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Coordination Chemistry Reviews 249 (2005) 2277–2307

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Review

Structural and spectroscopic properties of rhenium nitrosyl complexes

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Received 2 November 2004; accepted 18 March 2005
Available online 15 April 2005

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Abstract

This paper presents a comprehensive survey on structural and spectroscopic properties of mono- and polynuclear rhenium nitrosyl complexes with the exception of organometallic nitrosyl rhenium species.

Keywords: Rhenium complexes; Nitrosyl; X-ray; Spectroscopic investigation

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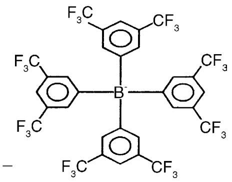

Abbreviations: BAr$^F{}_4$, [B{3,5-$(F_3C)_2C_6H_3$}$_4$]$^-$; COE, cyclooctene; dmpc, *trans*-1,2-bis(dimethylphosphine)cyclopentane; dmpm, 1,2-bis(dimethylphosphine)methane; dppe, 1,2-bis(diphenylphosphine)ethane; dppee, 1,2-bis(diphenylphosphine)ethene; dppm, 1,2-bis(diphenylphosphine)methane; pc^{2-}, phthalocyaninato dianion; picH, picolinic acid; tacn, 1,4,7-triazacyclononane ($C_6H_{15}N_3$)

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0010-8545/$ – see front matter
doi:10.1016/j.ccr.2005.03.022

1. Introduction

For many years, much attention has been focussed on the synthesis and study of a variety of nitrosyl transition metal complexes. These compounds have been the centre of interest to those scientists engaged in basic research and to those trying to employ these complexes in catalysis, production of organonitrogen compounds and pollutant control (reduction of NO in exhaust fumes). The recent discovery of the key role of nitric oxide in human cardiovascular, nervous systems and in the immune response to pathogen invasion has resulted in further interest in nitrosyl transition metal complexes. Therefore, the attention of scientists has focussed on the synthetic aspects, structural and spectroscopic properties of transition metal nitrosyl complexes as well as the reactivity of the coordinated NO group. Reactions of nitrosyl ligand are interesting in their own right and in relation to environmental, catalytic and biochemical background. In the last context, one of the principal problems associated with the reactivity of coordinated NO^+ concerns its reducibility. It has been recently suggested that the one-electron redox relatives of NO, the nitrosonium cation (NO^+), the nitroxide anion (NO^-) and the conjugate acid of NO^-, nitroxyl (HNO), is responsible for some aspects of the biological chemistry of nitric oxide. HNO has also been postulated as an intermediate in photochemical and free-radical reactions, and its formation and decomposition may play a role in the mechanism for combustion of nitrogen-containing fuels and oxidation of atmospheric nitrogen. The potential applications of nitrosyl complexes for the assembly of devices with novel optical and magnetic properties are also attractive. Many reviews concerning nitrosyl complexes and nitrosyl-related topics have appeared [1–28].

This article is intended to provide a comprehensive survey on structural and spectroscopic properties of mono- and polynuclear rhenium nitrosyl complexes, but it does not contain a discussion of organometallic nitrosyl rhenium species. In the previous reviews, the synthesis methods and properties for the selected individual rhenium compounds have been simply referenced rather than being presented and discussed in detail. Due to the favourable nuclear properties of ^{186}Re and ^{188}Re nuclides in diagnostic nuclear medicine and radioimmunotheraphy [29], a detailed discussion of the structural and spectroscopic properties of rhenium nitrosyls is surely useful.

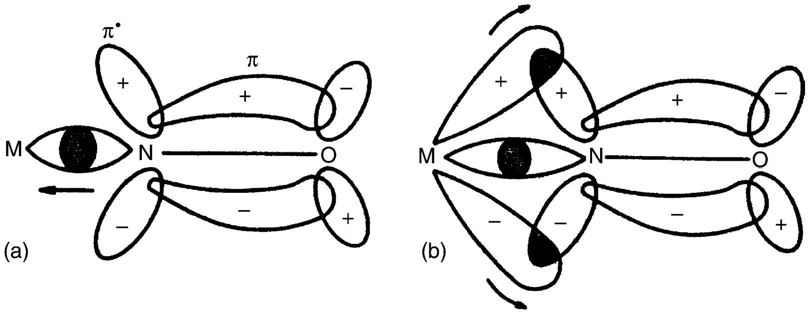
2. The bonding of nitric oxide a metal centre

The NO molecule can bind to a metal centre via the N or O atoms to give nitrosyl (M–NO) or isonitrosyl (M–ON) ligands, respectively. In practice, the bonding of NO involves attachment of the N atom to the metal centre, and the M–N–O angles may be essentially linear or bent, up to ca. 120°. Some metastable complexes generated photochemically in low-temperature solids have η^2-NO coordinated with the N–O bond perpendicular to the metal–ligand axis. It is also possible for NO to bridge two or more metal centres. In this case, the NO group is attached to more than one metal centre either via the N atom or via both N and O atoms. In metal complexes, the NO ligand may exist in three different oxidation states NO^+ (a nitrosonium cation), $NO^\bullet$ and NO^- (nitroxide anion) [1–27].

In a molecular orbital approach, the bonding of NO to a metal is considered to be made up of two components. The first involves donation of electron density from a σ-type orbital of NO onto the metal, and the second—back-donation from the metal d orbitals to the π^* orbitals of NO. Two components of the M–NO bonding: (a) σ-donation, (b) back-donation are presented schematically in Scheme 1 [19].

In the Enemark–Feltham formalism, nitrosyl containing species are described as $\{MNO\}^n$ (regardless of the co-ligands), where n stands for the number of electrons associated with the metal d and π^*(NO) orbitals (or equivalently to the number of d electrons on the metal when the nitrosyl ligand is formally considered as NO^+) [1–25]. The extension of Walsh's concepts to the $\{MNO\}^n$ moiety, discussed in great detail in paper [5], can be used to predict the bond angles of the $\{MNO\}^n$ unit. Fig. 1 presents the molecular orbital description for the $\{MNO\}^n$ unit in $C_{\infty v}$ symmetry.

The MNO triatomic unit with a d-block metal (M) requires 18 electrons to fill all bonding and non-bonding orbitals. Additional electrons will occupy the antibonding 3π orbital. Therefore, if Walsh's arguments are also applicable to the $\{MNO\}^n$ moiety, then partial occupation of the 3π orbital should lead to bending of the $\{MNO\}^n$ group [22].



Scheme 1.

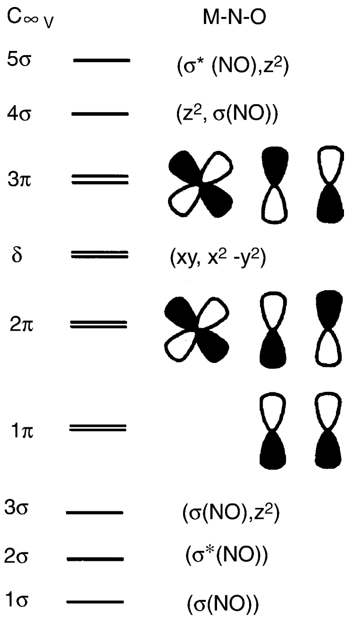


Fig. 1. Molecular orbital diagram for the $\{MNO\}^n$ unit in $C_{\infty v}$ symmetry [22].

3. Structural properties of nitrosyl rhenium complexes

3.1. Six-coordinate mononitrosyls

A typical arrangement of molecular orbitals in six-coordinate $\{MNO\}^n$ complexes with $n \leq 6$ is shown in Fig. 2a. The M–N–O bond defines the z-axis, the metal $d_{x^2-y^2}$ and d_z^2 interact with the σ ligand orbitals, the d_{xz} and d_{yz}orbitals interact with the π^*_{NO} orbitals, whereas the d_{xy} is relatively unperturbed in this arrangement [26].

For $\{MNO\}^n$ complexes with $n \leq 6$, the M–N–O moiety will be essentially linear, the electronic configuration for $\{MNO\}^6$ is $(e_1)^4(b_2)^2$. Octahedral complexes with $n \leq 6$ are described as bound to the nitrosyl cation (NO^+). For $\{MNO\}^7$ complexes, the added electron will occupy an antibonding π-type orbital (e_2) involving M, N and O. According to Walsh's rules, the bending of the M–N–O moiety will occur. This will lead to a change in symmetry and relative energies of the metal d orbitals and π^*_{NO} orbitals. Fig. 2b shows the arrangement of molecular orbitals in six-coordinate with a bent M–N–O unit. The electronic configuration of $\{MNO\}^7$ and $\{MNO\}^8$ are $\ldots(a')^1(a'')^0$ and $\ldots(a')^2(a'')^0$, respectively, which corresponds to the coordination of $NO^\bullet$ and NO^-, respectively (Scheme 2) [26]. There are dramatic changes in the M–N–O bond angles from 6 to 7 and 8 in the six-coordinate complexes. The average bond angles for $\{MNO\}^7$ and $\{MNO\}^8$ have been calculated to be 145 ± 10° and 125 ± 10°, respectively [19].

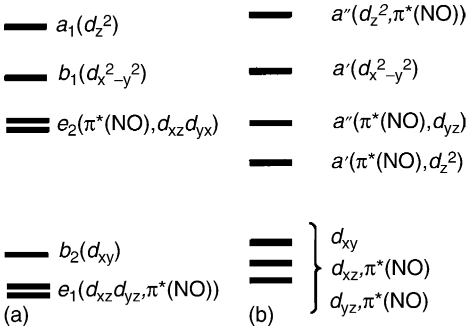


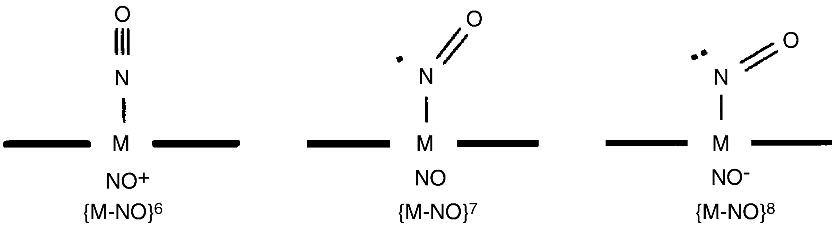
Fig. 2. The molecular orbital scheme in six-coordinate $\{MNO\}^n$ when M–N–O is 180° (a) and 120° (b) [26].

The molecular orbital scheme shown in Fig. 2 concerns strong ligand field complexes. For the first-row transitions metals, the energies of $d_{x^2-y^2}$ and d_z^2 orbitals might lie close to, or even lower than, the π^*_{NO} orbitals, and significant spin multiplicity could result, the coupling between spins on the metal and NO then being governed by spin-polarization. This has been discussed in detail for iron nitrosyl complexes [26].

Table 1 contains structural data for six-coordinate $\{ReNO\}^n$ complexes in order of increasing n. As can be seen from Table 1 only $\{ReNO\}^n$ complexes with n = 4–6 have been structurally characterised so far.

Some six-coordinate $\{ReNO\}^8$, $[Re(NO)(HNO)Cl_2(PPh_3)_2]$ [30], $[Re(NO)(HNO)Cl(I)(PPh_3)_2]$ [30], $[Re(HNO)Cl(CO)_2(PPh_3)_2]$ [31], $[Re(HNO)Cl(CO)_2(PCy_3)_2]$ [31] and $[Re(HNO)(CO)_3(PPh_3)_2](O_3SCF_3)$ [32], were isolated, but they were only characterised by IR or/and ^1H–^{15}N NMR.

The unusual characteristics of HNO as a molecule and ligand are yet not fully understood. Nitrosyl hydride (HNO) is isoelectronic with dioxygen, so the coordination chemistry of HNO ligand is described with special focus on its interaction with hemes and heme model complexes. There are some data suggesting that HNO is the primary product of the enzymatic conversion of L-arginine to cirtulline. Therefore, further study of the synthesis and reactivity of metal–HNO complexes is of high significance. To date, there are only four X-ray structural



Scheme 2.

Table 1
Structural data for six-coordinate mononitrosyl rhenium complexes

Complex	Re–N (Å)	N–O (Å)	Re–N–O (°)	References
$\{ReNO\}^4$				
$[Re(NO)Cl_4(MeCN)]$	2.07 (5)	1.11 (8)	166 (5)	[70]
$[Re(NO)Cl_3(NPPh_3)(OPPh_3)]$	1.734 (10)	1.183 (13)	174.1 (9)	[71]
$[Re(NO)Br_3(Ph)(PPh_3)]$	1.830 (12)	1.034 (13)	177.5 (10)	[72]
$[Re(NO)(CO)Cl_2(Ph)\{\eta^1\text{-}o\text{-}(NH)(NHPh)C_6H_4\}]$	1.789 (17)	1.166	177.6	[48]
$\{ReNO\}^5$				
$[Re(NO)Cl_2(OReO_3)(PPh_3)(OPPh_3)]$	1.736 (8)	1.18 (1)	175.8 (9)	[41]
$4[Re(NO)Cl_2(OPPh_3)_3](ReO_4)$	1.72 (1)	1.19 (1)	171.9 (12)	[41]
$[Re(NO)Cl_2(OReO_3)(OPPh_3)_2]$	1.76 (1)	1.16 (2)	175.3 (13)	[41]
$[Re(NO)Cl_3(PPh_3)_2]$	1.765 (9)	1.200 (11)	180	[34]
$[Re(NO)Cl_3(AsPh_3)_2][ReCl_4(AsPh_3)_2]$	1.816 (10)	1.092 (2)	176.0 (9)	[36]
$[Re(NO)Br_3(PPh_3)_2]$	1.769 (12)	1.12 (2)	180	[35]
$[Re(NO)Br_3(AsPh_3)_2]$	1.740 (11)	1.177 (13)	180	[36]
$[Re(NO)Cl_3(OPPh_3)_2]$	1.72 (3)	1.21 (3)	172 (4)	[42]
$[Re(NO)Br_3(OPPh_3)_2]$ (monoclinic)	1.757 (12)	1.261 (13)	172.6 (13)	[35]
$[Re(NO)Br_3(OPPh_3)_2]$ (orthorhombic)	1.87 (2)	0.94 (1)	175 (1)	[43]
$[Re(NO)Br_3(OAsPh_3)_2]$	1.749 (5)	1.156 (6)	176.8 (5)	[36]
$[Re(NO)Cl_3(OPPh_3)(PPh_3)]$	1.747 (5)	1.165 (8)	176.0 (6)	[38]
$[Re(NO)Cl_3(OPPh_3)(pyz)]$	1.740 (4)	1.184 (4)	178.2 (3)	[73]
$[Re(NO)Br_3(MeCN)(PPh_3)]$	1.763 (7)	1.146 (9)	177.4 (7)	[39]
$[Re(NO)Br_3(pzH)(AsPh_3)]$	1.755 (7)	1.149 (8)	178.5 (7)	[40]
$(Net_4)[Re(NO)Cl_4(py)]$	1.749 (6)	1.171 (9)	178.9 (7)	[44]
$(Net_4)[Re(NO)Br_4(EtOH)]$	1.723 (15)	1.19 (2)	169 (3)	[45]
$(Net_4)[Re(NO)Br_4(MeCN)]$	1.771 (11)	0.99 (2)	178 (6)	[45]
$(AsPh_4)[Re(NO)Cl_4\{OC(NH_2)CH_3\}]$	1.762 (9)	1.161 (13)	173.4 (9)	[46]
$K[Re(NO)(CN)_4(OH_2)]\cdot(Phen)_5\cdot MeOH\cdot 3H_2O$	1.71 (1)	1.23 (2)	172.2 (14)	[47]
$K_2[Re(NO)(CN)_5]\cdot(Phen)_6\cdot 4.5H_2O$	1.801 (6)	1.204 (9)	178.4 (8)	[47]
$[Re(NO)Cl(dppe)_2](NO_3)_2$	1.730 (13)	1.24 (2)	174.7 (11)	[68]
$[ReBr_3(NO)(dppe)]_{0.6}[ReBr_4(dppe)]_{0.4}$	1.69 (4)	1.31 (8)	175 (3)	[74]
$[Re(NO)(CO)_2Cl_2\{\eta^1\text{-}o\text{-}(NH_2)(NHPh)C_6H_4\}]$	1.831 (11)	1.175	174.4	[49]
$[Re(NO)(OPPh_3)(pc)]I_3\cdot CH_2Cl_2$	1.77 (1)	1.15 (1)	176 (1)	[75]
$\{ReNO\}^6$				
$[Re(NO)(CO)Cl_2L_2]$	1.829 (6)	1.157 (8)	180	[34]
$L = PPh_3$	1.89 (4)	1.16 (5)	167.2	[50]
$L = P(O\text{-}^iPr)_3$	1.827 (4)	1.180	178.6	[51]
L = dppm	1.773 (6)	1.178 (9)	177.0 (6)	[51]
L = 1/2 dmpc	1.888 (11)	1.138 (16)	179.1	[51]
$L = 1/2\ 4,4'\text{-}Me_2\text{-}bipy$	1.853 (8)	1.158	178.7	[49]
$[Re(NO)(CO)Br_2(PPh_3)_2]\cdot NO$	1.783 (9)	1.094 (2)	175.8 (9)	[52]
$[Re(NO)(CO)Cl(I)\{P(O\text{-}^iPr)_3\}_2]$	1.88 (2)	1.162	178.5	[50]
$[Re(NO)(CO)\{O_2SO(C_6H_4Me)\}\{P(O\text{-}^IPr)_3\}_2]$	1.821 (8)	1.17 (1)	178.7	[50]
$[Re(NO)(CO)Cl(H)(PMe_3)_2]$	1.921 (8)	1.182	171	[53]
$[Re(NO)(CO)H_2\{P(OMe)_3\}_2]$	1.78 (1)	1.287	178	[53]
$[Re(NO)(CO)H_2(PMe_3)_2]\cdot indole$	1.866 (9)	1.179 (14)	179.4 (9)	[54]
$[Re(NO)(CO)H(p\text{-}OC_6H_4NO_2)(PMe_3)_2]$	1.796 (11)	1.182 (16)	167.7 (10)	[54]
$[Re(NO)(CO)H(OOCCF_3)(PMe_3)_2]$	1.813 (7)	1.177 (10)	171	[55]
$[Re(NO)(CO)(O_3SCF_3)_2(PEt_3)_2]$	1.801 (4)	1.186	178.7	[56]
$[Re(NO)(CO)Cl(MeCN)_2(PEt_3)](O_3SCF_3)$	1.944	1.144	177.9	[56]
$[Re(NO)(CO)(MeCN)_2\{P(OMe)_3\}_2](O_3SCF_3)_2$	1.869	1.157	175.3	[56]
$[Re(NO)(CO)F(PPh_3)_3](BF_4)$	1.76 (2)	1.20 (3)	176 (2)	[57]
$[Re(NO)(CO)(NH_3)(tacn)]Br_2$	1.818 (8)	1.185 (10)	177.7 (7)	[58]
$[Re(NO)Cl(PhN{=}NC_6H_4)\{P(O\text{-}^iPr)_3\}_2]$	1.92 (3)	1.18 (4)	168.7	[50]
$\{N(PPh_3)_2\}[Re(NO)(CO)_2Cl_3]$	1.923	1.199	174.8	[59]
$[Re(NO)(CO)_2H(PPh_3)_2]\ (SO_3CF_3)$	1.829 (5)	1.185 (6)	178.1 (4)	[31]
$[Re(NO)(CO)_2Cl_2(THF)]$	1860 (12)	1.147 (18)	178.6	[51]
$[Re(NO)(CO)_2Br(N,O\text{-}pic)]$	1.893	1.138	177.7	[60]
$[Re(NO)Cl_2(MeCN)(PMe_3)_2]$	1.814	1.218	173.5	[65]
$[Re(NO)(OPPh_3)(pc)]$	1.76 (1)	1.18 (1)	179.6 (5)	[75]
$[ReCl_2(NO)(py)_3]$	1.843 (19)	1.107 (10)	160 (3)	[66]
	1.92 (2)	1.104 (10)	174 (9)	
$[ReCl_2(NO)(SbPh_3)_3]$	1.832 (19)	1.13 (4)	178 (2)	[67]
	1.753 (17)	1.32 (4)	175 (2)	

Table 1 (*Continued*)

Complex	Re–N (Å)	N–O (Å)	Re–N–O (°)	References
$[Re(NO)Br_2(py)_3]_{0.58}[ReBr_3(py)_3]_{0.42}$	1.68 (5)	1.38 (10)	172 (5)	[43]
$[Re(NO)H_2(PPh_3)_3]$ 1/2C_6H_6				[61]
Molecule I	1.77 (2)	1.25 (3)	175 (2)	
Molecule II	1.73 (2)	1.24 (3)	177 (2)	
$[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$	1.768 (4)	1.166 (5)	176.4 (4)	[62]
$(AsPh_4)_2[Re(NO)(CN)_4(H_2O)]\cdot 5H_2O$	1.732 (7)	1.181 (8)	178.4 (7)	[64]
$(AsPh_4)_2[Re(NO)(CN)_4\{SC(NH_2)_2\}]$	1.736 (11)	1.146 (13)	177.7 (11)	[63]
$[Re(NO)F(dppe)_2](BF_4)$	1.874 (10)	1.11 (2)	175.6 (14)	[69]
$[Re(NO)Cl(dppee)_2](BF_4)$	1.803 (16)	1.178 (21)	163	[51]
$[Re(NO)(CO)_2Cl(bipy)][Re(NO)(CO)_2Cl_3]$				[51]
Cation	1.770 (9)	1.163 (13)	178.8	
Anion	1.850 (11)	1.154 (14)	176.5	

reports of metal–HNO complexes; three of these reveal N-binding of the HNO ligand to the metal (Os, Ir and Ru), and one reveals a side-on η^2-binding of the HNO ligand in molybdenum complex [27,28,33].

