Coordination Chemistry Reviews, 51 (1983) 69–98
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TRANSITION METAL NITROSYLS IN ORGANIC SYNTHESIS AND IN POLLUTION CONTROL

KRISHNA KUMAR PANDEY *

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen (West Germany)

(Received 15 September 1982; in revised form 22 February 1983)

CONTENTS

STRUCTURES

(I)	4-Vinylcyclohexene
(II)	1,4-Dimethyl-4-vinylcyclohexene
(III)	1,5-Dimethyl-5-vinylcyclohexene
(IV)	4-Isopropenyl-1-methylcyclohexene
(V)	5-Isopropenyl-1-methylcyclohexene
(VI)	1,3-Dimethyl-4-vinylcyclohexene
(VII)	2,4-Dimethyl-4-vinylcyclohexene
(VIII)	Exo-*trans*-exo norbornadiene dimer
(IX)	Exo-*trans*-endo norbornadiene dimer

---

* On leave from the Department of Chemistry, University of Indore, India.

0010-8545/83/$09.00

(X) Norbornadiene dimer
(XI) Benzonorbornadiene dimer
(XII) 7-Isopropylidenebenzonorbornadiene dimer
(XIII) 7-Oxobenzonorbornadiene dimer
(XIV) Crossed dimer of benzonorbornadiene and norbornadiene

A. INTRODUCTION

The metal nitrosyls have had a curious and dramatic history. As early as 1934, it had been recognized that nitric oxide could lose or gain one electron in its bonding interaction with transition metals [1] to give complexes of NO^+ and NO^- [2] or complexes in which NO serves as a three-electron donor or a one-electron donor [3]. As pointed out by Ibers and co-workers [4], the mode of coordination of the metal nitrosyl group in a complex is dependent on the relative energies of the π^* orbital of the NO and the *d* orbital of the metal. If there exists an empty low energy *d* orbital on the metal, the pair of electrons forming the coordinated bond will be localized on the metal and the ligand may be described as NO^+; if not, the electrons will fill the π^* orbital of the nitrosyl and the species may be written as NO^-.

A number of review articles treating different aspects of chemistry of metal nitrosyl complexes have been published [5–18]. Several of these are comprehensive [6,9,11,14], while others are specialized in the areas of nitrosyl structure [10,18], NO bonding [12], organometallic nitrosyls [7], synthetic methods and reactions of coordinated NO [17]. This article treats the chemistry of metal nitrosyls from the standpoint of organic synthesis and pollution control.

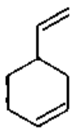
B. TRANSITION METAL NITROSYLS IN ORGANIC SYNTHESIS

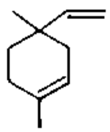
(i) Introduction

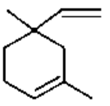
The electronic and steric properties of the nitric oxide ligand are similar to those of the carbonyl ligand. The transition metal nitrosyls have as yet attracted less attention than metal carbonyls. Some metal nitrosyls are useful as selective homogeneous catalysts, while others undergo reactions at the coordinated nitric oxide ligand to give N-bonded organic compounds. The purpose of this section of the article is to summarize the latest developments of transition metal nitrosyls in organic synthesis. The reactions of metal nitrosyls can be divided into two main groups. They are (a) catalytic reactions and (b) reactions of the coordinated NO group.

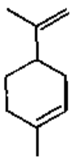
(ii) Oligomerization

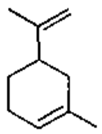
A wide variety of olefin self-condensation reactions occur via transition metal nitrosyl complexes and lead to oligomers. The dimerization of butadiene, isoprene and norbornadiene have been known for a considerable time. The catalytic routes to the products have been extensively investigated as thermal dimerization is a rather inefficient process. The oligomerization of butadiene, isoprene, norbornadiene (nbd) and phenylacetylene has been achieved using a number of nitrosyl complexes of iron and cobalt (Table 1). Codimerization of butadiene with isoprene, chloroprene, and norbornadiene is dominated by the formation of (I). This indicates that the dimerization of butadiene occurs first followed by the codimerization reactions [19]. The higher percentage conversion with (π-allyl) $Fe(CO)_2(NO)$ (97%) as compared to $Fe(CO)_2(NO)_2$ (77%) indicates that the reaction of butadiene with $Fe(CO)_2(NO)_2$ proceeds through π-allyl derivatives. The dimerization of butadiene is not observed with $Ni(CO)_4$ alone which indicates that in the catalytic systems $M(NO)_2X + Ni(CO)_4$ ($M = Fe$ or Co), the catalyst is not a nickel species but rather iron or cobalt nitrosyl moieties. The catalytic activity decreases from chloride to iodide ($Cl > Br > I$) which is in order of increasing M–X bond strength and increasing *trans* effect [25]. The yield of isoprene dimers in the case of BF_4^-, PF_6^-, or ClO_4^- is 5%, while with BPh_4^- the yield is 90%. This difference in yield was explained by an increase of the cationic character of the cobalt(I) ion.

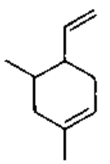

(I)

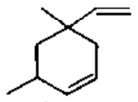

(II)

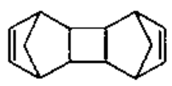

(III)

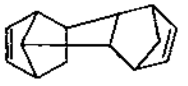

(IV)


(V)


(VI)


(VII)


(VIII)


(IX)

$Fe(NO)_2(PPh_3)_2$ does not dimerize the nbd because the triphenylphos-

TABLE 1

Oligomerization of olefins

Substrate	Catalyst	Products	Ref.
Butadiene	$Fe(CO)_2(NO)_2$	(I) (100%)	19
	$Fe(CO)_2(NO)_2$–$Al(C_2H_5)_3$ (1 : 1)	(I)	19
	$Fe(CO)_2(NO)_2$–PPh_3 (1 : 1)	(I)	19
	$Fe(CO)_2(NO)_2$–C_5H_5N (1 : 1)	(I)	19
	(π-allyl)–$Fe(CO)_2(NO)$	(I)	19
	$Co(CO)_3(NO)$	(I) (5%)	19
	$Mn(CO)(NO)_3$	(I) (5%)	19
	$[Fe(NO)_2Cl]_2 + Zn$ (or Cu)	(I) (100%)	20
	$Na[Fe(CO)_3(NO)]$	(I) (100%)	21
	$Na[Fe(CO)_3(NO)] + A$	(I) (99.5–100%)	21
	($A = HgCl_2$, $Hg(CN)_2$, $ZnCl_2$, $CoCl_2$, $FeCl_2$, $FeBr_2$, FeI_2, $NiCl_2$, $FeCl_3$)		
	$Na[Fe(CO)_3(NO)]\,[Fe(NO)_2Cl]_2$	(I) (100%)	21,22
	$Na[Fe(CO)_3(NO)] + [Fe(NO)_2Br]_2$	(I) (100%)	21,22
	$Na[Fe(CO)_3(NO)] + [Fe(NO)_2I]_2$	(I) (100%)	21,22
	$Na[Fe(CO)_2(C_5H_5)] + [Fe(NO)_2Cl]_2$	(I) (100%)	21,22
	$Na[Co(CO)_4] + [Fe(NO)_2Cl]_2$	(I) (100%)	21,22
	$Na[Co(CO)_4] + Co(NO)_2Cl$	(I) (Conversion, 58%)	21,22
	$Fe(NO)_2Cl + C_3H_5MgBr$	(I) (100%)	23
	$Fe(NO)_2Cl + (C_3H_5)_4Sn$	(I) (100%)	24
	$Fe(NO)_2X + Ni(CO)_4$	(I) (100%)	25
	$Fe(NO)_2X + Fe(CO)_5$	(I) (100%)	25
	$Co(NO)_2X + Ni(CO)_4$	(I) (100%)	25
	$Co(NO)_2X + Fe(CO)_5$	(I) (100%)	25
	($X = Cl$, Br, I)		
	$Fe(NO)_2(THF)_n$	(I) (100%)	26

Isoprene	$Fe(CO)_2(NO)_2$	**(II)** (40%), **(III)** (30%), **(IV)** (25%)	19
	(π-allyl)$Fe(CO)_2(NO)$	**(II)**, **(III)**, **(IV)**	19
	$[Co(NO)_2Br]_2$	**(II)**, **(IV)**, **(VI)**	27
	$[Co(NO)_2Cl]_2 + AgBF_4$	**(II)**, **(VI)**, 1,2,4-triphenylbenzene	27
	$[Co(NO)_2Cl]_2 + AgPF_6$	1,2,4-Triphenylbenzene	27
	$[Co(NO)_2Cl]_2 + AgClO_4$	**(II)**	27
	$[CO(NO)_2Cl]_2 + NaBPh_4$	1,2,4-Triphenylbenzene	27
	$[Fe(NO)_2Cl]_2 + Zn$ (or Cu)	**(II)**, **(VII)** (96%)	20
	$[Fe(NO)_2Cl] + Ni(CO)_4$	**(II)**+**(III)** (68%); **(IV)** (32%)	25
	$[Fe(NO)_2Cl] + Ni(CO)_4$	**(II)**+**(III)** (73%); **(IV)** (27%)	25
	$[Fe(NO)_2(THF)_n]$	**(II)**+**(VII)** (94%); **(IV)**+**(V)** (6%)	26
Isoprene + butadiene	$Fe(CO)_2(NO)_2$	**(I)**, **(II)**, **(III)**, **(IV)** and methyl substituted **(I)**	19
Norbornadiene	$Fe(CO)_2(NO)_2$	**(VIII)** (87%), **(IX)** (13%)	28
	$Co(CO)_3(NO)$	**(VIII)**, **(IX)**, **(X)**	28
	$[Co(NO)_2(nbd)]PF_6$	Five dimers	27
	$[Co(NO)_2Cl]_2 + AgPF_6$	Five dimers	27
	$[Co(NO)_2Cl]_2 + NaBPh_4$	**(VIII)** (98%)	27
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + AgBF_4$	**(VIII)** (88%)	30
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + AgPF_6$	**(VIII)** (94%)	30
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + NaBPh_4$	**(VIII)** (95%)	30
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + AgClO_4$	**(VII** (95%)	30
	$[Fe(NO)_2Cl]_2 + Zn$ (or Cu)	**(VIII)**	20
	$Fe(NO)_2Cl + Ni(CO)_4$	**(VIII)** (90%), **(IX)** (9.5%)	25
	$Fe(NO)_2Cl + Fe(CO)_5$	**(VIII)** (87.5%), **(IX)** (11.5)	25
	$Fe(NO)_2(THF)_n$	**(VIII)** (93%), **(IX)** (7%)	26
Benzonorbornadiene	$Fe(CO)_2(NO)_2$	**(XI)**	29
7-Isopropylidene benzonorbornadiene	$Fe(CO)_2(NO)_2$	**(XII)**	29
7-Oxo benzonorbornadiene	$Fe(CO)_2(NO)_2$	**(XIII)**	29
Benzonorbornadiene + norbornadiene	$Fe(CO)_2(NO)_2$	**(VIII)**, **(XI)**, **(XIV)**	29

TABLE 1 (continued)

Substrate	Catalyst	Products	Ref.
Phenylacetylene	$[Co(NO)_2Br]_2$	1,4-Diphenylbutadiene, 1,2,4-triphenylbenzene and linear oligomers	27
	$[Co(NO)_2(Me_2CO)_n]BPh_4$	1,4-Diphenylbutadiene (25%), 1,2,4-triphenylbenzene (25%), linear oligomers (50%)	27
	$[Fe(NO)_2Cl]_2$ + Zn (or Cu) + THF	1,2,4-Triphenylbenzene (55%)	20
2-Methylpropene	$[Rh(NO)(NCMe)_4][BF_4]_2$	Dimers (19%), trimers (40%), tetramers (14%)	31

phine ligands are not replaced by nbd. This indicates that dimerization proceeds via the replacement of carbonyl groups from $Fe(CO)_2(NO)_2$ by the diene [28]. Refluxing nbd for 63 h with the complex $[Co(NO)_2(nbd)]PF_6$ yields a mixture of five dimers, while no reaction occurs at room temperature [27]. The mixture $[Co(NO)_2Cl]_2 + NaBPh_4$ dimerizes nbd easily to one isomer (**VIII**) even at 0°C. These significant results were explained by the tightness of the $[Co]^+X^-$ ion pair and the propensity of the BPh_4^- ion to interact with metallic centers. The dimerization of nbd with the catalytic system $[Fe(NO)_2Cl]_2$ + Cu (or Zn) is solvent dependent, the activity of the system increasing with polarity. The systems with dichloromethane, tetrahydrofuran and acetone are more active than with the more strongly coordinating acetonitrile and methanol [20].

