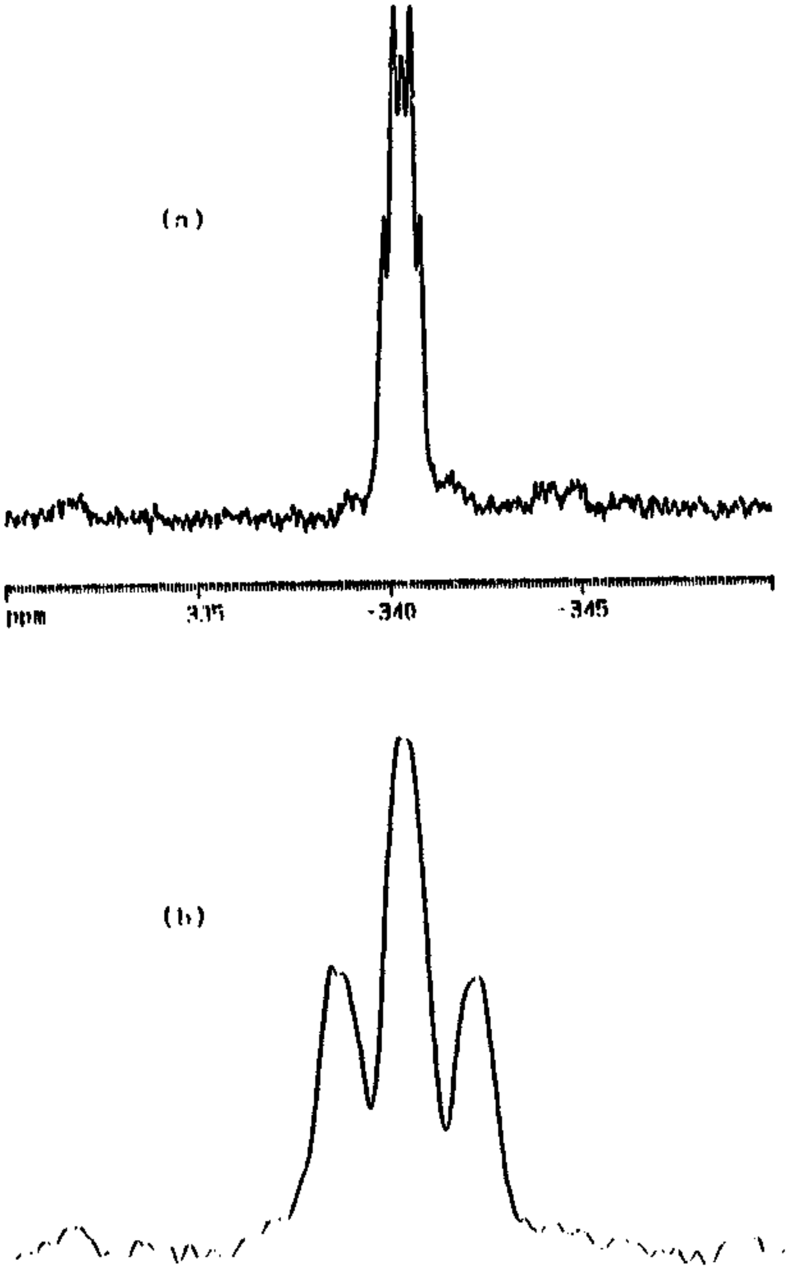
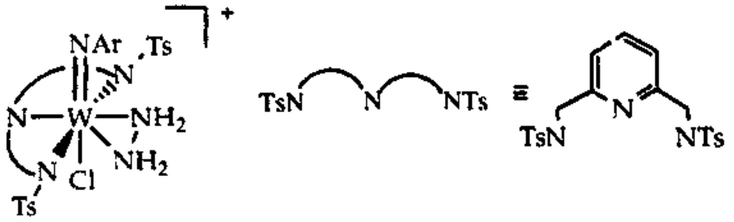


Fig. 4. Direct ^{15}N NMR spectra of $[\{Rh(PPh_3)_2\}_2(\mu_2\text{-}^{15}N_2H_4)_2]^{2+}$ (59) at 243 K: (a) with ^1H-decoupling; (b) without ^1H-decoupling.

2.3. Bidentate η^2-hydrazine complexes

Such complexes are still relatively scarce and the present crystallographically characterised complexes containing η^2-N_2H_4 are shown in Table 7.

A preliminary report of the structure of (**66**) has appeared and the preparation of (**66**) results from protonation of the analogous η^2-NHNH$_2$ complex which has also been crystallographically characterised [64]. Only one broad ^{1}H NMR resonance, 8.6 ppm, was observed for the N_2H_4 ligand consistent with rapid H-exchange.



