

The Reactions of Hydrazine with Transition-metal Complexes

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1 Introduction

In reactions with transition-metal complexes hydrazine may act both as a ligand and redox-reagent. Audrieth and Ogg¹, reviewing the subject in 1951, listed complexes apparently containing hydrazine, but the nature of many of these has been established only recently. Since that review, efforts have also been made to build on the work of Browne² on redox reactions between hydrazine and transition-metal complexes. Reactions between hydrazine and the heavier transition metals have been investigated recently, and new ligands discovered as a result (*e.g.*, nitride, molecular nitrogen). This Review summarises these findings. It is clear, despite recent work, that the subject is still in its (somewhat prolonged) infancy.

2 Hydrazine as a Ligand

Hydrazine and its alkyl- or phenyl- derivatives are potentially unidentate, bidentate, or bridging-ligands. Transition-metal complexes containing unidentate and bridging hydrazines are well documented, but [with the possible exception of $(\text{Pr}^f\text{O})_4\text{M}(\text{N}_2\text{H}_4)$ ($\text{M} = \text{Ti}$ or Zr)³] complexes containing bidentate hydrazines have not been found. The monomeric complexes $\text{Me}_3\text{Al}(\text{Me}_2\text{NNMe}_2)$, $\text{Et}_3\text{Al}(\text{Me}_2\text{NNMe}_2)$, $\text{Et}_2\text{ClAl}(\text{Me}_2\text{NNMe}_2)$, and $\text{EtCl}_2\text{Al}(\text{Me}_2\text{NNMe}_2)$ showed n.m.r. equivalence of the protons of all four *N*-methyl groups⁴⁻⁶. Therefore, they were believed to contain bidentate tetramethylhydrazine, although further work is desirable to prove some fast exchange process is not occurring.

The hydrazinium(+1) ion, N_2H_5^+ , is potentially a unidentate ligand, and complexes containing it are known.

A. Complexes Containing Unidentate Hydrazines.—Table 1 lists complexes containing unidentate hydrazines which have been well-characterised. Other complexes, *e.g.*, $[\text{Pt}^{\text{II}}\text{Cl}_2(\text{N}_2\text{H}_4)(\text{N}_2\text{H}_5)]\text{ClO}_4$,⁷ thought to contain unidentate hydrazine on the basis of analysis, require further investigation.

¹ L. F. Audrieth and B. A. Ogg, 'The Chemistry of Hydrazine', Wiley, New York, 1951.

² R. E. Kirk and A. W. Browne, *J. Amer. Chem. Soc.*, 1928, **50**, 337; and references therein.

³ M. S. Bains and D. C. Bradley, *Canad. J. Chem.*, 1962, **40**, 1351.

⁴ N. R. Fetter and B. Bartocha, *Canad. J. Chem.*, 1961, **39**, 2001.

⁵ N. R. Fetter, B. Bartocha, F. E. Brinckman, and D. W. Moore, *Canad. J. Chem.*, 1963, **41**, 1359.

⁶ D. F. Clemens, W. S. Bray, and H. H. Sisler, *Inorg. Chem.*, 1963, **2**, 1251.

⁷ N. G. Klyuchnikov and F. I. Para, *Zhur. neorg. Khim.*, 1967, **12**, 1219.

The Reactions of Hydrazine with Transition-metal Complexes

Table 1 Complexes containing unidentate hydrazines

Complex	Method of preparation	Ref.
$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{N}_2\text{H}_4)]\text{X}$ X = BPh ₄ or [Cr ^{III} (NH ₃) ₂ (SCN) ₄] M = Mo or W	$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}] + \text{N}_2\text{H}_4$ (96%) in dichloromethane	a
$[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{N}_2\text{H}_4)]\text{X}$ X = BPh ₄ or [Cr ^{III} (NH ₃) ₂ (SCN) ₄]	$[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}] + \text{N}_2\text{H}_4$ (96%) in benzene	b
$[\text{Mo}(\text{CO})_5(\text{N}_2\text{H}_3\text{R})]$ R = H or Ph	$(\text{Et}_4\text{N})[\text{Mo}(\text{CO})_5\text{X}] + \text{N}_2\text{H}_3\text{R}$ (85%) aqueous (X = Cl or I) in water	c
<i>mer</i> - $[(\text{Me}_2\text{PhP})_3\text{M}^{\text{II}}\text{X}_2(\text{N}_2\text{H}_3\text{R})]$ M = Ru or Os for R = H or Ph and X = Cl M = Ru for R = H and X = Br	<i>mer</i> - $[(\text{Me}_2\text{PhP})_3\text{M}^{\text{III}}\text{X}_3] + \text{N}_2\text{H}_3\text{R}$ (85% aqueous) in ethanol*	d, e
$[(\text{R}_3\text{P})_2\text{Rh}^{\text{III}}\text{Cl}_3(\text{N}_2\text{H}_3\text{Ph})]$ R = Et, or Bu ⁿ	$[(\text{R}_3\text{P})_3\text{Rh}^{\text{III}}\text{Cl}_3] + (\text{H}_3\text{N})\text{NNHPhCl}^\dagger$ in methanol	f
<i>trans</i> - $[\text{Rh}^{\text{III}}\text{en}_2\text{Cl}(\text{N}_2\text{H}_4)]^{2+}$ (en = ethylenediamine)	<i>trans</i> - $[\text{Rh}^{\text{III}}\text{en}_2\text{Cl}_2]^+ + \text{N}_2\text{H}_4^\dagger$	g
<i>trans</i> - $[\text{Rh}^{\text{III}}\text{en}_2(\text{N}_2\text{H}_4)_2]^{3+}$	<i>trans</i> - $[\text{Rh}^{\text{III}}\text{en}_2\text{Cl}(\text{N}_2\text{H}_4)]^{2+} + \text{N}_2\text{H}_4^\dagger$	g
<i>trans</i> - $[p\text{-FC}_6\text{H}_4\text{N}_2\text{H}_3\text{Pt}^{\text{II}}\text{Cl}(\text{Et}_3\text{P})_2]\text{BF}_4$	<i>trans</i> - $[(p\text{-FC}_6\text{H}_4\text{N}=\text{NH})\text{Pt}^{\text{II}}\text{Cl}(\text{Et}_3\text{P})_2]^+ + \text{H}_2$	h
$[\text{TiX}_4(\text{N}_2\text{H}_3\text{Ph})_2]^\S$ X = Cl, Br, or I	$\text{TiX}_4 + \text{N}_2\text{H}_3\text{Ph}$ (anhydrous) in anhydrous nitromethane	i
$[\text{TiX}_4(\text{H}_2\text{NNMe}_2)_4]^\parallel$ X = Cl, Br, or I	$\text{TiX}_4 + \text{H}_2\text{NNMe}_2$ (anhydrous) in anhydrous nitromethane	i
$[\text{Co}^{\text{II}}(\text{H}_2\text{NNHR})_6]\text{Cl}_2$ R = H or Me	$\text{Co}^{\text{II}}\text{Cl}_2 + \text{N}_2\text{H}_3\text{R}$ (anhydrous) no solvent	j
$[\text{Co}^{\text{II}}(\text{H}_2\text{NNMe}_2)_6]\text{Cl}_2$	$\text{Co}^{\text{II}}\text{Cl}_2 + \text{H}_2\text{NNMe}$ (anhydrous) no solvent	j
$[\text{Ni}^{\text{II}}(\text{N}_2\text{H}_3\text{Me})_6]\text{Cl}_2$	$[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]\text{Cl}_2 + \text{N}_2\text{H}_3\text{Me}$ (excess) in ethanol	k
$[\text{Zn}(\text{N}_2\text{H}_3\text{Ar})_2\text{X}_2]$ X = Cl, Br, or I; Ar = C ₆ H ₅ , <i>o</i> -ClC ₆ H ₄ , <i>o</i> -BrC ₆ H ₄ , <i>p</i> -BrC ₆ H ₄ , or <i>o</i> -, <i>m</i> -, <i>p</i> -CH ₃ OC ₆ H ₄	$\text{ZnX}_2 + \text{N}_2\text{H}_3\text{Ar}$ (anhydrous) in ethanol	l
$[\text{M}^{\text{II}}(\text{N}_2\text{H}_4)_2(\text{N}_2\text{H}_3\text{CO}_2)_2]$ M = Mn, Co, Ni, or Zn	$\text{M}^{2+} + \text{N}_2\text{H}_4$ (85% aqueous) + CO ₂ in aqueous ammonia	m—q

The preparation of $[p\text{-FC}_6\text{H}_4\text{N}_2\text{H}_3\text{Pt}^{\text{I}}\text{Cl}(\text{PEt}_3)_2]^+$ by hydrogenation of $[(p\text{-FC}_6\text{H}_4\text{N}=\text{NH})\text{Pt}^{\text{I}}\text{Cl}(\text{PEt}_3)_2]^+$ was suggested as part of a model for biochemical nitrogen fixation^{8,9}. On further hydrogenation $p\text{-FC}_6\text{H}_4\text{NH}_2$ and $\text{trans}[(\text{Et}_3\text{P})_2\text{Pt}^{\text{I}}\text{HCl}]$ were formed.

The structure of $[\text{Zn}(\text{N}_2\text{H}_4)_2(\text{N}_2\text{H}_3\text{CO}_2)_2]$ was determined by X -ray methods;¹⁰ Mn, Co, and Ni form complexes isomorphous with the Zn analogue¹¹ (Figure 1). Within experimental error the N—N (N_2H_4) bond length, 1.46(4) Å*, is the same as in hydrazine [1.453(5) Å from infrared,¹² 1.449(4) Å by electron diffraction,¹³ and 1.46(2) Å by X -ray¹⁴] and complexes containing bridging hydrazine (*vide infra*).

With substituted hydrazines linkage isomers are possible. There is evidence that the site of protonation of Me_2NNH_2 , PhNHNH_2 , and Ph_2NNH_2 is determined by electronic effects. The inductive effect of methyl compared to hydrogen results in protonation of the methyl-nitrogen, whereas with phenyl, mesomeric electron withdrawal results in protonation of the amido-nitrogen.¹⁵ However, there is a

* Standard deviations (relating to the least significant digit), where available, are given in parentheses.

⁸ G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822.

⁹ E. K. Jackson, G. W. Parshall, and R. W. F. Hardy *J. Biol. Chem.*, 1968, **243**, 4952.

¹⁰ A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Z. Krist.*, 1965, **122**, 259.

¹¹ A. Ferrari, A. Braibanti, G. Bigliardi, A. M. Lanfredi, and A. Tiripicchio, *Nature*, 1966, **211**, 1174.

¹² A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S-I. Mizushima, *Spectrochim. Acta.*, 1960, **16**, 1471.