The complex $[Rh(NO)(NCMe)_4](BF_4)_2$ catalyzes the oligomerization of 2-methylpropene to give dimers, trimers and tetramers, although the formation of the trimer is suppressed in the presence of *cis*-2-butene. This suggests that alkene coordination to an η^3-allyl intermediate is an essential step [31].

(iii) Polymerization of olefins

The rhodium nitrosyl complex $[Rh(NO)(NCMe)_4](BF_4)_2$ catalyzes the polymerization of 1,3-butadiene to *trans*-1,4-polybutadiene (95%) [31]. Some cationic nitrosyl complexes of cobalt and iron with different counter anions have been reported to induce polymerization of olefins (Table 2). The higher yield of polyisoprene for $X = PF_6^-$ than for BPh_4^- is thought to be due to an

TABLE 2

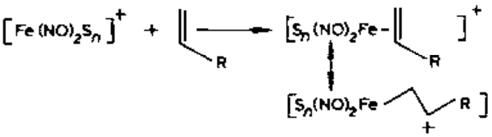
Polymerization of olefins

Unsaturated substrate	Catalyst	Reaction conditions		Selectivity (%)	Ref.
		T(°C)	t(h)		
Isoprene	$[Co(NO)_2Cl]_2 + AgX$ $(X = BF_4, PF_6, ClO_4)$	34	19	95	27
	$[Co(NO)Cl]_2 + NaBPh_4$	34	19	10	27
Acrylonitrile	$\frac{1}{2}[Fe(NO)_2Cl]_2 + NaBPh_4$	78	22	100	30
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + AgX$ $(X = BF_4, PF_6)$	78	22	100	30
	$[Fe(NO)_2L_n]BPh_4$ $(L = CH_3CN, C_2H_3CN)$	78	22	100	30
Styrene	$[Co(NO)_2Cl]_2 + AgPF_6$ (or $NaBPh_4$)	25	19	100	27
	$\frac{1}{2}[Fe(NO)_2Cl]_2 + AgX + CH_2Cl_2$	0	22	100	30,32
	$[Fe(NO)_2(MeCN)_n]PF_6$	0	22	100	30
	$[Fe(NO)_2(PPh_3)_2]PF_6$	0	22		30

increase in the cationic character of the cobalt(I) ion which is evidenced with a concomitant shift of the NO stretching frequencies in the complexes $[\mathrm{Co(NO)_2(CH_3CN)_2}]\,\mathrm{PF_6}$ and $[\mathrm{Co(NO)_2(CH_3CN)}]\mathrm{BPh_4}$ (respectively 1910, 1810 and 1750, 1720 $\mathrm{cm^{-1}}$). The cationic iron nitrosyl complexes $[\mathrm{Fe(NO)_2S}_n]^+\ \mathrm{X}^-$ (S = solvent), prepared by a metathetical exchange between Cl^- and the counter anion of Ag^+ or Tl^+ (eqn. 1), are active catalysts for the polymerization of acrylonitrile, styrene, α-methylstyrene, isobutene, tetrahydrofuran and styrenemethylmethacrylate [30,32].

$$[\mathrm{Fe(NO)_2Cl}]_2 + 2\,\mathrm{AgX} \xrightarrow{\text{solvent}} 2[\mathrm{Fe(NO)_2S}_n]^+\mathrm{X}^- + 2\,\mathrm{AgCl} \tag{1}$$

Polymer yields increase with temperature: 3% at −20°C, 39% at −10°C, 70% at 0°C and 100% at 20°C in the case of $[\mathrm{Fe(NO)_2S}_n]\mathrm{BF_4}$. Polymerization activity with $[\mathrm{Fe(NO)_2(PPh_3)_2}]^+$ and $[\mathrm{Fe(NO)_2(MeCN)}_n]^+$ has been examined. This suggests that styrene polymerization requires free coordination sites on the metal ion, since coordinated acetonitrile is displaced to some extent by excess styrene, while triphenylphosphine is not [32]. The mechanism of the polymerization reactions is not clear, but the initiation step has been attributed to coordination of the monomer to the metal ion (eqn. 2) [32].



(2)

(iv) Chemical oxidation

The Pd(II) and Pt(II) catalyzed oxidations of olefins are important reactions in organic synthesis. An aqueous solution of palladous chloride in the presence of nitric oxide oxidizes alkenes of the type $\mathrm{RCH{=}CH_2}$ (R = H or alkyl) to ketones. For example, propene is oxidized to acetone [33] (eqns. 3 and 4).

$$2\,\mathrm{PdCl_2} + 2\,\mathrm{NO} + \mathrm{H_2O} \rightarrow \mathrm{Pd(NO)Cl} + [\mathrm{Pd(NO)_2Cl_3}]^{2-} + 2\,\mathrm{H}^+ \tag{3}$$

$$[\mathrm{Pd(NO)_2Cl_3}]^{2-} + \mathrm{RCH{=}CH_2} \rightarrow \mathrm{Pd(NO)Cl} + \mathrm{RCOCH_3} + 2\,\mathrm{Cl}^- \tag{4}$$

The catalytic oxidation of triphenylphosphine to the oxide using ruthenium nitrosyl complexes such as $\mathrm{Ru(NO)X(O_2)(PPh_3)_2}$ (X = Cl, OH, CN or NCS) has been reported [34,35]. The catalytic activity is dependent on X^- and decreases in the order $\mathrm{NCS}^- > \mathrm{CN}^- > \mathrm{Cl}^- > \mathrm{OH}^-$. The proposed mechanism using $\mathrm{Ru(CO)(NO)(NCS)(PPh_3)_2}$ and $\mathrm{Ru(NO)(NCS)(O_2)(PPh_3)_2}$ as catalysts is given in the following scheme.

$$Ru(CO)(NO)(NCS)(PPh_3)_2 \underset{CO}{\overset{O_2}{\rightleftharpoons}} Ru(NO)(NCS)(O_2)(PPh_3)_2 \qquad (5)$$

$$\begin{tikzcd} Ru(NO)(NCS)(O_2)(PPh_3)_2 \arrow[r, leftrightharpoons, "PPh_3"] & Ru(NO)(NCS)(O_2)(PPh_3)_3 \arrow[d, "\text{slow}"] \\ Ru(NO)(NCS)(PPh_3)_2 \arrow[u, "{O_2,\ \text{fast}}"] & Ru(NO)(NCS)(PPh_3)(OPPh_3)_2 \arrow[l, "PPh_3", "(-2OPPh_3)"'] \end{tikzcd}$$

The $Ru(NO)(NCS)(O_2)(PPh_3)_2$ complex also catalyzes the oxidation of triphenylarsine, 1-hexene and cyclohexene [35].

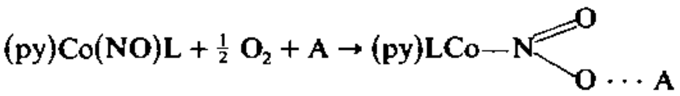
Tovrog et al. have recently shown that the cobalt nitrosyl complex [Co(NO)(saloph)] (saloph = N,N^1-bis(salicylidene)-*o*-phenylenediamine) reacts with O_2 in the presence of a Lewis base (pyridine) to give the complex $(py)Co(NO_2)(saloph)$ which catalyzes the O_2 oxidation of PPh_3 to $OPPh_3$ (eqns. 6 and 7) [36].

$$Co(NO)(saloph) + py + \tfrac{1}{2}\, O_2 \rightarrow (py)Co(NO_2)(saloph) \qquad (6)$$

$$(py)Co(NO_2)(saloph) + PPh_3 \rightarrow (py)Co(NO)(saloph) + OPPh_3 \qquad (7)$$

The catalytic cycle is completed by reoxidation of the nitrosyl ligand by O_2. The catalytic activity of the system decreases on decreasing the amount of pyridine due to the formation of the less active $Co(NO_2)(saloph)(PPh_3)$. The cobalt thionitrosyl complexes $Co(NS)Cl_2L_2$ ($L = P(OPh)_3$ or PPh_3) are easily oxidized by O_2 to the thionitro complexes $Co(NSO)Cl_2L_2$ which catalyze the oxidation of triphenylphosphine without the presence of base [37].

The complexes [(py)Co(NO)(saloph)] and [(py)Co(NO)(TPP)] (TPP = tetraphenylporphyrin) react with oxygen in the presence of Lewis acids A ($A = BF_3 \cdot C_2H_5O$ or $LiPF_6$) to give the nitro complexes $[(py)Co(NO_2)L \cdot A]$, which stoichiometrically oxidize primary alcohols to aldehydes and secondary alcohols to ketones [38]. A possible mechanism has been put forward (eqns. 8–10)



$$(py)Co(NO)L + \tfrac{1}{2}\, O_2 + A \rightarrow (py)LCo{-}N\begin{smallmatrix} \nearrow O \\ \searrow O \cdots A \end{smallmatrix} \qquad (8)$$

complex

$$\text{complex} + C_6H_5CH_2OH \rightarrow (py)LCo(NO)A + C_6H_5CHO + H_2O \qquad (9)$$

$$\text{complex} + RR'CHOH \rightarrow (py)LCo(NO)A + RR'C{=}O + H_2O \qquad (10)$$

RR′CHOH = cyclopentanol, cyclohexanol and cycloheptanol

The addition of Lewis acids increases the electrophilicity of the nitro group by associating with it (eqn. 8) and enhances the oxidizing capacity of these nitrocobalt(III) complexes. Co(NO)(TPP) is a better catalyst than (py)Co(NO_2)(TPP) because the interaction of Lewis acids with pyridine, liberated from the latter after reduction to the 5-coordinated nitrosyl complex, decreases the concentration of the Lewis acid and, therefore, the reaction rate.

The combination of the cobalt complexes Co(NO)L (L = saloph or TPP) with $PdCl_2(PhCN)_2$ in 1,2-dichloroethane catalyzes quantitatively the O_2 oxidation of ethylene to acetaldehyde and propylene to acetone [39]. In acetic acid, the co-oxidation of ethylene catalyzed by a combined palladium acetate and nitrocobalt catalyst affords vinyl acetate. The role of Pd(II) complexes is to activate olefins towards a nucleophilic attack by coordinating them. The mechanism involves oxygen transfer from the nitro ligand to the cobalt nitro complexes to palladium(II)-bound olefins followed by reoxidation of the reduced nitrosyl ligands by O_2.