(**66**)

Schrock et al. have prepared a number of η^2-N_2H_4 complexes and the pseudo-octahedral 17-electron complex (**67**), which has been crystallographically characterised, is prepared as shown in Eq. (16). Complex (**67**) undergoes ready deprotonation but is remarkably stable when compared with the neutral analogue of (**67**) which has not yet been detected spectroscopically [65]. Related to (**67**) are [Cp*MoMe$_3$(η^2-N_2H_4)]$^+$ [68,69], [Cp*ReMe$_3$(η^2-N_2H_4)]$^+$ [70,71] and [Cp*WMe$_4$(η^2-N_2H_4)]$^+$ [72,73]. For [Cp*ReMe$_3$(η^2-N_2H_4)], two ^{15}N resonances are observed consistent with a structure similar to (**67**), but it is also possible that there is an $\eta^1 \rightleftharpoons \eta^2$ equilibrium of the coordinated hydrazine. For [Cp*WMe$_4$(η^2-N_2H_4)], one ^{15}N and two ^{1}H resonances for N_2H_4 are observed and this is attributed to the N atoms being equivalent with two H atoms pointing towards and away from Cp* [68]. These data are summarised in Table 8.

Protonation of the crystallographically characterised hydrazido complex [Co(tripod)(η^2-NHNH$_2$)]$^+$ (tripod = MeC(CH$_2$PPh$_2$)$_3$) gives (**68**). Although it is difficult to be sure that it is η^2-N_2H_4 that is coordinated rather than some other 'N_2H_x' fragment, the magnetic moment 3.84 μ_B indicates three unpaired electrons consistent with a high spin d^7 electron configuration for square pyramidal geometry.

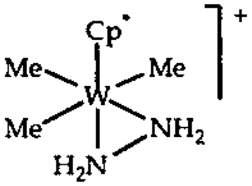
Table 7
Hydrazine structural data for complexes containing η^2-N_2H_4

Complex		d(M–N) (Å)	d(N–N) (Å)	$\widehat{\text{MNN}}$ (deg)	Reference
[W(NAr)(N(NTs)$_2$)Cl(η^2-N_2H_4)]^a	(**66**)	2.15	1.42		[64]
[Cp*WMe$_3$(η^2-N_2H_4)]$^+$	(**67**)	2.152(7)	1.43(1)	70.6(4)	[65]
[Co(tripod)(η^2-N_2H_4)]$^{2+\,b}$	(**68**)	1.945(10)	1.446(17)		[66]
[Cp$^*_2$Sm(THF)(η^2-N_2H_4)]$^+$	(**69**)	2.507(2)	1.471(3)	72.9(1)	[67]

^{a} Ar = 2,6-$C_6H_3{}^iPr_2$; N(NTs)$_2$ = 2,6-$NC_5H_3(CH_2Ts)_2$. ^{b} tripod = MeC(CH$_2$PPh$_2$)$_3$.

$$[Cp^*WMe_3(OTf)] \underset{H(OTf)}{\overset{N_2H_4}{\rightleftharpoons}} [Cp^*WMe_3(\eta^2\text{-}N_2H_4)](OTf)$$

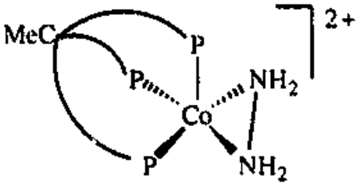
(67)



(67)

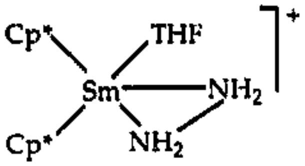
(16)

This suggests the N_2H_x must be formally neutral. Furthermore, the Co—N distances are the same, suggesting that N_2H_x is symmetrical; the N—N distance is in the range for hydrazine but outside the ranges observed for η^2-N_2H_2 or η^2-N_2, and the IR shows four ν(NH) bands (3148–3310 cm^{-1}), as would be expected for the assigned structure [66].



(68)

The preparation of (**69**), which is shown schematically below, also involves protonation, as shown in Eq. (17). Integration of the ^1H NMR resonances support this formulation (see Table 8).



(69)

$$[\{Cp^*_2Sm(THF)\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}NHNH)] + 2(Et_3NH)BPh_4 \xrightarrow{THF} [\{Cp^*_2Sm(THF)(\eta^2\text{-}N_2H_4)\}]BPh_4 + [Cp^*_2Sm(THF)_2]BPh_4 \qquad (17)$$

(69)

Table 8
NMR data for η^2-hydrazine complexes

Complex	$\delta(N_\alpha H)$	$\delta(N_\beta H)$	$\delta(N_\alpha)$	$\delta(N_\beta)$	$^1J(N_\alpha H)$	$^1J(N_\beta H)$	Reference
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)][OTf]$	5.25	5.02					[68]
$[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)][PF_6]$	4.93	4.37	−352.4	−352.4	80, 83	80, 83	[68]
$[Cp^*ReMe_3(\eta^2\text{-}NH_2NH_2)][OTf]$	6.4	5.7	−331.0[a]	−362.2[a]	84	84	[71]
$[Cp^*_2Sm(THF)(\eta^2\text{-}NH_2NH_2)][BPh_4]$	0.37	0.37					[67]

[a] Assignments could be reversed.