¹³ Y. Morino, T. Iiyima, and Y. Murata, *Bull. Chem. Soc. Japan.*, 1960, **33**, 46.

¹⁴ R. L. Collin and W. N. Lipscomb, *Acta. Cryst.*, 1951, **4**, 10.

¹⁵ R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 1963, 3151.

Footnotes to Table 1 on facing page.

* Other products of this reaction were H_2 , N_2 , and $\text{N}_2\text{H}_5\text{Cl}$.^{d,e} On warming in petroleum *mer*- $[(\text{Me}_2\text{PhP})_3\text{RuCl}_2(\text{N}_2\text{H}_4)]$ lost one Me_2PhP , forming $\{[(\text{Me}_2\text{PhP})_2\text{RuCl}_2]_2(\text{N}_2\text{H}_4)_2\}$ (see bridging hydrazines). A large excess of hydrazine yielded a mixture containing some $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{N}_2]^{2+}$.^d

† N_2H_4 gave a hydrazine complex of unknown formula which was also obtained from hydrated rhodium trichloride and N_2H_4 .^f

‡ In this review N_2H_4 is written when the form of hydrazine is not specified in the literature.

§ These complexes are believed to contain equal amounts of $\text{H}_3\text{NHNHPhCl}$ and polymeric $\text{TiX}_3(\text{NHNHPh})_2$.

|| The probable formula of this complex is $\text{TiX}_2(\text{HNNMe}_2)_2 \cdot 2\text{Me}_2\text{NHNH}_2 \cdot \text{X}$.

^a E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1964, **2**, 230; ^b E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1966, **5**, 63; ^c H. D. Murdoch and R. Henzi, *J. Organometallic Chem.*, 1966, **5**, 463; ^d J. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 854; ^e J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1969, 1674; ^f J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508; ^g D. J. Baker and R. D. Gillard, *Chem. Comm.*, 1967, 520; ^h G. W. Parshall, *J. Amer. Chem. Soc.*, 1967, **89**, 1822; ⁱ D. Nicholls and R. Swindells, *J. Chem. Soc.*, 1964, 4204; ^j D. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc. (A)*, 1966, 950; ^k D. Nicholls and R. Swindells, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2211; ^l L. M. Ku'len and M. S. Novokovskii, *Zhur. neorg. Khim.*, 1968, **13**, 2403; ^m P. V. Gogorishvili M. V. Korkarashvili, and L. D. Tsitsishvili, *Zhur. neorg. Khim.*, 1956, **1**, 1731; ⁿ P. V. Gogorishvili, M. V. Korkarashvili, and L. D. Tsitsishvili, *Zhur. neorg. Khim.*, 1957, **2**, 532; ^o A. Braibanti, G. Bagliardi, and R. C. Padovani, *Gazzetta*, 1965, **95**, 877; ^p A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Z. Krist.*, 1965, **122**, 259. ^q A. Ferrari, A. Braibanti, G. Bigliardi, A. M. Lanfredi, and A. Tiripicchio, *Nature*, 1966, **211**, 1174.

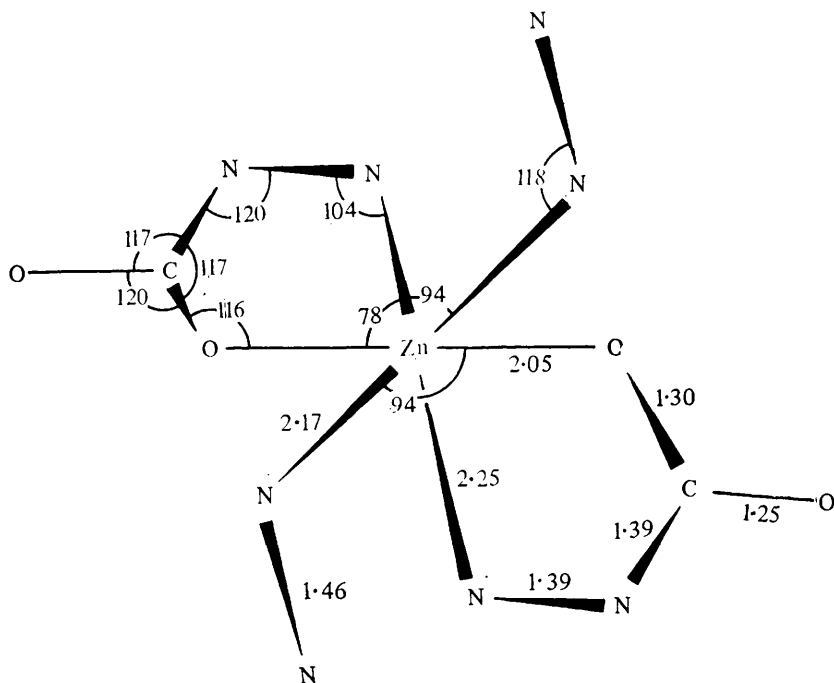


Figure 1 The structure of $[Zn(N_2H_4)_2(N_2H_3CO_2)_2]$ as determined by X-rays

reduction in basicity with increasing alkylation of hydrazine, as measured by the acid dissociation constants.¹⁶ There is no direct evidence of the co-ordination site in the relevant complexes in Table 1, though for $[Co^{II}(MeNHNH_2)_6]Cl_2$ co-ordination *via* the methyl-nitrogen was postulated from consideration of electronic effects.¹⁷ Complexes containing bridging phenylhydrazines have not been prepared, probably for steric reasons.^{18,19} Therefore, unidentate phenylhydrazines co-ordinate *via* the NH_2 -nitrogen.

Infrared spectra of $[Co^{II}(N_2H_4)_6]Cl_2$,¹⁷ and $[M(N_2H_4)_2(N_2H_3CO_2)_2]$ ($M = Co, Ni,$ or Zn)²⁰ have been reported (spectra of other complexes in Table 1 have been recorded, but absorption bands due to N_2H_4 vibrations were not reported). For $[Co^{II}(N_2H_4)_6]Cl_2$ the absorption band at 928 cm^{-1} was assigned to ν_{N-N} ,¹⁷ and the same band appeared at $936\text{--}931\text{ cm}^{-1}$ for $[M(N_2H_4)_2(N_2H_3CO_2)_2]$ ²⁰ (*vide infra*).

B. Complexes Containing Bridging Hydrazines.—Table 2 lists complexes con-

¹⁶ R. L. Hinman, *J. Org. Chem.*, 1958, **23**, 1587.

¹⁷ D. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc. (A)*, 1966, 950.

¹⁸ J. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 854.

¹⁹ J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

²⁰ A. Braibanti, F. Dallavalle, M. A. Pellinghelli, and E. Laporati, *Inorg. Chem.*, 1968, **7**, 1430.

Table 2 Complexes containing bridging hydrazines

Complex	Preparation	Ref.
$[M^{II}(N_2H_4)_2X_2]_n$ M = Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd; X = Cl, Br, I, CH ₃ , CO ₂ , or NCS	$M^{2+} + N_2H_4(85\% \text{ aqueous})^*$ in water	a—j
$[M^{II}(N_2H_3Me)_2Cl_2]$ M = Co or Ni	$[M^{II}(H_2O)_6]Cl_2(\text{excess}) + N_2H_3Me$ in ethanol	b, k
$[M^{II}(N_2H_4)_3](NO_3)_2$ M = Mn, Fe, Co, Ni, Zn, or Cd	$[M^{II}(H_2O)_6](NO_3)_2 + N_2H_4(85\% \text{ aqueous})$ in aqueous ammonia	b, l
$[Cu^I(CN)(N_2H_4)]_n$	†	m
$[\{(R_2PhP)_2Ru^{II}X_2\}_2(N_2H_4)_2]$ R = Me, Et, Bu ⁿ , or Ph for X = Cl R = Me or Et for X = Br	<i>mer</i> - $[(R_2PhP)_3Ru^{III}X_3] + N_2H_4(85\% \text{ aqueous})$ refluxed in ethanol	n
$[\{(Et_2PhP)_2Os^{II}Cl_2\}_2(N_2H_4)_2]$	<i>mer</i> - $[(Et_2PhP)_3Os^{III}Cl_3] + N_2H_4(85\% \text{ aqueous})$ refluxed in ethanol‡	n
$[\{(R_3P)_2Rh^{III}Cl_3\}_2(N_2H_4)]$ R = Et, Bu ⁿ , or n-Pentyl	<i>fac</i> - $[(R_3P)_3Rh^{III}Cl_3] + N_2H_5Cl$ refluxed in methanol	o

* Earlier references to the preparation of $[M^{II}(N_2H_4)_2X_2]$ are given by Audrieth and Ogg.¹

† Preparation not reported.

‡ The reaction between hydrazine and $[(Bu^nP)_3OsCl_3^{III}]$ yielded a mixture of starting material and $[(Bu^nP)_3Os^{III}Cl_2(N_2)]^p$ (*vide infra*). A complex $[\{(Bu^nPhP)_2Os^{III}Cl_3\}_2N_2H_4]$ has been briefly mentioned.^q

^aH. D. Murdoch and R. Henzi, *J. Organometallic Chem.*, 1966, **5**, 463; ^bD. Nicholls and R. Swindells, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2211; ^cA. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, 1965, **19**, 548; ^dA. Braibanti, F. Dallavalle, M. A. Pellinghelli, and E. Laporati, *Inorg. Chem.*, 1968, **7**, 1430; ^eA. Ferrari, A. Braibanti, G. Bigliardi, and F. Dallavalle, *Z. Krist.*, 1963, **119**, 284; ^fL. Sacconi and A. Sabatini, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1389. ^gA. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, 1963, **16**, 498; ^hA. Ferrari, A. Braibanti, and A. M. Lanfredi, *Gazzetta*, 1961, **91**, 69; ⁱA. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Gazzetta*, 1963, **93**, 937; ^jG. B. Kauffman and N. Sugisaka, *Z. anorg. Chem.*, 1966, **344**, 92; ^kD. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc. (A)*, 1966, 950; ^lA. Ferrari, A. Braibanti, and A. M. Lanfredi, *Ann. Chim. (Italy)*, 1958, **48**, 1238; ^mD. T. Cromer, A. C. Larson, and R. B. Roof, *Acta Cryst.*, 1966, **20**, 279. ⁿJ. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 854; ^oJ. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508; ^pJ. Chatt, G. J. Leigh, and D. M. P. Mingos, *Chem. and Ind.*, 1969, 109; ^qG. J. Leigh and D. M. P. Mingos, *J. Chem. Soc.*, (A), 1970, 587.