As predicted from the molecular orbital treatment (Figs. 1 and 2), the Re–N–O fragment in the six-coordinate rhenium nitrosyls with $n = 4\text{–}6$ is linear [34–75].

The rhenium atom, nitrosyl group and one of the halogen ligands in the $[Re(NO)X_3(PPh_3)_2]$ (X = Cl, Br) [34,35], $[Re(NO)Br_3(AsPh_3)_2]$ [36] and $[Re(NO)(CO)Cl_2(PPh_3)_2]$ [34] complexes are sited on a crystallographic two-fold axis of the *C*2/*c* space group. A thermal ellipsoid plot of $[Re(NO)Br_3(PPh_3)_2]$ is shown in Fig. 3.

The number of known $[Re(NO)X_3(PPh_3)_2]$ and $[Re(NO)X_3(AsPh_3)_2]$ complexes is relatively small, but considering structural data for other transition metal nitrosyl [37], it seems that the *C*2/*c* space group with four formula units per unit cell is the preferred one for neutral pseudooctahedral bis(triphenylphosphine) or bis(triphenylarsine) complexes with four ligands of low steric bulk in the equatorial plane. The *trans*-arrangement of the two steric demanding phosphine or arsine molecules in these complexes causes the *cis*-location of the nitrosyl group with respect to π-acid ligands ($AsPh_3$ or PPh_3), which is supported by the electronic influence of the multiply bonded ligand. It forces the metal non-bonding d electrons to lie in the plane perpendicular to the M–NO bond axis. The *cis*-location of the nitrosyl group with respect to $AsPh_3$ or PPh_3 molecules is observed in the *mer*-$[Re(NO)X_3L^1L^2]$ complexes (X = Cl or Br; $L^1 = PPh_3$ or $AsPh_3$; $L^2 = OPPh_3$, MeCN or pzH) [38–40].

A *trans*-arrangement of $OPPh_3$ molecules has been confirmed only for the $[Re(NO)Cl_2(OPPh_3)_2(OReO_3)]$ complex [41]. All other $[Re(NO)X_3L_2]$ complexes (X = Cl or Br; L = $OPPh_3$ or $OAsPh_3$) possess a *cis* geometry of $OPPh_3$ or $OAsPh_3$ molecules [35,36,42,43], which results in a significant angular deformation around the rhenium centre and larger deviation of the Re–N–O unit from linearity in comparison with the *mer*, *trans*-$[Re(NO)X_3L_2]$ complexes.

The $[Re(NO)X_4L]^-$ anions of the $(NEt_4)[Re(NO)Cl_4(py)]$ [44], $(NEt_4)[Re(NO)Br_4(EtOH)]$ [45], $(NEt_4)[Re(NO)Br_4(MeCN)]$ [45], $(AsPh_4)[Re(NO)Cl_4\{OC(NH_2)CH_3\}]$ [46] and $K[Re(NO)(CN)_4(H_2O)]$ [47] complexes display distorted octahedral coordination geometries with the

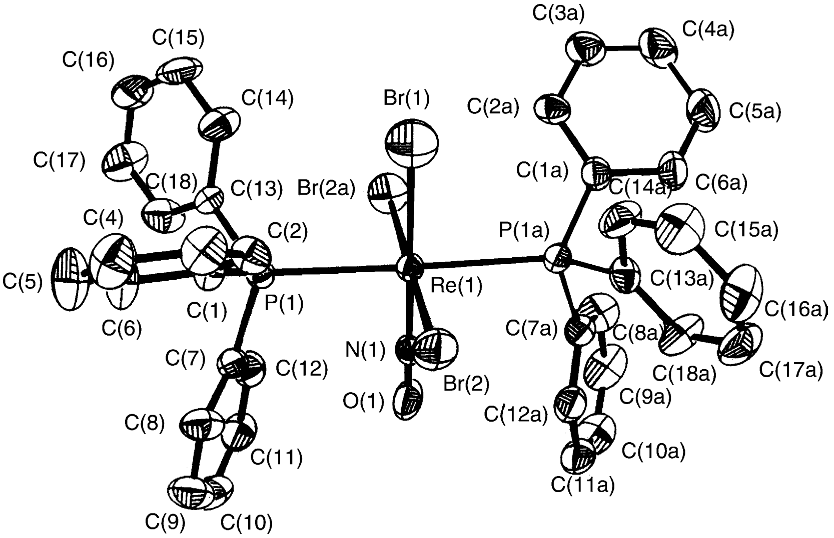


Fig. 3. Molecular structure of $[Re(NO)Br_3(PPh_3)_2]$ [35].

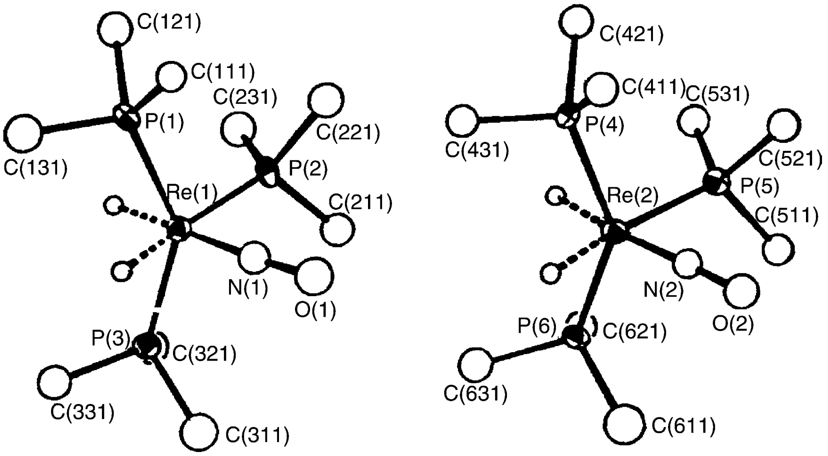


Fig. 4. Perspective drawings of the two independent $[Re(NO)H_2(PPh_3)_3]$ molecules [61].

four X ligands lying on an equatorial plane, and the nitrosyl group and ligand L in the axial positions. The rhenium atom of these compounds is significantly displaced out of the plane defined by the X ligands towards the nitrosyl group. The Re–NO bond distance in $[Re(NO)(CN)_4(H_2O)]^-$ is shorter with respect to that in $[Re(NO)(CN)_5]^{2-}$. Π-back-bonding from Re → NO is more pronounced in the $[Re(NO)(CN)_4(H_2O)]^-$ complex, in which the nitrosyl group is in a *trans*-position to the H_2O molecule being a σ-bonding ligand.

Carbonyl–nitrosyl species are sparse among $\{ReNO\}^5$ complexes, whereas they dominate in $\{ReNO\}^6$ chemistry [48–60]. The rhenium atom becomes more electron rich and is generally more available than the d^5 ion to electron exchange with π-ligands. Most of the structurally characterised six-coordinate $\{ReNO\}^6$ carbonyl–nitrosyls possess the $[Re(NO)(CO)(PR_3)_2]$ unit with *cis* arranged nitrosyl and carbonyl groups and *trans* arranged phosphine ligands [50–56]. Transition metal complexes containing the nitrosyl group in *trans*-position to the carbonyl ligand are instable [48]. Both NO and CO are considered as π-acceptor ligands; however, there are significant differences in the nature of the electron distributions in the Re–N–O and Re–C–O links. The rhenium–nitrogen bond is strong and the N–O bond is relatively weak, whereas the Re–C bond is relatively weak, and the C–O bond is strong. NO is more electronegative than CO; thus, it is a better electron acceptor but weaker σ-donor. Consequently, the NO group better stabilizes π-donating ligands in the *trans*-position. The analysis of the Re–C/Re–N and N–O/C–O bond lengths and the temperature factors of the nitrogen and carbon atoms sometimes allows one to distinguish carbonyl and nitrosyl ligands. However, in many carbonyl–nitrosyl complexes, the NO and CO groups are positionally disordered. As a result of this, the Re–N/Re–C and N–O/C–O distances and the temperature factors of the N and C atoms are similar. Non-resolvable disorder in the CO and NO positions was found in $[Re(NO)(CO)Cl_2(4,4'\text{-}Me_2\text{-bipy})]$, $[Re(NO)(CO)_2Cl_2(THF)]$, *cis, trans*-$[Re(NO)(CO)Cl_2(\eta^1\text{-dpmm})_2]$ [51], $[Re(NO)(CO)Cl(H)(PMe_3)_2]$ [53], $[Re(NO)(CO)(O_3SCF_3)_2(PEt_3)_2]$ [56] and $[Re(NO)(CO)(MeCN)_2\{P(OMe)_3\}_2](O_3SCF_3)$ [56].

The phosphine molecules of $[Re(NO)H_2(PPh_3)_3]$ in axial positions are markedly bent towards the hydrido-atoms. The P–Re–P angles are equal to 143.4(3)° and 143.0(3)° in the two crystallographically independent $[Re(NO)H_2(PPh_3)_3]$ molecules. Such substantial bending of the triphenylphosphine molecules results mainly from low steric hindrance of the hydrido ligands. Nevertheless, the electronic factors also favour the bending of the π-acceptor axial ligands towards the purely σ-donating hydride ligands and away from the nitrosyl group, a strong π-acceptor. A *trans* relationship between the nitrosyl ligand, the most proficient π-acceptor ligand in this complex, and the strong σ-donor hydride ligand contributes to the thermodynamic stability of the compound [61]. The perspective drawings of the two independent $[Re(NO)H_2(PPh_3)_3]$ molecules are depicted in Fig. 4.

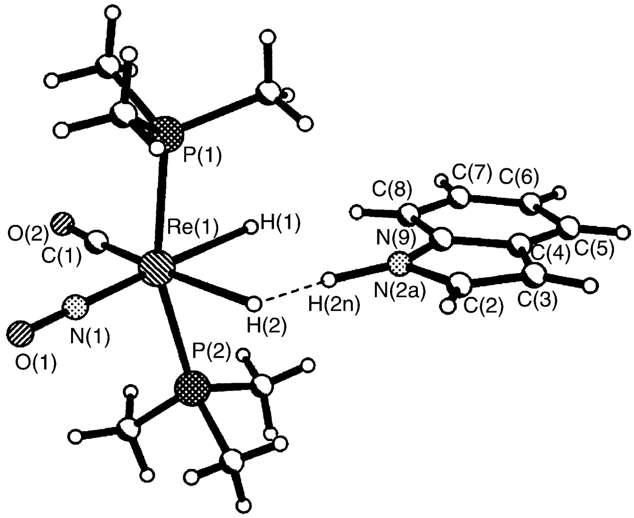


Fig. 5. The molecular structure of the $[Re(NO)(CO)H_2(PMe_3)_2]$-indole adduct [54].

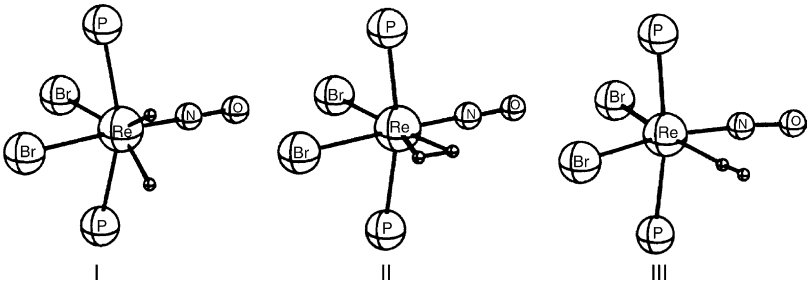


Fig. 6. Coordination geometries for the HH ligand in $[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$ [62].

Similar deviations from ideal octahedral geometry are observed in the other rhenium hydrido-nitrosyls: the P–Re–P angles are 163.5(1)° and 160.0(2)° for $[Re(NO)(CO)Cl(H)(PMe_3)_2]$ and $[Re(NO)(CO)H_2\{P(OMe)_3\}_2]$, respectively [53]. In *trans, trans*-$[Re(NO)(CO)_2(H)(PPh_3)_2](SO_3CF_3)$ both the triphenylphosphine and carbonyl ligands are significantly bent towards the hydride site (P–Re–P = 161.46(4)°, C–Re–C = 163.8(2)°) [31].

The interaction of the rhenium hydrido-nitrosyls $[Re(NO)(CO)H_2(PR_3)_2]$ (R = Me, Et, *i*Pr) with a series of proton donors has been studied. The hydrogen bonded complex of $[Re(NO)(CO)H_2(PMe_3)_2]$ with indole has been characterised by single-crystal X-ray diffraction [54]. The molecular structure of the $[Re(NO)(CO)H_2(PMe_3)_2]$-indole adduct is shown in Fig. 5.

The Re–H bonds of the adduct are non-equivalent: Re–H(1) = 1.63(3) Å and Re–H(2) = 2.36(3) Å. The Re–H(2) bond is positioned in front of an elongated NH fragment of indole, and the H(2)···H(2*n*)–N(2a) is equal to 1.79(5) Å. The indole molecule is coplanar with the plane of the [Re(NO)(CO)] fragment [54].

Several dihydrogen rhenium nitrosyls have been obtained, and X-ray diffraction studies have been carried out for one of them—$[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$. Unfortunately, the hydrogen atoms of the η^2-H_2 moiety could not be found in the difference Fourier maps. Their most probable positions in the molecule have been traced by an extensive search based on DFT calculations. It is known that there are three different possibilities for the binding of the HH unit to the metal centre: side-on in-plane (I), side-on perpendicular (II) and end-on (III). The different coordination geometries for the HH ligand in $[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$ are depicted in Fig. 6.

The bonding of dihydrogen to a metal in a side-on way consists of two components. The first one involves σ-donation of electron density from the σ_{HH} orbital to the metal d_σ orbital, and the second—back-donation from the d_π metal orbitals to the σ^*_{HH}. For the end-on coordination mode, only the σ_{HH} to the d_σ interaction is possible; thus, the side-on modes are in

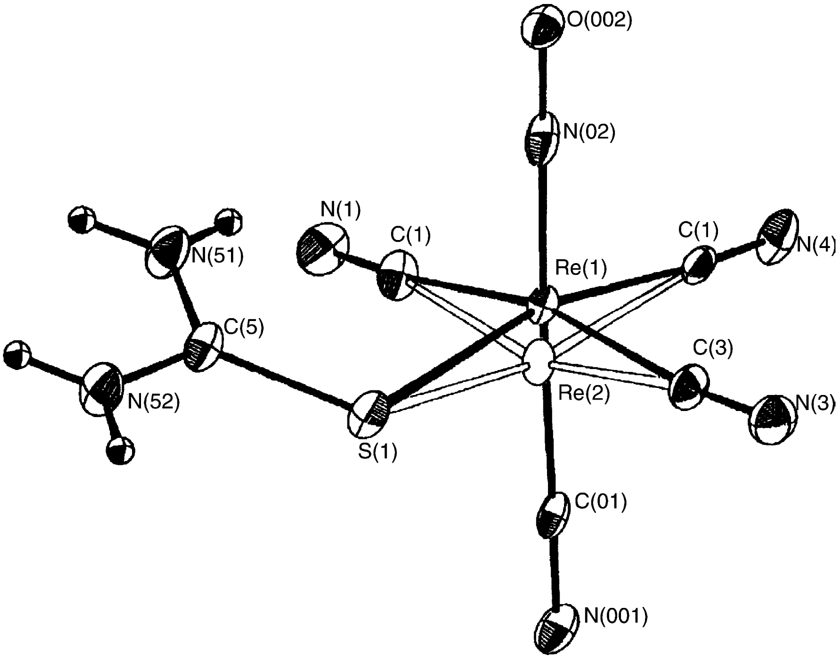


Fig. 7. Perspective drawing of the $[Re(NO)(CN)_4\{SC(NH_2)_2\}]^{2-}$ ion with the disorder in the rhenium atom [63].

favour over the end-on coordination. DFT calculations carried out for structures of types I and II of $[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$ reveal that the structure of type I is more stable, and the energy differences between the two geometric arrangement (I and II) is equal to 59 kJ/mol [62].

The numbering scheme of the $[Re(NO)(CN)_4\{SC(NH_2)_2\}]^{2-}$ ion as well as the disorder observed for the central atom is shown in Fig. 7.

The *cis* orientation of the thiourea with respect to the nitrosyl group in the $(AsPh_4)_2[Re(NO)(CN)_4\{SC(NH_2)_2\}]$ [63] complex is surprising and somewhat unexpected. It is in contrast to $(AsPh_4)_2[Re(NO)(CN)_4(H_2O)]$ and all other crystallographically characterised transition metal mono-substituted cyano-complexes [64]. The rhenium atom of $[Re(NO)(CN)_4(H_2O)]^{2-}$ anion is surrounded by four cyano groups in the equatorial plane, and the nitrosyl and aqua ligands in axial positions.

Both anion and cation of the $[Re(NO)(CO)_2Cl(bipy)][Re(NO)(CO)_2Cl_3]$ complex possess an octahedrally coordinated Re centre. In the cation, the nitrosyl group is in *trans*-position to the chloride ligand, and the 2,2′-bipyridine moiety is located *trans* to the carbonyl groups. In the anion, the chloride ligands are *facially* coordinated to the Re atom, and the nitrosyl group is *cis* arranged to the CO ligands [51].

The $[Re(NO)Cl_2(MeCN)(PMe_3)_2]$ complex is an example of a transition metal complex with $Z' = 11$, being the largest Z' value for this class of compounds observed up to now. The unusual high number of independent molecules in the asymmetric unit results from the dense network of hydrogen bonds. Both the two chlorides and the oxygen atoms of the nitrosyl ligands serve as acceptor sites, whereas methyl groups of either the phosphines or nitriles act as hydrogen donors. A projection onto the *a*, *c* plane of the unit cell of this compound is shown in Fig. 8. The $[Re(NO)Cl_2(MeCN)(PMe_3)_2]$ molecules exhibit a distorted octahedral coordination. The two Cl ligands are coordinated in *cis* configuration, and are located *trans* to π-accepting moieties. The phosphorus donors are in *trans*-position, and they are slightly bent towards the Cl ligands, which enhances π-back-donation from the metal centre to the acceptor groups [65].

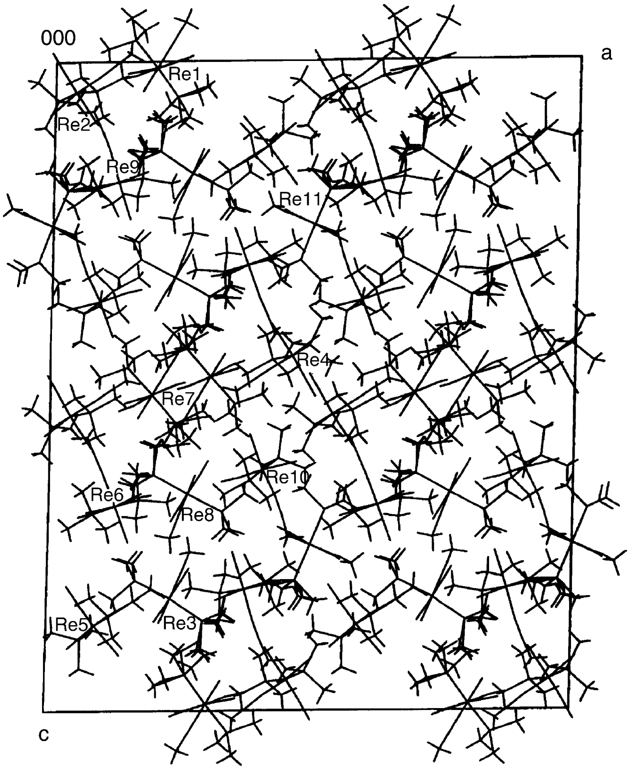


Fig. 8. A projection onto the *a*, *c* plane of the unit cell of $[Re(NO)Cl_2(MeCN)(PMe_3)_2]$ [65].