Table 9
^{15}N chemical shift of hydrazine and substituted hydrazines (referenced to $MeNO_2$)

Ligand	$\delta(N_1)$[a] (ppm)	$\delta(N_2)$[a] (ppm)	Reference	$\delta(N_\alpha)$ (ppm)	$\delta(N_\beta)$ (ppm)	Reference
NH_2NH_2	−335.9		[74]			
NH_2NHMe	−305.6	−328.1	[74]	−329.0[b]	−306.0[b]	[76]
NH_2NMe_2	−281.5	−322.8	[74]	−282.0[b]	−324.3[b]	[76]
NHMeNHMe	−306.7		[74]			
$NHMeNMe_2$	−307.8	−285.4	[74]			
NMe_2NMe_2	−277.7		[74]			
NH_2NHPh	−319.6	−294.3	[74]			
NH_2NPh_2	−320.0[c]	−294.8[c]	[75]			

[a] The values of $\delta(^{15}N)$ with respect to HNO_3 [72,73] have been converted to $\delta(^{15}N)$ with respect to $MeNO_2$(liq) using $\delta(Me^{15}NO_2) = -\delta(H^{15}NO_3) - 6.2$.

[b] With respect to $MeNO_2$ at room temperature.

[c] At 303 K.

3. Substituted hydrazines

Although direct ^{15}N NMR data have been reported on substituted hydrazines, $N_2H_xR_{4-x}$ (R = Me, $x = 1 \ldots 4$; R = Ph, $x = 1, 2$) (Table 9) [74,75], the resonances were not until recently assigned to N_α and N_β, and unambiguous assignments for the unsymmetrically substituted hydrazines have only recently become available for NH_2NHMe and NH_2NMe_2 [76] (see Table 9). The continuing proliferation of different reference standards by different groups causes real problems in making ^{15}N NMR measurements useful, and these problems are accentuated when conversions are done inaccurately. We have adopted the suggestion in Mason's authoritative review, which recommends the use of external $MeNO_2$ as a universal standard [5]. However, in a different compilation [77] the ^{15}N chemical shifts for hydrazines are all quoted as positive when they should actually be negative, since they all resonate at higher field compared with $MeNO_2$.

Substituted hydrazines $N_2H_xR_{4-x}$ ($x = 1, 2, 3$; R = Me, Ph) can act as ligands and, as found for hydrazine itself, examples of complexes containing $N_2H_xR_{4-x}$ in terminal, μ_2- or η^2-modes of bonding are now known. Nevertheless, for unsymmetrically substituted hydrazines it is difficult to be sure whether the substituted or unsubstituted nitrogen atom will preferentially coordinate to the metal because of competing steric/electronic effects. Thus, studies on substituted hydrazines suggest that they are all less basic than hydrazine itself, but this has to be contrasted with methylamines which are all more basic than ammonia [78]. However, data have not yet been reported which distinguish the basicities of the inequivalent nitrogens, although there is some evidence that protonation of the unsymmetrically alkyl-substituted hydrazine occurs at the substituted nitrogen atom, N_β [79].

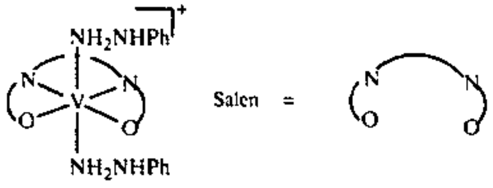
4. Substituted hydrazine complexes

4.1. Complexes containing monodentate substituted hydrazine(s)

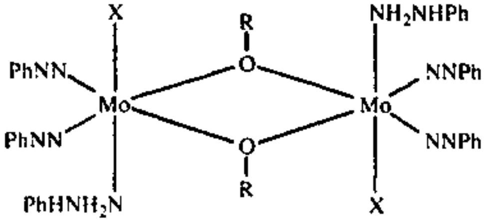
As mentioned earlier, it is difficult to be sure, especially for Me-substituted hydrazines, whether coordination will be preferred at the substituted (N_α) or substituted (N_β) nitrogen. The structures, which have presently been crystallographically characterised, are shown in Table 10; for unsymmetrically substituted hydrazines it is always the unsubstituted nitrogen N_α which is coordinated to the metal. Nevertheless, it is possible for coordination to occur via a substituted nitrogen, as evidenced by the structure of $[RhCl_4(PPh_3)(NHMeNHMe)]^-$ (**76**) [84].