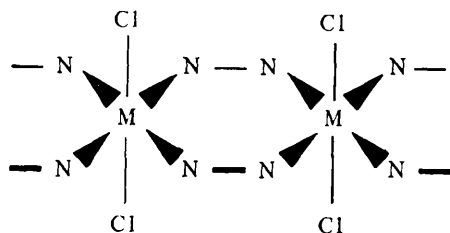
taining bridging hydrazines. The insoluble, unreactive complexes $[M^{II}(N_2H_4)_2X_2]_n$ are the usual product of reactions between excess hydrazine hydrate and first-row transition-metal complexes.

X-Ray investigation of $[Mn^{II}(N_2H_4)_2Cl_2]_n$,²¹ and $[Zn^{II}(N_2H_4)_2Cl_2]_n$ ²² showed

²¹ A. Ferrari, A. Braibanti, G. Bigliardi, and F. Dallavalle, *Z. Krist.*, 1963, **119**, 284.

²² A. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, 1963, **16**, 498.

The Reactions of Hydrazine with Transition-metal Complexes



both have infinite-chain structures with *cis*-bridging hydrazine molecules and *trans*-Cl ions.

Other $[M^{II}(N_2H_4)_2X_2]_n$ complexes have similar structures²³⁻²⁶. $[Cu^I(CN)(N_2H_4)]_n$ contains bridging cyanide and bridging hydrazine, with the copper(I) having distorted tetrahedral co-ordination²⁷ (Figure 2). The compounds

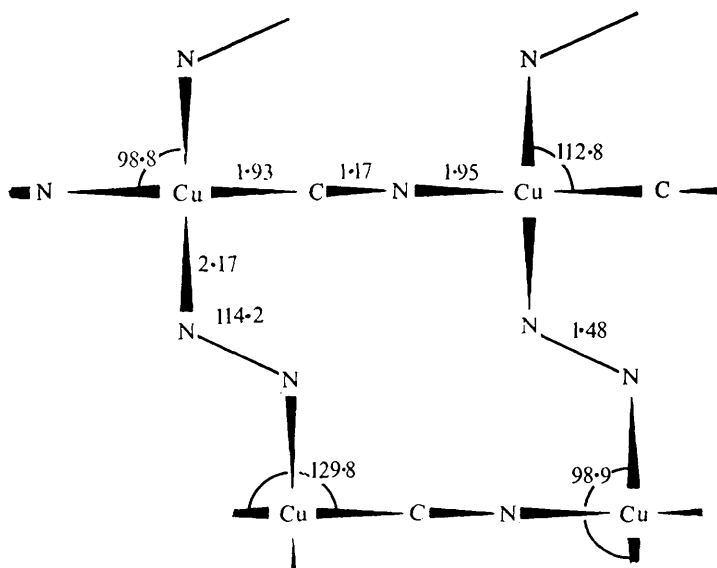


Figure 2 The structure of $[Cu^I(CN)(N_2H_4)]_n$ as determined by X-rays

$Cu^I Cl(N_2H_4)_2$, $(Cu^I Cl)_2 N_2 H_3 Me$, and $(Cu^I Cl)_2 H_2 NNMe_2$, of unknown structure, have been reported.²⁸ In all complexes the N—N bond length is between 1.45 and

²³ A. Ferrari, A. Braibanti, and G. Bigliardi, *Acta Cryst.*, 1965, **19**, 548.

²⁴ A. Ferrari, A. Braibanti, and A. M. Lanfredi, *Gazzetta*, 1961, **91**, 69.

²⁵ A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Gazzetta*, 1963, **93**, 937.

²⁶ A. Braibanti, G. Bigliardi, R. C. Padovani, and F. Dallavalle, *Gazzetta*, 1965, **95**, 1212.

²⁷ D. T. Cromer, A. C. Larson, and R. B. Roof, *Acta Cryst.*, 1966, **20**, 279.

²⁸ D. Nicholls and R. Swindells, *J. Inorg. Nuclear. Chem.*, 1969, **31**, 3313.

1.48 Å, which is the same as in hydrazine or complexes containing monodentate hydrazine.

The complexes $[M^{II}(N_2H_4)_3](NO_3)_2$ are believed, from i.r.^{20,29} and preliminary X-ray³⁰ investigation, to have chain structures with three bridging hydrazine molecules linking octahedrally co-ordinated metal ions.

Sacconi and Sabatini³¹ investigated the i.r. spectra of $[M^{II}(N_2H_4)_2Cl_2]_n$ ($M = Mn, Fe, Co, Ni, Cu, Zn, \text{ or } Cd$) and $[Cd^{II}(N_2D_4)_2Cl_2]_n$ from 4000 to 300 cm^{-1} . In addition to bands assigned to N—H modes of vibration, $\nu N-N$ was in the region 985—960 cm^{-1} (and followed the Irving-Williams order of complex stability^{20,31-33}) and $\nu M-N$, 440—340 cm^{-1} . Braibanti and co-workers²⁰ noted an increase in frequency of $\nu N-N$ from hydrazine (875 cm^{-1})^{34,35} to complexes containing unidentate hydrazine (circa 930 cm^{-1})^{17,20} to complexes containing bridging hydrazine (between 985 and 948 cm^{-1})^{20,29,30}. This increase is paralleled by the increase in $\nu N-N$ on protonation of N_2H_4 (N_2H_5Cl , 973³⁶; $N_2H_6Cl_2$, 1027 cm^{-1})³⁷, and both results were ascribed to changes in electron pair repulsion as the hydrazine lone pairs become involved in bonding.²⁰ However, the approximation that the fundamental vibration concerned consists solely of $\nu N-N$ must become less accurate as co-ordination of hydrazine increases. Also, assignment of the band at 875 cm^{-1} in the spectrum of hydrazine to $\nu N-N$ was questioned by Durig and co-workers,³⁸ who assigned this band to a NH_2 rocking vibration and the band at 1126 cm^{-1} to $\nu N-N$. Despite these reservations, the frequency of $\nu N-N$ is a useful indication of the type of co-ordinated hydrazine.

The reaction between $HgCl_2$ and hydrazinium(+1) chloride yielded $[Hg(N_2H_4)_2]Cl_2$ and $[Hg(N_2H_4)]Cl_2$.³⁹ By analogy with ammonia and amide complexes of mercury, Broderson³⁹ assigned a polymeric structure containing bridging hydrazine to $[Hg(N_2H_4)]Cl_2$ and a monomeric structure with unidentate hydrazine to $[Hg(N_2H_4)_2]Cl_2$, and interpreted the i.r. spectra of the complexes on this basis. $\nu N-N$ was at 952 cm^{-1} for $[Hg(N_2H_4)_2]Cl_2$ and 976 cm^{-1} for $[Hg(N_2H_4)]Cl_2$. Further work appears necessary to confirm the structures. $[Hg_2(N_2H_2)]Cl_2$ was also obtained from $HgCl_2$ and hydrazinium(+1) chloride or hydrazinium(+2) chloride.³⁹⁻⁴¹ This highly explosive complex, from i.r.³⁹ and X-ray powder⁴⁰ measurements, has chains of quadridentate $N_2H_2^{2-}$ linking Hg^{2+} ions.

C. Complexes Containing Hydrazinium Ion as Ligand.—Complexes containing

²⁹ D. Nicholls and R. Swindells, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2211.

³⁰ A. Ferrari, A. Braibanti, and A. M. Lanfredi, *Ann. Chim. (Italy)*, 1958, **48**, 1238.

³¹ L. Sacconi and A. Sabatini, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1389.

³² L. Sacconi and A. Sabatini, *Nature*, 1960, **186**, 549.

³³ M. S. Barvinok and I. S. Bukhareva, *Zhur. fiz. Khim.*, 1967, **41**, 525.

³⁴ P. A. Giguère and I. D. Lui, *J. Chem. Phys.*, 1952, **20**, 136.

³⁵ E. Catalano, R. H. Sanborn, and J. W. Frazer, *J. Chem. Phys.*, 1963, **38**, 2265.

³⁶ J. C. Decius and D. P. Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 2436.

³⁷ R. G. Snyder and J. C. Desius, *Spectrochim. Acta*, 1959, **13**, 280.

³⁸ J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, 1966, **44**, 4238.

³⁹ K. Broderson, *Z. anorg. Chem.*, 1957, **290**, 24.

⁴⁰ K. Broderson, *Z. anorg. Chem.*, 1956, **285**, 5.

⁴¹ A. Meuwesen and G. Weiss, *Z. anorg. Chem.*, 1957, **289**, 5.

N_2H_5^+ have been postulated, e.g., $[\text{M}^{\text{II}}(\text{N}_2\text{H}_5)_2(\text{N}_2\text{H}_3\text{CO}_2)_2]\text{CO}_3$ ($\text{M} = \text{Co}$ or Ni)^{42,43} but only $[\text{M}^{\text{II}}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]_n$ ($\text{M} = \text{Cr}, \text{Co}, \text{Ni}, \text{Cu},$ or Zn) are adequately characterised. These have essentially the same structure as the zinc complex,⁴⁴ shown by *X*-ray studies to be a chain of metal ions linked by bridging bidentate sulphate groups, with N_2H_5^+ completing a distorted octahedron.⁴⁵ The N—N bond length, 1.55 Å, is significantly longer than was found in complexes of N_2H_3 , or unco-ordinated N_2H_5^+ (1.42 to 1.47₅ Å⁴⁶). However, twinning of the crystals and consequently a less accurate analysis may account for the observed bond length.⁴⁵ The complex $(\text{N}_2\text{H}_5)_3\text{CdCl}_5$ contains bridging chloride ions and unco-ordinated hydrazinium cations.⁴⁷

3 Redox-reactions of Hydrazine

The information on redox-reactions between hydrazine and transition-metal complexes may be divided into two categories. On one hand are investigations which focus attention on the kinetics and mechanism of hydrazine oxidation in aqueous solution. Here the role played by the different transition-metal complexes used as oxidants has received little attention. On the other hand are investigations of reactions between hydrazine and second- and third-row transition-metal complexes, which focus attention on the product containing the metal, and here the fate of hydrazine is often a mystery. To some extent this division reflects the interests of the investigators, although the obvious complexity of many reactions in the second category indicates the mystery may remain for some time.

A. Mechanism of Hydrazine Oxidation in Aqueous Solution.—The problem of the variation in products when hydrazine was oxidised by different compounds was first approached by Kirk and Browne². They classified oxidants according to the presence or absence of hydrazoic acid in the products of hydrazine oxidation, and noted (for acid solutions) that only two-electron oxidants produced hydrazoic acid. A mechanism for hydrazine oxidation, based on reactions of organic derivatives of hydrazine, was proposed to explain this. In 1953 Higginson⁴⁸ investigated the formation of all products of hydrazine oxidation (hydrazoic acid, ammonia, and nitrogen; hydroxylamine was also proposed⁴⁹ but, with possibly one exception,⁵⁰ has not been observed, probably because of the very negative standard potentials for oxidation of hydrazine to hydroxylamine⁴⁹). Hydrazoic

⁴² P. V. Gogorishvili, M. V. Karkarashvili, and L. D. Tsitsishvili, *Zhur. neorg. Khim.*, 1956, **1**, 2753.