The N–O bond lengths in the six-coordinate rhenium nitrosyls are generally in the range 1.10–1.20 Å, as expected for NO^+ ligand [19]. In some cases, a significant lengthening or shortening of the N–O distance is observed. Generally, this results from steric ligand interactions, disorder problems or thermal motion of atoms. The disorders of the nitrosyl ligands affect also the accuracy of the Re–N bond lengths and Re–N–O angles. A lengthening of the Re–N distances in the $[Re(NO)(CO)Cl_2(4,4'\text{-}Me_2\text{-}bipy)]$, $[Re(NO)(CO)_2Cl_2(THF)]$, $[Re(NO)(CO)Cl_2(dppm)_2]$ [51] and $[Re(NO)(CO)H_2(PMe_3)_2]$-indole [54] complexes is a consequence of non-resolvable disorder in the NO and CO groups. The structures of *mer*-$[ReCl_2(NO)(py)_3]$ [66] and *mer*-$[ReCl_2(NO)(SbPh_3)_3]$ [67] have been modelled with the *trans* Cl and NO ligands disordered over two sites, and consequently a large discrepancy is observed in the Re–N and N–O bond lengths. A similar trend is observed for the $[Re(NO)Cl(dppe)_2](NO_3)_2$ [68], $[Re(NO)F(dppe)_2](BF_4)$ [69] and $[Re(NO)Cl(dppee)_2](BF_4)$ [51] complexes with the two chelating ligands in the equatorial positions. These complexes have crystallographically imposed C_i symmetry, so that the axial ligands are disordered in the two positions with equal occupancy factors.

3.2. Five-coordinate mononitrosyls

Five-coordinate complexes can adopt either tetragonal pyramidal (TP) or trigonal bipyramidal (TBP) structures. The nitrosyl group in TBP complexes may occupy either the apical or equatorial position. Table 2 contains structural data for five-coordinate rhenium mononitrosyls.

The geometries of the $[Re(NO)H(BH_4)(P^iPr_3)_2]$ and $[Re(NO)H(BH_4)(PPh_3)_2]$ compounds may be viewed in two ways depending on the number of coordination sites occupied by the BH_4^- ligand. If the bridging BH_4^- is considered to occupy a single site in the coordination sphere, the structures of these complexes can be described as distorted trigonal bipyramids. Alternatively, if we assume that bridging borohydride occupies two coordination positions, the structures might be referred as a very distorted octahedron. Unfortunately, the positional disorder of the borohydride and nitrosyl ligands does not allow further discussion of geometrical data, although the actual coordination arrangement around the rhenium is clearly established. The

Table 2
Structural data for five-coordinate mononitrosyl rhenium complexes

Complex	Re–N (Å)	N–O (Å)	Re–N–O (°)	References
$[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$	1.781 (16)	1.167 (24)	173.6 (14)	[76]
$[Re(NO)H(BH_4)(P^iPr_3)_2]$	1.748 (6) 1.58 (2)	1.17 (1) 1.27 (2)	169.4	[62]
$[Re(NO)H(BH_4)(PPh_3)_2]$	1.75 (2) 1.86 (2)	1.18 (2) 1.10 (3)	170.9	[62]

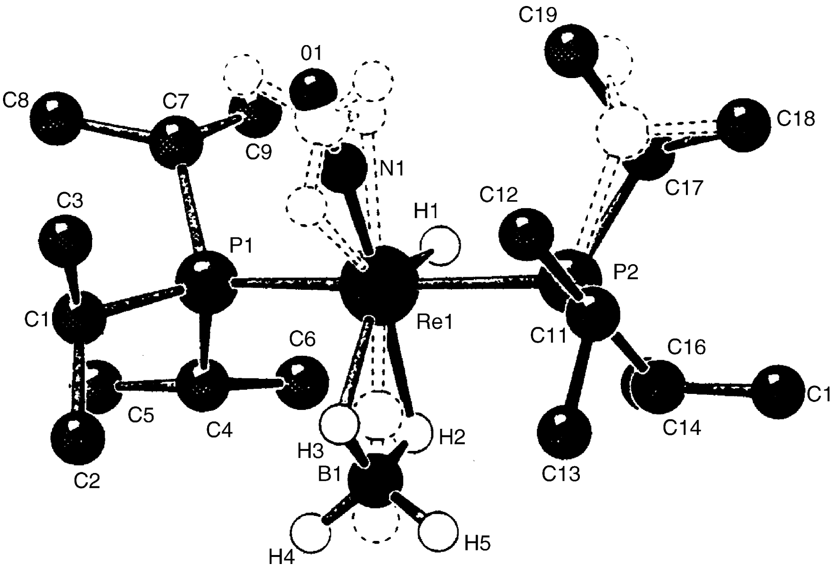


Fig. 9. The molecular structure of $[Re(NO)H(BH_4)(P^iPr_3)_2]$ [62].

phosphine molecules of the $[Re(NO)H(BH_4)(P^iPr_3)_2]$ and $[Re(NO)H(BH_4)(PPh_3)_2]$ complexes are placed in axial positions. The NO group, the hydride ligand and the bridging borohydride form the equatorial plane [62]. The molecular structure of $[Re(NO)H(BH_4)(P^iPr_3)_2]$ is shown in Fig. 9.

The geometry around the rhenium atom in the $[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$ compound is best described as a trigonal bipyramid. The nitrosyl group of the $[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$ complex occupies the apical position, two of the equatorial aromatic ligands are directed towards (*endo*) the NO and one away (*exo*). The axial aromatic group is oriented so as to occupy the space left between the equatorial aromatic ligands [76]. The structure of $[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$ is depicted in Fig. 10.

3.3. Dinitrosyl mononuclear complexes

In dinitrosyl complexes, the NO ligands may be arranged *trans* or *cis*, although the majority of dinitrosyl species adopt a *cis* geometry. Fig. 11 presents the correlation diagram relating the molecular orbitals for a linear $M(NO)_2$ group with $D_{\infty h}$ symmetry (a) to those for C_{2v} symmetry (b) [5].

Complexes containing the $\{M(NO)_2\}^4$ moiety could have either linear *trans* or bent *cis* structures, although the *trans* form minimizes the repulsion of the two NO groups. Additional electrons will occupy δ_g orbital in $D_{\infty h}$ symmetry. The δ_g orbital is non-bonding with respect to M and N. Thus, an $\{M(NO)_2\}^6$ and $\{M(NO)_2\}^8$ species should adopt a bent structure. The $\{M(NO)_2\}^{10}$ complexes in C_{2v} symmetry will have the electron configuration:

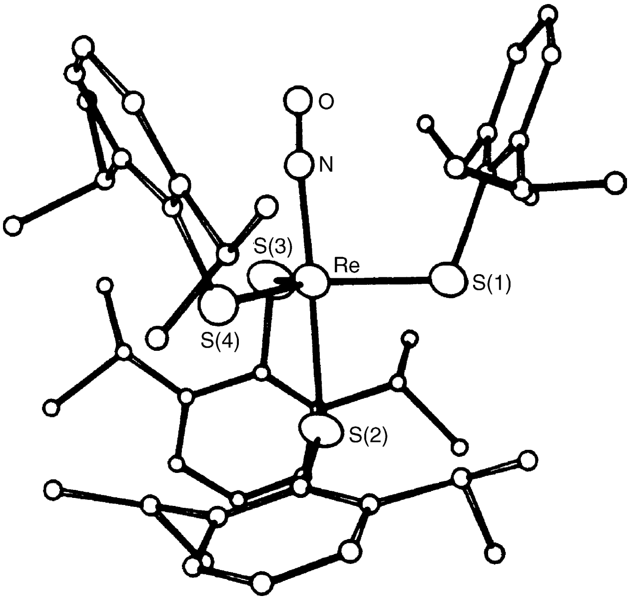


Fig. 10. Perspective drawing of $[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$ [76].

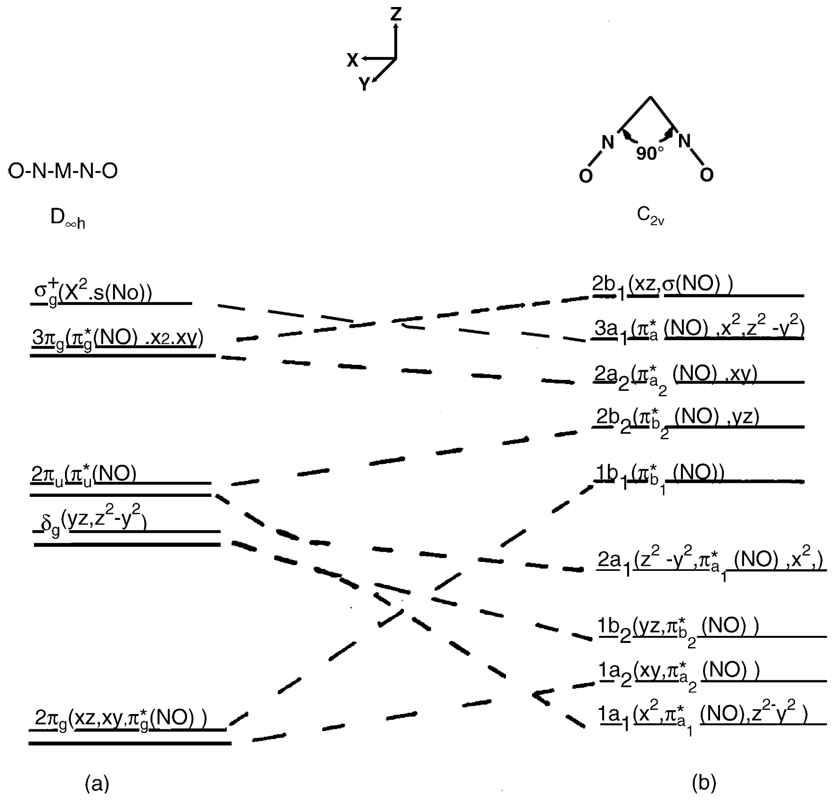


Fig. 11. A correlation diagram relating the molecular orbitals for a linear $M(NO)_2$ group with $D_{\infty h}$ symmetry (a) to those for C_{2v} symmetry (b) [5].

$(1a_2)^2(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^2$. The $1b_1$ orbital is entirely localized on the NO groups. Population of this orbital is expected to cause the N–M–N angle to increase and could also lead to changes in the M–N–O angles. Two conformations, *attracto* and *repulso*, have been confirmed for $\{M(NO)_2\}^{10}$ complexes. The *attracto* conformation, with the N–Re–N angle less than ca. 130° and the two O atoms bent towards each other, is characteristic for the first-row transition metal dinitrosyls with good π-accepting ligands. The second- and third-row transition metal dinitrosyls with poor π-acceptors usually have *repulso* conformations, with N–Re–N angles larger than ca. 130° [5,19].

Table 3 presents structural data for dinitrosyl mononuclear rhenium complexes [75,77–80]. The nitrosyl groups of the $[Re(NO)_2(pc)]^-$ compound are *trans* arranged, which results from the presence of the tetradendate ligand in the equatorial plane [75].

In all the other structurally characterised mononuclear dinitrosyl rhenium complexes, the NO ligands adopt a *cis* arrangement. The $[Re(NO)_2Cl_2(SbPh_3)_2]$ [77], $[Re(NO)_2Br_4]^-$ [78] and $[Re(NO)_2Cl_3(MeCN)]$ [79] complexes display distorted octahedral coordination geometries.

The $[Re(NO)_2(PCy_3)_2]^+$ cation can be described as a distorted C_{2v} butterfly unit, which is obtained on removing one equatorial ligand from an ideal trigonal bipyramidal arrangement. Structures of a variety of $[M(NO)_2(PR_3)_2]^{n+}$ compounds ($n = 0$ or 1; M = Fe, Ru, Os, Co, Rh or Ir) are described in the literature. However, all these complexes exhibit the coordination geometry of a distorted tetrahedron, and therefore cannot be compared with $[Re(NO)_2(PCy_3)_2]^+$. The molecular structure of $[Re(NO)_2(PCy_3)_2]^+$ is shown in Fig. 12.

The phosphorus atoms are bent away from the NO groups; the P–Re–P bond angle is equal to 159.93(8)°. The NO ligands show a *cisoid* bend of about 15°, and the N–Re–N angle is 115.9(4)° [80].

The $[Re(NO)_2(P^iPr_3)_2(H)]$ complex and the $[Re(NO)_2(PCy_3)_2(CO)]^+$ cation display distorted TBP geometries with the phosphine molecules in the apical positions. The P^iPr_3molecules of $[Re(NO)_2(P^iPr_3)_2(H)]$ are markedly bent towards the hydrido-ligand; the P–Re–P angle is 153.89(6)°. The bending of the phosphine molecules towards the hydride site polarizes the rhenium d_{xz} orbital in the direction of the π-accepting nitrosyl groups. It provides better d_{xz}–π^*_{NO} overlap and enhances the amount of back-donation to NO.

A strong polarization of d_{xz} in the direction of the π-accepting nitrosyl groups is not favourable in the $[Re(NO)_2(PCy_3)_2(CO)]^+$ cation. In this case, the carbonyl ligand competes with the NO groups for back-donation. The P–Re–P angle of $[Re(NO)_2(PCy_3)_2(CO)]^+$ is considerable larger—169.62(5)° [80] (Scheme 3).

The benzaldehyde ligand of $[Re(NO)_2(PCy_3)_2(C_6H_5CHO)](BAr^F{}_4)$ is coordinated in a asymmetrical fashion, as can be seen in Fig. 13.

The coordination of the benzaldehyde ligand to the $[Re(NO)_2(PR_3)_2]$ fragment leads to bending of one of the

Table 3
Structural data for dinitrosyl mononuclear rhenium complexes

Complex	Re–N (Å)	N–O (Å)	Re–N–O (°)	N–Re–N	References
$[Re(NO)_2(PCy_3)_2](BAr^F{}_4)$	1.735 (10) 1.766 (8)	1.225 (12) 1.180 (11)	166.9 (9) 165.7 (9)	115.9(4)	[80]
$[Re(NO)_2(P^iPr_3)_2(H)]$	1.804 (7) 1.780 (7)	1.193 (9) 1.227 (9)	173.1 (8) 175.4 (7)	127.4(3)	[80]
$[Re(NO)_2(PCy_3)_2(CO)](BAr^F{}_4)$	1.790 (7) 1.825 (5)	1.191 (9) 1.176 (1)	174.0 (6) 176.3 (6)	121.5(3)	[80]
$[Re(NO)_2(PCy_3)_2(C_6H_5CHO)](BAr^F{}_4)$	1.758 (4) 1.811 (4)	1.199 (5) 1.204 (5)	150.9 (3) 175.9 (4)	108.8(2)	[80]
$[Re(NO)_2Cl_2(SbPh_3)_2]$ Molecule I	1.909 (8) 2.064 (96)	0.941 (10) 1.080 (97)	178.3 (9) 176.0 (14)	95.1(19) 90.0(7)	[77]
Molecule II	2.003 (22) 1.921 (14)	1.043 (26) 1.030 (17)	178.1 (12) 178.5 (17)		
$(PPh_4)[Re(NO)_2Br_4]\cdot 2CCl_4$	1.844 (18) 1.798 (21)	1.143 (26) 1.005 (28)	176.1 (18) 177.1 (21)	91.2(9)	[78]
$[Re(NO)_2Cl_3(MeCN)]$	1.76 (6) 1.59 (6)	1.23 (9) 1.36 (9)	173.7 161.9	91.9	[79]
$\{N(PPh_3)_2\}[Re(NO)_2(pc)]$	2.120	0.917	174.4	180	[75]

nitrosyl groups. The geometry of $[Re(NO)_2(PCy_3)_2(C_6H_5CHO)]^+$ is better described by a distorted tetragonal pyramid than a trigonal bipyramid [80].

3.4. Lewis acid adducts

Transition metal nitrosyls can react with Lewis acids to form adducts via (i) the oxygen atom of the nitrosyl group, (ii) the metal or (iii) the ancillary ligands such as CO or halide. Structural data for rhenium nitrosyl/Lewis adducts are listed in Table 4 [62,81].

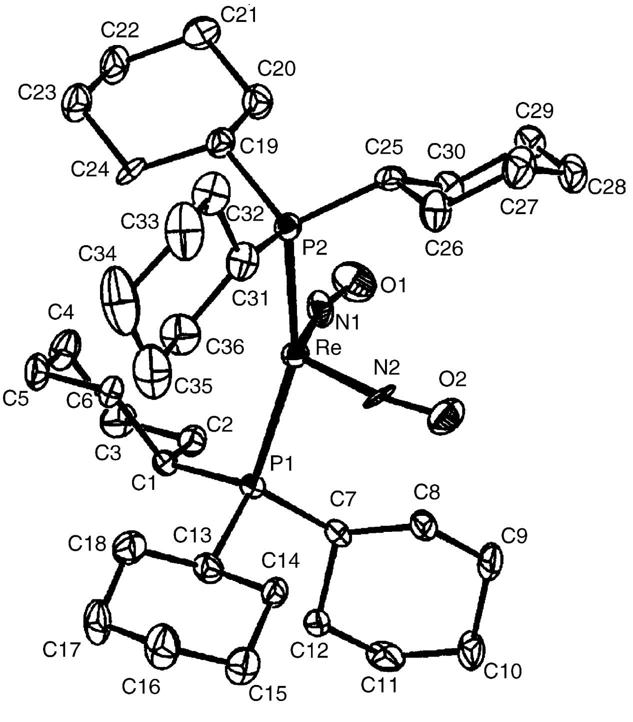
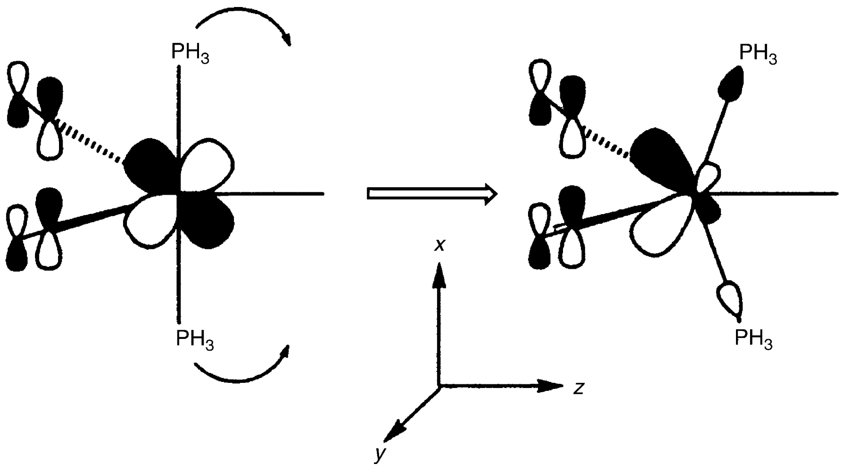


Fig. 12. The molecular structure of $[Re(NO)_2(PCy_3)_2]^+$ [80].

The ligand geometry around the rhenium in $[Re(NO)(NOBF_3)(H)(P^iPr_3)_2]$ [62], $[Re(NO)(NOSiEt_3)(H)(P^iPr_3)_2](BAr^F{}_4)$ and $[Re(NO)\{NOH_2NC_5H_6(CH_3)_4\}(H)(PCy_3)_2](BAr^F{}_4)$ [81] is best described as a distorted trigonal bipyramid. The NO group, the hydride ligand and the NOL fragment are located in the trigonal plane of the molecule. The phosphine ligands occupy the apical positions and they are strongly bent towards the position of the hydride ion. The coordination of the $SiEt_3$ and BF_3 moieties to the nitrosyl ligand results in a significant lengthening of the respective N–O bond, but only a slight shortening of the corresponding Re–N distance is observed. The lengthening of the N–O bond is interpreted in terms of increased electronic donation from the metal centre to the NO unit initiated by the attachment of the Lewis acid. The nitrosyl ligand remains essentially linear after attachment of $SiEt_3$ or BF_3, the Re–N–O angle is close to 170°. The N–O–Si/N–O–B linkage is sharply bent with a N–O–Si/N–O–B angle close to 120°, indicating an sp^2 hybridization at the oxygen atom. The molecular structure of $[Re(NO)(NOSiEt_3)(H)(P^iPr_3)_2]^+$ cation is shown in Fig. 14.

In the solid-state of $[Re(NO)\{NOH_2NC_5H_6(CH_3)_4\}(H)(PCy_3)_2](BAr^F{}_4)$ complex, the ammonium cation is situated in the bridging position between the nitrosyls groups of the two crystallographically different molecules. As can be seen from Fig. 15, both hydrogen atoms of the ammonium cation are involved in hydrogen bonding with the nitrosyl ligands (NO···HN distances of 1.908 and 1.987 Å, respectively) [81].



Scheme 3.