In all cases the N−N bond distances are as expected for coordination of $N_2H_xR_{4-x}$ ($x = 2,3$) via donation of a single lone pair, and the values for $\widehat{MNN}$ are similar to those found for the unsubstituted hydrazines (Table 1) with the smaller angles being found in the less sterically hindered square planar complexes.

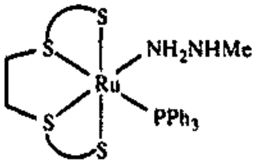
The structures of these compounds are shown below:



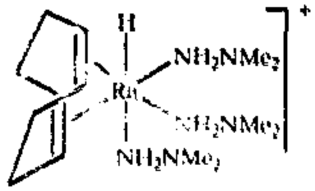
(70)



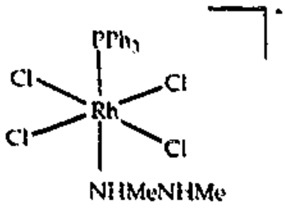
(71) $X = OMe, R = Me$
(72) $X = Cl, R = Pr$
(73) $X = Cl, R = Me$



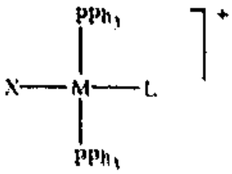
(74)



(75)



(76)



(77) $M = Rh, X = CO, L = NH_2NHMe$
(78) $M = Rh, X = CO, L = NH_2NMe_2$
(79) $M = Rh, X = CO, L = NH_2NHPh$
(80) $M = Pt, X = Cl, L = NH_2NHp\text{-}FC_6H_4$

Table 10
Structural data for the substituted hydrazine in complexes containing monodentate substituted hydrazine(s)

Complex		M−N$_\alpha$	d(M−N) (Å)	d(N−N) (Å)	$\widehat{MNN}$ (deg)	Reference
$[V(salen)(NH_2NHPh)_2]^+$	**(70)**	NH_2	2.170(4)	1.434(6)	110.8(3)	[80]
$[\{Mo(N_2Ph)_2(OMe)(NH_2NHPh)\}_2(\mu_2\text{-}OMe)_2]$	**(71)**	NH_2	2.267(3)	1.423(4)	115.5(2)	[81]
			2.265(5)	1.445(9)	115.4(3)	[82]
$[\{Mo(N_2Ph)_2Cl(NH_2NHPh)\}_2(\mu_2\text{-}OPr)_2]$	**(72)**	NH_2	2.248(6)	1.413(9)	115.8(5)	[81]
$[\{Mo(N_2Ph)_2Cl(NH_2NHPh)\}_2(\mu_2\text{-}OMe)_2]$	**(73)**	NH_2	2.22(1)	1.41(1)	118.3(8)	[81]
$[Ru('S_4')(PPh_3)(NH_2NHMe)]$	**(74)**	NH_2	not yet reported			[83]
$[RuH(COD)(NH_2NMe_2)_3]^+$	**(75)**	NH_2	2.19(1)^a 2.28(1)^b	1.47(1)	118.9(7)	[33]
$[RhCl_4(PPh_3)(NHMeNHMe)]^-$	**(76)**	NHMe	2.216(8)	1.405(9)	117.4(5)	[84]
$[Rh(CO)(PPh_3)_2(NH_2NHMe)]^+$	**(77)**	NH_2	2.12(2)	1.46(2)	109(1)	[85]
$[Rh(CO)(PPh_3)_2(NH_2NMe_2)]^+$	**(78)**	NH_2	2.16(1)	1.45(2)	110.1(7)	[85]
$[Rh(CO)(PPh_3)_2(NH_2NHPh)]^+$	**(79)**	NH_2	2.14(1)	1.46(4)	111.8(8)	[85]
$[PtCl(PEt_3)_2(NH_2NH\textit{p}\text{-}FC_6H_4)]^+$	**(80)**	NH_2	2.081(7)	1.436(11)	113.2(5)	[86]

^{a} Trans to COD. ^{b} trans to H.

It is worthwhile commenting upon the preparation and structures of complexes listed in Table 10 where analogous unsubstituted hydrazine derivatives are unknown.