⁴³ P. V. Gogorishvili and T. M. Khonelidze, *Zhur. neorg. Khim.*, 1961, **6**, 1291.

⁴⁴ D. W. Hand and C. K. Prout, *J. Chem. Soc. (A)*, 1966, 168.

⁴⁵ C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1961, 4177.

⁴⁶ S. A. Hady, I. Nahrngbauer, and I. Olovsson, *Acta Chem. Scand.*, 1969, **23**, 2764; and references therein.

⁴⁷ A. Braibanti and A. Tiripicchio, *Gazzetta*, 1966, **96**, 1580.

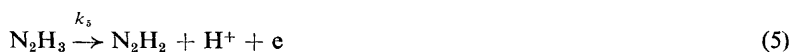
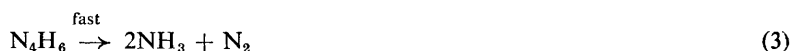
⁴⁸ W. C. E. Higginson, D. Sutton, and P. Wright, *J. Chem. Soc.*, 1953, 1380.

⁴⁹ W. M. Latimer, 'Oxidation Potentials', 2nd edn., Prentice-Hall, Englewood Cliffs, New Jersey, 1952, p. 99.

⁵⁰ S. Ostrowetsky and D. Brinon, *Compt. rend.*, 1966, **263**, C, 406.

acid was obtained only with two-electron oxidants, and its production was optimum at elevated temperature (*ca.* 80 °C) and pH < 1.0, under which conditions ammonia was also produced.⁴⁸ At 20 °C and pH from 1.0 to 2.0 no oxidant produced hydrazoic acid, and some (particularly main-group oxidants) gave no ammonia or only small quantities. No clear relation between the nature of the oxidant and ammonia production is apparent. At pH > 6 ammonia was produced, sometimes in low yield, by many oxidants, and traces of azide were observed for two-electron oxidants. Nitrogen was produced under all conditions.

Higginson and co-workers⁵¹⁻⁵³ and, independently, Cahn and Powell⁵⁴ investigated the products, kinetics and mechanism of the reaction between hydrazine and $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ in acid solution. From the results a general mechanism for hydrazine oxidation was proposed,^{53,54} based on that of Kirk and Browne:²



This mechanism accounted for one-electron oxidation of hydrazine. Two-electron oxidation was postulated to occur by the mechanism:



An alternative to removal of N_2H_2 by (6) and (8) was:



⁵¹ W. C. E. Higginson, *Chem. Soc. Special Publ.* No. 10, 1957, 95.

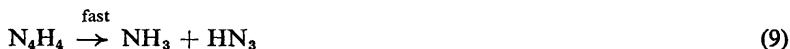
⁵² W. C. E. Higginson and D. Sutton, *J. Chem. Soc.*, 1953, 1042.

⁵³ W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1955, 1551.

⁵⁴ J. W. Cahn and R. E. Powell, *J. Amer. Chem. Soc.*, 1954, 76, 2568.

Cahn and Powell⁵⁴ reported that copper(II) did not oxidise hydrazine, but when added to the hydrazine-iron(III) reaction, it increased the ratio $[\text{N}_2] : [\text{NH}_3]$ produced, without increasing the reaction rate. Therefore reaction (4) was postulated and a value of 0.15 obtained for the ratio k_4/k_2 . However, reaction (-1) was not included in this scheme. Higginson and Wright⁵³ and (using a different experimental method) Pollard and Nickless⁵⁵ found k_4/k_2 to be 0.015 (± 0.015) and therefore considered (4) to be unimportant. Rosseinsky⁵⁶ found that the addition of copper(II) increased *both* the rate *and* the ratio $[\text{N}_2] : [\text{NH}_3]$, and this could be explained by suppression of reaction (-1) due to an increase in the rate of (5), a result confirmed by Pollard and Nickless.⁵⁵

Cahn and Powell⁵⁴ proposed an alternative mechanism for hydrazoic acid formation:



or



Higginson⁵¹ criticised reactions (11–13) because the precursor, N_4H_6 , is produced by one-electron oxidants, and hence this mechanism does not explain the difference between one- and two-electron oxidants.

B. The Nature of the Hydronitrogen Intermediates.—Before considering application of the mechanism to transition-metal oxidants it is appropriate to consider the independent evidence for the existence of the intermediates N_2H_3 , N_2H_2 , N_3H_3 , N_4H_4 , and N_4H_6 . Some of this evidence derives from gas-phase experiments. While not proving that the species exist in solution, such evidence indicates that postulating them as reaction intermediates is reasonable. As noted by Higginson,⁵¹ any of these may be protonated and there is evidence that this occurs for N_2H_3 ,^{57,58} and N_2H_2 .⁵⁹ Protonation may, indeed, confer increased stability on N_2H_3 .⁶⁰

The hydrazine radical, N_2H_3 , prepared by thermal or electrodeless discharge decomposition of hydrazine, was identified by its mass spectrum.⁶¹ Di-imide, N_2H_2 , obtained by passing an electrodeless discharge through hydrazine⁶² or

⁵⁵ F. H. Pollard and G. Nickless, *J. Chromatog.*, 1960, **4**, 196.

⁵⁶ D. R. Rosseinsky, *J. Chem. Soc.*, 1957, 4685.

⁵⁷ J. Q. Adams and J. R. Thomas, *J. Chem. Phys.*, 1963, **39**, 1904.

⁵⁸ H. R. Falle, *Canad. J. Chem.*, 1968, **46**, 1703.

⁵⁹ S. Karp and L. Meites, *J. Amer. Chem. Soc.*, 1962, **84**, 906.

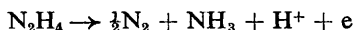
⁶⁰ G. Davies and K. Kustin, *J. Phys. Chem.*, 1969, **73**, 2288.

⁶¹ S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1958, **28**, 719.

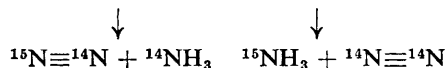
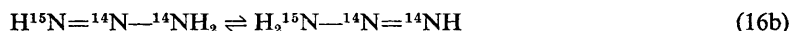
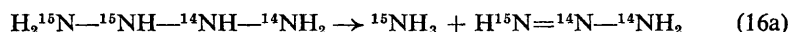
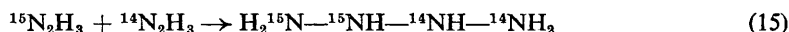
⁶² S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 1959, **29**, 442.

hydrazoic acid,⁶¹ by photolysis of hydrazoic acid,⁶³ or by thermal decomposition of anthracene 9,10-bi-imine,⁶⁴ was identified by its mass^{61,62,64} and i.r.⁶³ spectra. Di-imide, generated *in situ*, is now a well-known reductant, and its chemistry as such has been reviewed.⁶⁵ Mono- and di-substituted derivatives of di-imide have attracted attention and copper(I) complexes containing these ligands were prepared by oxidation of the appropriate hydrazine.⁶⁶

Evidence for tetrazene, N_4H_6 , and triazene, N_3H_3 , was obtained from investigation of $[Fe^{III}(H_2O)_6]^{3+}$ oxidation of hydrazine containing $^{15}N_2H_4$.^{62,64} The overall equation for oxidation was:



50% of the molecular nitrogen produced had random isotopic composition and 50% had the same isotopic composition as the parent hydrazine. This was explained by the following mechanism (Scheme 1):



Scheme 1

If reactions (16a) and (16b) are correct, this would preclude (12) and (13) as the source of HN_3 , since (16) is fast whereas (13) is slow, and hence N_3H_3 would yield ammonia and nitrogen, not hydrazoic acid.

A compound believed to be N_4H_6 was prepared by pyrolysis of hydrazine. A yellow diamagnetic solid (which decomposed to nitrogen and ammonia on heating) was trapped at $-195^\circ C$. Randomisation of $H_2^{14}N-^{15}NH_2$ was observed, but the extent was not measured.⁶⁷

Tetrazene, N_4H_4 , and triazene, N_3H_3 , were observed in the mass spectrum of the solid trapped at $-195^\circ C$ after submitting hydrazine to an electrodeless discharge.⁶¹ N_4H_4 , not present in the gaseous products, was believed to result from a reaction at the cold trap surface.

C. Mechanism of Reactions between Hydrazine and Transition-metal Complexes.—

The reaction between hydrazine and $[Fe^{III}(H_2O)_6]^{3+}$ was used to develop the general mechanism⁵¹⁻⁵⁶ (*vide supra*). This mechanism has been used to interpret

⁶³ K. Rosengren and G. C. Pimentel, *J. Chem. Phys.*, 1965, **43**, 507.

⁶⁴ E. J. Corey and W. L. Mock, *J. Amer. Chem. Soc.*, 1962, **84**, 685.

⁶⁵ S. Hunig, H. R. Muller, and W. Thier, *Angew. Chem. Internat. Edn.*, 1965, **4**, 271.

⁶⁶ D. Petredis, A. Burke, and A. L. Balch, *J. Amer. Chem. Soc.*, 1970, **92**, 428; and references therein.

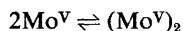
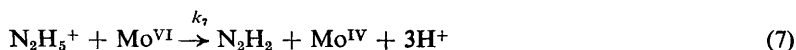
⁶⁷ F. O. Rice and F. Sherber, *J. Amer. Chem. Soc.*, 1955, **77**, 291.

The Reactions of Hydrazine with Transition-metal Complexes

the reactions between hydrazine and $[\text{Fe}^{\text{III}}\text{Y}]^-$ ($\text{Y} = \text{ethylenediaminetetraacetate}$),⁶⁸ $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$,⁶⁹ $[\text{Mn}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$,⁶⁰ $[\text{Mo}^{\text{VI}}\text{O}_4]^{2-}$,⁷⁰ and Ag_2O .⁷¹ The reaction between hydrazine and $[\text{MnO}_4]^-$ was investigated earlier,⁷² and the proposed mechanism criticised,⁵¹ but interpretation awaits further investigation.

The reactions between hydrazine and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ ⁶⁹ and hydrazine and $[\text{Fe}^{\text{III}}\text{Y}]^-$ ⁶⁸ were investigated in alkaline solution. No ammonia was produced by $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ and only a small amount by $[\text{Fe}^{\text{III}}\text{Y}]^-$, implying that reaction (2) is unimportant compared to (5) for these oxidants. Reaction (-1), extremely important for $[\text{Fe}^{\text{III}}\text{Y}]^-$ ($k_{-1}/k_5 \approx 140$), was not observed for $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$.