The molybdenum nitrosyl complexes $Mo(NO)_2Cl_2L_2$ and $Mo(NO)Cl_3L_2$ (L = hexamethyl phosphortriamide HMPT, dimethyl formamide, 1/2 (2,2-bipyridine, C_2H_5CN, $OPPh_3$, PPh_3, $AsPh_3$ or $SbPh_3$) catalyze the epoxidation of cyclohexene with tert-butyl hydroperoxide. The analogous chromium and tungsten nitrosyl complexes are less active. The epoxidations of cyclohexene with cyclohexenylhydroperoxide, and of cyclopentene, cycloheptene, cyclooctene and octene-1 with tert-butyl hydroperoxide are catalyzed by the $Mo(NO)_2Cl_2(HMPT)_2$ complex [40].

(v) Homogeneous hydrogenation of unsaturated compounds

Since the first observation of the homogeneous hydrogenation of benzoquinone in quinoline solution in the presence of cupric acetate [41], a variety of other homogeneous hydrogenation systems have been investigated [42], including the use of transition metal nitrosyl complexes.

The ruthenium nitrosyl complexes catalyze the hydrogenation of styrene, propionaldehyde, acetone and crotonaldehyde (Table 3). The much lower activity of $RuH(NO)(PMePh_2)_3$ as compared with $RuH(NO)L_3$ (L = PPh_3, PPr^iPh_2 or $P(C_6H_{11})Ph_2$) is due to the different mode of NO bonding [45]. The increase in catalytic activity of $RuH(NO)(PPh_3)_3$ with water indicates the assistance of water either in the formation of the catalytic species or its decomposition to the product alcohol [47]. The osmium nitrosyl complex $OsH(NO)(PPh_3)_3$ displays similar catalytic activity for the hydrogenation of styrene [43].

The rhodium(−I) nitrosyls $Rh(NO)L_3$ (L = PPh_3, P(*p*-tolyl)$_3$, P(*p*-FC_6H_4)$_3$, $PMePh_2$ and $AsPh_3$) are effective catalysts for homogeneous hydrogenation of olefins and alkynes [48–50]. The activity, based on crude

TABLE 3

Homogeneous hydrogenation catalyzed by ruthenium nitrosyl complexes

Substrate	Catalyst	Product	Ref.
Styrene	$RuH(NO)(PPh_3)_3$	Ethylbenzene	43
	$RuH(NO)(PPr^iPh_2)_3$	Ethylbenzene	43
	$RuH(NO)[P(C_6H_{11})Ph_2]_3$	Ethylbenzene	43
Propionaldehyde	$RuH(NO)(PPh_3)_3$	Propanol	45
Acetone	$RuH(NO)(PPh_3)_3$	2-Methoxyethanol (22%)	46
	$RuH(NO)(PPh_3)_3 + 2.5\%\ H_2O$	2-Methoxyethanol (97%)	46
Crotonaldehyde	$Ru(NO)Cl_3(PPh_3)_2$	Butanol	47

rates of reduction of 1-hexene, decreases in the order: $L = P(p\text{-tolyl})_3 > PPh_3 > P(p\text{-}FC_6H_4)_3 \equiv AsPh_3 > PMePh_2$. Substrates are reduced by $Rh(NO)(PPh_3)_3$ in the order: 1-alkyne > 2-alkyne > 1-olefin > *exo*-methylene ⩾ cyclohexene ⩾ *cis*-2-alkene > *trans*-2-alkene > trisubstituted olefin ≫ tetrasubstituted olefin. The rate of reduction for non-conjugated, non-chelating dienes is the same as for mono-olefins, but for conjugated and chelating dienes the rate of reduction is much slower, possibly due to blocking of coordination sites needed for oxidative addition for H_2.

Collman et al. [48] have demonstrated the stereochemistry of the $Rh(NO)(PPh_3)_3$-catalyzed hydrogenation of olefins. While dimethylmaleate shows *cis* addition of D_2 (90%), cyclohexene with D_2 yields d_2-cyclohexene, and hydrogenation of 2-hexene produces *cis*-2-hexene.

$Ir(NO)(PPh_3)_3$ catalyzes the reduction of heptenes, styrene derivatives, and 1-hexene, with slower rates than those for $Rh(NO)(PPh_3)_3$. The difference in catalytic activities of these complexes has been attributed to: (i) a much lower degree of phosphine dissociation from $Ir(NO)(PPh_3)_3$ ($\alpha_D = 0.25$) than from $Rh(NO)(PPh_3)_3$ ($\alpha_D = 2.0$) [49]; and (ii) differences in nitrosyl bonding (M–NO angle, 153° for $Rh(NO)(PPh_3)_3$ and 180° for $Ir(NO)(PPh_3)_3$) to give the required free coordination site. $Rh(NO)Cl_2(PPh_3)_2$ catalyzes the reduction of 3- and 4-alkylcyclohexanones and 3- and 4-alkylcyclohexanol [51].

(vi) Isomerization

Some transition metal nitrosyl complexes catalyze the isomerization of 1-pentene and 1-hexene. The complex $Mo(NO)_2Cl_2(PPh_3)_2$ with cocatalyst $C_2H_5AlCl_2$ catalyzes the isomerization of 1-pentene together with disproportionation of the olefin [52]. The cocatalyst $(CH_3)_3Al_2Cl_3$ is much less effective. The complexes $RuH(NO)L_3$ ($L = PPh_3$, $PPrPh_2$) and $OsH(NO)(PPh_3)_3$ isomerize 1-hexene efficiently to internal olefins [43]. The rate using

TABLE 4

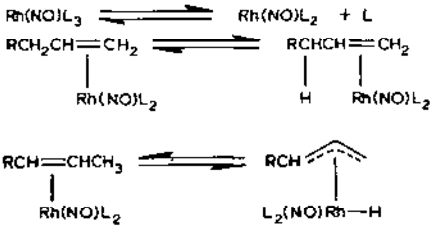
Metathesis of olefins

Olefin	Catalyst	Products	Ref.
1-Pentene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	4-Octene(48%), ethylene	52,56,57
	$Mo(NO)_2Cl_2(PPh_3)_2 + C_2H_5AlCl_2$	Butene(18%), pentene-2(25%), hexenes(28%), heptene(11%), octene(16%), ethylene and propene	52
	$Mo(NO)_2Cl_2 + (CH_3)_3Al_2Cl_3$	4-Octene(24%)	52
	$MoCl_3(C_6H_5CO_2)_2 + NO$	4-Octene(60%)	52
	$Mo\ O_2(CH_3COCHCOCH_3)_2 + NO$	4-Octene(18%)	52
	$Mo\ OCl_3 + NO$	4-Octene(55%)	52
	$Mo\ Cl_5 + NO$	4-Octene(43%)	52
	$Mo\ Cl_5 + OPPh_3 + NO$	4-Octene(45%)	52
	$Mo\ Cl_5 + OP(n\text{-}C_8H_{17})_3 + NO$	4-Octene(17%)	52
	$Mo\ Cl_5 + P(n\text{-}C_4H_9) + NO$	4-Octene(58%)	52
2-Pentene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	2-Butene and 3-hexene	52,58
	$Mo(NO)_2Cl_2(PPh_3)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene	52,58
	$W(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	2-Butene(9%), 3-hexene(15%) and heptene(1%)	52
	$W(NO)_2Cl_2(PPh_3)_2 + C_2H_5AlCl_2$	2-Butene (14%), 3-hexene(28%) and 2-heptene(3%)	52
	$Mo(NO)Cl_3 + C_2H_5AlCl_2$	2-Butene and 3-hexene(53% conversion in 5 min.)	60–62
	$Mo(NO)Cl_3(CH_3CN)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene(51%)	60–62
	$Mo(NO)Cl_3(DMF)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene(52%)	60–62
	$Mo(NO)Cl_3(pyridine)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene(42%)	60–62
	$Mo(NO)Cl_3(bipy) + C_2H_5AlCl_2$	No metathesis	60–62
	$Mo(NO)Cl_3(OPPh_3)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene(52%)	60–62
	$Mo(NO)Cl_3(DMSO)_2 + C_2H_5AlCl_2$	2-Butene and 3-hexene(51%)	60–62
	$Mo(NO)Cl(Salen) + C_2H_5AlCl_2$	2-Butene and 3-hexene (13%)	60–62
	$Mo(NO)(CO)_2Cl + CH_3AlCl_2$	2-Butene and 3-hexene	63
	$Mo(NO)(CO)_2Cl + C_2H_5AlCl_2$	2-Butene and 3-hexene	63
1,5-Hexadiene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	1,5,9-Decatriene(24%), 1,5,9,13-tetradecatetraene(7%), 1,5,9,13,17-octadecapentaene and ethylene	52

2-Heptene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	2-Butene(12%) and 5-decene(27%)	52
2-Heptene + ethylene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	Propylene(6%), 2-butene(5%), 1-hexene(19%) and 5-decene(15%)	52
1-Octene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	7-Tetradecene(37%)	52
	$Mo(NO)_2Cl_2(PPh_3)_2 + C_2H_5AlCl_2$	7-Tetradecene(12%)	52
	$Mo(NO)_2Cl_2(py)_2 + (CH_3)_3Al_2Cl_3$	7-Tetradecene(60%)	52
	$Mo(NO)_2Cl_2(py)_2 + C_2H_5AlCl_2$	Tridecene(5%) and	52
		7-tetradecene(64%)	52
	$Mo(NO)_2Cl_2(py)_2 + (C_2H_5)_3Al_2Cl_3$	7-Tetradecene(49%)	52
	$MoCl_4(PPh_3)_2 + NO + (CH_3)_3Al_2Cl_3$	7-Tetradecene(48%)	52
	$MoCl_4(py)_2 + NO + (CH_3)_3Al_2Cl_3$	7-Tetradecene(47%)	52
	$MoCl_5 + C_5H_5N + NO + (CH_3)_3Al_2Cl_3$	7-Tetradecene(38%)	52
	$WCl_6 + C_5H_5N + NO + (CH_3)_3Al_2Cl_3$	7-Tetradecene(29%)	52
	$WCl_6 + C_5H_5N + NO + C_2H_5AlCl_2$	7-Tetradecene(42%) with trace of C_9, C_{10} and C_{13} olefins	52
1,7-Octadiene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	Cyclohexene(91%) and 1,7,13-tetradecatriene(3%)	52,57
Cyclooctene + ethylene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	1,9-Decadiene(17%)	52
1,5-Cycloocta-diene + ethylene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	1,5,9-Decatriene(4.9%)	52
Cyclododecene + ethylene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	1,13-Tetradecadiene(13%)	52
2,8-Decadiene	$Mo(NO)_2Cl_2(PPh_3)_2 + (CH_3)_3Al_2Cl_3$	Propene(90%), dimethylethylene and cyclohexene	65

$RuH(NO)(PMePh_2)_3$ is 10^{-3} times slower than the rate with $RuH(NO)(PPh_3)_3$. The difference in activities may be due to different modes of NO bonding [44].