The formation of **(70)** cannot be achieved by direct halide displacement and a more indirect route (Eq. (18)) had to be employed [80].

$$[\{VO(salen)\}_2][I_5] \xrightarrow[NH_2NHPh,MeCN]{AlEt_2(OEt)} \underset{\textbf{(70)}}{[V(salen)(NH_2NHPh)_2]I} \qquad (18)$$

The resulting d^2 V(II) complex exhibits strong H-bonding of one of the hydrogens on each NH_2 group with the anion, leading to a linear N−H···I configuration. **(71)**, **(72)** and **(73)** all contain linear phenyl diazenido ligands and have been prepared according to Eqs. (19) and (20) [81,82].

$$[MoO_2(acac)] \xrightarrow[ROH]{\text{excess } NH_2NHPh} \underset{\textbf{(71)}\ R = Me}{[\{Mo(N_2Ph)_2(OR)(NH_2NHPh)\}_2(\mu_2\text{-}OR)_2]} \qquad (19)$$

$$[MoOCl_4(H_2O)]^- \xrightarrow[ROH]{\text{excess } NH_2NHPh} \underset{\textbf{(72)}\ R = Pr,\ \textbf{(73)}\ R = Me}{[\{Mo(N_2Ph)_2Cl(NH_2NHPh)\}_2(\mu_2\text{-}OR)_2]} \qquad (20)$$

The preparation of the only crystallographically characterised complex which contains a substituted N$_\alpha$ atom is simply achieved by the reaction of $[RhCl(PPh_3)_3]$ with NHMeNHMe·2HCl [84].

Table 11
^1H and ^{13}C NMR data and IR measurements relating to the substituted hydrazine in complexes containing monodentate substituted hydrazines

Complex	$\delta(N_\alpha H)$	$\delta(N_\beta H)$	$\delta(N_\alpha CH_3)$	$\delta(N_\beta CH_3)$	$\delta(N_\alpha CH_3)$	$\delta(N_\beta CH_3)$	IR	Reference
$[Cp^*V(CO)_3(NH_2NHMe)]$	4.35	2.15		2.44			√	[18]
$[Cp^*V(CO)_3(NH_2NH_2NMe)_2]$	4.11			2.26			√	[18]
$[Cp^*V(CO)_3(NHMeNHMe)]$	4.45	2.70	2.42	2.31			√	[18]
$[VCl_3(THF)_2(NH_2NMe_2)]$	8.57			2.70			√	[88]
$[VCl_3(THF)_2(NH_2NC_5H_{10})]$	7.98						√	[88]
$[VCl_3(dmpe)_2(NH_2NMe_2)]$	7.79			2.61			√	[88]
$[VCl_3(tdmp)_2(NH_2NMe_2)]^a$	7.67			2.62			√	[88]
$[MoCpI_2(NO)(NH_2NHMe)]$							√	[89]
$[MoCpI_2(NO)(NH_2NMe_2)]$							√	[89]
$[MoCpI_2(NO)(NHMeNMe_2)]$	6.17		3.56	3.56, 3.36	41.5	57.3, 49.9	√	[89]
$[MoCpI_2(NO)(NH_2NHPh)]$							√	[89]
$[MoCpI_2(NO)(NH_2NHC_6F_5)]$	5.40	6.62					√	[89]
$[MoCpBr_2(NO)(NH_2NHC_6F_5)]$							√	[89]
$[MoCpI_2(NO)(NH_2NHp\text{-}(NO_2)C_6H_4)]$	6.40	8.0					√	[89]
$[MoCpI_2(NO)(NH_2NHp\text{-}MeC_6H_4)]$							√	[89]
$[MoCpI(NO)(NH_2NMe_2)]^+$							√	[89]
$[MoCpI(NO)(NHMeNMe_2)]^+$	7.70		3.36	3.53, 3.30	41.5	57.0, 49.1	√	[89]
$[MoCpI(NO)(NH_2NHPh)]^+$							√	[89]
$[MoCpI(NO)(NMeEtNMe_2)]^+$							√	[89]
$[Fe(CO)\{P(OEt)_3\}_4(NH_2NHp\text{-}MeC_6H_4)]^{2+}$	6.35	4.8					√	[90]
$[Fe(CO)\{P(OEt)_3\}_4(NH_2NHp\text{-}(MeO)C_6H_4)]^{2+}$	6.16	4.7					√	[90]
$[Fe(CO)\{P(OEt)_3\}_4(NH_2NHp\text{-}(NO_2)C_6H_4)]^{2+}$	7.82	5.2					√	[90]
$[Ru(CNR)_4(NH_2NHMe)_2]^+$ ($R = {}^tBu$)	5.07	3.27		2.57			√	[91]
$[Ru(CNR)_4(NH_2NHMe)_2]^+$ ($R = CH_2Ph$)	5.37	3.47		2.47				[91]
$[Ru(CNR)_4(NH_2NHMe)_2]^+$ ($R = 2,6\text{-}Me_2C_6H_5$)	6.0 to	3.1br		2.43		42		[91]