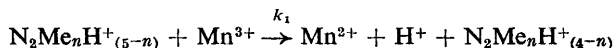
The reaction between hydrazine and $[\text{Mo}^{\text{VI}}\text{O}_4]^{2-}$ was investigated in acid solution.⁷⁰ Because di-imide was identified as an intermediate, it was concluded that molybdenum(vi) acted as a two-electron oxidant, although the final product was molybdenum(v). In view of reaction (5), the presence of di-imide is not unequivocal evidence for two-electron oxidation, though observation of hydrazoic acid in molybdenum(vi) oxidation of hydrazine at 80 °C⁴⁸ indicates this is probably correct (in the investigation under discussion only nitrogen was observed). A complicated relation between rate of reaction and pH was found. The mechanism proposed was as follows (Scheme 2):



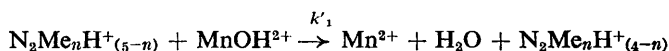
Scheme 2

The reaction between hydrazine and Ag_2O in acid solution showed an induction period, attributed to formation of a silver(i)-hydrazine complex. No attempt was made to detect products other than nitrogen. The rate increased rapidly with pH, the mechanism being similar to that of hydrazine- $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$.⁷¹

The reaction between $\text{N}_2\text{Me}_n\text{H}^+_{(5-n)}$ ($n = 0 - 4$) and $[\text{Mn}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ was investigated in highly acidic solutions.⁶⁰ No product analysis was made, but the rate was dependent on the acid concentration:



or



⁶⁸ H. Minato, E. J. Meehan, I. M. Kolthoff, and C. Auerbach, *J. Amer. Chem. Soc.*, 1959, **81**, 6168.

⁶⁹ E. J. Meehan, I. M. Kolthoff, and K. Mitsuhashi, *Suomen Kem.*, 1969, **42B**, 159.

⁷⁰ T. Huang and J. T. Spence, *J. Phys. Chem.*, 1968, **72**, 4198.

⁷¹ R. J. Hodges and W. F. Pickering, *Austral. J. Chem.*, 1966, **19**, 981.

⁷² E. Abel, *Monatsh.*, 1953, **84**, 754.

k'_1 was at least one order of magnitude greater than k_1 when $n = 0-3$, but for $n = 4$, $k_1 > k'_1$, indicating the dominant mode of oxidation when $n = 0-3$ was hydrogen atom transfer, but for $n = 4$, where this is impossible, electron transfer was dominant.

Karp and Meites⁵⁹ studied the effect of pH on the two-electron electrochemical oxidation of hydrazine, and found ammonia was produced at intermediate pH, but not at low or high pH. This was explained, using the reaction sequences (7), (6), or (7), (8), (9), by protonation of N_2H_2 , giving $N_2H_3^+$, or deprotonation, giving N_2H^- . Dimerisation of N_2H_2 to N_4H_4 would be inhibited by formation of charged species, and reaction (6) predominates under such conditions.

From the work described the reaction scheme leading to different products when hydrazine is oxidised by transition-metal complexes is now understood, and seems generally applicable. It is less clear how varying the transition-metal complex affects the rate of a particular reaction within the scheme, thus giving the different products. There is evidence, for one-electron oxidants, that complexes labile to substitution oxidise hydrazine *via* N_4H_6 [reactions (2) and (3)] to nitrogen and ammonia, whereas complexes inert to substitution oxidise *via* N_2H_2 [reactions (5) and (6)], producing N_2 alone.⁷³ An investigation of this problem is apparently being made.⁷³ From the work of Karp and Meites⁵⁹ it is clear that pH has an important effect on the rate of some reactions, a factor which has been little considered.

4 Reactions between Hydrazine and Complexes of Second- and Third-row Transition-metals

Reactions between hydrazine and complexes of second- and third-row transition-metals of Groups VII and VIII yield, in addition to hydrazine complexes (*vide supra*), complexes which are the result of redox-reactions of hydrazine. Some contain a ligand obviously derived from hydrazine (*e.g.*, nitride), in others no such ligand is present {*e.g.*, formation of $[(Ph_3P)_4Pt^0]$ }. Some reactions yield hydride complexes, and with these it is never clear whether the hydride is derived directly from hydrazine or is abstracted from the solvent.

There is some correlation between transition-metal group and products of reaction with hydrazine. Nitrido-complexes are often obtained with rhenium, molecular nitrogen complexes with ruthenium and osmium, and hydrides, or complexes of reduced oxidation state, with rhodium, iridium, palladium, and platinum. Therefore discussion of the reactions is divided into these groups.

A. Reactions between Hydrazine and Complexes of Rhenium.—Early investigations of the reaction between hydrazinium(+2) chloride and perrhenate in the presence of triphenylphosphine indicated that $'[(Ph_3P)_2ReCl_2]'$ and $'[(Ph_3P)_2-$

⁷³ A. Brown and W. C. E. Higginson, *Chem. Comm.*, 1967, 725.

The Reactions of Hydrazine with Transition-metal Complexes

ReCl_3] were obtained.⁷⁴⁻⁷⁶ Chatt and co-workers⁷⁷ showed $[(\text{Ph}_3\text{P})_2\text{ReCl}_2]$, was actually a nitrido-complex of rhenium(v), $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$, and other five-co-ordinate $\{[(\text{R}_3\text{P})_2\text{Re}^{\text{V}}\text{NX}_2]$ ($\text{R}_3\text{P} = \text{Pr}^n\text{Ph}_2\text{P}$ or EtPh_2P for $\text{X} = \text{Cl}$; Ph_3P for $\text{X} = \text{Br}$)} and six-co-ordinate $\{[(\text{R}_3\text{P})_3\text{Re}^{\text{V}}\text{NX}_2]$ ($\text{R}_3\text{P} = \text{Et}_2\text{PhP}$ for $\text{X} = \text{Cl}$, Br , or I ; $\text{R}_3\text{P} = \text{Me}_2\text{PhP}$ for $\text{X} = \text{Cl}$ or Br ; $\text{R}_3\text{P} = \text{Et}_3\text{P}$, Pr^n_3P , Pr^n_2PhP , Bu^n_2PhP , MePh_2P , EtPh_2P , or $\text{Pr}^n\text{Ph}_2\text{P}$ for $\text{X} = \text{Cl}$)} derivatives were obtained.^{77,78} The steric requirements of the tertiary-phosphine apparently determine the co-ordination number of the complex.⁷⁸ Recently $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}(\text{NCH}_3)\text{Cl}_3]$ was prepared from 1,2-dimethylhydrazine and $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{OCl}_3]$, and a metathetical reaction gave $[(\text{Et}_2\text{PhP})_2\text{Re}^{\text{V}}(\text{NCH}_3)\text{Cl}_3]$.⁷⁹ From X-ray studies of $[(\text{Et}_2\text{PhP})_3\text{Re}^{\text{V}}\text{NCl}_2]$,⁸⁰ $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$ ⁸¹ and $[(\text{Et}_2\text{PhP})_2\text{Re}^{\text{V}}(\text{NCH}_3)\text{Cl}_3]$ ⁸² Re—N bond lengths of 1.778(11), 1.603(9) and 1.685(11) Å respectively, were determined. $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$ is a very distorted square pyramid.⁸¹ The other molecules are octahedral with chloride *trans*- to the nitrido- or methylimido-ligand.^{80,81}

Chatt,⁷⁶ Wilkinson,⁸³ and co-workers proved that $[(\text{Ph}_3\text{P})_2\text{ReCl}_3]$ was also a rhenium(v) complex, $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{OCl}_3]$, but $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{Cl}_2]$ (which has been prepared by other methods),^{76,83} could be obtained from the reaction also.⁸³ The puzzling situation in which three products $\{[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$, $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{OCl}_3]$ and $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{Cl}_2]\}$ were obtained in high yield from the same reaction was clarified by the discovery that in aqueous ethanol, hydrazinium(+2) chloride, perrhenate, and excess triphenylphosphine yielded $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{Cl}_2]$, but in anhydrous ethanol,⁷⁸ or in the presence of excess hydrochloric acid⁸⁴, $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{OCl}_3]$ was obtained. The latter did not react with hydrazinium(+2) to yield $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$ unless water and excess phosphine were present, when $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{Cl}_2]$ was formed as the first step.⁷⁸ In the formation of $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$ from $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{O}(\text{OEt})\text{Cl}_2]$ and hydrazinium(+2) chloride in aqueous tetrahydrofuran as solvent, ethanol, triphenylphosphineoxide, and ammonium chloride were detected. It was therefore suggested that reduction of a hydrazinium(+1) ligand in an intermediate rhenium(III) complex yielded rhenium(v), ammonium chloride, and the nitrido-ligand. In agreement with this, substitution of $\text{N}_2\text{H}_4(\text{R})\text{Cl}$ ($\text{R} = \text{H}$ or Ph) for $\text{N}_2\text{H}_6\text{Cl}_2$ gave similar products (although yields were lower) but hydrazine hydrate did not give a nitrido-complex.⁷⁸ These reactions are, schematically:

⁷⁴ R. Colton, R. Levitus, and G. Wilkinson, *J. Chem. Soc.*, 1960, 4121.

⁷⁵ M. Freni and V. Valenti, *J. Inorg. Nuclear Chem.*, 1961, 16, 240.

⁷⁶ J. Chatt and G. A. Rowe, *Chem. and Ind.* 1962, 92; *J. Chem. Soc.*, 1962, 4019.

⁷⁷ J. Chatt, J. D. Garforth, and G. A. Rowe, *Chem. and Ind.*, 1963, 332; with N. P. Johnson, *J. Chem. Soc.*, 1964, 1012.

⁷⁸ J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. (A)*, 1969, 2288.

⁷⁹ J. Chatt and J. R. Dilworth, quoted by D. A. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, 8, 703.