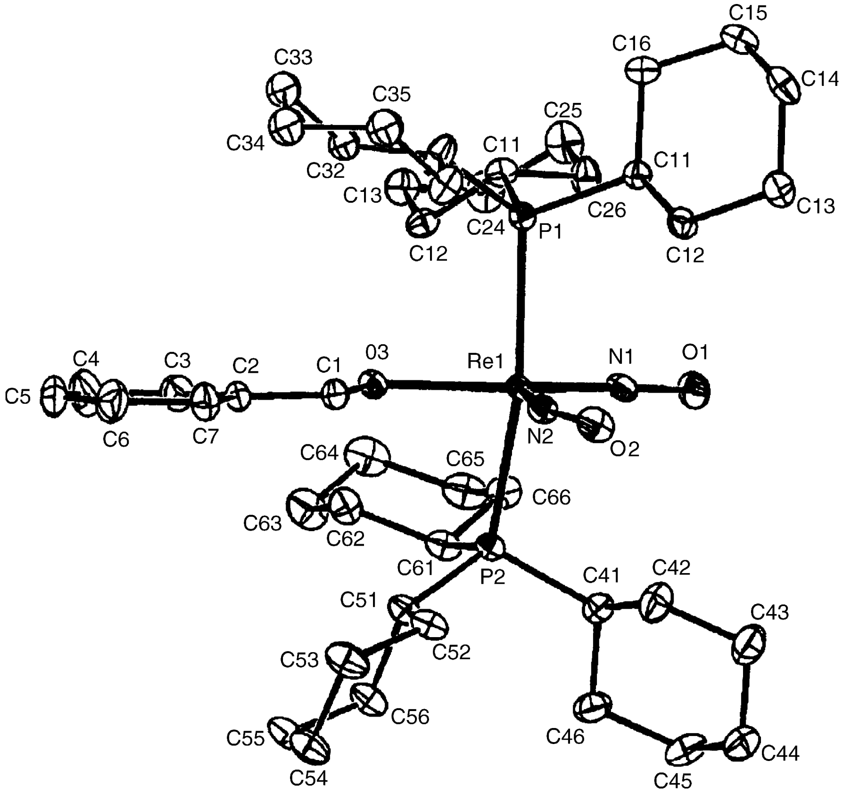


Fig. 13. The molecular structure of $[Re(NO)_2(PCy_3)_2(C_6H_5CHO)]^+$ [80].

Table 4
Structural data for five-coordinate mononitrosyl rhenium complexes

Complex	Re–N (Å)	N–O (Å)	Re–N–O (°)	References
$[Re(NO)(NOBF_3)(H)(P^iPr_3)_2]$	1.775 (5) 1.749 (5)[a]	1.212 (7) 1.304 (7)[a]	168.7 (5) 170.0 (4)[a]	[62]
$[Re(NO)(NOSiEt_3)(H)(P^iPr_3)_2](BAr^F{}_4)$	1.790 (4) 1.765 (4)[a]	1.194 (5) 1.321 (5)[a]	167.7 (4) 174.0 (4)[a]	[81]
$[Re(NO)\{NOH_2NC_5H_6(CH_3)_4\}(H)(PCy_3)_2](BAr^F{}_4)$	1.782 (4) 1.781 (3)[a]	1.213 (5) 1.237 (4)[a]	174.1 (4) 175.7 (3)[a]	[81]

[a] These values correspond to (NOL) group.

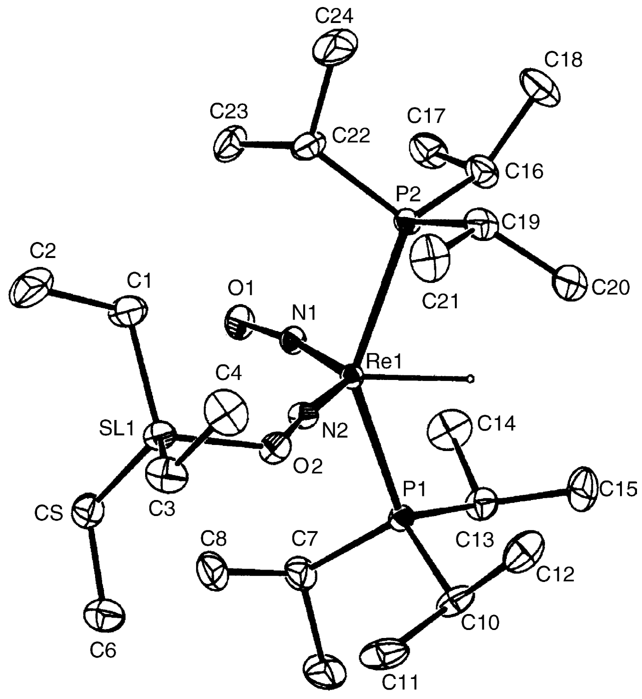


Fig. 14. Molecular structure of [Re(NO)(NOSiEt$_3$)(H)(P^{i}Pr$_3$)$_2$]$^+$ [81].

3.5. Bridging nitrosyl rhenium complexes

The nitrosyl ligand can bridge two, three or even four metal atoms. It can bind to metal centres of polynuclear species only through the N atom, or both N and O atoms. Although dinuclear complexes with the NO ligand bridging two centres via the N atom seem to be the simplest, they have not been obtained for rhenium. The only structurally characterised bridging nitrosyl rhenium compounds are [Re$_2$(H)(μ-η^2-NO)(NO)$_3$(P^{i}Pr$_3$)$_4$](BAr^F$_4$) [80] and (NEt$_4$)[{Re$_3$(μ-H)$_3$(CO)$_{10}$}$_2$(μ$_4$-η^2-NO)] [82]. The molecular structure of the [Re$_2$(H)(μ-η^2-NO)(NO)$_3$(P^{i}Pr$_3$)$_4$]$^+$ cation is shown in Fig. 16.

The [Re$_2$(H)(μ-η^2-NO)(NO)$_3$(P^{i}Pr$_3$)$_4$](BAr^F$_4$) compound can be considered as an adduct of [Re(NO)$_2$(P^{i}Pr$_3$)$_2$](BAr^F$_4$) and [Re(NO)$_2$(P^{i}Pr$_3$)$_2$(H)]. The oxygen atom of one of the nitrosyl groups of [Re(NO)$_2$(P^{i}Pr$_3$)$_2$(H)] is apparently a Lewis base strong enough to interact with a Lewis acid—[Re(NO)$_2$(P^{i}Pr$_3$)$_2$]$^+$.

A view of the [{Re$_3$(μ-H)$_3$(CO)$_{10}$}$_2$(μ$_4$-η^2-NO)]$^-$ anion is depicted in Fig. 17. It consists of two centrosymmetrically related triangular cluster units [Re$_3$(μ-H)$_3$(CO)], joined by a nitrosyl ligand disordered about an inversion centre. The Re–N–O, Re–N–Re and Re–O–Re angles are close to 120°, which indicate an sp^2 hybridization of the N and O atoms. The nitrosyl group lies fairly well in the plane of four atoms [82]. Structural data for bridging nitrosyl rhenium complexes are presented in Table 5.

3.6. Dinuclear and polynuclear rhenium compounds with terminal NO ligands

Structural data for dinuclear and trinuclear rhenium complexes with terminal nitrosyl ligands are listed in Table 5 [51,56,83–87]. The two bridging dmpm ligands of

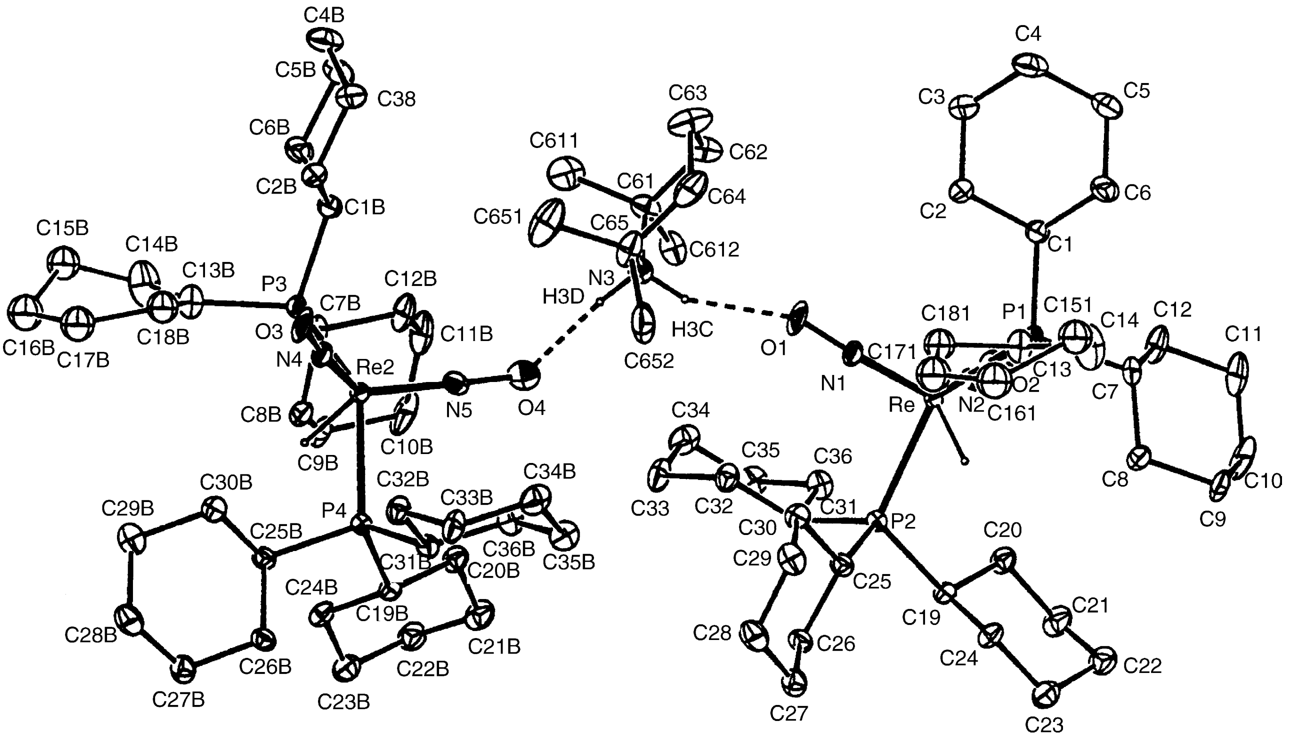


Fig. 15. Hydrogen bonding in the solid sate of [Re(NO){NOH$_2$NC$_5$H$_6$(CH$_3$)$_4$}(H)(PCy$_3$)$_2$](BAr^F$_4$) [81].

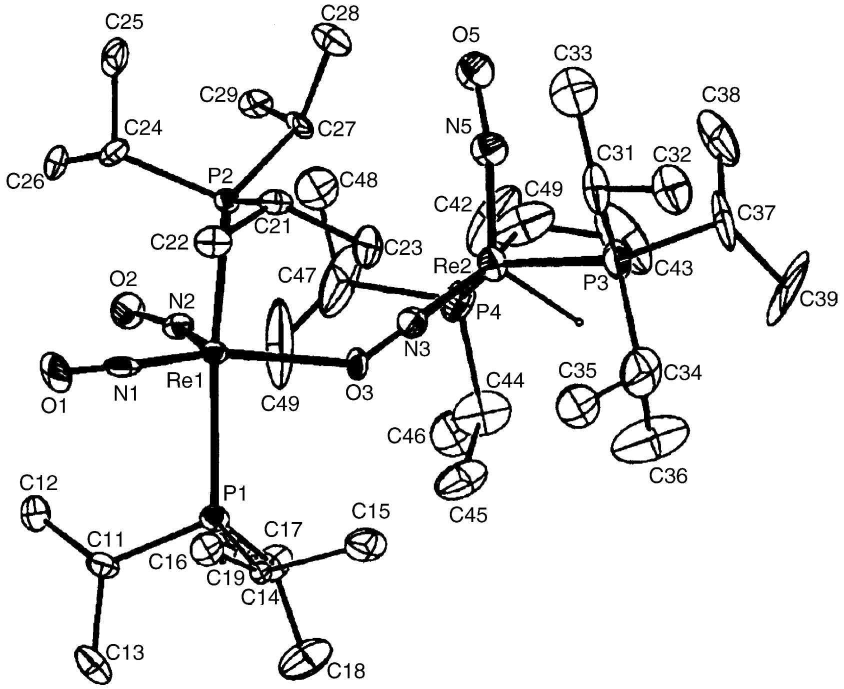


Fig. 16. Molecular structure of the $[\mathrm{Re_2(H)(\mu\text{-}\eta^2\text{-}NO)(NO)_3(P^iPr_3)_4}]^+$ cation [80].

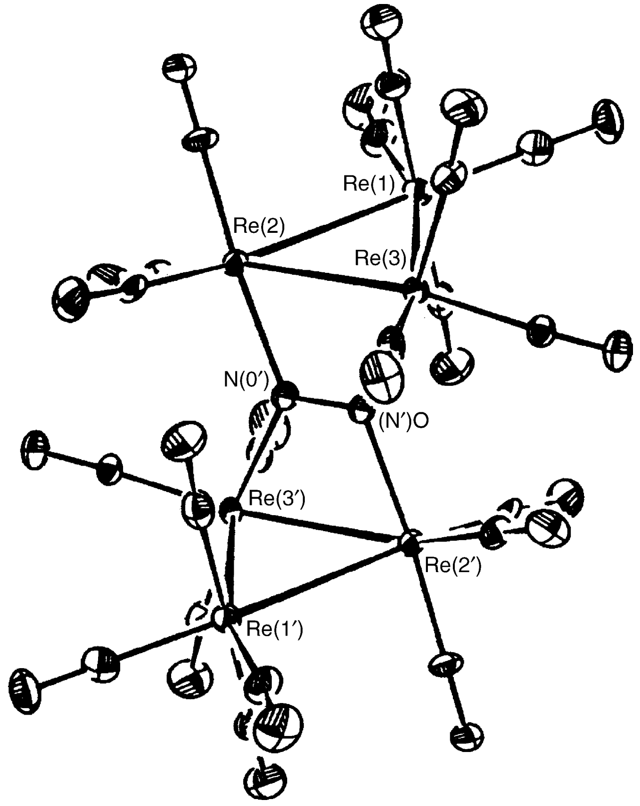


Fig. 17. Molecular structure of the $[\{\mathrm{Re_3(\mu\text{-}H)_3(CO)_{10}}\}_2(\mu_4\text{-}\eta^2\text{-}\mathrm{NO})]^-$ anion [82].

$[\mathrm{Re_2(NO)Cl_5(\mu\text{-}dmpm)_2}]$ are bound in such a way that a rarely encountered *cis*, *trans* disposition of phosphorus atoms at the two metal centres is observed [83] (Fig. 18).

The short Re–Re bond distance [2.379(1) Å)] in $[\mathrm{Re_2(NO)Cl_5(\mu\text{-}dmpm)_2}]$ indicates the presence of a triple bond between the rhenium atoms. The weakening of the Re≡Re bond of $[\mathrm{Re_2(NO)Cl_5(\mu\text{-}dmpm)_2}]$ in comparison with other triply bonded dirhenium halide complexes results from Re → π^*_{NO} back-bonding. The Re–Re bond distances of $[\mathrm{Re_2(\mu\text{-}H)(\mu\text{-}Br)[P(O)Ph_2]Br_2(NO)(\mu\text{-}dppm)_2}]^+$

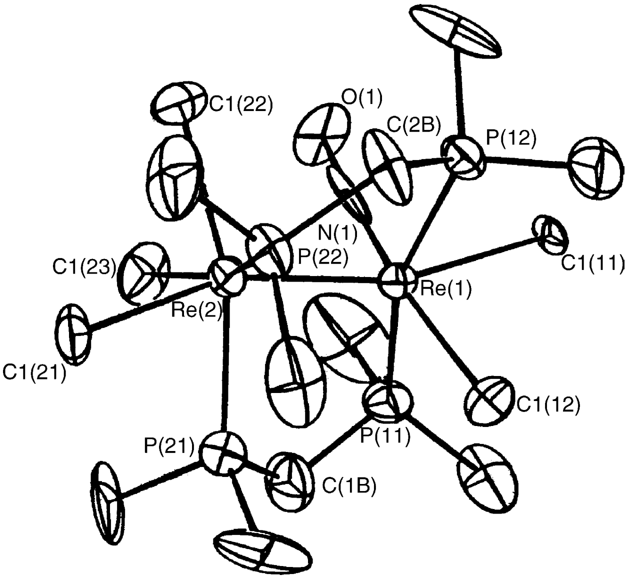


Fig. 18. Molecular structure of $[\mathrm{Re_2(NO)Cl_5(\mu\text{-}dmpm)_2}]$ [83].

Table 5
Structural properties of dinuclear rhenium nitrosyls and heteronuclear clusters with terminal nitrosyl groups bound to Re atoms

Complex	Re–N/O (Å)	N–O (Å)	Re–N–O (°)	References
Bridging nitrosyl rhenium complexes				
$[Re_2(H)(\mu\text{-}\eta^2\text{-NO})(NO)_3(P^iPr_3)_4](BAr^F{}_4)$	1.78 (1)	1.20 (1)	158 (1)	[80]
	1.80 (2)	1.17 (2)	172 (1)	
$(NEt_4)[\{Re_3(\mu\text{-}H)_3(CO)_{10}\}_2(\mu_4\text{-}\eta^2\text{-NO})]$	2.133 (av)	1.34 (av)	114.4 (av)	[82]
Dinuclear rhenium complexes with one or two terminal nitrosyl ligands				
$[Re_2(NO)Cl_5(\mu\text{-dmpm})_2]$	1.68 (3)	1.28 (3)	174 (1)	[83]
$[Re_2(\mu\text{-}H)(\mu\text{-}Br)[P(O)Ph_2]Br_2(NO)(\mu\text{-dppm})_2](ReO_4)$	1.76 (1)	1.18 (1)	178 (1)	[84]
$(PPh_4)[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$	1.721 (18)	1.191 (25)	176.5 (17)	[76]
	1.638 (27)	1.305 (32)	173.6	
$[Re(NO)(CO)Cl(\mu\text{-}Cl)(COE)]_2$	1.760 (13)	1.168 (18)	170.3 (12)	[51]
$[Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2(O_3SCF_3)_2$	1.762 (5)	1.190 (7)	177.2 (5)	[56]
$[\{Re(NO)(CO)(tacn)\}_2(\mu\text{-}CH_2OCH_2)]I_2$	1.77 (3)	1.26 (4)	176.3	[87]
	1.70 (3)	1.24 (4)	173.9	
$[\{Re(NO)(CO)_2Cl\}_2(\mu\text{-}SCMe_3)_2]$	1.785 (13)	1.187 (18)	177.0 (14)	[85]
	1.840 (18)	1.182 ((23)	177.1 (14)	
$[\{Re(NO)(CO)_2\}_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)]$	1.861 (28)	1.21 (5) av	169.7 (33)	[85]
	1.793 (51)		172.0 (33)	
$[Re_2(NO)_2(CO)_3(SCMe_3)(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]$	1.744 (14)	1.175 (20)	177.1 (15)	[85]
	1.808 (21)	1.131 (29)	174.4 (17)	
$[Re_2(NO)_2(CO)_2(SCMe_3)_2(\mu\text{-}SCMe_3)_2(\mu\text{-}OH)]\{Na(THF)(Et_2O)\}$	1.742 (14)	1.181 (19)	176.6 (13)	[85]
	1.802 (14)	1.168 (20)	176.9 (13)	
Trinuclear rhenium clusters with the nitrosyl group at each Re atom				
$[Re_3(NO)_3(CO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}S)(\mu_3\text{-}Cl)]$	1.704 (27)	1.18 (4) av	177.8 (25)	[85]
	1.813 (35)		175.7 (33)	
	1.815 (29)		174.3 (30)	
$[Re_3(NO)_3(CO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)]$	1.759 (16)	1.204 (22)	176.1 (16)	[85]
Trinuclear antiferomagnetic clusters with Cr_2Re_2 core and nitrosyl ligand bound to Re				
$[Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(NO)I]$	1.901 (21)	1.011 (34)	157.5 (26)	[88]
$[Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(NO)(CO)]$	1.807 (28)	1.165 (41)	176.7 (13)	[89]
cis-$[Cp_2Cr_2(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2ReCl_2(NO)(CO)_2]$	1.77 (3)	1.25 (4)	177.6 (31)	[90]
trans-$[Cp_2Cr_2(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2ReCl_2(NO)(CO)_2]$	1.780 (2)	1.16 (2)	174.2 (10)	[90]
Trinuclear antiferomagnetic clusters with $CrRe_2$ core and nitrosyl ligands bound to Re atoms				
$[CpCr(\mu\text{-}SCMe_3)Re(NO)(CO)(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)Re(NO)(CO)_2]$	1.767 (8)	1.199 (11)	175.3	[88]
	1.839 (9)	1.162 (13)	173.6	
$[CpCr(\mu\text{-}SCMe_3)Re(NO)(CO)(\mu_3\text{-}S)_2(\mu_3\text{-}SCMe_3)\ (\mu\text{-}SCMe_3)Re(CO)_3]$	1.775 (10)	1.195 (16)	176	[88]
$[CpCr(\mu_3\text{-}S)(\mu\text{-}OSCMe_3)_2Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(NO)_2(CO)_2]$	1.785 (12)	1.19 (2)	178.9	[90]
	1.823 (14)	1.19 (2)	175.9	
Tetranuclear antiferromagnetic clusters with Cr_2Re_2 core and nitrosyl ligands bound to Re atoms				
$[CpCr(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2Re(NO)(CO)]_2$	1.789 (5)	1.176 (7)	178.6 (5)	[90]

[84] and $[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]^-$ [76] are considerably longer than for $[Re_2(NO)Cl_5(\mu\text{-dmpm})_2]$ (2.6273(8) and 2.783(1), respectively), but still indicative of some degree of Re–Re multiple bonding.