The isomerization of terminal olefins is not catalyzed by the rhodium complex $Rh(NO)(PPh_3)_3$ in the absence of H_2 and O_2. However, in the presence of traces of air, $Rh(NO)(PPh_3)_3$ in CH_2Cl_2 isomerizes 1-hexene (10% conversion) into internal isomers [48]. Under H_2 atmosphere $Rh(NO)L_3$ ($L = PPh_3$ or $PMePh_2$) does not catalyze the isomerization in CH_2Cl_2, but in benzene and tetrahydrofuran it effectively catalyzes the isomerization. For example, the reduction of 1-hexene by $Rh(NO)(PMePh_2)_3$ under 1 atm. H_2 occurs slowly in CH_2Cl_2 without isomerization, while in benzene, the reaction is two times faster and results in a mixture of 34.2% hexene, 45% *trans*-2-hexene and 20.5% *cis*-2-hexene; in THF the reaction is five times faster and leads to a mixture of 60.2% hexene, 16.5% *trans*-2-hexene and 23.8% *cis*-2-hexene. $Ir(NO)(PPh_3)_3$ catalyzes the isomerization of 1-hexene in benzene at 85°C [50]. The initial step in the isomerization involves the dissociation of a phosphine ligand in solution, which facilitates generation of a coordinatively unsaturated metal olefin complex, and allows formation of a π-allyl metal hydride intermediate



(vii) Metathesis

The metathesis of acyclic and cyclic olefins has been intensively investigated [53–55], but this reaction has seen limited use in organic synthesis. With transition metal nitrosyls, the major homogeneous catalyst systems for the metathesis of olefins are prepared from molybdenum or tungsten nitrosyl complexes and alkylaluminium cocatalysts (Table 4).

Kinetic studies on the metathesis of 2-pentene, using $Mo(NO)_2Cl_2L_2$ ($L = PPh_3$, C_2H_5N or $OPPh_3$) with organo-aluminium systems, have been investigated. The rate is first order in catalyst and variable in olefin; the effectiveness of the cocatalysts decreases in the order $(CH_3)_3Al_2Cl_3 > C_2H_5AlCl_2 > (C_2H_5)_3Al_2Cl_3$ [64].

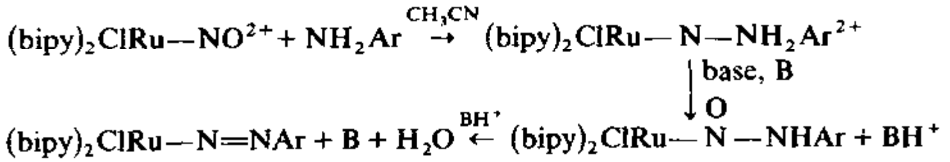
The metathesis of olefins containing quaternary ammonium groups gives α–ω bifunctional olefins in the presence of $Mo(NO)_2Cl_2$—$(PPh_3)_2$—

$C_2H_5AlCl_2$. For example, *trans*-$[Me_3NCH{=}CH(CH_2)_3NMe_3]I$ results in the formation of 2-butene and $[Me_3N(CH_2)_2CH{=}CH(CH_2)_2\text{-}NMe_3]^{2+}$. The inactivity of olefins with amino groups indicates that the metathesis of such olefins may be possible by diminishing the basic character of the nitrogen [66].

(viii) Miscellaneous preparations

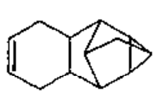
(a) Organic synthesis via diazotization of aromatic amines using ruthenium nitrosyl complexes

Reaction of the amines *p*-$NH_2C_6H_4{-}Y$ (Y = OCH_3, CH_3 or H) with the complex $[Ru(NO)Cl(bipy)_2][PF_6]_2$ in polar solvents results in the formation of diazonium complexes in which the useful synthetic intermediate (ArN_2) is stored in a stable chemical form (eqn. 11) [67].

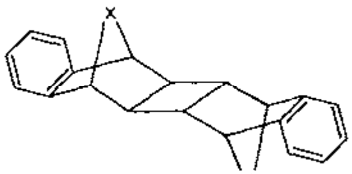


$$\begin{array}{l} (bipy)_2ClRu{-}NO^{2+} + NH_2Ar \xrightarrow{CH_3CN} (bipy)_2ClRu{-}N{-}NH_2Ar^{2+} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{base, B} \\ (bipy)_2ClRu{-}N{=}NAr + B + H_2O \xleftarrow{BH^+} (bipy)_2ClRu{-}\overset{}{\underset{\displaystyle O}{N}}{-}NHAr + BH^+ \end{array} \qquad (11)$$

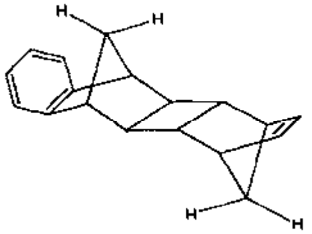
The bound diazonium group can be converted to the corresponding hydrocarbon by a one-electron reduction or by hydrogen atom abstraction, e.g. from α-hydrogen-containing ketones. For example, reaction with acetone



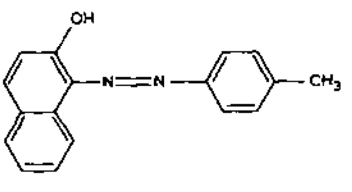
(X)



(XI) X = CH_2
(XII) X = $C{=}CMe_2$
(XIII) X = O



(XIV)



(XV)

liberates toluene, while KI in the presence of a catalytic amount of I_2 gives *p*-iodotoluene. The reaction of $[RuCl(bipy)_2(p\text{-}N_2C_6H_4OCH_3)]^{2+}$ with β-naphthol in methanol in the presence of K_2CO_3 affords $[RuCl(OH)(bipy)_2]$ and the azo-coupling product (**XV**).

(b) Formation of geminal dihalides

The copper halide nitrosyls $[Cu(NO)X_2]_2$ (X = Cl or Br) react with primary amine complexed to a copper(II) halide to give *gem*-dihalides, alcohols, alkyl halides and nitriles. For example, treatment of coordinated 2-phenylethylamine in acetonitrile with $[Cu(NO)Cl_2]_2$, followed by addition of ethylenediamine and aqueous NaOH, gives four products (eqn. 12) [68].

$$\begin{aligned}C_6H_5CH_2CH_2NH_2\cdot CuCl_2 + [Cu(NO)Cl_2]_2 &\rightarrow \underset{(58\%)}{C_6H_5CH_2CHCl_2}\\ &+ \underset{(3\%)}{C_6H_5CH_2CN} + \underset{(9\%)}{C_6H_5CH_2CH_2Cl} + \underset{(5\%)}{C_6H_5CH_2CH_2OH} \qquad (12)\end{aligned}$$

The yields of the *gem*-dihalides decrease if free amine reacts with the nitrosyl halide prior to reaction of the coordinated amine (Table 5). The reaction of free amine appears to have at least three components (eqns. 13–15).

$$2\,RCH_2NH_2 + [Cu(NO)X_2]_2 \rightarrow 2\,RCH_2NH_2\cdot CuX_2 + 2\,NO \qquad (13)$$

$$2\,RCH_2NH_2 + [Cu(NO)X_2]_2 \rightarrow RCH_2X + RCH_2OH + CuX + N_2 + H_2O \qquad (14)$$

$$2\,RCH_2NH_2 + [Cu(NO)X_2]_2 \rightarrow 2\,RCHX_2 + 2\,CuX + 2\,N_2 + 2\,HX + 2\,H_2O \qquad (15)$$

1-Phenylethylamine coordinated to $CuCl_2$ reacts with $[Cu(NO)Cl_2]_2$ to give styrene (17%), 1-chloro-1-phenylethane (25%) and 1-phenylethanol (28%). Similarly, 1-adamantamine gives 1-chloroadamantane (31%) and 1-adamantanol (28%). No formation of *gem*-dihalides is observed in these reactions.

(c) Carbonylation of benzylic halides

The carbonylation of benzylic halides RCH_2X with $Co(CO)_3(NO)$ as catalyst, gives the corresponding benzylic acids RCH_2COOH together with other products depending on the organic substrate (Table 6) [69]. All the reactions are carried out at room temperature and 1 atm. CO using sodium hydroxide (5 N), benzene, and dodecyltrimethylammonium chloride as a phase transfer catalyst. The most plausible explanation for these reactions is

TABLE 5

Yields of *gem*-dihalides from oxidative deamination of amines by $[Cu(NO)X_2]_2$

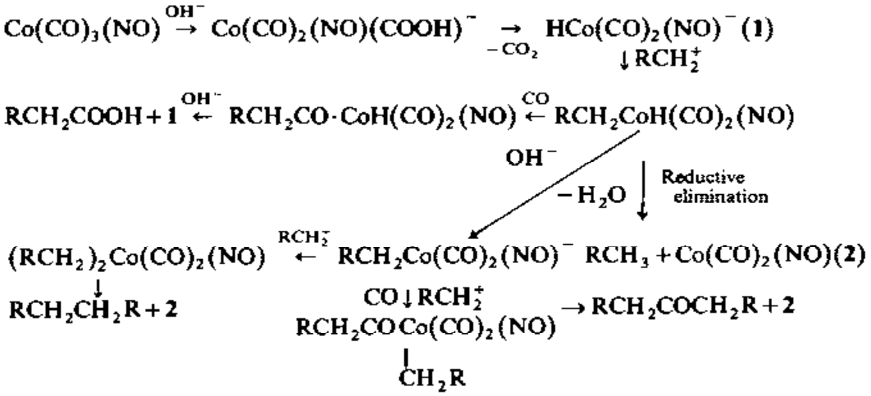
RCH_2NH_2	CuX_2	$RCHX_2$	Yield
R	X		(%)
C_6H_5	Cl	$C_6H_5CHCl_2$	14
	Br	$C_6H_5CHBr_2$	30
$C_6H_5CH_2$	Cl	$C_6H_5CH_2CHCl_2$	58
	Br	$C_6H_5CH_2CHBr_2$	54
$C_6H_5CH_2CH_2$	Cl	$C_6H_5CH_2CH_2CHCl_2$	34
$C_6H_5(CH_2)_3$	Cl	$C_6H_5(CH_2)_3CHCl_2$	12
$CH_3(CH_2)_5$	Cl	$CH_3(CH_2)_5CHCl_2$	34
	Br	$CH_3(CH_2)_5CHBr_2$	39
$CH_3(CH_2)_8$	Cl	$CH_3(CH_2)_8CHCl_2$	20
	Br	$CH_3(CH_2)_8CHBr_2$	37
$C_2H_5O_2(CH_2)_4$	Cl	$C_2H_5O_2C(CH_2)_4CHCl_2$	30
HO $CH_2(CH_2)_4$	Cl	HO $CH_2(CH_2)_4CHCl_2$	39
Cyclohexyl	Cl	$(CH_2)_5CH\ CHCl_2$	26

TABLE 6

Carbonylation of benzylic halides with $Co(CO)_3(NO)$ [69]

RCH_2X		Products	Yield
R	X		(%)
Ph	Br	$PhCH_2COOH$	58
		$PhCH_2CH_2Ph$	9
		$(PhCH_2)_2CO$	7
		PhCHO	4
p-CNC_6H_4	Br	*p*-$COOHC_6H_4CH_2COOH$	80
		(*p*-$CNC_6H_4CH_2)_2CO$	2
		p-$CNC_6H_4CH_3$	
		(*p*-$CNC_6H_4CH_2)_2$	
β-naphthyl	Br	β-$C_{10}H_7CH_2COOH$	44
		β-Methylnaphthalene	6
		β-Naphthaldehyde	5
		(β-$C_{10}H_7CH_2)_2$	
		(β-$C_{10}H_7CH_2)_2CO$	
o-$CH_3C_6H_4$	Br	*o*-$CH_3C_6H_4CH_2COOH$	68
		(*o*-$CH_3C_6H_4CH_2)_2$	12
		(*o*-$CH_3C_6H_4CH_2)_2CO$	10
		o-Xylene	4
		o-$CH_3C_6H_4CHCOCOOH$	
		o-$CH_3C_6H_4CH_2$	
p-$CH_3C_6H_4$	Cl	*p*-$CH_3C_6H_4CH_2COOH$	48
		p-$CH_3C_6H_4CH_2COCOOH$	6
		p-$CH_3C_6H_4CHCOCOOH$	6
		p-$CH_3C_6H_4CH_2$	

thought to involve initial addition of hydroxide ion to a carbonyl carbon.



$$Co(CO)_2(NO) + CO \rightarrow Co(CO)_3(NO) \tag{16}$$

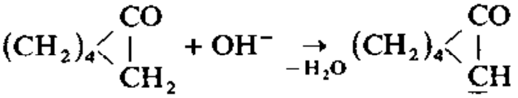
(d) Preparation of oximes (R = NOH)

Acetone reacts with nitroprusside ion $[Fe(CN)_5(NO)]^{2-}$ under basic conditions to give the intermediate anion, $[Fe(CN)_5N(O)CHCOMe]^{4-}$ which then hydrolyzes to give 2-oxopropanol-1-oxime (eqn. 17) [70].