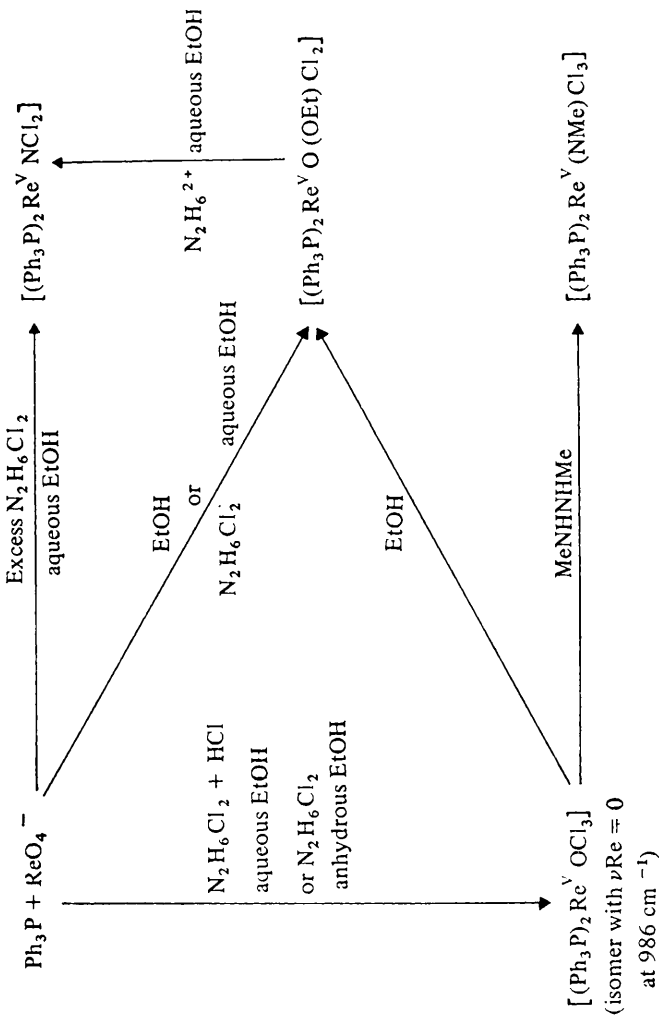
⁸⁰ P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, 6, 197.

⁸¹ R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, 6, 204.

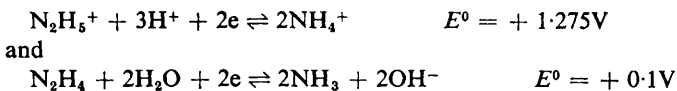
⁸² D. A. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, 8, 703.

⁸³ C. J. L. Lock and G. Wilkinson, *Chem. and Ind.*, 1962, 40; with N. P. Johnson, *J. Chem. Soc.*, 1964, 1054.

⁸⁴ N. P. Johnson, *J. Chem. Soc. (A)*, 1969, 1843.



In addition to these reactions, $[(\text{Et}_2\text{PhP})_3\text{Re}^{\text{III}}\text{Cl}_3]$ was oxidised to $[(\text{Et}_2\text{PhP})_2\text{Re}^{\text{V}}\text{Cl}_4]$ by chlorine or hydrazinium(+2) chloride.⁸⁵ This is one of the few reactions in which hydrazine is clearly an oxidant. Standard potentials for the reactions:



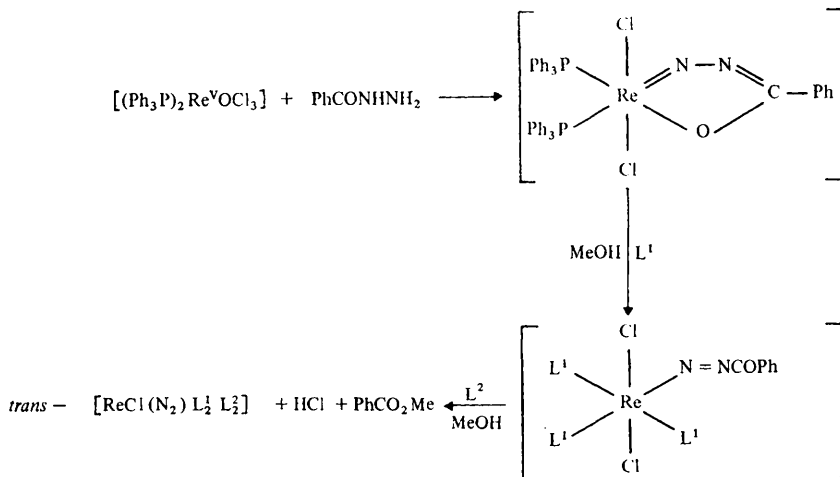
⁸⁵ J. Chatt, J. D. Garforth, N P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 601.

The Reactions of Hydrazine with Transition-metal Complexes

indicate hydrazine is thermodynamically a good oxidant, but for kinetic reasons these reactions are rarely observed.⁴⁹ Other examples of such oxidation are known, *e.g.*, hydrazine oxidised titanium(III) to titanium(IV) in acid-aqueous solution (but not in non-aqueous media)⁸⁶ and $[\text{Ru}^{\text{II}}(\text{NH}_3)_6]^{2+}$ was oxidised to $[\text{Ru}^{\text{III}}(\text{NH}_3)_6]^{3+}$ by hydrazinium(+1) chloride⁸⁷ (*vide infra*). Hydrazine was reported to oxidise chromium(II) to chromium(III)⁸⁸ but this has been questioned.⁸⁹

Re-investigation of $\text{K}_3[\text{Re}^{\text{V}}\text{O}_2(\text{CN})_4]$, prepared by refluxing aqueous potassium cyanide, perhenate, and hydrazine hydrate,⁹⁰ proved the product was a mixture of $\text{K}_3[\text{Re}^{\text{V}}\text{O}_2(\text{CN})_4]$ and $\text{K}_2[\text{Re}^{\text{V}}\text{N}(\text{CN})_4\text{H}_2\text{O}]$.⁹¹ The latter was obtained pure using a large excess of hydrazine and prolonged refluxing,⁹¹ or from excess potassium cyanide and $[(\text{Ph}_3\text{P})_2\text{Re}^{\text{V}}\text{NCl}_2]$.⁸⁴ Structural investigation showed ' $\text{K}_2[\text{Re}^{\text{V}}\text{N}(\text{CN})_4\text{H}_2\text{O}]$ ' contained lattice water, an asymmetrically *trans*-bridging nitrido-ligand ($\text{Re}-\text{N} = 1.53, 2.44 \text{ \AA}$) and, surprisingly, nitrogen-bonded cyanide with a $\text{Re}-\widehat{\text{N}}-\text{C}$ angle of 136° ,⁹² and hence should be reformulated as *trans*- $\text{K}_{2n}[\text{Re}^{\text{V}}(\text{NC})_4\text{N}]_n.n\text{H}_2\text{O}$.

Formation of nitride is the predominant feature of reactions between hydrazine and rhenium complexes. However, reactions yielding molecular nitrogen complexes were discovered recently. Hydrazine and $[\text{Re}(\text{CO})_3\text{L}^1\text{L}^2\text{X}]$ ($\text{L}^1 = \text{PMe}_2\text{Ph}$; $\text{L}^2 = \text{L}^1$ or CO) gave $[\text{Re}(\text{CO})_2(\text{NH}_2)_2\text{N}_2\text{L}^1\text{L}^2]$.⁹³ This reaction may be a special case of general synthesis of $[\text{ReCl}(\text{N}_2)\text{L}_2^1\text{L}_2^2]$ ($\text{L}^1 = \text{mono- or}$



⁸⁶ D. Nicholls and R. Swindells, *J. Chem. Soc.*, 1964, 4204.

⁸⁷ F. Bottomley, *Canad. J. Chem.*, 1970, **48**, 351.

⁸⁸ C. F. Wells and M. A. Salam, *J. Chem. Soc. (A)*, 1968, 1568.

⁸⁹ W. Schmidt, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1968, **7**, 1984.

⁹⁰ G. Morgan and G. R. Davies, *J. Chem. Soc.*, 1938, 1858.

⁹¹ C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 2281.

⁹² W. O. Davies, N. P. Johnson P. Johnson, and A. J. Graham, *Chem. Comm.*, 1969, 737.

⁹³ J. T. Moelwyn-Hughes and A. W. B. Garner, *Chem. Comm.*, 1969, 1309.

equivalent di-tertiary phosphine; $L^2 = L^1$ or CO), developed using benzoyl-hydrazine (see facing page).⁹⁴

The reduction of $[Re^{III}(\text{diars})_2X_2]X$ (diars = *o*-phenylenebisdimethylarsine; X = Cl, Br, or I) to $[Re^{II}(\text{diars})_2X_2]$ by hydrazine hydrate has been mentioned briefly.⁹⁵

B. Reactions between Hydrazine and Complexes of Ruthenium and Osmium.—

Goremykin and Avtokratora⁹⁶ reported $K_2[Ru^{III}Cl_5H_2O]$ and aqueous saturated hydrazinium(+1) chloride formed a red compound, $[Ru_2(N_2H_5)_4(N_2H_4)Cl_6]Cl_4 \cdot HCl$ at room temperature, and a yellow compound, $[Ru_2Cl_2(N_2H_4)_5]Cl_4$, on warming. Powell and Prout⁹⁷ proved ' $[Ru_2Cl_2(N_2H_4)_5]Cl_4$ ' was actually $[Ru^{III}(NH_3)_5Cl]Cl_2 \cdot [Ru_2(N_2H_5)_4(N_2H_4)Cl_6]Cl_4 \cdot HCl$ [which can be obtained only using hydrazinium(+2) chloride] was reformulated as $N_2H_5[Ru^{III}Cl_5N_2H_5] \cdot \frac{1}{2}N_2H_5Cl$,⁹⁷ but further work is obviously necessary on this complex.

Allen and Senoff⁹⁸ and co-workers obtained $[Ru^{II}(NH_3)_5N_2]X_2$ (X = Cl, Br, I, BF_4 , or PF_6) from hydrazine hydrate and chloro-aquo-complexes of ruthenium(III) or (IV). The product was contaminated with $[Ru^{II}(NH_3)_6]X_2$ ^{98b} and a hydrazine complex⁹⁹, and at $-23^\circ C$ a mixture of hydrazine, and nitrogen and dinitrogen complexes of ruthenium(II) was obtained.¹⁰⁰ Pure $[Ru^{II}(NH_3)_5N_2]X_2$ was obtained from $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and N_3^- ,^{98b} and structural investigation indicated a linear $Ru-N \equiv N$ moiety.¹⁰¹ Oxygen is necessary for formation of $[Ru^{II}(NH_3)_5N_2]^{2+}$ from hydrazine and ruthenium complexes, and from the electronic spectrum of the reaction a mechanism involving oxygen oxidation of the intermediate $[Ru^{II}(NH_3)_5(NH=NH)]^{2+}$ was proposed.⁹⁷

Hydrazinium(+1) chloride oxidised $[Ru^{II}(NH_3)_6]^{2+}$ or $[Ru^{II}(NH_3)_5N_2]^{2+}$ to $[Ru^{III}(NH_3)_6]^{3+}$, subsequent substitution giving $[Ru^{III}(NH_3)_5Cl]Cl_2$. Similar oxidation reactions are an integral part of all reactions between ruthenium complexes and hydrazine which yield $[Ru^{III}(NH_3)_5Cl]Cl_2$.⁹⁷ In schematic form the reactions are shown in Scheme 3.