The $[Re(NO)(CO)Cl(\mu\text{-}Cl)(COE)]_2$ [51] complex and the $[Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2{}^{2+}$ cation [56] are built from two identical mononuclear fragments related by a centre of inversion. The O and P atoms of the two bridging $\{(MeO)_2P(O)\}$ fragment and two Re atoms of $[Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2{}^{2+}$ cation form a planar heteronuclear six membered ring. Fig. 19 presents the molecular structure of the $[Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2{}^{2+}$ cation.

The terminal nitrosyl groups of the trinuclear $[Re_3(NO)_3(CO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)]$ complex occupy the *trans*-positions to the oxo ligand, whereas the carbonyl groups are *trans* arranged with respect to the $\mu_3\text{-}SCMe_3$ bridge [85]. The molecular structure of the $[Re_3(NO)_3(CO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)]$ is depicted in Fig. 20.

The cubane-type cluster $[Re(\mu_3\text{-}O)(CO)_2(NO)]_4$ was isolated in the reaction of the $[ReCl_3(CO)_2(NO)]^-$ complex

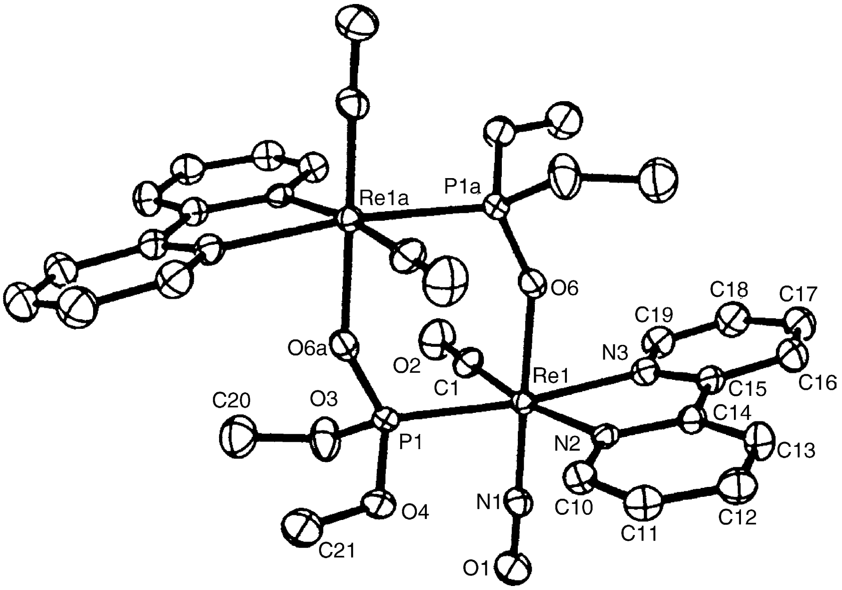


Fig. 19. Molecular structure of the $[Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2^{2+}$ cation [56].

with water, and characterised by IR and mass spectroscopy. The basic structure is a Re_4O_4-unit (Scheme 4) [86].

Table 5 contains also structural data for a variety of antiferromagnetic heteronuclear clusters containing a nitrosyl group bound to a Re atom [88–90]. Although these compounds are organometallic species, they have been included in Table 5. The rhenium atoms of the clusters are not bound to carbon atom of organic ligands. Most of these clusters have been synthesised by fission of the binuclear rhenium complex applying organometallic chromium complexes as ligands. Chart 1 presents the structural formulae of selected heteronuclear clusters.

3.7. Short comparison with manganese and technetium

The number of structurally characterised nitrosyl coordination compounds is considerable larger for rhenium than manganese or technetium.

X-ray structures were determined for some six-coordinate $\{TcNO\}^5$ and $\{TcNO\}^6$ complexes. The first group includes $(AsPh_4)[Tc(NO)Cl_3(acac)]$ [91] and $(NBu^n{}_4)[Tc(NO)Cl_4(MeOH)]$ [92] (similar to $(NEt_4)[Re(NO)Br_4(EtOH)]$). The second class comprises the following compounds: $[Tc(NO)Br_2(CNBu^t)_3]$ [93], $[Tc(NO)Cl_2(HN{=}NC_6H_4N)(PPh_3)]$ [94], $[Tc(NO)Cl(diars)_2]^+$ [95] (similar to $[Re(NO)X(L–L)]^+$), $[Tc(NO)(Phen)_2(NH_3)]^{2+}$ [96], $[Tc(NO)Cl_2(pyPPh_2\text{-}P,N)(py\text{-}PPh_2\text{-}P)]$ [97] and $[Tc(NO)Cl_2(py)_3]$ [98] (analogous to $[Re(NO)Cl_2(py)_3]$). Π-acceptor donors, such as phosphines, arsines and/or

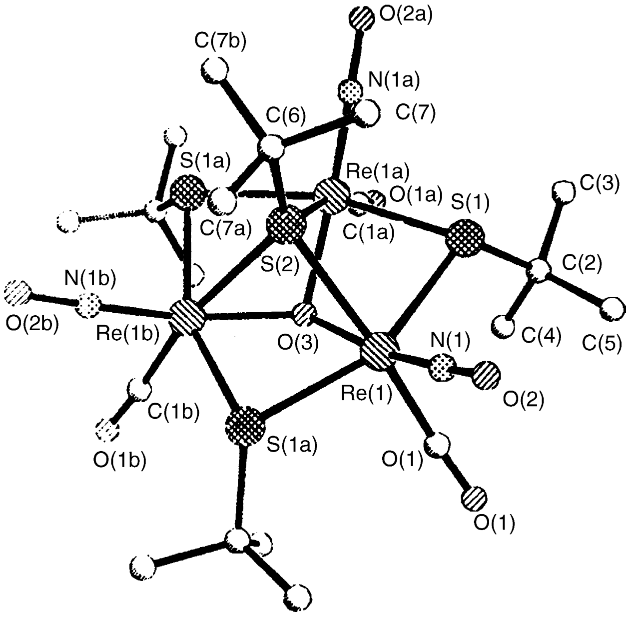
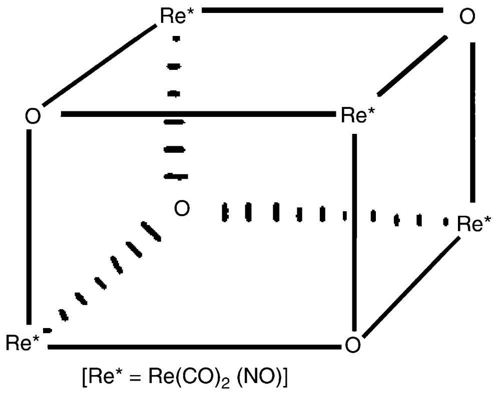


Fig. 20. Molecular structure of the $[Re_3(NO)_3(CO)_3(\mu\text{-}SCMe_3)_3(\mu_3\text{-}SCMe_3)(\mu_3\text{-}O)]$ [85].



Scheme 4.

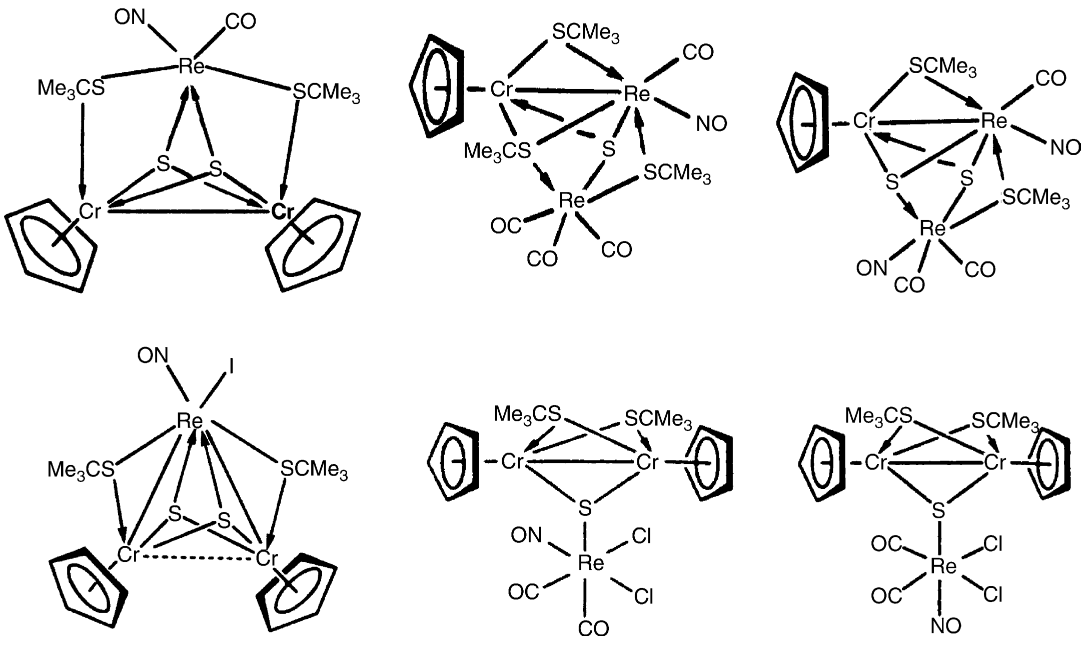


Chart 1.

pyridine-like ligands, usually complete the coordination sphere of $\{TcNO\}^6$ complexes. Only one five-coordinate technetium nitrosyl complex has been structurally characterised—$[Tc(NO)Cl(2,3,5,6\text{-}Me_4SC_6H)_3]$ [99]. The geometry about the technetium atom is trigonal bipyramidal with the chloride and linear NO group in the axial positions. For rhenium, a series of $[Re(NO)(SR)_4]$ was obtained, and X-ray structure was determined for $[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_4]$.

For manganese, some mono- and dinitrosyl five-coordinate complexes were structurally characterised. The $[Mn(NO)(CO)_4]$ [100], $[Mn(NO)(CO)_3(PPh_3)]$ [101], $[Mn(NO)(CO)_2(PHPh_2)_2]$ [102] and $[Mn(NO)(CO)_2(PPh_3)_2]$ [103] compounds have TPB geometry with the linear NO group in the equatorial plane. Although $[Re(NO)(CO)_4]$ is unknown, the $[Re(NO)(CO)_2(PPh_3)_2]$ derivative was isolated, but it was not structurally characterised.

In the (2,8,16,22-tetra-azatricyclo(21.5.0.0^{9,15})octacosa-1,9,11,13,15,23,25,27-octane)(nitrosyl)manganese(III) [104], the nearly linear NO group lies in the trigonal plane, rather than occupying the axial position of a square pyramid as occurs in the porphyrin analogue—[Mn(NO)(TTP)] [105].

In the five-coordinate dinitrosyls – $[Mn(NO)_2\{PPh(OMe)_2\}_3]^+$ [106], $[Mn(NO)_2(Cl)\{PPh(OMe)_2\}_2]$ [107] and $[Mn(NO)_2(H)(PMe_3)_2]$ [108] – the coordination about the Mn atom is trigonal bipyramidal with the nearly linear nitrosyl groups in the equatorial plane. Some similar rhenium five-coordinate rhenium dinitrosyls are presented in Section 3.3. The pentacyano anion, $[Mn(NO)(CN)_5]^{2-}$ [109], porphyrin complex, [Mn(NO)(4-MePip)(TPP)] [105], and series of nitrosylmanganese phthalocyaninates [Mn(NO)(ONO)(pc)], [Mn(NO)(NCO)(pc)], $[Mn(NO)(OPPh_3)(pc)]$ and $[Mn(NO)_2(pc)]^-$ [75] are structurally characterised six-coordinate nitrosyl complexes of manganese. A similar series of nitrosylrhenium phthalocyaninates were obtained, and the X-ray structure of $[Re(NO)(CN)_5]^{2-}$ was determined.

Four-coordinate structurally characterised manganese nitrosyl species, $[Mn(NO)_3(PPh_3)]$ [110] and $[Mn(NO)_2(CO)_2]^-$ [111], possess tetrahedral geometry with essentially linear NO groups. They are formally d^{10} nitrosyls and do not have analogues among rhenium and technetium nitrosyl complexes.

3.8. Structural trans-effects of nitrosyl ligand

The ‘structural trans-effect’ (STE) is defined as the effect of a ligand on a bond distance to a *trans* ligand. ‘Kinetic trans-effect’ (KTE) refers to the effect on the lability of a *trans* ligand [112].

A thorough analysis of the bond lengths in octahedral transition metal nitrosyls allowed one to get information on the ‘structural trans-effects’ of the nitrosyl ligand. The linearly bonded nitrosyl ligand is a poor σ-donor, and a very strong π-acceptor. The STEs of NO^+ depend on the bonding properties of the ligand being affected (in *trans*-position to the nitrosyl). Fig. 21 presents the simplified orbital representations of the bonding in linear metal nitrosyl complexes with different types of *trans* ligand.

The NO^+ ligand shows moderate STE with respect to π-acceptor ligands, negligible STE, to a purely σ-donating ligand, and inverse STE (i.e., the *trans* bonds are shortened) when occupies *trans*-position to π-donors [112].

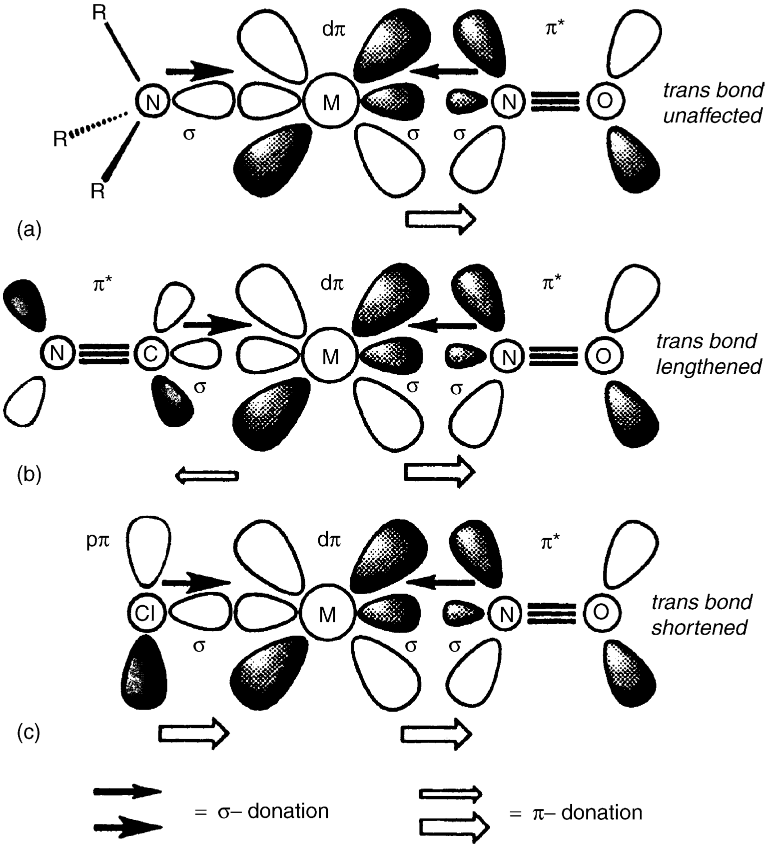


Fig. 21. Simplified orbital representations of the bonding in linear metal nitrosyl complexes with different types of *trans* ligand: (a) σ-donor ligand; (b) σ-donor–π-acceptor ligand; (c) σ-donor–π-donor ligand [112].

The number of rhenium nitrosyls with σ-donor ligands in the coordination sphere is sparse. The [Re(NO)(CO)(NH_3)(tacn)]Br_2 complex (tacn = 1,4,7-triazacyclonanane) seems to be the best example. The X-ray crystallographic investigation confirms negligible STE of the nitrosyl group on the the Re–N_{amine} bond length. The Re–N_{amine} distance (2.149(6) Å) in *trans*-position to the nitrosyl is almost the same as the Re–N_{amine} bond *trans* to the NH_3 molecule (2.154(6) Å), and shorter in comparison with the third Re–N_{amine} bond (2.169(6) Å) *trans* to the carbonyl ligand [58].

For the $(AsPh_4)_2$[Re(NO)$(CN)_4${SC$(NH_2)_2$}], the rhenium-cyano bond length *trans* to the nitrosyl is significantly longer (2.229(11) Å) than the average rhenium-cyano distance *cis* to the nitrosyl group (2.121(12) Å) [63]. A similar trend is observed for (NEt_4)[Re(NO)Cl_4(py)] [44]. The Re–N_{py} bond (2.218(6) Å) is considerable longer in comparison with the value obtained from the sum of the relevant covalent radii (2.08 Å) or average value of the Re–N_{py} distances (2.12 Å) in *mer*-[Re$X_3$$(py)_3$] (X = Cl, Br) [112].

An inverse structural trans-effect of the linearly bonded nitrosyl ligand has been observed for structures: (PPh_4)[Re$(NO)_2$$Br_4$] [78] and ($AsPh_4$)[Re$(NO)_2$$Cl_4$][79]. The perspective drawing of the [Re$(NO)_2$$Br_4$]$^-$ with bond lengths is depicted in Fig. 22.

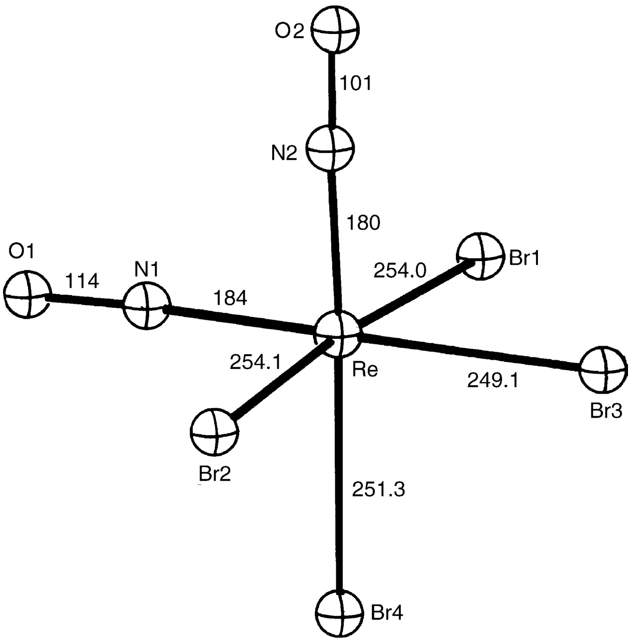


Fig. 22. Perspective drawing of the [Re$(NO)_2$$Br_4$]$^-$ with bond lengths (ppm) [78].

For the *mer*, *trans*-$[Re(NO)X_3(PPh_3)_2]$ (X = Cl, Br) [34,35], $[Re(NO)Br_3(AsPh_3)_2]$ [36] compounds a significant lengthening of the Re–Cl and Re–Br distances is observed. This probably results from the fact that the halogen atoms in the *cis* positions to the NO group take part in weak intramolecular hydrogen bonds. The formation of the hydrogen bond causes local deficiency of electron density on the halogen ions and consequently these ligands are closer to the rhenium atom in the experimental structures.

The strong STE of $NO^{\bullet}$ and NO^- in the octahedral mononitrosyls can be explained on the basis molecular orbital scheme presented in Fig. 2. The highest occupied molecular orbital in the six-coordinate $\{MNO\}^7$ and $\{MNO\}^8$ complexes is constituted of the π^*_{NO} orbital and d_z^2 metal orbital. This orbital combination must be antibonding with respect to the binding of the ligand in *trans*-position to the NO. A partial population of the d_z^2 orbital by an unpaired electron (or electrons) derived from the $NO^{\bullet}$ or NO^- ligand leads to weakening of the metal–ligand bond *trans* to the nitrosyl. This can be demonstrated by the structural studies of the porphyrin [M(NO)(4-MePip)(TPP)] complexes. For $\{MnNO\}^6$ complex, the Mn–NO angle is nearly linear (176°) and the $Mn–N_{pip}$ bond length is relatively short (2.20 Å). For $\{FeNO\}^7$complex, the Fe–NO angle equals to 142° and the bond to 4-methylpiperidine nitrogen is significantly weakened (2.46 Å). In the $\{CoNO\}^8$ species, the Co–NO angle is 128° and a stable complex with 4-methylpiperidine could not be isolated. The structural trans-effect is apparently the mechanism by which NO acts as a messenger and turns on the enzyme guanylate cyclase. NO as a signalling agent coordinates to a five histidine-ligated heme; the consequent NO trans-effect leads to a breaking of the *trans* iron–histidine bond. The structural trans-effect of $NO^{\bullet}$ leads to a greater than 0.20 Å lengthening of the bond *trans* to NO. The structural data for complexes with a nitroxyl ligand show that NO^- has a particularly strong STE, greater than $NO_2{}^-$, CN^- and Me^- [26,113,114].