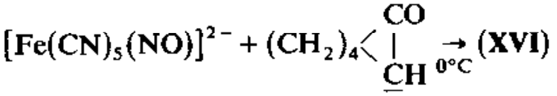
$$CH_3COCH_3 + [Fe(CN)_5(NO)]^{2-} \xrightarrow{OH^-/H_2O} [Fe(CN)_5(H_2O)]^{3-}$$

$$+ CH_3C(O)CH{=}NOH \tag{17}$$

Similarly, treatment of cycloalkanones under alkaline conditions in methanol gives red-brown or red-violet complexes $[(CN)_5FeN(O)\underset{\displaystyle CO}{\underset{|}{C}}H(CH_2)_n]^{3-}$ **(XVI)**, the alkaline hydrolysis of which results in the formation of ω-(hydroxyimino)alkanoic acids [71]. The products of acid hydrolysis of **(XVI)** are the ω-cyanoalkanoic acids and their methyl esters (Table 7) [72]. A possible reaction mechanism, for example, with cyclohexanone is thought to be as follows (eqns. 18–21)



$$(CH_2)_4\!\left\langle \begin{matrix} CO \\ | \\ CH_2 \end{matrix} \right. + OH^- \xrightarrow[-H_2O]{} (CH_2)_4\!\left\langle \begin{matrix} CO \\ | \\ \underline{C}H \end{matrix} \right. \tag{18}$$

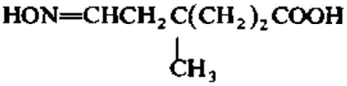


$$[Fe(CN)_5(NO)]^{2-} + (CH_2)_4\!\left\langle \begin{matrix} CO \\ | \\ \underline{C}H \end{matrix} \right. \xrightarrow[0°C]{} \textbf{(XVI)} \tag{19}$$

$$\textbf{(XVI)} + H_2O \rightarrow [Fe(CN)_5(H_2O)]^{3-} + HON{=}CH(CH_2)_4COOH \tag{20}$$

TABLE 7

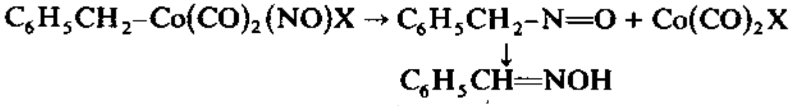
Hydrolysis products of cycloalkanone–nitroprusside complexes

Cycloalkanone	Medium	Products	Yield (%)
Cyclopentanone	Acid	$NC(CH_2)_3COOCH_3$	23.6
		$NC(CH_2)_3COOH$	5.0
		Glutarimide	8.9
	Alkaline	$HON{=}CH(CH_2)_3COOH$	38.0
Cyclohexanone	Acid	$NC(CH_2)_4COOCH_3$	17.8
		$NC(CH_2)_4COOH$	27.8
	Alkaline	$HON{=}CH(CH_2)_4COOH$	50
Cycloheptanone	Acid	$NC(CH_2)_5COOCH_3$	0.7
		$NC(CH_2)_5COOH$	35.6
	Alkaline	$HON{=}CH(CH_2)_5COOH$	25
4-Methylcyclohexanone	Alkaline	 $HON{=}CHCH_2\underset{\displaystyle CH_3}{C}(CH_2)_2COOH$	40
Cyclooctanone	Acid	$NC(CH_2)_6COOCH_3$	Trace
		$NC(CH_2)_6COOH$	45.2
Cyclododecanone	Acid	$NC(CH_2)_{10}COOH$	37.9

$$(XVI) + H^+ \rightarrow [Fe(CN)_5(H_2O)]^{3-} + NC(CH_2)_4COOH + NC(CH_2)_4COOCH_3 \qquad (21)$$

The reactions of benzyl halides, *p*-nitrobenzylchloride, *o*-chlorobenzylchloride and *p*-phenylbenzylchloride with $N(C_4H_9)_4[Co(CO)_2(NO)X]$ result in the formation of corresponding aldoximes in 30–50% yield, depending on X [73]. Phenylacetic acid (5–10%) is also isolated as a secondary product. The mechanism of the reaction is not clear but probably the first step involves oxidative addition of the benzyl halide to cobalt, followed by the migration of the benzyl group to the nitrogen of the nitrosyl group with the formation of an aldoxime (eqns. 22 and 23) [73].

$$C_6H_5CH_2Cl + [Co(CO)_2(NO)X]^- \xrightarrow[-Cl^-]{} C_6H_5CH_2\text{–}Co(CO)_2(NO)X \qquad (22)$$



$$C_6H_5CH_2\text{–}Co(CO)_2(NO)X \rightarrow \underset{\displaystyle C_6H_5CH{=}NOH}{\underset{\downarrow}{C_6H_5CH_2\text{–}N{=}O}} + Co(CO)_2X \qquad (23)$$

The formation of benzaldoximes together with other organic compounds also occurs in the reactions of benzyl bromide with $Ru(NO)_2(PPh_3)_2$ in refluxing toluene under CO atmosphere [74]. The organic products after 48 h are $PhCONH_2$ (77%), PhCN (17%), PhCH=NOH (9%) and PhCHO (5%). A plausible mechanism for the reaction involves the electrophilic addition of $PhCH_2^+$ to the coordinated NO group to the $RuN(O)CH_2Ph$ moiety. Other nitrosyl complexes which undergo denitrosylation with benzyl bromide are [Ru(NO)(diphos)], $Ru(NO)_2[P(OC_2H_5)_3]_2$, $Rh(NO)(PPh_3)_3$, $Rh(NO)Cl_2(PPh_3)_2$, and $Co(NO)L_3$ ($L = PPh_3$ or $P(OC_2H_5)_3$).

The allyl complexes, $Ru(CO)(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$ and $[M(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]PF_6$ (M = Rh or Ir) react rapidly with CO to give acrolein oxime (eqns. 24 and 25) [75,76]. The formation of an acrolein oxime complex $Ni(CH_2{=}CHCH{=}NOH)(NO)Br$ from the reaction of NO with $[Ni(\eta^3\text{-}C_3H_5)Br]_2$ suggests an acrolein oxime intermediate in these reactions [77].

$$Ru(CO)(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2 + CO \rightarrow Ru(CO)_3(PPh_3)_2 + CH_2{=}CHCH{=}NOH \qquad (24)$$

$$[M(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+ + CO \rightarrow [M(CO)_3(PPh_3)_2]^+ + CH_2{=}CHCH{=}NOH \qquad (25)$$

C. THE POTENTIAL OF TRANSITION METAL NITROSYLS IN POLLUTION CONTROL

(i) Introduction

Ninety nine percent of dry atmosphere consists of oxygen and nitrogen. Nitrous oxide is the most important of all the oxides of nitrogen in the lower layer of the atmosphere, the total volumetric concentration of all the remaining nitrogen oxides on the Earth's surface is of the order of 10^{-8}. Associated with the combustion of fuels is the production of pollutants such as nitric oxide, carbon monoxide, partially oxidized hydrocarbon molecules and sulfur dioxide. The major pollutants are CO and NO, although unburnt hydrocarbons contribute substantially to the formation of smog. Other minor but significant pollutants are sulfur oxides, lead compounds and halogens. In recent years there has been considerable interest in the conversion of NO to the less harmful products N_2, N_2O and NH_3. This interest has largely stemmed from attempts to remove, or at least diminish, the concentration of pollutant NO in exhaust gases emitted by internal combustion engines.

Several papers related to heterogeneous catalytic conversion of NO to N_2, N_2O or NH_3 using transition metals have been reported [78–99]. The most successful systems are those containing platinum metals, especially Pd, Pt and Ru. Under reducing conditions Pd- and Pt-based catalysts convert NO to NH_3, while Ru-based catalysts are effective in converting NO to N_2 in the presence of CO. However, the following section of this review is restricted to homogeneous processes concerning the conversion of NO to N_2, N_2O or NH_3 using transition metal complexes.

(ii) Applications of transition metal nitrosyls

(a) Formation of N_2

The cobalt complexes $[Co(NO)_2X]_2$ (X = Cl, Br) react with PPh_3, $AsPh_3$ and $SbPh_3$, to form N_2 gas (eqn. 26) [100].

$$\begin{aligned}&[Co(NO)_2X]_2 + 6\ PPh_3\\&\quad \rightarrow Co(NO)(PPh_3)_3 + CoX_2(OPPh_3)_2 + OPPh_3 + 3/2\ N_2\end{aligned} \tag{26}$$

Treatment of $[Ir(NO)X_5]^-$ with ammonia gives $[Ir(NH_3)X_5]^{2-}$ and N_2 [101]. In molten triphenylphosphine, $[Fe(NO)_2Br]_2$ dissolves forming $Fe(NO)Br(PPh_3)_2$, $Fe(NO)_2(PPh_3)_2$, $OPPh_3$ and N_2; $[Fe(NO)_2I]_2$ behaves similarly with $P(C_6H_{11})_3$, but the reaction of $Fe(NO)_3I$ with pyridine gives $[Fe(py)_6](NO_2)I$ and N_2 [102].

The chemical and electrochemical reduction of diazonium complexes $[Ru(bipy)_2(N_2Ar)Cl](PF_6)_2$ (see Section B(viii)) is accompanied by N_2 evolution (eqn. 27) [67, 103].

$$\begin{aligned}&CH_3CN + [Ru(bipy)_2(p\text{-}N_2C_6H_4CH_3)Cl]^{2+} + e^-\\&\quad \rightarrow [Ru(bipy)_2(CH_3CN)Cl]^+ + N_2 + C_6H_5CH_3\end{aligned} \tag{27}$$

Reaction of trithiazyltrichloride with $Rh(NO)(PPh_3)_3$ and $Rh(NO)X_2(PPh_3)_2$ (X = Cl, Br) in THF affords $[Rh(\mu\text{-}NS)Cl_2(PPh_3)]_2$, $OPPh_3$, $SPPh_3$ and N_2 [104].