The sole product of the reaction between hydrazine hydrate and $(NH_4)_2[Os^{IV}Cl_6]$ was $[Os^{II}(NH_3)_5N_2]X_2$ (X = Br, I, BF_4 , BPh_4 , PF_6 , or ClO_4), which is more inert than the analogous ruthenium complex.¹⁰² A mixture of $[(Bu^n_2PhP)_3Os^{II}Cl_2(N_2)]$ and $[(Bu^n_2PhP)_3Os^{III}Cl_3]$ (a mixture first thought to be a paramagnetic hydride complex¹⁰³) was obtained from *mer*- $[(Bu^n_2PhP)_3Os^{III}Cl_3]$ and

⁹⁴ J. Chatt, J. P. Dilworth, and G. J. Leigh, *J. Organometallic Chem.*, 1970, **21**, P49; *Chem. Comm.*, 1969, 687.

⁹⁵ J. E. Fergusson, *Co-ordination Chem. Rev.*, 1966, **1**, 459.

⁹⁶ V. I. Goremykin and T. D. Avtokratora, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk.*, 1947, 427.

⁹⁷ C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1962, 137.

⁹⁸ (a) A. D. Allen and C. V. Senoff, *Chem. Comm.*, 1965, 621; (b) with F. Bottomley, R. O. Harris, and V. P. Reinsalu, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

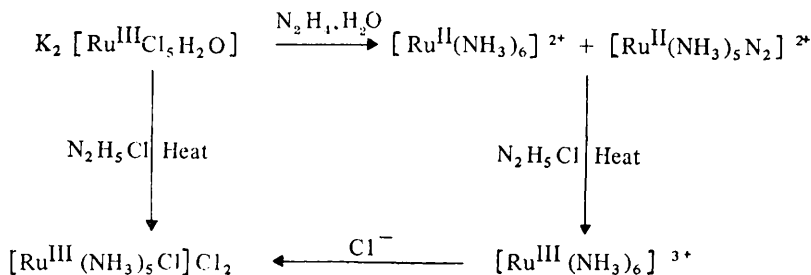
⁹⁹ J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Fergusson, *Nature*, 1969, **221**, 551; with J. L. Love and A. B. Nikolsky, *J. Chem. Soc. (A)*, 1970, 1479.

¹⁰⁰ J. E. Fergusson and J. L. Love, *Chem. Comm.*, 1969, 399.

¹⁰¹ F. Bottomley and S. C. Nyburg, *Chem. Comm.*, 1966, 897; *Acta Cryst.*, 1968, **B24**, 1289.

¹⁰² A. D. Allen and J. R. Stevens, *Chem. Comm.*, 1967, 1147.

¹⁰³ J. Chatt, G. J. Leigh, and R. J. Paske, *Chem. Comm.*, 1967, 671.



Scheme 3

hydrazine hydrate.¹⁰⁴ A series of complexes $[(\text{R}_3\text{P})_3\text{Os}^{\text{II}}\text{X}_2(\text{N}_2)]$ ($\text{X} = \text{Cl}$ for $\text{R}_3\text{P} = \text{Me}_2\text{PhP}$, Et_2PhP , Pr^n_2PhP , Bu^n_2PhP , EtPh_2P , or Et_3P ; $\text{X} = \text{Br}$ for $\text{R}_3\text{P} = \text{Me}_2\text{PhP}$ or Et_2PhP) has now been prepared by reduction of *mer*- $[(\text{R}_3\text{P})_3\text{Os}^{\text{III}}\text{Cl}_3]$ with zinc in tetrahydrofuran under nitrogen.¹⁰⁶ However, in the presence of excess Pr^n_3As , reduction of $[(\text{Pr}^n_3\text{As})_2\text{Os}^{\text{IV}}\text{Cl}_4]$ with hydrazine hydrate gave $[(\text{Pr}^n_3\text{As})_3\text{Os}^{\text{III}}\text{Cl}_3]$.¹⁰⁸ In the light of results with phosphine complexes, this reaction would bear re-investigation.

Hydrazine catalysed the *mer*- to *fac*- isomerisation of *mer*- $[(\text{Bu}^n_2\text{PhP})_3\text{Os}^{\text{III}}\text{Cl}_3]$.¹⁰⁷ In view of the known reduction of $[(\text{Bu}^n_2\text{PhP})_3\text{Os}^{\text{III}}\text{Cl}_3]$ to $[(\text{Bu}^n_2\text{PhP})_3\text{Os}^{\text{II}}\text{Cl}_2(\text{N}_2)]$ ¹⁰⁴ it is possible the isomerisation proceeds *via* redox reactions of hydrazine and osmium(III).

In contrast to rhenium, reduction of $\text{K}[\text{Os}^{\text{VIII}}\text{O}_3\text{N}]$ with hydrazinium(+ 2) chloride in ethanol in the presence of Et_2PhP gave $[(\text{Et}_2\text{PhP})_3\text{Os}^{\text{III}}\text{Cl}_3]$, and a mixture of hydrazinium(+ 2) chloride, $\text{K}[\text{Os}^{\text{VIII}}\text{O}_3\text{N}]$ and triphenylphosphine gave $[(\text{Ph}_3\text{P})_2\text{Os}^{\text{III}}(\text{NH}_3)\text{Cl}_3]$, which was also obtained from hydrazinium(+ 2) chloride and $[(\text{Ph}_3\text{P})_2\text{Os}^{\text{V}}\text{OCl}_3]$.¹⁰⁸

C. Reactions between Hydrazine and Complexes of Rhodium and Iridium.—Bath and Vaska¹⁰⁸ reported a remarkable reaction in which excess 95% aqueous hydrazine and ethanolic *trans*- $[(\text{Ph}_3\text{P})_2\text{M}^{\text{I}}\text{Cl}(\text{CO})]$ ($\text{M} = \text{Rh}$ or Ir) formed $[(\text{Ph}_3\text{P})_3\text{M}^{\text{I}}\text{H}(\text{CO})]$. The rhodium complex is a trigonal-bipyramid with CO *trans*- to hydride and an Rh—H bond length of 1.60(12) Å.¹⁰⁹

Hydrazine catalytically increases the rate of substitution of ligands at rhodium(III). Such reactions have been studied kinetically, *e.g.*, hydrolysis of *trans*- $[\text{Rh}^{\text{III}}\text{en}_2\text{XY}]^+$ ($\text{X} = \text{Cl}$, Br , or I for $\text{Y} = \text{Cl}$, Br , or I)^{110, 111} (from which reaction hydrazine complexes were isolated¹¹⁰) and displacement of X by Y

¹⁰⁴ J. Chatt, G. J. Leigh, and D. M. P. Mingos, *Chem. and Ind.*, 1969, 109.

¹⁰⁵ J. Chatt, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1969, 515.

¹⁰⁶ J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. (A)*, 1968, 2636.

¹⁰⁷ J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1969, 1674.

¹⁰⁸ S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, 85, 3500.

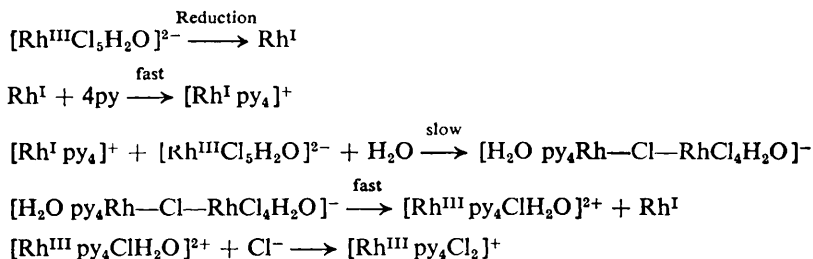
¹⁰⁹ S. J. LaPlaca and J. A. Ibers, *Acta Cryst.*, 1965, 18, 511.

¹¹⁰ D. J. Baker and R. D. Gillard, *Chem. Comm.*, 1967, 520.

¹¹¹ F. Basolo, E. J. Bounsall, and A. J. Poe, *Proc. Chem. Soc.*, 1963, 366.

in *trans*-[Rh^{III} en₂XY]⁺ (X = I; Y = Cl or Br).¹¹² Similar catalytic reactions were employed in the synthesis of rhodium(III) complexes starting from hydrated rhodium trichloride or K₂[Rh^{III}Cl₅H₂O], e.g., *trans*-[Rh^{III} py₄Cl₂]Cl (py = pyridine),^{113,114} [Rh^{III} bipy₂Br₂]Br (bipy = 2,2'-bipyridyl),¹¹¹ and [Rh^{III} phen₂Cl₂]Cl (phen = 1,10-phenanthroline).^{114,115} The latter complexes appear to be *cis*-isomers, although this has not been proven conclusively.¹¹⁶

Hydrazine and sodium borohydride were very efficient catalysts, although other compounds (e.g., hypophosphorous acid¹¹⁴) were used, and the solvent (ethanol) also acts as a catalyst.¹¹³ Because these compounds produced hydride complexes in other reactions, it was postulated that hydrides were the reactive intermediates in rhodium(III) catalysis.^{112,114} However, investigation of the formation of *trans*-[Rh^{III} py₄Cl₂]Cl showed [Rh^I(CO)₂Cl]₂ was a better catalyst than sodium borohydride,¹¹⁵ indicating a hydride complex was not involved. Kinetic results were consistent with the mechanism given in Scheme 4.¹¹³



Scheme 4

This is in agreement with the observation that the product was exclusively the *trans*-isomer and [Rh^{III} py₃Cl]²⁺ was not obtained even with excess pyridine. The [Rh^I(CO)₂Cl]₂ catalysed reaction was inhibited by 1,10-phenanthroline, probably due to rapid formation of a non-oxidisable 1,10-phenanthroline complex of rhodium(I),¹¹⁵ thus removing rhodium(I) from reaction. This inhibition cannot be explained by a hydride intermediate.

The synthesis of *cis*-[Rh^{III} phen₂Cl₂]Cl¹¹⁴ is not a true catalytic reaction, since the quantity of hydrazine used and the reaction conditions (boiling ethanol) are sufficient to reduce all the rhodium(III) to rhodium(I).¹¹⁵ No [Rh^{III} phen₂Cl₂]Cl was formed using catalytic quantities of hydrazine. Formation of the *cis*-isomer precludes the chain-mechanism, but from the evidence rhodium(I) must be involved, though how it is re-oxidised to rhodium(III) is unknown. The results with rhenium and ruthenium suggest the oxidant may be hydrazine.

Finally, substitution reactions of *trans*-[Ir^{III} en₂Cl₂]⁺ were not catalysed by hydrazine or hypophosphorous acid, in contrast to the rhodium analogue, and this was ascribed to the unfavourable standard potential for reduction of

¹¹² H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc. (A)*, 1966, 1275.

¹¹³ J. V. Rund, F. Basolo, and R. J. Pearson, *Inorg. Chem.*, 1964, 3, 658.