$[Ru(P(OMe)_2Ph)_4(NH_2NHMe)_2]^{2+}$		6.05br			2.45		✓	[30]
$[RuH(COD)(NH_2NHMe)_3]^+$	5.9			4.3	2.45		✓	[30]
$[RuH(COD)(NH_2NMe_2)_3]^+$	5.97		to	6.17	2.20 to 2.45		✓	[30]
$[Ru(COD)(NH_2NMe_2)_4]^{2+}$	4.7		to	1.8	2.52		✓	[30]
$[Ru(\eta^6\text{-}C_6H_6)(NH_2NMe_2)_3]^{2+}$	6.64		to	6.71	2.44 to 2.49		✓	[31]
$[Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)(NH_2NMe_2)_3]^{2+}$	6.39		to	6.54	2.43 to 2.52		✓	[31]
$[Ru('S_4')(PPh_3)(NH_2NHMe)]$	3.9			1.9	2.15		✓	[83]
$[Ru('S_4')(PPh_3)(NH_2NHPh)]$		3.0br					✓	[83]
$[OsCl(COD)(NH_2NMe_2)]^+$					2.65			[32,91]
$[Cp^*RhCl_2(NH_2NMe_2)]$	4.30				2.60	50.2		[92]
$[Cp^*RhBr_2(NH_2NMe_2)]$	3.76				2.70	50.1		[92]
$[Cp^*RhI_2(NH_2NMe_2)]$	3.55				2.58			[92]
$[Cp^*RhCl_2(NH_2NMePh)]$					3.11	44.7		[92]
$[Cp^*RhCl_2(NH_2NHC_6F_5)]$	5.45			6.50				[92]
$[PtCl(PEt_3)_2(NH_2NHp\text{-}FC_6H_4)]$	3.7			3.2				[87]

[a] tdmp = $P\{(CH_2)_3PMe_2\}_3$.

The preparation of mono-dentate hydrazine complexes by displacement of weakly bonded groups provides a good route. This is further illustrated by the displacement of the O-bonded perchlorato group from *trans*-$[Rh(PPh_3)_2(CO)(OClO_3)]$ by substituted hydrazines to give (**77**), (**78**) and (**79**) [85].

The formation of (**80**) is a classic example of early work for the indirect preparation of substituted hydrazines involving the reactions shown in Eq. (21) [87].

$$[PtHCl(PEt_3)_2] \xrightarrow[R = p\text{-}FC_6H_4]{[RN_2]^+} [PtCl(NHNR)(PEt_3)_2]^+ \xrightarrow{H_2}$$

$$[PtCl(NH_2NHR)(PEt_3)_2]^+ \qquad (21)$$

(80)

Other complexes containing mono-dentate substituted hydrazines which have been claimed on the basis of NMR and/or IR spectroscopic data of the complexed ligand are shown in Tables 11 and 12, together with the complexes included in Table 10 where appropriate.

It is worthwhile commenting upon some of the structures in Table 11.

A variety of complexes containing different arenes/substituted hydrazines have been prepared and examined by ^{51}V NMR [18]. The structures are all similar to (**19**) described earlier, except for $[V(CO)_3(\eta^5\text{-}C_5H_4SiMe_3)(NH_2NHPh)]$ and $[V(CO)_3(\eta^5\text{-}C_5H_3\text{Mecetyl})(NH_2NHPh)]$ for which ^{51}V NMR spectra suggest that bonding of the monodentate hydrazine occurs either through the NH_2- or NHPh-groups to about an equal extent [18].

Displacement of the aryldiazene (ArNHN) from the corresponding complex with excess NH_2NHAr' gives $[Fe(CO)\{P(OEt)_3\}_4(NH_2NHAr')]^{2+}$ which from ^{31}P NMR studies has been shown to have the cis-configuration [90].

Use of the INEPT pulse sequence to obtain ^{15}N spectra can easily distinguish which nitrogen in unsymmetrically substituted hydrazines is coordinated to rhodium [76] (Table 12).

On the basis of electronic and susceptibility measurements, $[Co(NH_2NHMe)_6]^{2+}$, together with the blue complex $[CoCl_2(NH_2NHMe)_2]_n$, have been reported, with the latter complex being polymeric and suggested to contain both bridging and bidentate NH_2NHMe groups [37].

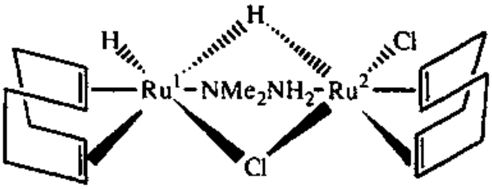
Table 12
^{15}N NMR data for complexes containing monodentate substituted hydrazines

Complex	$\delta(N_\alpha)$	$\delta(N_\beta)$	$^1J(Rh-N_\alpha)$	$^2J(P_{trans}-N_\alpha)$	Reference
$[Rh(PPh_3)_3(NH_2NHMe)]^+$	−317.8	−313.8	11.2	29.5	[76]
$[RhCl(PPh_3)_2(NH_2NHMe)]$	−312.1	−316.6	10.6	36.8	[76]
$[RhCl(PPh_3)_2(NH_2NMe_2)]$	−291.8	[a]	11.7	38.1	[76]
$[Rh(PPh_3)_2(NH_2NHMe)_2]^+$	−320.1	−316.6	15.0	29.0	[76]
$[Rh(PPh_3)_2(NH_2NMe_2)_2]^+$	−295.0	−[a]	10.6	28.5	[76]

[a] Could not be detected from $^{15}N-\{^1H\}$ INEPT measurements.