4. Spectroscopic properties of nitrosyl rhenium complexes

4.1. IR spectroscopy

The MNO group is expected to exhibit ν_{NO}, ν_{MN} and δ_{MNO} in the IR spectra of metal nitrosyl complexes, but only ν_{NO} has been identified in most cases. The stretching frequency for uncoordinated NO is 1870 cm^{-1}, and on binding to a metal ν_{NO} may increase or decrease. It is a consequence of the synergetic electronic interaction between σ-donation of electron density from NO to metal d orbitals and back-donation of electron density from M to NO. A net donation of electron density from NO group to a metal centre results in a stronger N–O bond, and a higher ν_{NO} can be expected. Conversely, an increased back-donation of electron density from M to NO leads to the population of π^*_{NO} orbitals and lowering of ν_{NO}. The position of ν_{NO} is influenced by many other factors, such as electronic configuration of the metal centre, electronic effects of other ligands, the overall charge of the complex and the structure of the complex. Although IR spectroscopy is the most widely used technique for the characterisation of metal nitrosyls, it cannot be used to unambiguously assign the mode of linkage of NO group to a metal centre. There is no reliable correlation between a position of ν_{NO} and M–N–O geometry [1–25]. The IR stretching frequencies for nitrosyl rhenium complexes are summarized in Tables 6–9.

In general, only one ν_{NO} is observed in the IR spectra of the mononitrosyl rhenium complexes. The splitting in the ν_{NO} bands in the IR spectra of the $[Re(NO)(CO)Cl(bipy)(PR_3)](O_3SCF_3)$ complexes (R = OMe, Et) is connected with the presence of two isomers in an approximate 2:1 ratio [56]. Unfortunately, all attempts to separate the isomers by chromatography were unsuccessful. In other cases, the splitting of the ν_{NO} bands results from the solid-state effect or the choice of solvent medium for recording the IR spectrum of the complex [36,57,62,115,116].

The ν_{NO} vibrations of the rhenium nitrosyl complexes appear at lower wavenumbers than that of free NO. This indicates a contribution of electronic back-donation from the metal centre to the π^*_{NO} orbitals. A significant shift to lower wavenumbers is typical for the $\{ReNO\}^6$ compounds with strong σ/π-donors in the coordination sphere.

The highest NO stretching frequency is observed for the $[Re(NO)(CO)(MeCN)_2(PEt)_3)_2](O_3SCF_3)$ complex. In comparison with $[Re(NO)(CO)(MeCN)_2\{P(OMe)_3\}_2](O_3SCF_3)$ and $[Re(NO)(CO)(bipy)\{P(OMe)_3\}_2](O_3SCF_3)$, a decrease in π-back-bonding to the nitrosyl group can be noted [56].

On changing the halogen from chlorine to bromine, the ν_{NO} frequency of $(NEt)_2[Re(NO)X_5]$ compounds increases, although an opposite behaviour could be expected on the basis of the trend in electron affinity [117–119]. The substitution of the halide *trans* to NO in the $(NEt)_2[Re(NO)X_5]$ complexes by a neutral π-acceptor ligand L causes an increase of the ν_{NO} frequency. The ligand L successfully competes with the electron transfer from the metal to the NO group. The variations in ν_{NO}, however, are not a measure of the π-acceptor properties of the ligands L [117,120].

Table 10 presents NO stretching frequencies for $[M(NO)(CN)_5]^{n-}$ (M = Mn, Re, Fe, Ru, Os; n = 2, 3). The ν_{NO} of $[Re(NO)(CN)_5]^{n-}$ (n = 2 or 3) is considerably lower in comparison with $[M(NO)(CN)_5]^{2-}$ (M = Fe, Ru, Os) and the manganese $[Mn(NO)(CN)_5]^{n-}$ (n = 2 or 3) analogues. The ν_{NO} of $[Re(NO)(CN)_5]^{2-}$ is even lower than the NO stretching frequency observed for the $\{Mn(NO)\}^6$ complex. This indicates a large contribution of electronic back-donation from the Re atom to the π^*_{NO} orbitals. The decrease of ν_{NO} for $[Re(NO)(CN)_4(OH_2)]^{1-}$ in comparison with $[Re(NO)(CN)_5]^{2-}$ is consistent with the fact that π-back-bonding from Re to NO is more pronounced in the

Table 6
NO stretching frequencies for six-coordinate mononitrosyl rhenium complexes

Complex	ν(NO) ($\mathrm{cm^{-1}}$)	References
$\{\mathrm{ReNO}\}^4$		
$[\mathrm{Re(NO)Cl_4(MeCN)}]$	1912; 1810	[70]
$[\mathrm{Re(NO)Cl_3(NPPh_3)(OPPh_3)}]$	1737	[71]
$(\mathrm{AsPh_4})[\mathrm{Re(NO)Cl_5}]\cdot\mathrm{H_2O}$	1740/1750	[115]
$(\mathrm{PPh_4})[\mathrm{Re(NO)Cl_5}]\cdot\mathrm{H_2O}$	1730	[115]
$(\mathrm{AsPh_4})[\mathrm{Re(NO)Br_5}]\cdot\mathrm{H_2O}$	1740	[115]
$(\mathrm{PPh_4})[\mathrm{Re(NO)Br_5}]\cdot\mathrm{H_2O}$	1740	[115]
$[\mathrm{Re(NO)Cl_4(phen)}]\cdot\mathrm{H_2O}$	1770/1740	[115]
$[\mathrm{Re(NO)Br_4(phen)}]\cdot\mathrm{H_2O}$	1762/1733	[115]
$\{\mathrm{ReNO}\}^5$		
$(\mathrm{NEt_4})_2[\mathrm{Re(NO)Cl_5}]$	1718^{a}, 1740^{2}	$[117^{a},118^{b}]$
$\mathrm{K_2}[\mathrm{Re(NO)Cl_5}]$	1730	[118]
$\mathrm{Cs_2}[\mathrm{Re(NO)Cl_5}]$	1710^{a}	[118]
$(\mathrm{NEt_4})_2[\mathrm{Re(NO)Br_5}]$	1734^{a}, 1715^{b}	$[117^{a},119^{b}]$
$(\mathrm{bipyH})_2[\mathrm{Re(NO)I_5}]$	1700	[129]
$\mathrm{Cs_2}[\mathrm{Re(NO)I_5}]$	1700	[129]
$\mathrm{Rb_2}[\mathrm{Re(NO)I_5}]$	1720	[129]
$(\mathrm{NMe_4})_2[\mathrm{Re(NO)(SCN)_5}]$	1765	[131]
$\mathrm{K_2}[\mathrm{Re(NO)(SCN)_5}]$	1755	[131]
$\mathrm{K}[\mathrm{Re(NO)(CN)_4(OH_2)}]\cdot(\mathrm{Phen})_5\cdot\mathrm{MeOH}\cdot3\mathrm{H_2O}$	1700	[47]
$\mathrm{K_2}[\mathrm{Re(NO)(CN)_5}]\cdot(\mathrm{Phen})_6\cdot4.5\mathrm{H_2O}$	1660	[47]
$(\mathrm{NEt_4})[\mathrm{Re(NO)Cl_4(L)}]$		
L = MeCN	1765	[117]
L = py	1753	[117]
L = 3-Cl-py	1735	[117]
L = 2-pic	1755	[117]
L = 2,4-lut	1750	[120]
$(\mathrm{NEt_4})[\mathrm{Re(NO)Br_4(L)}]$		
L = MeCN	1770	[117]
L = py	1762^{a}, 1755^{b}	$[117^{a},120^{b}]$
L = 3-Br-py	1740^{a}, 1733^{b}	$[117^{a},120^{b}]$
L = 3-pic	1758	[117]
L = 4-pic	1755	[120]
L = 3,5-lut	1755	[120]
L = $\mathrm{C_6H_5NH_2}$	1741	[120]
L = 4-Me-$\mathrm{C_6H_4NH_2}$	1743	[117]
$(\mathrm{AsPh_4})[\mathrm{Re(NO)Cl_4\{OC(NH_2)CH_3\}}]$	1735	[46]
$[\mathrm{Re(NO)(CO)(NH_3)(tacn)}]\mathrm{Br_3}$	1740	[58]
$[\mathrm{Re(NO)(OH)_3(phen)}]\cdot\mathrm{H_2O}$	1680	[115]
$[\mathrm{Re(NO)(OH)_3(bipy)}]\cdot\mathrm{H_2O}$	1680	[115]
$[\mathrm{Re(NO)X_3(bipy)}]$		
X = Cl	1740	[124]
X = Br	1730–1740	[120]
X = I	1755	[129]
$[\mathrm{Re(NO)X_3(phen)}]$		
X = Cl	1760	[124]
X = Br	1730–1740	[120]
X = I	1700	[129]
$[\mathrm{Re(NO)Cl(dppe)_2}](\mathrm{NO_3})_2$	1700	[68]
$[\mathrm{Re(NO)Cl(dppe)_2}](\mathrm{BF_4})_2$	1680	[68]
$[\mathrm{ReBr_3(NO)(dppe)}]_{0.6}[\mathrm{ReBr_4(dppe)}]_{0.4}$	1742	[74]
$[\mathrm{Re(NO)Cl_2X(PPh_3)_2}]$		
X = Cl	1734^{a}, 1760^{b}	$[34^{a},119^{b}]$
X = OMe	1727	[57]
X = OEt	1728	[57]
$[\mathrm{Re(NO)Cl_2(OReO_3)(PPh_3)(OPPh_3)}]$	1745	[41]
$[\mathrm{Re(NO)Cl_2(OPPh_3)_3}](\mathrm{ReO_4})$	1760	[41]
$[\mathrm{Re(NO)Br_3L_2}]$		
L = $\mathrm{PPh_3}$	1776^{a}, 1750^{b}	$[35^{a},119^{b}]$
L = $\mathrm{AsPh_3}$	1773	[36]
$[\mathrm{Re(NO)Cl_3(AsPh_3)_2}][\mathrm{ReCl_4(AsPh_3)_2}]$	1738	[36]

Table 6 (*Continued*)

Complex	ν(NO) (cm^{-1})	References
$[Re(NO)X_3(OPPh_3)_2]$		
X = Cl	1734	[42]
X = Br (monoclinic)	1738	[35]
X = Br (orthorhombic)	1754	[43]
$[Re(NO)X_3(OAsPh_3)_2]$		
X = Cl	1721	[36]
X = Br	1733	[36]
$[Re(NO)Cl_3(OPPh_3)(PPh_3)]$	1745	[38]
$[Re(NO)Cl_3(OPPh_3)(pyz)]$	1762	[73]
$[Re(NO)Br_3(MeCN)(PPh_3)]$	1749	[39]
$[Re(NO)Br_3(pzH)(AsPh_3)]$	1754	[40]
$\{ReNO\}^6$		
$(AsPh_4)_2[Re(NO)(CN)_4(H_2O)]\cdot 5H_2O$	1677	[64]
$[Re(NO)Cl_2(MeCN)(PMe_3)_2]$	1678	[65]
$[Re(NO)Cl_2(CNR)_2(PPh_3)]$	1726	[57]
$[Re(NO)Cl_2L_3]$		
L = $P(OMe)_3$ (CH_2Cl_2)	1755	[53]
L = PPh_3	1693/1658	[57]
L = $SbPh_3$	1683	[67]
L = py	1650	[66]
$[Re(NO)Br_2L_3]$		
L = py	1665	[120]
L = $SbPh_3$	1681	[67]
L = 4-picol	1660	[120]
$[Re(NO)(I)L_2]PtCl_6$		
L = phen	1665	[129]
L = bipy	1675	[129]
$[Re(NO)BrL_2]Br$		
L = phen	1660	[120]
L = bipy	1660	[120]
$[Re(NO)Cl(dppee)_2](BF_4)$	1714	[51]
$[Re(NO)Cl(dppe)_2](BF_4)$	1690	[68]
$[Re(NO)(OEt)(C_7H_7NC)_2(PPh_3)_2](PF_6)$	1693	[116]
$[Re(NO)(OEt)(C_7H_7NC)_2(PPh_3)_2](ClO_4)$	1702	[116]
$[Re(NO)(OMe)(C_7H_7NC)_2(PPh_3)_2](PF_6)$	1694	[116]
$[Re(NO)(OMe)(C_7H_7NC)_2(PPh_3)_2](ClO_4)$	1701	[116]
$[Re(NO)(CO)Cl_2L_2]$		
L = $P(OMe)_3$ (CH_2Cl_2)	1755	[53]
L = $P(O\text{-}^iPr)_3$ (hexane)	1750	[53]
L = PMe_3 (CH_2Cl_2)	1733	[53]
L = PEt_3 (CH_2Cl_2)	1728	
L = PEt_3 (hexane)	1716	[53]
L = $P(i\text{-}Pr)_3$ (hexane)	1716	[53]
L = PCy_3 (CH_2Cl_2)	1717	[53]
L = PPh_3	1722[a], 1738[b], 1730[c]	[34[a],57[b],130[c]]
L = dppm	1734	[51]
L = 1/2 bipy	1725	[51]
L = 1/2 (4,4′-Me_2-bipy)	1718	[51]
L = 1/2 dmpc		
Enacjomer I	1747	[51]
Enacjomer II	1711	[51]
	1755	[53]
$[Re(NO)(CO)Br_2(PPh_3)_2]$	1740	[130]
$[Re(NO)(CO)Br_2(PPh_3)_2]\cdot NO$	1743/1726	[52]
$[Re(NO)(CO)Cl(I)\{P(O\text{-}^iPr)_3\}_2]$	1757	[50]
$[Re(NO)(CO)\{O_2SO(C_6H_4Me)\}\{P(O\text{-}^iPr)_3\}_2]$	1775	[50]
$[Re(NO)(CO)Cl(H)L_2]$		
L = $P(OMe)_3$ (hexane)	1701	[53]
L = $\{P(i\text{-}PrO)_3\}_2$ (hexane)	1693	[53]
L = PMe_3 (CH_2Cl_2)	1668	[53]

Table 6 (*Continued*)

Complex	ν(NO) (cm^{-1})	References
L = PEt_3 (hexane)	1669	[53]
L = $P(i\text{-}Pr)_3$ (hexane)	1671	[53]
$[Re(NO)(CO)(H)X(PPh_3)_2]$		
X = OCH_3	1669	[116]
X = F (*trans* to NO)	1698	[116]
X = F (*trans* to CO)	1662	[116]
X = Cl	1715/1710/1704	[116]
X = Br	1717/1709/1702	[116]
X = N_3	1704, 1700	[116]
X = NCO	1702	[116]
X = I	1719	[116]
X = SCN	1726	[116]
$[Re(NO)(CO)H(OOCCF_3)L_2]$		
L = PMe_3	1723	[55]
L = $P(i\text{-}Pr)_3$	1724	[55]
L = $P(i\text{-}PrO)_3$	1730	[55]
$[Re(NO)(CO)(OOCCF_3)_2L_2]$		
L = PMe_3	1763	[55]
L = $P(i\text{-}Pr)_3$	1755	[55]
L = $P(i\text{-}PrO)_3$	1785	[55]
$[Re(NO)(CO)F(X)(PPh_3)_2]$		
X = F	1711	[57]
X = OMe	1694	[57]
X = D	1675	[57]
$[Re(NO)(CO)H_2L_2]$		
L = $P(OMe)_3$ (hexane)	1681	[53]
L = $P(i\text{-}PrO)_3$ (hexane)	1671	[53]
L = PMe_3 (hexane)	1655	[53]
L = PEt_3 (hexane)	1652	[53]
L = $P(i\text{-}Pr)_3$ (hexane)	1650	[53]
L = PCy_3 (hexane)	1623	[53]
$[Re(NO)(CO)F(PPh_3)_3](BF_4)$	1742	[57]
$[Re(NO)(CO)H(p\text{-}OC_6H_4NO_2)(PMe_3)_2]$	1665	[54]
$[Re(NO)(CO)Cl(MeCN)_2\{P(OMe)_3\}](O_3SCF_3)$ (in MeCN)	1778	[56]
$[Re(NO)(CO)Cl(MeCN)_2(PEt_3)](O_3SCF_3)$ (in MeCN)	1760	[56]
$[Re(NO)(CO)Cl(bipy)\{P(OMe)_3\}](O_3SCF_3)$	1748/1781	[56]
$Re(NO)(CO)Cl(bipy)(PEt_3)](O_3SCF_3)$	1737/1760	[56]
$[Re(NO)(CO)Cl(O_3SCF_3)\{P(OMe)_3\}_2]$	1770	[56]
$[Re(NO)(CO)Cl(O_3SCF_3)(PEt_3)_2]$	1744	[56]
$[Re(NO)(CO)(O_3SCF_3)_2\{P(OMe)_3\}_2]$	1802	[56]
$[Re(NO)(CO)(O_3SCF_3)_2(PEt_3)_2]$	1767	[56]
$[Re(NO)(CO)(MeCN)_2\{P(OMe)_3\}_2](O_3SCF_3)_2$	1826	[56]
$[Re(NO)(CO)(MeCN)_2(PEt_3)_2](O_3SCF_3)_2$	1793	[56]
$Re(NO)(CO)(bipy)\{P(OMe)_3\}_2](O_3SCF_3)_2$	1764	[56]
$[Re(NO)(CO)_2(tacn)](BF_4)_2$	1800	[125]
$[Re(NO)(CO)(NH_3)(tacn)]Br_2$	1720	[58]
$[Re(NO)(CO)(CF_3SO_3)(tacn)](CF_3SO_3)$	1760	[58]
$[Re(NO)(CO)Cl(tacn)][(1S\text{-}C_{10}H_{14}BrO_4S]$	1700	[87]
$[Re(NO)(CO)(MeCN)(tacn)]\ (BF_4)_2$	1740	[58]
$[Re(NO)(CO)(NMe_3)(tacn)]\ (BF_4)_2$	1740	[58]
$[Re(NO)(CO)(NCO)(tacn)](BF_4)$	1700	[58]
$[Re(NO)(CO)(HCO)_2(tacn)]\ (BF_4)$	1680	[58]
$[Re(NO)(CO)\{NH(CO)(OCH_3)\}(tacn)]\ I$	1680	[58]
$[Re(NO)(CO)\{NH(CO)(OC_2H_5)\}(tacn)]\ I$	1680	[58]
$[Re(NO)(NCO)_2(tacn)]$	1620	[58]
$[Re(NO)(CO)_2Cl_2(L)]$		
L = THF	1779	[51]
L = py	1761	[126]
L = 4-pic	1763	[126]
L = 3,4-lut	1765	[126]
L = C_4H_8S	1772	[126]

Table 6 (*Continued*)

Complex	ν(NO) (cm^{-1})	References
L = C_5H_5NO	1761	[126]
L = $OPPh_3$	1761	[126]
L = PBu_3	1770	[126]
$[Re(NO)(CO)_2I_2(py)]$	1763	[126]
$[Re(NO)(CO)_2Br_2(py)]$	1769	[126]
$[Re(NO)(CO)_2Cl(PPh_3)_2]Cl_3$	1810	[126]
$[Re(NO)(CO)_2Br(PPh_3)_2]Br_3$	1805	[30]
$(NEt_4)[Re(NO)(CO)_2Cl_3]$	1770	[59]
$(NMe_4)[Re(NO)(CO)_2(NO_3)_3]$	1794	[59]
$[Re(NO)(CO)_2Cl(bipy)](BF_4)$	1818	[51]
$[Re(NO)(CO)_2H(PPh_3)_2]$ (SO_3CF_3)	1766	[31]
$[Re(NO)H(X)(PPh_3)_3]$		
X = H	1640	[132]
X = F	1655	[116]
X = Cl	1664/1656/1651	[116]
X = Br	1665/1656/1651	[116]
X = OCH_3	1634	[116]
X = N_3	1660	[116]
X = NCO	1661, 1657	[116]
$[Re(NO)H(X)(C_7H_7NC)(PPh_3)_2]$		
X = F	1656	[116]
X = Cl	1668	[116]
X = Br	1667	[116]
X = I	1676	[116]
X = OCH_3	1646	[116]
X = N_3	1675	[116]
X = NCO	1679	[116]
X = SCN	1686	[116]
$[Re(NO)H(BH_4)L_2]$		
L = P^iPr_3	1660	[62]
L = PCy_3	1660	[62]
L = PPh_3	1687/1666	[62]
$[Re(NO)H(MeOH)(PPh_3)_3](ClO_4)]$	1700	[116]
$[Re(NO)Br_2(\eta^2\text{-}H_2)(P^iPr_3)_2]$	1722	[62]
$[Re(NO)Br_2(\eta^2\text{-}H_2)(PCy_3)_2]$	1706	[62]
$[Re(NO)(CO)_2Cl(bipy)][Re(NO)(CO)_2Cl_3]$		
Cation	1807	[51]
Anion	1766	
$[Re(NO)(NOBF_3)(H)(P^iPr_3)_2]$	1637 (N–O) 1363 (N–OBF_3)	[62]
$[Re(NO)(NOBF_3)(H)(PCy_3)_2]$	1646 (N–O) 1377 (N–OBF_3)	[62]
$[Re(NO)(HNO)Cl_2(PPh_3)_2]$	1720 (N–O), 1370 (HNO)	[30]
$[Re(NO)(HNO)Cl(I)(PPh_3)_2]$	1745 (NO) 1380 (HNO)	[30]
$[Re(HNO)Cl(CO)_2(PPh_3)_2]$	1376	[31]
$[Re(HNO)Cl(CO)_2(PCy_3)_2]$	1335	[31]
$[Re(HNO)(CO)_3(PPh_3)_2]OTf$	1391	[32]

Most of the spectra are measured in KBr disks, otherwise the solvent is given in round brackets. The superscript letters (a–c) indicate the number of reference.

monoanion where the nitrosyl ligand is *trans* to the aqua group [47,121–123].