¹¹⁴ R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 1951.

¹¹⁵ J. V. Rund, *Inorg. Chem.*, 1968, 7, 24.

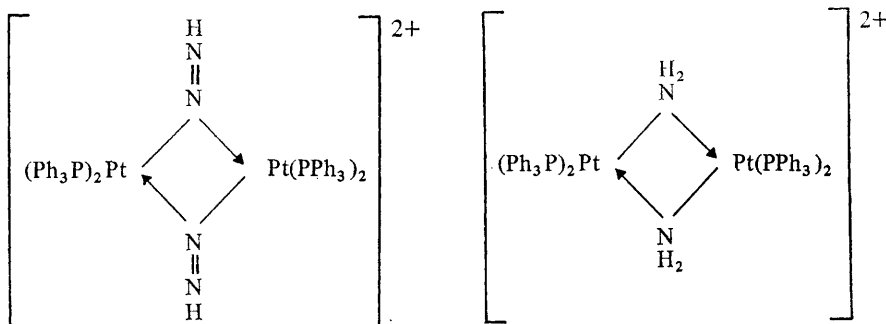
¹¹⁶ R. D. Gillard and B. T. Heaton, *J. Chem. Soc. (A)*, 1969, 451.

trans-[Ir^{III}en₂Cl₂]⁺ to iridium(i).¹¹⁷

D. Reactions between Hydrazine and Complexes of Palladium and Platinum.—Reactions between hydrazine and *cis*-dihalogenobis(tertiary phosphine)platinum(II) have received considerable attention for over ten years. Chatt, Duncanson, and Shaw¹¹⁸ prepared the first air-stable hydride complexes, *trans*-[(R₃P)₂Pt^{II}HX] (R₃P = Ph₃P, Me₃P, Prⁿ₃P, Et₃P, or EtPh₂P; X = Cl or Br) by refluxing 85% aqueous hydrazine hydrate and *cis*-[(R₃P)₂Pt^{II}Cl₂] in ethanol. A product believed to be *cis*-[(Ph₃P)₂Pt^{II}HCl], obtained from the same reaction in methanol,¹¹⁹ has been shown to be a different crystalline form of *trans*-[(Ph₃P)₂Pt^{II}HCl].¹²⁰ Malatesta and co-workers,^{121–123} from a similar reaction to that of Chatt *et al.*, but using 10% alcoholic *anhydrous* hydrazine, obtained the planar triangular complex [(Ph₃P)₃Pt⁰].

Refluxing [(R₃M)₂Pt^{II}X₂] (M = P for R = Ph or PhO and X = Cl or Br; M = As for R = Ph or *p*-ClC₆H₄ and X = Cl or Br) with 10% alcoholic anhydrous hydrazine and excess tertiary phosphine or arsine gave [(R₃M)₄Pt⁰], though {[(*p*-ClC₆H₄)₃P]₂Pt^{II}Cl₂} yielded {[(*p*-ClC₆H₄)₃P]₃Pt⁰}, the tetrakis-complex being unobtainable.¹²¹ [(Ph₃P)₂Pd^{II}I₂] and 10% alcoholic anhydrous hydrazine produced palladium metal, but with excess of the appropriate phosphine [(Ph₃P)₃Pd⁰] and {[(*p*-CH₃C₆H₄)₃P]₃Pd⁰} were obtained.¹²⁴

Mason and co-workers¹²⁵ obtained a compound of empirical formula (Ph₃P)₂PtClN₂H {which decomposed on warming in benzene to give [(Ph₃P)₂Pt^{II}HCl]} on cooling ethanolic 85% aqueous hydrazine hydrate and [(Ph₃P)₂Pt^{II}Cl₂] to -78 °C. The structure of a tetraphenylborate salt (prepared by metathesis) showed it contained a mixture of bridged amido- and dehydrodi-imide-complexes:¹²⁵



¹¹⁷ R. A. Bauer and F. Basolo, *Chem. Comm.*, 1968, 458.

¹¹⁸ J. Chatt, L. A. Duncanson, and B. L. Shaw, *Proc. Chem. Soc.*, 1957, 343; J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

¹¹⁹ J. C. Bailar and H. Itatani, *Inorg. Chem.*, 1965, 4, 1618.

¹²⁰ A. F. Clemmit and F. Glockling, *J. Chem. Soc. (A)*, 1969, 2163.

¹²¹ L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

¹²² L. Malatesta and R. Ugo, *J. Chem. Soc.*, 1963, 2080.

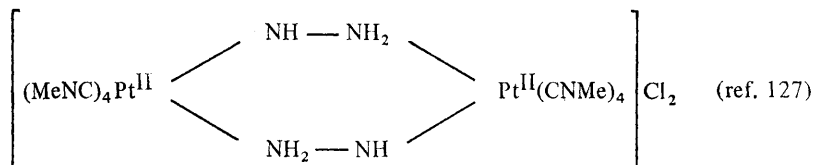
¹²³ V. Albano, P. L. Ballon, and V. Scatturin, *Chem. Comm.*, 1966, 507.

¹²⁴ L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186.

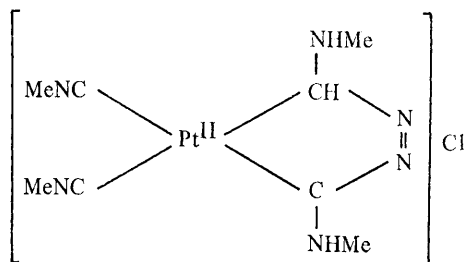
¹²⁵ G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Comm.*, 1967, 739.

The asymmetric species with one bridging amide and one bridging dehydrodiimide may also be present. An analogous but less stable palladium complex was obtained. With *excess* hydrazine at 40—50 °C a mixture of $[(\text{Ph}_3\text{P})_2\text{Pt}^0]$ ¹²⁶ and $[(\text{Ph}_3\text{P})_3\text{Pt}^0]$ was obtained, this mixture also being formed by treatment of $[(\text{Ph}_3\text{P})_2\text{Pt}^{\text{II}}\text{HCl}]$ with excess hydrazine.¹²⁵ This suggests *trans*- $[(\text{Ph}_3\text{P})_2\text{Pt}^{\text{II}}\text{HCl}]$ is the initial product of all reactions of hydrazine with *cis*- $[(\text{Ph}_3\text{P})_2\text{Pt}^{\text{II}}\text{Cl}_2]$, and the different reactions of 85% aqueous hydrazine and anhydrous hydrazine may be rationalised as the effect of concentration.

Addition of hydrazine to aqueous tetrachloroplatinite(II) containing excess methyl isocyanide gave a complex formulated as



This formulation was shown to be incorrect, and the structure



proposed.¹²⁸ Carbene complexes of platinum(II) have been obtained independently, from primary amines and isocyanide complexes.¹²⁹

5 Reactions of Hydrazines resulting in Insertion of a Nitrogen Atom into a Metal–Carbon Bond

Fischer and Aumann¹³⁰ reported the reaction:

¹²⁶ R. Ugo, F. Ceriati and G. LaMonica, *Chem. Comm.*, 1966, 868.

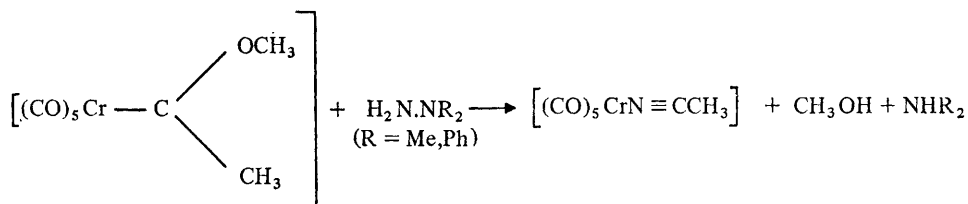
¹²⁷ L. Chugaev, M. Skanavy, and A. Posniak, *Z. anorg. Chem.*, 1925, **148**, 37.

¹²⁸ G. Rouschias and B. L. Shaw, *Chem. Comm.*, 1970, 183.

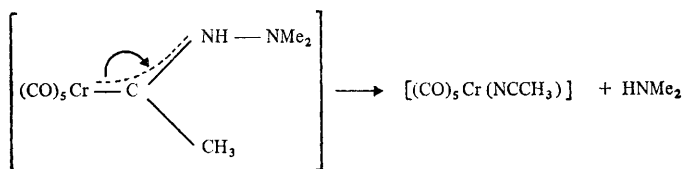
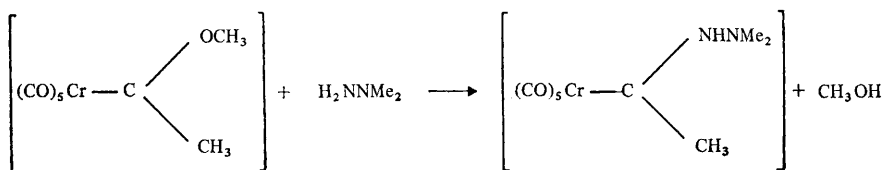
¹²⁹ E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Comm.*, 1969, 1322.

¹³⁰ E. O. Fischer and R. Aumann, *Angew. Chem. Internat. Edn.*, 1967, **6**, 181.

The Reactions of Hydrazine with Transition-metal Complexes

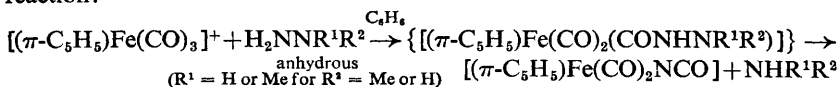


The mechanism was thought to involve nucleophilic attack of hydrazine at the carbene-carbon atom:



By a similar reaction, *cis*-[(Ph₃P)(CO)₄W(C(OCH₃)CH₃)] gave *cis*-[(Ph₃P)(CO)₄W(NCCH₃)].

Angelici and Busetto¹³¹ prepared isocyanate complexes by the insertion reaction:



For N₂H₄ and N₂H₃Me a very unstable intermediate was isolated, which, from i.r. evidence and by analogy with the known [(π-C₅H₅)Fe(CO)₂(CONHR)],¹³² was thought to be [(π-C₅H₅)Fe(CO)₂(CONHNHR)]. Therefore the reaction was believed to proceed *via* nucleophilic attack of hydrazine at a carbonyl-carbon atom. By a similar reaction (although no attempt was made to isolate the intermediate) (Ph₄As)[W(CO)₅NCO] was obtained from [W(CO)₆] and hydrazine.

The author thanks Dr. J. Passmore for helpful comments on this review.

¹³¹ R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, 1969, **91**, 3197.

¹³² L. Busetto and R. J. Angelici, *Inorg. Chim. Acta.*, 1968, **2**, 391.