4.2. *Bridging substituted hydrazines*

There is only one crystallographically characterised example of a bridging substituted hydrazine, i.e. $[\{Ru(COD)Cl\}(\mu_2\text{-}H)(\mu_2\text{-}Cl)(\mu_2\eta^1,\eta^1\text{-}NH_2NMe_2)\{Ru(COD)H\}]$ (**81**) [92] and the structural data are given in Table 13.



(81)

Each Ru is octahedral and the value of $d(Ru^1-NMe_2)$ is significantly longer than $d(Ru^2-NH_2)$ probably due to steric effects. The presence of hydride and chloride rather than two bridging chlorides has also been ascribed to minimisation of steric effects, but unfortunately (**81**) is too insoluble to obtain spectroscopic data to confirm this. Nevertheless, there is crystallographic evidence for the bridging hydride and IR (nujol mull) evidence for the terminal hydride (ν(Ru–H) 2055 and 2035 cm^{-1}). The preparation of (**81**), which was originally misformulated [30], is shown in Eq. (22). However, it is unclear why the substituted hydrazine occupies the bridging position in (**81**).

$$[RuH(COD)(NH_2NMe_2)_3]^+ \xrightarrow[(X = Cl\ or\ Br)]{LiX} \underset{\mathbf{(81)}}{[\{Ru(COD)XH\}_2(\mu_2\text{-}NH_2NMe_2)]^+} \qquad (22)$$

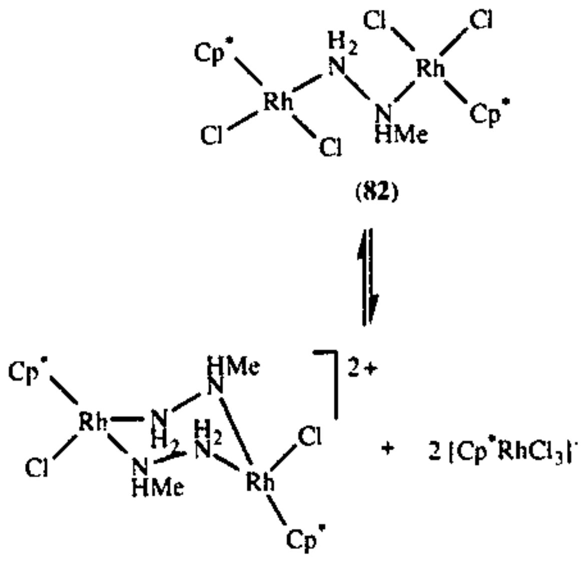
Reaction of $[\{Cp^*RhX\}_2(\mu_2\text{-}X)_2]$ (X = Cl, Br, I) with NH_2NHMe gives $[\{Cp^*Rh\}_2X_4(NH_2NHMe)]$ (**82**), unlike the reaction with mono-aryl-, 1,1-dimethyl- and 1-methyl-1-phenyl-hydrazines which gave 1 : 1 adducts (see Table 11). Detailed variable temperature measurements on (**82**) have been carried out and evidence has been obtained for the equilibrium in Eq. (23) [91].

By contrast, chloride displacement from (**82**) gives (**83**), which is found not to be fluxional, and the structure shown below has been proposed [91].

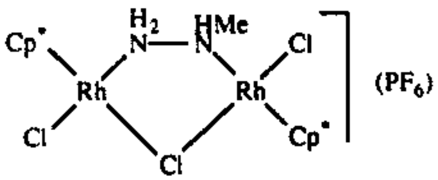
Table 13
Structural data for the bridging-substituted-hydrazine complex, (**81**)

Complex	$d(Ru^1-N)$	$d(Ru^2-N)$	$d(N-N)$	$\widehat{Ru^1NN}$	$\widehat{Ru^2NN}$	Reference
$[\{Ru(COD)Cl\}(\mu_2\text{-}H)(\mu_2\text{-}Cl)(\mu_2\text{-}NMe_2NH_2)\{Ru(COD)H\}]^a$ (**81**)	2.24(2)	2.12(2)	1.51(4)	103(1)	114(2)	[92]

[a] See (**81**) in text for labelling scheme.