(b) Formation of N_2O

The $[Rh(NO)_2Cl]_4$ tetramer undergoes a disproportionation reaction with PPh_3, $AsPh_3$ and $SbPh_3$, at room temperature to give N_2O (eqn. 28) [105], while reduction of the complexes $[M(NO)_2Cl]_n$ (M = Co, Rh) with sodium amalgam in THF in the presence of excess PPh_3 gives $M(NO)(PPh_3)_3$ and N_2O (eqn. 29) [105,106].

$$\begin{aligned}&[Rh(NO)_2Cl]_4 + 12\ PPh_3\\&\quad \rightarrow 2\ Rh(NO)(PPh_3)_3 + 2\ Rh(NO)Cl_2(PPh_3)_2 + 2\ OPPh_3 + 2\ N_2O\end{aligned} \tag{28}$$

$$[M(NO)_2Cl]_n + 4\ PPh_3 \xrightarrow[THF]{Na/Hg} M(NO)(PPh_3)_3 + OPPh_3 + N_2O \tag{29}$$

Treatment of *cis*-$Mo(NO)_2(S_2CNEt_2)_2$ with N_3^- or NCO^- gives N_2O and

$Mo(NO)(S_2CNEt_2)_3$ [107]. Reaction of NO with $RhCl(PPh_3)_3$ or $Rh(CO)ClL_2$ ($L = PPh_3$ or $AsPh_3$) affords N_2O and nitrosyl–nitro complexes [108,109]. Titanium(III) cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_5)TiCl]_2$ and $(\eta^5\text{-}C_5H_5)Ti(NCO)$ convert NO to N_2O quantitatively (eqns. 30 and 31) [110,111].

$$\left[(\eta^5\text{-}C_5H_5)TiCl\right]_2 + 2\,NO \rightarrow \left[(\eta^5\text{-}C_5H_5)TiCl\right]_2O + N_2O \tag{30}$$

$$2(\eta^5\text{-}C_5H_5)Ti(NCO) + 2\,NO \rightarrow \left[(\eta^5\text{-}C_5H_5)Ti(NCO)\right]_2O + N_2O \tag{31}$$

Nucleophilic attack by hydroxylamine at the coordinated NO in iridium and iron nitrosyl complexes affords N_2O (eqns. 32 and 33) [101,112,113].

$$[Ir(NO)X_5]^- + NH_2OH + H_2O \rightarrow [Ir(H_2O)X_5]^{2-} + N_2O + H_3O^+ \tag{32}$$

$$[Fe(NO)(CN)_5]^{2-} + NH_2OH + H_2O \rightarrow [Fe(H_2O)(CN)_5]^{3-} + N_2O + H_3O^+ \tag{33}$$

Nitric oxide reacts with transition metal nitrosyls to give N_2O and either nitro (NO_2^-) or hyponitrito ($N_2O_2^{2-}$) complexes. In general, hyponitrito complexes react with H^+ to liberate N_2O. Some examples of reactions of NO with nitrosyl complexes, and the formation of reactions of hyponitrito complexes with acid (H^+) are shown in eqns. (34–36) [114]; (37) [115]; (38) and (39) [116]; (40) and (41) [117]; and (42–45) [118–120].

$$[Co(NO)(en)_2Cl]Cl + 2\,NO \xrightarrow{CH_3OH} [Co(NO_2)(en)_2Cl]Cl + N_2O \tag{34}$$

$$[Co(NO)(en)_2(MeOH)]Cl_2 + 2\,NO \xrightarrow{CH_3OH} [Co(NO_2)(en)_2Cl]Cl + N_2O \tag{35}$$

$$[Co(NO)(DMGH)_2(MeOH)] + 2\,NO \xrightarrow{CH_3OH/C_5H_5N} Co(NO_2)(DMGH)_2(py) + N_2O \tag{36}$$

$$Ir(NO)_2Br(PPh_3)_2 + 2\,NO \xrightarrow{\text{2-butanol}} Ir(NO)(NO_2)Br(PPh_3)_2 + N_2O \tag{37}$$

$$[Co(NH_3)_5(NO)]^{2+} + NO \rightarrow [Co(NH_3)_5(N_2O_2)]^{2+} \tag{38}$$

$$[Co(NH_3)_5(N_2O_2)]^{2+} + NO + H_3O^+ \rightarrow [Co(NH_3)_5(OH)]^{2+} + NO_2^- + N_2O \tag{39}$$

$$2\,Ni(CO)_2(PPh_3)_2 + 4\,NO \xrightarrow[-CO]{} \left[\{Ni(NO)(PPh_3)_2\}_2N_2O_2\right] \tag{40}$$

$$\left[\{Ni(NO)(PPh_3)_2\}_2N_2O_2\right] + H^+ \rightarrow 2\,Ni(NO)(OH)(PPh_3)_2 + N_2O \tag{41}$$

$$Rh(NO)Cl_2(PPh_3)_2 + NOBr_3\ (\text{excess}) \rightarrow \left[\{RhBr_2(PPh_3)_2\}_2N_2O_2\right] + 2\,Cl^- + Br^- \tag{42}$$

$$[\{RhBr_2(PPh_3)_2\}_2N_2O_2] + H^+ \rightarrow [RhBr(PPh_3)_2]_2 + Br^- + N_2O + H_2O \quad (43)$$

$$2\ Rh(NO)_2Cl(PPh_3)_2 \rightarrow [\{Rh(NO)(PPh_3)_2Cl\}_2N_2O_2] \quad (44)$$

$$[\{Rh(NO)(PPh_3)_2Cl\}_2N_2O_2] \xrightarrow{HCl} Rh(NO)Cl_2(PPh_3)_2 + N_2O + H_2O \quad (45)$$

(c) Formation of N_2O and CO_2 from NO and CO

Conversion of CO and NO to the less harmful gases CO_2 and N_2O is of intrinsic interest because of its environmental relevance (eqn. 46)

$$2\ NO + CO \rightarrow N_2O + CO_2 \quad (46)$$

Reaction (46) does not occur at 450°C in the absence of catalysts, but in the presence of heterogeneous catalysts [90], the reaction occurs at about 400°C. Several papers dealing with homogeneous catalysis of reaction (46) at low temperature have been reported. Since excellent reviews have been presented by Eisenberg and Meyer [14] and McCleverty [17], only recent work in this area will be considered here.

The reaction catalyzed by $[M(NO)_2(PPh_3)_2]^+$ ($M = Rh$, Ir) has been reported by Johnson and co-workers (eqn. 47), the catalytic cycle being

$$[M(NO)_2(PPh_3)_2]^+ + 4\ CO \rightarrow [M(CO)_3(PPh_3)_2]^+ + N_2O + CO_2 \quad (47)$$

completed by regeneration of $[M(NO)_2(PPh_3)_2]^+$ via reaction of NO with $[M(CO)_3(PPh_3)_2]^+$ [121–123]. In contrast to the rhodium and iridium complexes, $M(NO)_2(PPh_3)_2$ ($M = Ru$, Os) complexes react very slowly with CO at room temperature [123]. The $Pt(N_2O_2)(PPh_3)_2$ complex reacts with CO to give N_2O and CO_2 and *cis*-$Pt(CO)_2(PPh_3)_2$ (eqn. 48) [122].

$$Pt(N_2O_2)(PPh_3)_2 + 3\ CO \rightarrow Pt(CO)_2(PPh_3)_2 + N_2O + CO_2 \quad (48)$$

The most satisfactorily proposed mechanism involves attack of CO on $[M(NO)_2(PPh_3)_2]^+$ to give $[M(N_2O_2)(CO)(PPh_3)_2]^+$ which then reacts with additional CO to give CO_2 and N_2O. The reaction of NO with $[M(CO)_3(PPh_3)_2]^+$ also occurs via the formation of the same five-coordinate intermediate and produces CO_2, N_2O, and $[M(NO)_2(PPh_3)_2]^+$; the overall reactions are summarized as follows [123]

$$\begin{tikzcd}
{[M(NO)_2(PPh_3)_2]^+} \arrow[r, shift left, "+CO"] & {[M(NO)_2(CO)(PPh_3)_2]^+} \arrow[l, shift left, "-CO"] \arrow[r, "2\,NO"] & {[M(NO)_2(PPh_3)_2]^+ + N_2O + CO_2} \\
{[M(CO)_3(PPh_3)_2]^+ + N_2O + CO_2} \arrow[ur, "NO", "-2\,CO"'] & {[M(N_2O_2)(CO)(PPh_3)_2]^+} \arrow[l, "+CO"'] &
\end{tikzcd}$$

The catalytic activity of the metals is dependent on their tendency to back donate electrons to the NO ligand, and decreases from rhodium to iron ($Rh < Ir < Ru < Os < Co < Fe$) [123].

The catalysis of reaction (46) by rhodium and iridium nitrosyl complexes has also been reported by Haymore and Ibers [115]. At 20°C in butanol, $[Rh(NO)_2(PPh_3)_2]PF_6$ catalyzes the reaction slowly, while in dimethylformamide the catalytic reaction occurs rapidly at 62°C [124], proceeding via formation of an intermediate, $[Rh(NO)_2(DMF)_x(PPh_3)]^+$ ($x = 1$ or 2). An increase in rate observed upon addition of water in this system is considerably less than that found for the $[Rh(CO)(NO)_2Cl_2]^-$ catalyst [126]. The effect of water may arise from preferential complexation of H_2O over DMF to the rhodium monomer. Homogeneous catalysis of reaction (46) using rhodium(III)–rhodium(I) systems, e.g. $RhCl_3 \cdot 3H_2O$ in ethanol, $Ph_4As[Rh(CO)_2Cl_2] + HX$ ($X = Cl, ClO_4$), in the presence of H_3O^+ as cocatalyst, has been studied extensively by Eisenberg and co-workers [125–128].

Kubota and co-workers have reported catalysis of reaction (46) using $PdCl_2$–$CuCl_2$ (or CuCl) in aqueous HCl [129,130]. Use of $PdCl_2$ alone results in deposition of elemental palladium after 5–6 h, and therefore a reduction in the rate of N_2O formation. The overall reactions are

$$CO + PdCl_2 + H_2O \rightarrow Pd + CO_2 + 2\ HCl \tag{49}$$

$$Pd + 2\ NO + 2\ HCl \rightarrow N_2O + PdCl_2 + H_2O \tag{50}$$

$$Pd + 2\ CuCl_2 \rightarrow PdCl_2 + 2\ CuCl_2^- \tag{51}$$

$$2\ CuCl_2^- + 2\ NO + 2\ HCl \rightarrow N_2O + 2\ CuCl_2 + H_2O \tag{52}$$

The formation of CO_2 from CO is more rapid than the formation of N_2O from NO, the total conversion at 144 h yielding 94% CO_2 and 74% N_2O. The lower yield of the N_2O compared to CO_2 is due to formation of the inactive nitrosyl complexes $[Pd(NO)Cl]_x$ and $[Pd(NO)_2Cl_2]$. In the case of Eisenberg rhodium systems [125–128], the formation of N_2O is more rapid than in the $PdCl_2$–$CuCl_2$–HCl system.