The stretching frequency of the nitrosyl group in the $[ReX_3(NO)L_2]$ complexes (X = Cl, Br; L = phosphines, arsines and their oxides) is affected by both X and L ligands. The ν_{NO} frequency of $[ReCl_3(NO)L_2]$ (PPh_3 or $AsPh_3$) compounds is lower than for the bromo-species. The higher ν_{NO} frequencies are found for complexes containing phosphine and arsine ligands than their oxides, but this results not only from the different character of these ligands but also from the different arrangement of the ligands around the rhenium atom in these complexes. The lowering of the ν_{NO} for $[ReX_2(NO)L_3]$ complexes in relation to $[ReX_3(NO)L_2]$ corresponds to the lower oxidation state of the rhenium ion in $[ReX_2(NO)L_3]$, resulting in an increased back-donation of electron density from the filled rhenium d orbitals into the π^* antibonding orbital of the NO group [34–36,42,43,57,66,120,124].

The effect of spectator phosphine (PR_3) ligands is seen by comparison of ν_{NO} values observed in the [Re(NO)(CO)

Table 7
NO stretching frequencies for five-coordinate mononitrosyl rhenium complexes

Complex	ν(NO) (cm^{-1})	References
$\{ReNO\}^4$		
$[Re(NO)X_4]$	1758	[76]
$X = SC_6H_3{}^iPr_2$-2,6	1760	[76]
$X = SC_6H_2{}^iPr_3$-2,4,6	1757 (1763 cm)	[76]
$X = SC_6H_2Me_3$-2,4,6	1755 (1768 cm)	[76]
$[Re(NO)X_3(OMe)]$		
$X = SC_6H_2Me_3$	1747	[76]
$X = SC_6H_2{}^iPr_3$	1745	[76]
$[Re(NO)(SC_6H_3{}^iPr_2\text{-}2,6)_3(OEt)]$	1746	[76]
$Re(NO)(SC_6H_2{}^iPr_3\text{-}2,4,6)_3Cl]$	1780	[76]
$\{ReNO\}^5$		
$(PPh_4)[Re(NO)(OH)_4]\cdot H_2O$	1685	[115]
$(AsPh_4)[Re(NO)(OH)_4]\cdot H_2O$	1685	[115]
$\{ReNO\}^8$		
$[Re(NO)(CO)_2L_2]$		
$L = P(i\text{-}PrO)_3$ (CH_2Cl_2)	1612	[53]
$L = PMe_3$ (Et_2O)	1604	[53]
$L = PEt_3$ (hexane)	1609	[53]
$L = PCy_3$	1582	[31]
$L = PPh_3$	1620	[30]

$Cl_2(PR_3)_2]$, $[Re(NO)(CO)Cl(H)(PR_3)_2]$, $[Re(NO)(CO)(OOCCF_3)_2(PR_3)_2]$ and $[Re(NO)(CO)H_2(PR_3)_2]$ series. The stronger is the sigma donor strength of PR_3, the lower the ν_{NO} frequency is observed. The position of ν_{NO} in $[Re(NO)(CO)Cl_2L_2]$ species is considerable higher than in $[Re(NO)(CO)Cl(H)L_2]$ and $[Re(NO)(CO)H_2L_2]$. This is due to a strong σ-donor character of hydride ligands. A similar trend is also observed on changing chloride or bromide ligands by fluoride one [34,51,53,57,125,127].

Formation of the NO–L linkage (L = acidic substrate) dramatically affects the ν_{NO} vibrations in the IR spectrum. The attachment of an acidic substrate to the NO group leads to an increase in electron density donation from the metal to the NO unit. Consequently, the nitrogen–oxygen bond becomes weaker, as reflected by the lower IR wavenumber [62,81].

Nitroxyl (NO^-) complexes, as predicted by the Enemark–Feltham rules, have low ν_{NO} stretching frequencies indicative of occupation of the π^*_{NO} antibonding orbitals. Compounds of $[Re(X)(Cl)(NO)(HNO)(PPh_3)_2]$ composition (X = Cl, I) have both NO and HNO; their IR spectra show ν_{NO} stretches for the HNO and NO at 1370, 1720 cm^{-1} (X = Cl) and 1380, 1745 cm^{-1} (X = I) [30]. The IR spectra of $[Re(HNO)Cl(CO)_2(PPh_3)_2]$, $[Re(HNO)Cl(CO)_2(PCy_3)_2]$ [31] and $[Re(HNO)(CO)_3(PPh_3)_2](O_3SCF_3)$ [32] reveal strong bands assigned to ν_{NO} (HNO) in a similar range. The marked drop in ν_{NO} from that of free HNO at 1563 cm^{-1} indicates π-acceptor character of the HNO ligand. The effect of spectator ligands is seen by comparison of $[Re(HNO)Cl(CO)_2(PR_3)_2]$ where R equals phenyl (Ph) or cyclohexyl (Cy). The stronger sigma donor, PCy_3, resulted in a 40 cm^{-1} lowering of the ν_{NO} energy compared to that of the $[Re(HNO)Cl(CO)_2(PPh_3)_2]$ complex. A significantly smaller lowering observed for the ν_{CO} (only ca. 7 cm^{-1}) indicates that π-back-bonding in the $[Re(HNO)Cl(CO)_2(PR_3)_2]$ complexes is dominated by HNO [31,32].

For metal dinitrosyls with *trans*-arranged NO group, only one ν_{NO} is expected in the IR spectra. The symmetric vibration of the linear ON–M–NO unit does not alter the dipole moment, and is IR inactive. In the infrared spectra of metal dinitrosyls with *cis* geometry of the NO ligands, both the symmetric and antisymmetric stretching vibrations are IR active. The symmetric vibration occurs at higher energy than the antisymmetric stretching vibration.

The positions of the ν_{NO} bands for the rhenium dinitrosyls are gathered in Table 9. Crystallographically, a *trans*-arrangement of nitrosyl groups has been confirmed only in the $[Re(NO)_2(pc)]^-$ cation [75], but it is also predicted for the $[Re(NO)_2(dppe)_2](BF_4)$ complex [69]. The

Table 8
NO stretching frequencies for dinuclear and heteronuclear rhenium complexes

Complex	ν(NO) (cm^{-1})	References
$[Re(NO)(CO)_2Cl_2]_2$	1803 1807	[126]
$[Re(NO)(CO)_2Br_2]_2$ (chloroform)	1798	[126]
$[Re(NO)(CO)_2I_2]_2$ (chloroform)	1785	[126]
$[Re(NO)(CO)Cl(\mu\text{-}Cl)(COE)]_2$	1776	[51]
$Re(NO)(CO)(bipy)\{PO(OMe)_2\}_2]_2(O_3SCF_3)_2$	1764	[56]
$[Re_2(NO)Cl_5(\mu\text{-}dmpm)_2]$ (nujol)	1750	[83]
$[Re_2(\mu\text{-}H)(\mu\text{-}Br)[P(O)Ph_2]Br_2(NO)(\mu\text{-}dppm)_2](ReO_4)$	1736	[84]
$[\{Re(NO)(CO)(tacn)\}_2(\mu\text{-}CH_2OCH_2)]I_2$	1680	[87]
$(PPh_4)[Re_2(SPh)_7(NO)_2]$	1738, 1718	[76]
$(PPh_4)[Re_2(SC_6H_4Me\text{-}4)_7(NO)_2]$	1720, 1690	[76]
$[Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(NO)(CO)]$	1683	[89]
cis-$[Cp_2Cr_2(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2ReCl_2(NO)(CO)_2]$(*cis*)	1748	[90]
trans-$[Cp_2Cr_2(\mu_3\text{-}S)(\mu\text{-}SCMe_3)_2ReCl_2(NO)(CO)_2]$(*trans*)	1745	[90]
$[CpCr(\mu_3\text{-}S)(\mu\text{-}OSCMe_3)_2Re_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)(NO)_2(CO)_2]$	1709	[78]
$[CpCr(\mu\text{-}OSCMe_3)Re(NO)(CO)(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)Re(NO)(CO)_2]$	1741, 1707	[88]
$[CpCr(\mu\text{-}OSCMe_3)Re(NO)(CO)(\mu_3\text{-}S)_2(\mu_3\text{-}SCMe_3)$ $(\mu\text{-}SCMe_3)Re(CO)_3]$	1716	[88]
$[Cp_2Cr_2(\mu_3\text{-}S)_2(\mu\text{-}SCMe_3)_2Re(NO)I]$	1687	[88]

Table 9
Stretching NO frequencies for mononuclear dinitrosyl rhenium complexes

Complex	$\nu(NO)$ (cm^{-1})	References
$\{Re(NO)_2\}^6$		
$(AsPh_4)[Re(NO)_2Cl_4]$	1870, 1775	[79]
$(NBu_4)[Re(NO)_2Cl_4]$	1870, 1775	[115]
$(PPh_4)[Re(NO)_2Cl_4]\cdot 1.5H_2O$	1865, 1700	[115]
$(AsPh_4)[Re(NO)_2Cl_4]\cdot H_2O$	1870, 1762	[115]
$(PPh_4)[Re(NO)_2Br_4]\cdot 2CCl_4$	1870, 1755	[78]
$(NBu_4)[Re(NO)_2Br_4]$	1865, 1780	[115]
$(PPh_4)[Re(NO)_2Br_4]\cdot H_2O$	1860, 1750	[115]
$(AsPh_4)[Re(NO)_2Br_4]\cdot H_2O$	1860, 1740	[115]
$[Re(NO)_2Cl_3(MeCN)]$	1903, 1820	[79]
$[Re(NO)_2Br_2(PPh_3)_2]Br_3$	1890, 1800	[30]
$\{Re(NO)_2\}^7$		
$[Re(NO)_2X_2(PPh_3)_2]$		
$X = Cl$	1720	[127]
$X = Br$	1730	[127]
$X = I$	1725	[127]
$X = NO_3$	1740	[127]
$[Re(NO)_2Cl_2(SbPh_3)_2]$	1723, 1655	[77]
$\{Re(NO)_2\}^8$		
$[Re(NO)_2(PCy_3)_2](BAr^F{}_4)$ (Nujol)	1711, 1649	[80]
$[Re(NO)_2(P^iPr_3)_2](BAr^F{}_4)$ (Nujol)	1712, 1654	[81]
$[Re(NO)_2(PCy_3)_2(CO)](BAr^F{}_4)$ (CD_2Cl_2)	1717, 1675	[80]
$[Re(NO)_2(P^iPr_3)_2(CO)](BAr^F{}_4)$ (nujol)	1726, 1682	[81]
$[Re(NO)_2(PCy_3)_2(MeCN)](BAr^F{}_4)$ (nujol)	1663, 1625	[81]
$[Re(NO)_2(P^iPr_3)_2(MeCN)](BAr^F{}_4)$ (nujol)	1675, 1634	[81]
$[Re(NO)_2(PCy_3)_2(THF)](BAr^F{}_4)$ (nujol)	1664, 1585	[81]
$[Re(NO)_2(P^iPr_3)_2(THF)](BAr^F{}_4)$ (nujol)	1678, 1630	[81]
$[Re(NO)_2(PCy_3)_2(C_6H_5CHO)](BAr^F{}_4)$ (CD_2Cl_2)	1704, 1668	[80]
$Re(NO)_2(P^iPr_3)_2(C_6H_5CHO)](BAr^F{}_4)$ (nujol)	1674, 1618	[81]
$[Re(NO)_2(H)L_2]$		
$L = P^iPr_3$	1604	[62]
$L = PCy_3$	1602	[62]
$L = PPh_3$	1622	[62]
$[Re(NO)_2X(PPh_3)_2]$		
$X = Cl$	1650	[119]
$X = Br$	1650	[119]
$X = I$	1650	[119]
$[Re(NO)_2(dppe)_2](BF_4)$	1650	[69]
$\{N(PPh_3)_2\}[Re(NO)_2(pc)]$	1586	[75]

presence of a single strong ν_{NO} band in the IR spectrum of $[Re(NO)_2(dppe)_2](BF_4)$ seems to confirm a *trans* geometry of the NO groups. All the other rhenium dinitrosyls show two prominent ν_{NO} vibrations situated with a splitting of 50–165 cm^{-1} typical for *cis*-dinitrosyl complexes.

Table 10
NO stretching frequencies for $[M(NO)(CN)_5]^{n-}$ complexes ($M = Mn$, Re, Fe, Ru, Os; $n = 2, 3$)

Complex	$\nu(NO)$ (cm^{-1})	References
$[Mn(NO)(CN)_5]^{2-}$	1880	[122]
$[Re(NO)(CN)_5]^{2-}$	1700	[47]
$[Mn(NO)(CN)_5]^{3-}$	1730	[122]
$[Re(NO)(CN)_5]^{3-}$	1650	[121]
$[Fe(NO)(CN)_5]^{2-}$	1945	[123]
$[Ru(NO)(CN)_5]^{2-}$	1926	[123]
$[Os(NO)(CN)_5]^{2-}$	1897	[123]

Rhenium complexes with bridging NO group are very rare and IR data are available only for $[Re_2(H)(\mu\text{-}\eta^2\text{-}NO)(NO)_3(P^iPr_3)_4](BAr^F{}_4)$. As can be expected, the stretching frequencies of the bridging nitrosyl are split and shifted to lower wavenumbers: 1659, 1645, 1627 and 1609 cm^{-1} for $[Re_2(H)(\mu\text{-}\eta^2\text{-}NO)(NO)_3(P^iPr_3)_4](BAr^F{}_4)$ [80].

Detailed variable temperature IR spectroscopy studies are particularly suitable for examination of the reactions of nitrosyl complexes with proton donors (XH). These studies were carried out for the rhenium hydridonitrosyls of $[Re(NO)(CO)H_2(PR_3)_2]$ ($R = Me$, Et, ^iPr) and $[Re(NO)(CO)Cl(H)(PMe_3)_2]$ formulas. As these complexes possess several sites able to form hydrogen bonds (oxygen atoms of carbonyl and nitrosyl groups, hydride and chloride ligands and central atom), it is very important to establish the hydrogen-bonding site. It can be done by detailed variable temperature IR spectroscopy studies in the ranges of ν_{XH}, ν_{NO}, ν_{CO}, ν_{ReH} and ν_{ReCl}. The investigation is based on the following observations: (i) the intensities of ν_{XH} bands of the free X–H bond decrease and intense low-frequency ν_{XH}bands of hydrogen bonded complexes appear, (ii) hydrogen bond formation with the ligand L (CO, NO, H, Cl) leads to a low-frequency shift of the corresponding ν_L stretching band and (iii) the appearance of ν_L band at higher energy indicates that this ligand does not act as a proton acceptor [54,55,128].

4.2. UV–vis spectroscopy

Nowadays, two theoretical methods, namely density functional theory (DFT) and the semi-empirical INDO method, are commonly used to analyze the electronic structures and spectra of transition metal complexes. However, studies of electronic structure and electronic spectroscopy of transition metal nitrosyl complexes are dominated by investigations of the nitroprusside ion $[Fe(CN)_5(NO)]^{2-}$ [133–135] and ruthenium nitrosyls [136–138]. There are only a few studies, which include the detailed interpretation of the electronic spectra of rhenium nitrosyl complexes.

Paper [139] presents the detailed assignments of electronic bands of the $[Re(NO)Cl_5]^{2-}$ anion on the basis of the simplified molecular orbital diagram presented in Fig. 23.

The experimental band at 307 nm (5960) was attributed to the transition $(e^4b_2^1) \rightarrow (e^4e^{*1})$, whereas the band at 210 nm (5130) was assigned to the $(e^4b_2^1) \rightarrow (e^3b_2^1e^{*1})$ transition. Both the transitions are to a level, which is essentially localized on the NO, and they are considered as charge-transfer $d \rightarrow \pi^*_{NO}$ transitions.

The electronic spectra of the $[Re(NO)(CN)_5]^{2-}$ and $[Re(NO)(H_2O)(CN)_4]^-$ anions were discussed on basis of the simplified molecular scheme presented in Fig. 2 [47]. The electronic spectral bands, 424(130) nm for $[Re(NO)(CN)_5]^{2-}$ and 409(145) nm (4360) for $[Re(NO)(H_2O)(CN)_4]^-$, were assigned as $b_2 \rightarrow e_1$ transitions, which are essentially $M \rightarrow \pi^*_{NO}$ transitions. For the manganese analogue ($[Re(NO)(CN)_5]^{2-}$), the electronic absorption assigned to the $b_2 \rightarrow e_1$ transition is shifted to lower energy (538 nm) [140]. This can be explained by the stronger overlap of the d orbitals when going from Mn to Re. Similar trend can be noticed for $[M(NO)(CN)_5]^{2-}$ cyanonitrosyls (M = Fe, Ru, Os); the energies of the electronic absorptions, attributed to $M \rightarrow \pi^*_{NO}$ transitions, increase in the order Fe < Ru < Os [86].

DFT and time-dependent DFT (TDDFT) calculations were carried out for the following rhenium nitrosyls: $[ReBr_3(NO)(PPh_3)_2]$, $[ReBr_3(NO)(OPPh_3)_2]$ [141], $[ReBr_3(NO)(AsPh_3)(pzH)]$ [40], $[ReCl_3(NO)(OPPh_3)(pyz)]$ and $[ReCl_3(NO)(OPPh_3)(PPh_3)]$ [73]. As the investigated complexes are of large size, most of their molecular orbitals have a complicated character. The percent participations of the ligand atomic orbitals in the several highest occupied and lowest unoccupied molecular orbitals are discussed in detail in the papers [40,73,141]. The electronic configuration of the metal centre in all the investigated complexes is as follows: $(d_{xz})^2(d_{yz})^2(d_{xy})^1$. The d_{xy} rhenium orbital makes principal contributions into the HOMO with α-spin and LUMO with

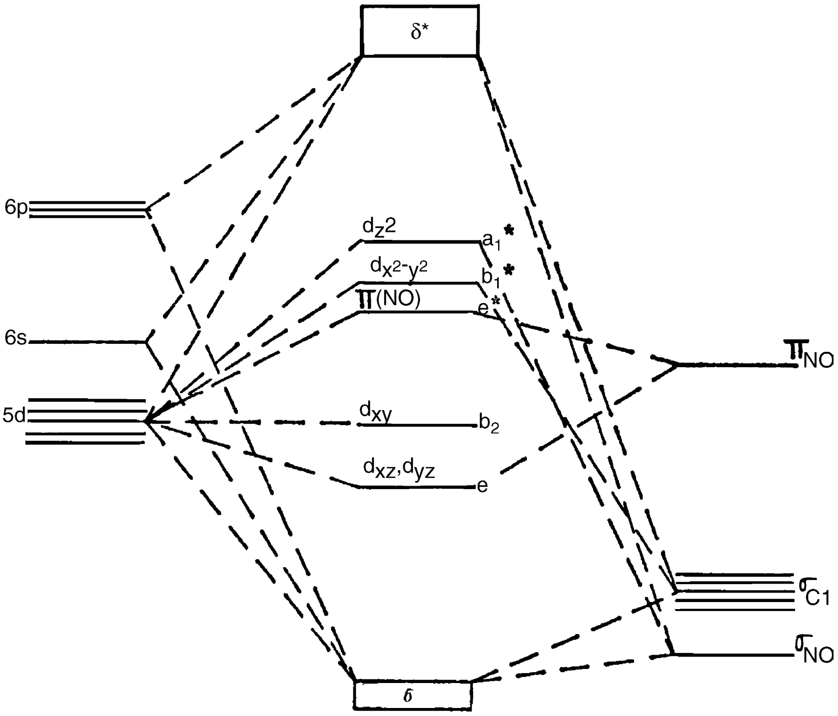


Fig. 23. Molecular orbital diagram for $[Re(NO)Cl_5]^{2-}$.