(23)



(83)

4.3. Bidentate η^2-substituted hydrazine complexes

Only two crystallographically characterised η^2-substituted hydrazine complexes have been reported (see Table 14) and their structures are shown below.

(**84**) was prepared by the reaction of $[VCl_3(MeCN)_3]$ with $MePhNNH_2$ and the coordination about V is approximately pentagonal bipyramidal with the axial positions occupied by Cl and NNMePh. There are four molecules in the unit cell with significant H-bonding between the NH_2 groups, axial Cl atoms and ionic chlorides [93].

For (**85**), a mono-substituted hydrazine is found to bond in a bidentate mode and the preparation involves protonation of the analogous phenylhydrazido(−I) complex [94,95].

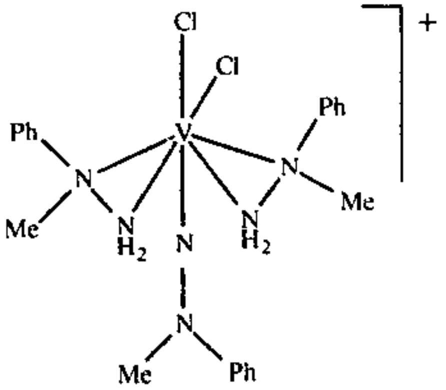
Table 14
Structural data for the substituted hydrazine in complexes containing bidentate substituted hydrazines

Complex		$d(M-NH_2)$ (Å)	$d(M-NRR')$ (Å)	$d(N-N)$ (Å)	Reference
$[VCl_2(NNMePh)(\eta^2\text{-}NH_2NMePh)_2]^+$	(**84**)	ca. 2.1	ca. 2.1	ca. 1.48	[93]
$[MoICp(NO)(\eta^2\text{-}NH_2NHPh)]^+$	(**85**)	2.134(3)	2.184(3)	1.430(5)	[94,95]

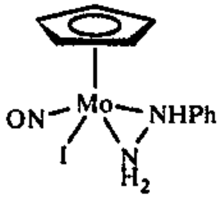
Table 15
^1H and ^{13}C NMR and IR data of η^2-substituted hydrazine complexes

Complex	$\delta(N_\alpha H)$	$\delta(N_\beta H)$	$\delta(N_\alpha CH_3)$	$\delta(N_\beta CH_3)$	$\delta(N_\alpha CH_3)$	$\delta(N_\beta CH_3)$	IR	Reference
$[Cp^*MoMe_3(\eta^2\text{-}NH_2NHMe)]^+$							✓	[69]
$[Cp^*MoMe_3(\eta^2\text{-}NH_2NMe_2)]^+$							✓	[69]
$[Cp^*MoMe_3(\eta^2\text{-}NHMeNHMe)]^+$							✓	[69]
$[Cp^*WMe_3(\eta^2\text{-}NH_2NHMe)]^+$							✓	[65]
$[Cp^*WMe_3(\eta^2\text{-}NH_2NMe_2)]^+$							✓	[65]
$[Cp^*WMe_3(\eta^2\text{-}NHMeNHMe)]^+$							✓	[65]
$[Cp^*WMe_4(\eta^2\text{-}NH_2NHMe)]^+$	4.37	5.73, 5.13		2.97^b				[73]
$[Cp^*ReMe_3(\eta^2\text{-}NH_2NHMe)]^+$	7.0	6.40		2.95		35.9	✓	[71]
$[Cp^*ReMe_3(\eta^2\text{-}NH_2NMe_2)]^+$	6.95			3.10		28.1	✓	[71]
$[Cp^*ReMe_3(\eta^2\text{-}NHMeNHMe)]^+$	6.65^a	6.05^a	2.93^a	2.86^a	33.9^a	30.2^a	✓	[71]

[a] Assignments may be interconverted. [b] $^3J(H-H) = 5.0$ Hz.



(84)



(85)

The presence of two and three orbitals, which are available for mono- or bidentate-hydrazine coordination in the 'Cp*MMe$_4$' and 'Cp*MMe$_3$' (M = Mo, W, Re) fragments respectively [96], undoubtedly assists η^2-coordination of substituted hydrazines, and the compounds reported so far are listed in Table 15. Substituted hydrazine complexes containing the 'Cp*MMe$_3$' (M = Mo, W) fragment are of course paramagnetic, and multinuclear NMR characterisation of the diamagnetic compounds is only possible on the analogous compounds containing the '[Cp*ReMe$_3$]$^+$' and 'Cp*MMe$_4$' (M = Mo, W) fragments. This facility has been exploited by Schrock et al. to monitor the site of deprotonation in both hydrazine and substituted hydrazine complexes, but these results fall outside the scope of this review and have been discussed recently [97,98].

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