(d) Formation of NH_3

In alcoholic and basic solution $Co(NO)(CO)_3$ decomposes to give N_2 and NH_3 (eqn. 53) [131].

$$\begin{aligned} &3\ Co(NO)(CO)_3 + 9\ OH^- \\ &\quad \rightarrow Co(CO)_4 + 2\ Co(OH)_2 + HCO_3^- + 3\ CO_3^- + N_2 + NH_3 \end{aligned} \tag{53}$$

The polarographic reduction of $[Cr(NO)(CN)_5]^{4-}$ gives NH_3 gas at pH 3 by a mechanism suggested to involve successive protonation of the NO group

[132,133].

$$\mathrm{Cr(NO)(CN)_5^{3-}} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{Cr(NO)(CN)_5^{4-}}$$

$$\overset{H^+}{\rightleftharpoons} \mathrm{Cr(NOH)(CN)_5^{3-}} \xrightarrow{H^+} \mathrm{Cr(NOH_2)(CN)_5^{2-}} \xrightarrow{+e^-} \mathrm{Cr(NOH_2)(CN)_5^{3-}}$$

$$\xrightarrow{H^+} \mathrm{Cr(NH_2OH)(CN)_5^{2-}} \xrightarrow{3e^-,\,2\,H^+} \mathrm{Cr^{2-}} + 5\,\mathrm{CN^-} + \mathrm{NH_3} + \mathrm{H_2O}$$

Reactions of $[Co(NO)_2(PPh_3)_2]^+$ and $Rh(NO)_2Cl(PPh_3)_2$ with $NaBH_4$ afford $Co(NO)(PPh_3)_3$ and $Rh(NO)(PPh_3)_3$, respectively, together with evolution of NH_3, indicating attack of H^- on one of the coordinated NO ligands [119, 134]. Nitrosyl chloride reacts with hydrated ruthenium trichloride in the presence of excess PPh_3 to give $NH_4[Ru(NO)Cl_5]$, $[Ru(NO)Cl_2(PPh_3)]_2$ and NH_4Cl [135], while quantitative conversion of NOCl to NH_4Cl has been observed in the presence of ferric chloride and triphenylphosphine [Fe : PPh_3 = 1 : 8].

(e) Formation of N_2 and N_2O

In earlier studies Stedman [136] and Lucien [137] suggested that reaction of NO^+ with N_3^- results in production of N_2 and N_2O via intermediate formation of [M–N_4O] species containing an N_4O ring system. In the case of reaction between $[Ru(NO)Cl(diars)_2]^{2+}$, isotopic labelling gave evidence for such an attack of N_3^- ion at coordinated NO [138]. In the reaction between $[Fe(NO)(CN)_5]^{2-}$ and N_3^-, kinetic and isotopic labelling experiments indicate the formation of the intermediate $[Fe(NO)N_3(CN)_5]^{3-}$ rather than [M–N_4O]. The intermediate then decomposes directly to give N_2 and N_2O [112]. The reactions of $[Ru(NO)Cl(bipy)_2]^+$ [139,140] and $[Ir(NO)Br_5]^{2-}$ [101] with azide ion also afford N_2 and N_2O.

In the reaction of amines RCH_2NH_2 ($R = C_6H_5$, $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, etc.), with the nitrosyl halides $[Cu(NO)X_2]_2$ in acetonitrile, N_2 and N_2O are evolved together with the formation of organic compounds (eqns. 13–15) [68]. The cobalt complex $Co(NO)(PPh_3)_3$ reacts with NO to give N_2 and N_2O (eqn. 54) [141].

$$\mathrm{Co(NO)(PPh_3)_3} + 7\,\mathrm{NO} \rightarrow \mathrm{Co(NO)_2NO_2(PPh_3)} + 2\,\mathrm{OPPh_3} + 2\,\mathrm{N_2O} + \tfrac{1}{2}\,\mathrm{N_2} \qquad (54)$$

The conversion of NO into N_2 and N_2O is catalyzed by *cis*- and *trans*-$[Co(en)_2(NO_2)_2]^+$ in aqueous solution in the presence of ammonia or aliphatic amines RNH_2 ($R = CH_3$, C_2H_5 or C_4H_9) [142]. The initial rate of formation of N_2 and N_2O is first order, dependent on the partial pressure of NO, the concentration of complex and the concentration of amine. The

TABLE 8

Decomposition of metal dinitrosyls at 150°C

Complex [a]	Solvent	Yield (%)		
		N_2	NO	N_2O
$[Co(NO)_2Cl]_2 + PMDT$	Dichlorobenzene	11	29	60
$[Co(NO)_2Cl]_2 + HMTT$	Mesitylene	6	27	67
$[Co(NO)_2Br]_2 + HMTT$		6	6	88
$[Co(NO)_2I]_2 + HMTT$		2	4	94
$Rh(NO)_2Cl + PMDT$	Dichlorobenzene	100	0	0
$+ TMED$		100	0	0
$+ HMTT$		100	0	0
$+ Ph_2PCH_2CH_2PPh_2$		25	0	75
$+ PhP(CH_2CH_2PPh_2)_2$		9	5	86
$+ OP(C_4H_9)_3$		15	1	84
$+ (C_4H_9)_3N$		43	0	57
+ diglyme		16	37	47
+ acetylacetone		14	55	31
$Rh(NO)_2Cl$		13	54	33
$[Rh(NO)_2Cl(PPh_3)_2]PF_6$		100	0	0

[a] PMDT, Pentamethyldiethylenetriamine; HMTT, *N,N,N′,N″,N‴, N‴*-hexamethyltriethylenetetramine; TMED, *N,N,N′,N′*-tetramethylethylenediamine.

amine reactivity is in the order: $CH_3NH_2 \geqslant C_2H_5NH_2 \geqslant C_4H_9NH_2 > NH_3$.

The catalytic disproportionation of NO into N_2 and O_2, and the decomposition of dinitrosyl complexes to N_2, NO and N_2O have been extensively studied [143]. Disproportionation of the dinitrosyls of first-row transition metals, where the two NO groups are well separated due to their tetrahedral stereochemistry, results in the formation of N_2O. The disproportionation of dinitrosyls of the second-row transition metals with trigonal bipyramidal structures favours the formation of N_2O in the presence of good π-acceptors, and the formation of N_2 in the presence of good σ-donors (Table 8).

ACKNOWLEDGEMENTS

I am grateful to Professor H.W. Roesky for his help and encouragement during the preparation of this review and to a referee for careful and constructive critical reading and for the modification of the review in the present form. I am also indebted to Mrs. A. Brinkmann for typing the manuscript and Mr. J. Schimkowiak for drawing the figures. Finally I thank the Alexander von Humboldt Foundation for financial support.

REFERENCES

1 N.V. Sidgwick and R.W. Bailey, Proc. R. Soc. London Ser. A, 144 (1934) 521.
2 T. Moeller, J. Chem. Educ., 23 (1946) 542.
3 M.L.H. Green, Organometallic Compounds, The Transition Elements, Methuen, London, 1968.
4 C.S. Pratt, B.A. Coyle and J.A. Ibers, J. Chem. Soc., (1971) 2146.
5 C.C. Addison and J. Lewis, Quart. Rev. (London), 9 (1955) 115.
6 B.F.G. Johnson and J.A. McCleverty, Prog. Inorg. Chem., 7 (1966) 277.
7 W.P. Griffith, Adv. Organomet. Chem., 7 (1968) 211.
8 J.A. Masek, Inorg. Chim. Acta Rev., 3 (1969) 99.
9 N.G. Connelly, Inorg. Chim. Acta Rev., 6 (1972) 48.
10 B.A. Frenz and J.A. Ibers, M.T.P. Int. Rev. Sci. Phys. Chem. Ser. 1, 11 (1972) 33.
11 J.A. McGinnety, M.T.P. Int. Rev. Sci. Inorg. Chem. Ser. 1, 5 (1972) 229.
12 J.H. Enemark and R.D. Feltham, Coord. Chem. Rev., 13 (1974) 339.
13 K.G. Caulton, Coord. Chem. Rev., 14 (1974) 317.
14 R. Eisenberg and C.D. Meyer, Acc. Chem. Res., 8 (1975) 26.
15 F. Bottomley, Acc. Chem. Res., 11 (1978) 158.
16 F. Bottomley, Coord. Chem. Rev., 26 (1978) 7.
17 J.A. McCleverty, Chem. Rev., 79 (1979) 53.
18 R.D. Feltham and J.H. Enemark, Topics Inorg. Organomet. Stereochem., 12 (1981) 155.
19 J.P. Candlin and W.H. Janes, J. Chem. Soc. C., (1968) 1856.
20 D. Ballivet, C. Billard and I. Tkatchenko, Inorg. Chim. Acta, 25 (1977) L58.
21 I. Tkatchenko, J. Organomet. Chem., 124 (1977) C39.
22 I. Tkatchenko, Fr. Demande, 2202061 (10,10,72).
23 P.L. Maxfield, U.S. Pat. 3377397 (10.22.65).
24 P.L. Maxfield, Fr. Pat. 1535936 (09.02.66).
25 I. Tkatchenko, J. Mol. Catal., 4 (1978) 163.
26 D. Ballivet-Tkatchenko, M. Riveccie and N.E. Murr, J. Am. Chem. Soc., 101 (1979) 2763.
27 D. Ballivet and I. Tkatchenko, J. Mol. Catal., 1 (1975) 319.
28 P.W. Jolly, F.G.A. Stone and K. Mackenzie, J. Chem. Soc., (1965) 6416.
29 L. Lombardo, D. Wege and S.P. Wilkinson, Aust. J. Chem., 27 (1974) 143.
30 D. Ballivet, C. Billard and I. Tkatchenko, J. Organomet. Chem., 124 (1977) C9.
31 N.G. Connelly, P.T. Draggett and M. Green, J. Organomet. Chem., 140 (1977) C10.
32 D. Ballivet-Tkatchenko, C. Billard and A. Revillon, J. Polym. Sci., 19 (1981) 1697.
33 J. Smidt and R. Jira, Chem. Ber., 93 (1960) 162.
34 B.W. Graham, K.R. Laing, C.J. O'Connor and W.R. Roper, J. Chem. Soc. Chem. Commun., (1970) 1272.
35 B.W. Graham, K.R. Laing, C.J. O'Connor and W.R. Roper, J. Chem. Soc. Dalton Trans., (1972) 1237.
36 B.S. Tovrog, S.E. Diamond and F. Mares, J. Am. Chem. Soc., 101 (1979) 270.
37 R.D. Tiwari, K.K. Pandey and U.C. Agarwala, Inorg. Chem., 21 (1982) 845; K.K. Pandey, personal communication.
38 B.S. Tovrog, S.E. Diamond, F. Mares and A. Szalkiewicz, J. Am. Chem. Soc., 103 (1981) 3522.
39 B.S. Tovrog, F. Mares and S.E. Diamond, J. Am. Chem. Soc., 102 (1980) 6616.
40 J. Fleischer, D. Schnurpfeil, K. Seyferth and R. Taube, J. Prakt. Chem., 319 (1977) 995.
41 M. Calvin, Trans. Faraday Soc., 34 (1938) 1181.
42 C.W. Bird, Transition Metal Intermediates in Organic Synthesis, Academic Press, London, 1967, p. 248.

43 S.T. Wilson and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 3068.
44 C.G. Pierpont and R. Eisenberg, Inorg. Chem., 11 (1972) 1094.
45 R.A. Sanchez-Delgado, A. Andriollo, O.L. Deochoa, T. Suarez and N. Valencia, J. Organomet. Chem., 209 (1981) 77.
46 R.A. Sanchez-Delgado and O.L. Deochoa, J. Organomet. Chem., 202 (1980) 427.
47 W. Strohmeier and K. Holke, J. Organomet. Chem., 193 (1980) C63.
48 J.P. Collman, N.W. Hoffman and D.E. Morris, J. Am. Chem. Soc., 91 (1969) 5659; G. Dolcetti, N.W. Hoffman and J.P. Collman, Inorg. Chim. Acta, 6 (1972) 531.
49 W. Strohmeier and R. Endres, Z. Naturforsch., 276 (1972) 1415.
50 G. Dolcetti, Inorg. Nucl. Chem. Lett., 9 (1973) 705.
51 V.Z. Sharf, L.Kh. Freidlin, U.N. Krutii and I.S. Shekoyan, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1330.
52 C.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kittleman, J. Am. Chem. Soc., 92 (1970) 528.
53 W.B. Hughes, Organomet. Chem. Synth., 1 (1972) 341.
54 D.J. Cardin, B. Cetinkaya, M.J. Doyle and M.F. Lappert, Chem. Soc. Rev., 2 (1973) 99.
55 R.J. Hains and G.J. Leigh, Chem. Soc. Rev., 4 (1975) 155.
56 E.A. Zuech, J. Chem. Soc. Chem. Commun., (1968) 1182.
57 E.A. Zuech, U.S. 4010217 (Cl 260 - 683D; C 07 C3/62) (1.3.1977); Chem. Abstr., (1977) 86: 189167 Z.
58 W.B. Hughes, J. Chem. Soc. Chem. Commun., (1969) 431.
59 W.B. Hughes, Adv. Chem. Ser., 132 (1974) 192.
60 K. Seyferth and R. Taube, Z. Chem., 14 (1974) 284.
61 K. Seyferth and R. Taube, Z. Chem., 14 (1974) 410.
62 K. Seyferth and R. Taube, Z. Anorg. Allg. Chem., 437 (1977) 313.
63 K. Seyferth and R. Taube, J. Organomet. Chem., 229 (1982) 275.
64 W.B. Hughes, J. Am. Chem. Soc., 92 (1970) 532.
65 R.H. Grubbs and C.R. Hoppin, J. Chem. Soc. Chem. Commun., (1977) 634.
66 J.P. Lavel and A. Latters, J. Chem. Soc. Chem. Commun., (1977) 502.
67 W.L. Bowden, W.F. Little and T.J. Meyer, J. Am. Chem. Soc., 99 (1977) 4340.
68 M.P. Doyle, B. Siegfried and J.J. Hammond, J. Am. Chem. Soc., 98 (1976) 1628.
69 S. Gambarotta and H. Alper, J. Organomet. Chem., 212 (1981) C23.
70 J.H. Swinehart and W.G. Schmidt, Inorg. Chem., 6 (1967) 232.
71 T. Shono, H. Nii and K. Shinra, Kogyo Kagaku Zasshi, 72 (1969) 1669.
72 A. Ishigaki, M. Oue, Y. Matsushita, I. Masuda and T. Shono, Bull. Chem. Soc. Jpn., 50 (1977) 726.
73 M. Foà and L. Cassar, J. Organomet. Chem., 30 (1971) 123.
74 J.A. McCleverty, C.W. Ninnes and I. Wolochowicz, J. Chem. Soc. Chem. Commun., (1976) 1061.
75 M.W. Schoonover and R. Eisenberg, J. Am. Chem. Soc., 99 (1977) 8371.
76 M.W. Schoonover, E.C. Baker and R. Eisenberg, J. Am. Chem. Soc., 101 (1979) 1880.
77 R.A. Clement, U. Klabunde and G.W. Parshall, J. Mol. Catal., 4 (1978) 87.
78 A. Amirnazmi, J.F. Benson and M. Boudart, J. Catal., 30 (1973) 55.
79 K.C. Taylor and R.L. Klimish, J. Catal., 30 (1973) 478.
80 S. Rakshit, B.K. Sen and P. Bandyopadyay, Z. Anorg. Allg. Chem., 401 (1973) 212.
81 M.R.S. Winter, J. Catal., 34 (1974) 440.
82 T.P. Kobylinski and B.W. Taylor, J. Catal., 33 (1974) 376.
83 R.J.H. Voorhoeve and L.E. Trimble, J. Catal., 38 (1975) 80.
84 A. Amirnazmi and M. Boudart, J. Catal., 39 (1975) 383.

85 N.W. Cant and P.W. Fredrickson, J. Catal., 37 (1975) 531.
86 I. Suzuki, K. Sasaki and Y. Kaneko, J. Catal., 37 (1975) 555.
87 K.A. Windhorst and J.H. Lunsford, J. Chem. Soc. Chem. Commun., (1975) 852.
88 K.A. Windhorst and J.H. Lunsford, J. Am. Chem. Soc., 97 (1975) 1407.
89 S.J. Tauster and L.L. Murrel, J. Catal., 41 (1976) 192.
90 J.D. Butler and D.R. Davis, J. Chem. Soc. Dalton Trans., (1976) 2249.
91 M.F. Brown and R.D. Gonzalez, J. Catal., 44 (1976) 477.
92 M.H. Matloob and M.W. Robert, J. Chem. Soc. Faraday Trans. 1, 73 (1977) 1393.
93 T. Seiyama, T. Arakawa, T. Matsuda, Y. Takita and N. Yamazoe, J. Catal., 48 (1977) 1.
94 D.W. Johnson, M.H. Matloob and M.W. Robert, J. Chem. Soc. Chem. Commun., (1978) 40.
95 R.J.H. Voorhoeve and L.E. Trimble, J. Catal., 53 (1978) 251.
96 R.J.H. Voorhoeve, C.K.H. Patel, L.E. Trimble and R.J. Kerl, Science, 200 (1978) 761.
97 C.C. Taylor, Diss. Abstr. B, (1979) 3183.
98 T. Inui, T. Otowa and Y. Takegami, J. Chem. Soc. Chem. Commun., (1980) 94.
99 Q. Edwards, Diss. Abstr. B, (1980) 5291.
100 W. Hieber and D.V. Pigenot, Chem. Ber., 89 (1965) 610.
101 F. Bottomley, S.G. Clarkson and S.B. Tong, J. Chem. Soc. Dalton Trans., (1974) 2344.
102 W. Hieber and R. Kramolowsky, Z. Anorg. Allg. Chem., 321 (1963) 94.
103 W.L. Bowden, W.F. Little and T.J. Meyer, J. Am. Chem. Soc., 95 (1973) S84.
104 K.K. Pandey and U.C. Agarwala, Inorg. Chem., 20 (1980) 1308; Indian J. Chem. A, 20 (1980) 74.
105 W. Hieber and K. Heinicke, Z. Anorg. Allg. Chem., 316 (1962) 321.
106 W. Hieber and K. Heinicke, Z. Anorg. Allg. Chem., 316 (1962) 305.
107 J.A. Broomhead, J. Bridge, W. Grundy and T. Norman, Inorg. Nucl. Chem. Lett., 11 (1975) 519.
108 W.B. Hughes, J. Chem. Soc. Chem. Commun., (1969) 1126.
109 S. Kiji, S. Yoskikawa and J. Furukawa, Bull. Chem. Soc. Jpn., 43 (1970) 3614.
110 F. Bottomley and H.H. Brintzinger, J. Chem. Soc. Chem. Commun., (1978) 234.
111 F. Bottomley and I.J.B. Lin, J. Chem. Soc. Dalton Trans., (1981) 271.
112 S.K. Wolfe, C. Andrade and J.H. Swinhart, Inorg. Chem., 13 (1974) 2567.
113 S. Lunak and J. Veprek-Siska, Collect. Czech. Chem. Commun., 39 (1974) 2719.
114 D. Gwost and K.G. Caulton, Inorg. Chem., 13 (1974) 414.
115 B.L. Haymore and J.A. Ibers, J. Am. Chem. Soc., 96 (1974) 3325.
116 P. Gans, J. Chem. Soc. A, (1967) 943.
117 R.D. Feltham, Inorg. Chem., 3 (1964) 119.
118 K.K. Pandey, S. Datta and U.C. Agarwala, Transition Met. Chem., 4 (1979) 337.
119 K.K. Pandey and U.C. Agarwala, J. Inorg. Nucl. Chem., 42 (1980) 293.
120 K.K. Pandey, K.C. Jain and U.C. Agarwala, Indian J. Chem. A, 22 (1982) 75.
121 B.F.G. Johnson and S. Bhaduri, J. Chem. Soc. Chem. Commun., (1973) 650.
122 S. Bhaduri, B.F.G. Johnson, C.J. Savory, J.A. Segal and R.H. Walter, J. Chem. Soc. Chem. Commun., (1974) 809.
123 S. Bhaduri and B.F.G. Johnson, Transition Met. Chem., 3 (1978) 156.
124 J.A. Kaduk, T.H. Tulip, J.R. Budge and J.A. Ibers, J. Mol. Catal., 12 (1981) 239.
125 J. Reed and R. Eisenberg, Science, 184 (1974) 568.
126 C.D. Meyer and R. Eisenberg, J. Am. Chem. Soc., 98 (1976) 1364.
127 D.E. Hendriksen and R. Eisenberg, J. Am. Chem. Soc., 98 (1976) 4662.
128 D.E. Hendriksen, C.D. Meyer and R. Eisenberg, Inorg. Chem., 16 (1977) 970.
129 M. Kubota, K.J. Evans, C.A. Koerntgen and J.C. Marsters, Jr., J. Am. Chem. Soc., 100 (1978) 342.

130 M. Kubota, K.J. Evans, C.A. Koerntgen and J.C. Marsters, Jr., J. Mol. Catal., 7 (1980) 481.
131 J. Ellermann and W. Hieber, Chem. Ber., 96 (1963) 1667.
132 D.I. Bustin and A.A. Vleek, Collect. Czech. Chem. Commun., 31 (1966) 2374.
133 D.I. Bustin and A.A. Vleek, Collect. Czech. Chem. Commun., 32 (1967) 1665.
134 B.F.G. Johnson, S. Bhaduri and N.G. Connelly, J. Organomet. Chem., 40 (1972) C 36.
135 K.K. Pandey, S.R. Ahuja, N.S. Poonia and S. Bharti, J. Chem. Soc. Chem. Commun., (1982) 1268.
136 G. Stedman, J. Chem. Soc., (1960) 1702.
137 H.W. Lucien, J. Am. Chem. Soc., 80 (1958) 4458.
138 P.G. Douglas and R.D. Feltham, J. Am. Chem. Soc., 94 (1972) 5254.
139 F.J. Miller and T.J. Meyer, J. Am. Chem. Soc., 93 (1971) 1294.
140 S.A. Adeyemi, F.J. Miller and T.J. Meyer, Inorg. Chem., 11 (1972) 994.
141 M. Rossi and A. Sacco, J. Chem. Soc. Chem. Commun., (1971) 694.
142 S. Naito, J. Chem. Soc. Chem. Commun., (1978) 175.
143 W.R. Moser, The Catalytic Chemistry of Nitric Oxides, Plenum Press, New York, 1975, p. 33.