β-spin. The occupied d_{yz} and d_{xz} rhenium orbitals participate in the back-donation from the central ion to the NO ligand. However, the d_{yz}/d_{xz} and π^*_{NO} orbitals are distributed among several occupied MOs to give considerable contribution into several HOMO and LUMO orbitals. For all the complexes, the bonding $\pi_{Re–NO}$ orbitals are localized mainly on the rhenium d orbitals, whereas the $\pi^*_{Re–NO}$ orbitals have prevalent NO character. The TDDFT calculations for $[ReX_3(NO)L_2]$ and $[ReX_3(NO)(L^1)(L^2)]$ complexes reveal that the electronic transitions from the rhenium d orbitals onto π^* orbitals of the nitrosyl group have small oscillator strengths and they do not contribute significantly to the overall shape of the spectrum. They are hidden under the more intense transitions of LMCT character. Such small values of the oscillator strengths seem to be typical of the $d \rightarrow \pi^*_{NO}$ transitions; they have been supported by calculations for other metal nitrosyls [138,139]. The $d \rightarrow \pi^*_{NO}$ transitions make contribution into the following absorption bands: 456 and 420 nm for $[ReBr_3(NO)(PPh_3)_2]$, 321 nm for $[ReBr_3(NO)(OPPh_3)_2]$, 476 and 390 nm for $[ReBr_3(NO)(AsPh_3)(pzH)]$, 459, 408 and 359 nm for $[ReCl_3(NO)(OPPh_3)(pyz)]$ and 421 and 356 nm for $[ReCl_3(NO)(OPPh_3)(PPh_3)]$.

The six-coordinate Re(I) complexes are diamagnetic. All of the bonding and non-bonding orbitals are filled—$e^4b_2{}^2$. In comparison with Re(II) nitrosyls, the metal becomes more electron rich and interacts more effectively with the π^*_{NO} level, weakening the N–O bond. The electronic spectra of $[Re(NO)X_2(py)_3]$ were discussed briefly in papers [43,66]. The charge-transfer ($d \rightarrow \pi^*_{NO}$) transitions were assigned to the experimental bands at 533 and 405 nm for $[Re(NO)Br_2(py)_3]$ [43], and 372 and 327 nm for $[Re(NO)Cl_2(py)_3]$ [66]. On passing from bromine to chlorine derivatives, the higher electronic frequency of the $d_\pi \rightarrow \pi^*_{NO}$ transition is in agreement with the greater electron affinity of chlorine. Papers [34,52] include a short discussion of the UV–vis spectra for carbonyl–nitrosyl $[Re(NO)(CO)X_2(PPh_3)_2]$ complexes. The $d \rightarrow \pi^*_{NO}$ transitions were assigned to the absorption bands at 680 and 275 nm for the chloride complex [34], and 635 and 270 nm for the bromide analogue [52].

4.3. NMR spectroscopy

Nitrogen NMR spectroscopy appears to be particularly suitable for distinguishing between bent and linear M–N–O conformations because of the large downfield shift (by hundreds of ppm) that is expected for the bent in comparison with the linear nitrosyl ligand. Due to low NMR sensitivities of the ^{14}N and ^{15}N nuclei, however, this technique has not been widely used in metal nitrosyl chemistry. The highly abundant nucleus ^{14}N is quadrupolar ($I = 1$), so lines given by molecules of the size of metal complexes may be very broad, especially for bent nitrosyls. ^{15}N has a nuclear spin of 1/2, but low natural abundance and very long relaxation times. However, the use of Fourier transforms methods, superconducting magnets, wide-bore spectrometers and clever pulse sequences have greatly improved the accessibility of ^{15}N work. Some metalloporphyrins (synthetic or natural), cobalt and ruthenium nitrosyl complexes have been examined by ^{15}N NMR spectroscopy [19,26,142,143].

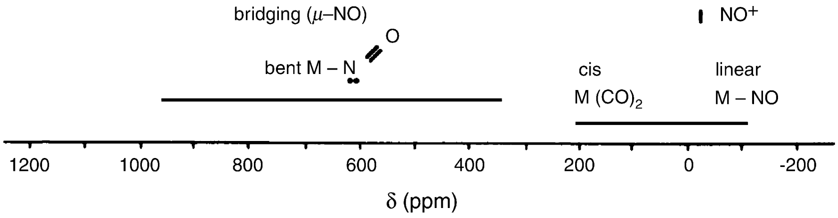
Typical ranges of N chemical shifts displayed by metal nitrosyl complexes are shown in Scheme 5 [19]:

As can be seen from scheme, the N chemical shifts vary over wide range and N chemical shifts of bent or bridging nitrosyls are more deshielded than those of the linear M–N–O systems and *cis*-$M(NO)_2$ species. For linear mononitrosyl complexes, the δ_N tends to increase across the transition metal series, and also down a particular group.

Much more information (about fluxionality between linear and bent M–N–O arrangements, fluxional behaviour in solution, motions of a bent nitrosyl ligand) can be obtained from shielding tensor analysis [19,26,142,143].

The ^1H NMR spectra of the nitrosyl hydride (HNO) complexes show a downfield resonance in the range of 13–23 ppm assigned to the proton of the HNO ligand, for $[Re(HNO)Cl(CO)_2(PPh_3)_2]$ [31], $[Re(HNO)Cl(CO)_2(PCy_3)_2]$[31] and $[Re(HNO)(CO)_3(PPh_3)_2](O_3SCF_3)$ [32] at 20.66, 21.35 and 21.66 ppm, respectively. The proton resonances of the rhenium nitrosyl hydride complexes are similar to those reported for the HNO ligand in other coordination complexes (for $[Os(HNO)Cl_2(CO)(PPh_3)_2]$, $[Ir(HNO)H(Cl)_2(PPh_3)_2]$ at 21.2 and 22.75 ppm, respectively), but are further downfield shifted relative to HNO resonances observed in heme model compounds (for [Ru(HNO)(ttp)(1-MeIm)] at 13.64 ppm). This upfield shift for the last examples is consistent with the contribution of the porphyrin ring current to the HNO resonance [33].

For ^{15}N isotopically labelled complexes this peak splits into doublets and values of $|^1J_{NH}|$ are close to 70Hz (for $[Re(H^{15}NO)Cl(CO)_2(PPh_3)_2]$, 66.2 Hz [31], and $[Re(H^{15}NO)(CO)_3(PPh_3)_2]$Otf, 72.5 Hz [32]), as expected



Scheme 5.

for a proton attached to an sp^2-hybidized nitrogen coordinated to a transition metal. If the HNO ligand were coordinated to metal through oxygen, the nitrogen atom would possess an uncomplexed lone pair and the magnitude of $|^1J_{NH}|$ would be reduced to ∼45 Hz.

5. Some remarks on the reactivity of rhenium nitrosyl complexes

The $[Re(NO)X_5]^{2-}$ complexes easily undergo replacement of their halide ligands (in *trans*-position to the NO group) by many types of neutral ligands to give $[Re(NO)X_4(L)]^-$ species. Refluxing $[Re(NO)X_5]^{2-}$ with pyridine or picolines in boiling diglyme leads to the isolation of the tri-substituted non-ionic $[Re(NO)X_2L_3]$ derivatives [120]. Tri-substituted neutral compounds were also isolated in the reactions of $[Re(NO)X_5]^{2-}$ with triphenylstibine in ethanol, whereas the reactions with PPh_3 and $AsPh_3$ lead to $[ReX_3(NO)(PPh_3)_2]$, $[ReBr_3(NO)(AsPh_3)_2]$ and $[ReCl_3(NO)(AsPh_3)_2][ReCl_4(AsPh_3)_2]$, respectively [35,67]. The smaller steric demand of $SbPh_3$ in comparison with PPh_3 and $AsPh_3$ explains the formation of $[ReX_2(NO)(SbPh_3)_3]$. The increase of M–E and E–C (E = P, As or Sb) bond lengths in the order P > As > Sb leads to the decrease of the EPh_3 cone angles [67]. The $[Re(NO)Br_5]^{2-}$ complex was used to prepare a series of mononitrosyl hydride and dihydrogen rhenium complexes: $[Re(NO)(H)(BH_4)(PR_3)_2]$ and $[Re(NO)Br_2(\eta^2\text{-}H_2)(PR_3)_2]$ (R = ^{I}Pr or Cy). The coordinated BH_3 of $[Re(NO)(H)(BH_4)(PR_3)_2]$ can be replaced by the H_2 or the NO ligand leading to $[Re(NO)(H)_4(PR_2)_2]$ or $[Re(NO)_2(H)(PR_3)_2]$ [62].

The reaction of $[Re(NO)(CO)Cl_2L_2]$ (L = PEt_3 or $P(OMe)_3$) with excess of AgO_3SCF_3 in boiling acetonitrile leads to an isomeric mixture of $[Re(NO)(CO)Cl(MeCN)_2L][O_3SCF_3]$ (approximately 2:1 ratio), whereas the same reaction performed in toluene with one or two equivalents of AgO_3SCF_3 gives the mono- or disubstituted complexes $[Re(NO)(CO)Cl(O_3SCF_3)L_2]$ and $[Re(NO)(CO)(O_3SCF_3)_2L_2]$. The replacement of the triflate ligands in the latter compounds proceeds very slowly and with retention of the molecular geometry to give the ionic $[Re(NO)(CO)(MeCN)_2L](O_3SCF_3)_2$ products. The $[Re(NO)(CO)Cl(MeCN)_2L](O_3SCF_3)$ complexes react with bipy to yield $[Re(NO)(CO)Cl(bipy)L](O_3SCF_3)$ derivatives, whereas $[Re(NO)(CO)(O_3SCF_3)_2\{P(OMe)_3\}_2]$ in the presence of bipy undergo in boiling toluene an Arbuzov-like phosphite dealkylation, producing a dinuclear $[Re(NO)(CO)(bipy)\{P(O)(OMe)_2\}]_2(O_3SCF_3)_2$ [56].

The hydrido-nitrosyls $[Re(NO)(CO)H_2(PR_3)_2]$ and $[Re(NO)(CO)Cl(H)(PR)_2]$ react with a series of proton donors (XH). The formation of $[Re(NO)(CO)H_2(PMe_3)_2]$ indole was observed in the reaction of $[Re(NO)(CO)H_2(PMe_3)_2]$ with indole in the solid-state [54]. Protonation of $[Re(NO)(CO)H_2(PR_3)_2]$ complexes (L = P^iPr_3, $P(O^iPr)_3$ and PMe_3) with stoichiometric or excess amounts of CF_3COOH yields the monohydrido trifluoroacetato compounds $[Re(NO)(CO)(H)(OOCF_3)L_2]$ and bis(trifluoroacetato) complexes $[Re(NO)(CO)(OOCF_3)_2L_2]$ [55].

Reaction of $[Re(NO)Cl_2(OMe)(PPh_3)_2]$ with a range of thiophenols under basic conditions gives one of two classes of products depending on the steric requirements of the thiols. Thiophenols with methyl and isopropyl substituents in their 2-position yield mononuclear rhenium(III) complexes of the composition $[Re(NO)(SR)_4]$, whereas sterically less demanding ligands without substituents in 2-position give dimeric $[Re_2(NO)_2(SR)_7]^-$ compounds. The $[Re(NO)(SR)_4]$ and $[Re_2(NO)_2(SR)_7]^-$ complexes were studied by cyclic voltammetry. The mononuclear compounds are reduced in a reversible one-electron process at potentials between −0.44 and −0.83 V versus saturated calomel electrode, at scan rates from 0.01 to 1.0 V s^{-1}. The reversible nature of the processes suggests that the $[Re(NO)(SR)_4]^-$ anions form without any substantial structural change. The $(PPh_4)[Re_2(NO)_2(SPh)_7]$ and $(PPh_4)[Re_2(NO)_2(SC_6H_4Me\text{-}4)_7]$ complexes are reduced irreversibly at more negative potentials −1.25 and −1.44 V, respectively [76].

Treatment of $[Re(NO)Cl_2(OMe)(PPh_3)_2]$ with $NaBH_4$ and PPh_3 in ethanol provides $[Re(NO)H_2(PPh_3)_3]$. The hydride nitrosyl reacts with HCl in ethanol to form air-sensitive $[Re(NO)Cl_2(PPh_3)_3]$, which in turn reacts with CO or CNR to give $[Re(NO)(CO)Cl_2(PPh_3)_2]$ and $[Re(NO)Cl_2(CNR)_2(PPh_3)]$, respectively. Reaction of $[Re(NO)H_2(PPh_3)_3]$ with HBF_4 or HPF_6 in the presence of CO leads to $[Re(NO)(CO)F(PPh_3)_3]^+$, which easily reacts with coordinating anions to give $[Re(NO)(CO)XF(PPh_3)_2]$ (X = H, OCH_3, F). The $[Re(NO)H(MeOH)(PPh_3)_3]ClO_4$ complex, formed in the reaction of $[Re(NO)H_2(PPh_3)_3]$ with alcoholic $HClO_4$, reacts with coordinating anions with loss of methanol to give $[Re(NO)X(H)(PPh_3)_3]$ (X = OCH_3, F, Cl, Br, I, N_3, NCO, SCN). These complexes can easily undergo replacements of one of the phosphine ligands by neutral ligands (CO or RCN) to give $[Re(NO)H(X)(L)(PPh_3)_2]$. Treatment of $[Re(NO)H(MeOH)(PPh_3)_3]ClO_4$ with *p*-tolylisocyanide provides $[Re(NO)(OMe)(CNR)_2(PPh_3)_3]ClO_4$. In this case, the substitution is accompanied by dihydrogen elimination [57,116].

Reaction of $[Re(NO)(CO)_2Cl(\mu\text{-}Cl)]_2$ with cyclooctene (COE) gives $[Re(NO)(CO)(COE)Cl(\mu\text{-}Cl)]_2$, whereas treatment with THF produces racemic $[Re(NO)(CO)_2Cl_2(THF)]$. Reaction of the last one with racemic *trans*-1,2-bis(dimethylphosphino)ethane (dmpc) proceeds with loss of the THF molecule and one CO group, affording diastereomeric mixture of $[Re(NO)(CO)Cl_2(dmpc)]$. The reaction of $[Re(NO)(CO)(COE)Cl(\mu\text{-}Cl)]_2$ with 1,2-bis(diphenylphosphino)methane gives *cis*, *trans*-$[Re(NO)(CO)Cl_2(\eta^1\text{-}dppm)]$, while the treatment with 1,2-bis(diphenylphosphino) ethane and $NaBF_4$ yields $[Re(NO)Cl(dppee)_2](BF_4)$. Refluxing of $[Re(NO)(CO)(COE)Cl(\mu\text{-}Cl)]_2$ with 2,2′ bipyridine or 4,4′-dimethyl-2,2′ bipyridine in CH_2Cl_2 leads to the isolation of $[Re(NO)(CO)Cl_2(L)]$. The $[Re(NO)(CO)_2Cl(\mu\text{-}Cl)]_2$ dimer can be converted to

$[Re(NO)(CO)Cl_2L_2]$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, PMe_3, PEt_3, PCy_3) by heating with L in acetonitrile. In the case of the reaction with $P(OMe)_3$, the trisubstituted compound *mer*-$[Re(NO)Cl_2\{P(OMe)_3\}_3]$ was also obtained. The Cl ligands of $[Re(NO)(CO)Cl_2L_2]$ can be replaced with Me groups by reacting them with MeLi in Et_2O. Treatment of $[Re(NO)(CO)Cl_2L_2]$ with $Li[BHEt_3]$ leads to substitution of one Cl by an H ligand with formation of $[Re(NO)(CO)(H)ClL_2]$. The hydride-transfer agent $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ transforms $[Re(NO)(CO)Cl_2L_2]$ into the *cis*-hydride $[Re(NO)(CO)H_2L_2]$ systems. Reductive carbonylation of $[Re(NO)(CO)Cl_2L_2]$ in the presence of Na/Hg and CO gives five-coordinate $[Re(NO)(CO)_2L_2]$ complexes [51,53].

Reaction of anhydrous HCl with $[Re(NO)(CO)_2(PR_3)_2]$ (R = Ph, Cy) results in a formal protonation of the nitrosyl ligand and addition of chloride to the central atom, giving the nitroxyl complex *cis*, *trans*-$[ReCl(NHO)(CO)_2(PR_3)_2]$. In contrast, addition of $HOSO_2CF_3$ to a solution of $[Re(NO)(CO)_2(PPh_3)_2]$ results in protonation at the metal and formation of *trans*, *trans*-$[ReH(NO)(CO)_2(PPh_3)_2](O_3SCF_3)]$ [31,32].

The $Re(NO)(CO)_2(tacn)](BF_4)$ complex reacts with a number of nucleophiles such as N_2H_4, H_2NNHMe, H_2NNMe_2, H_2NOH or N_3^- to give $[Re(NO)(CO)(NCO)(tacn)](BF_4)$. A mechanism of these reactions involves a nucleophilic attack at the coordinated carbonyl to give carbazoyl intermediates. $[Re(NO)(CO)(NCO)(tacn)](BF_4)$ undergoes a series of reactions at the coordinated isocyanate ligand, e.g., concentrated HBr forms $[Re(NO)(CO)(NH_3)(tacn)]Br_2$, whereas reaction with formic acid or trifluoromethene sulfonic acid gives complexes of the type $[Re(NO)(CO)(HCO_2)(tacn)]^+$ and $[Re(NO)(CO)(O_3SCF_3)(tacn)]^+$. In the presence of iodide anions, $[Re(NO)(CO)(NCO)(tacn)](BF_4)$ undergoes addition reactions in MeOH or EtOH to form complexes containing coordinated methyl- or ethylcarbamato ligands—$[Re(NO)(CO)\{NHCO(OR)\}(tacn)]I$. The $[Re(NO)(CO)(NH_3)(tacn)]Br_2$ complex can be oxidized electrochemically or chemically with Br_2 to give $[Re(NO)(CO)(NH_3)(tacn)]Br_3$ [58].

The $[Re(NO)(CN)_4(OH_2)]^{2-}$ anion substitutes the aqua ligand upon reactions with nucleophiles such as SCN^-, N_3^- and thiourea [63].

The $[Re(NO)(CN)_4(OH_2)]^-$ and $[Re(NO)(CN)_5]^{2-}$ complexes show three sequential metal centred reversible and quasi reversible cyclic responses in the scan range +0.3 to −0.9 V versus SCF. The interplay of all redox levels is shown in Eqs. (1)–(3) [47].

$$\begin{aligned} &[Re(NO)(CN)_5]^{2-} \underset{\substack{+e^- \\ (+0.28\,V)}}{\overset{-e^-}{\rightleftharpoons}} [Re(NO(CN)_5]^- \\ &[Re(NO)(CN)_4(H_2O)]^- \underset{\substack{+e^- \\ (+0.27\,V)}}{\overset{-e^-}{\rightleftharpoons}} [Re(NO(CN)_4(H_2O)] \end{aligned} \qquad (1)$$

$$\begin{aligned} &[Re(NO)(CN)_5]^{2-} \underset{\substack{-e^- \\ (-0.39\,V)}}{\overset{+e^-}{\rightleftharpoons}} [Re(NO(CN)_5]^{3-} \\ &[Re(NO)(CN)_4(H_2O)]^- \underset{\substack{-e^- \\ (+0.41\,V)}}{\overset{+e^-}{\rightleftharpoons}} [Re(NO(CN)_4(H_2O)]^{2-} \end{aligned} \qquad (2)$$

$$\begin{aligned} &[Re(NO)(CN)_5]^{3-} \underset{\substack{-e^- \\ (-0.76\,V)}}{\overset{+e^-}{\rightleftharpoons}} [Re(NO(CN)_5]^{4-} \\ &[Re(NO)(CN)_4(H_2O)]^{2-} \underset{\substack{-e^- \\ (-0.76\,V)}}{\overset{+e^-}{\rightleftharpoons}} [Re(NO(CN)_4(H_2O)]^{3-} \end{aligned} \qquad (3)$$

Due to the coordinate unsaturation, $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ (R = ^{I}Pr, Cy) react easily in solution with two electron donors to yield the addition derivatives $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ (L = MeCN, CO, C_6H_5CHO, THF). Except for THF, all these ligands appear to be strongly bound to the metal. Addition of an excess of $HSiEt_3$ to a solution of $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ results in formation of $[Re(NO)(NOSiEt_3)(H)((PR_3)_2](BAr^F{}_4)$. The reactivity of $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ towards dihydrogen was also examined, but the $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ complex was not isolated. In the presence of tetramethylpiperidine as a base, the reaction of $[Re(NO)_2(PR_3)_2](BAr^F{}_4)$ with H_2 produces $[Re(NO)\{NOH_2NC_5H_6(CH_3)_4\}(H)(PR_3)_2](BAr^F{}_4)$ [80,81].

6. Conclusions

Rhenium forms a relatively wide range of nitrosyl mono-, di- and polynuclear complexes, and their structural and spectroscopic properties have been discussed in this paper. However, only a few studies concern the electronic structure and electronic spectroscopy of rhenium nitrosyls.

The Re(I) dicarbonyl–nitrosyl complexes, such as $[Re(NO)(CO)_2X_3]^-$, show a tendency for coordination at carboxylic and amine groups of biomolecules. In a similar fashion conjugation of $[^{188}Re(CO)_2(NO)]^{2+}$ to proteins or antibodies is feasible. This provides a path to a potentially new class of radiopharmaceuticals.

Although only $\{ReNO\}^n$ complexes with $n = 4$–6 have been structurally characterised, some six-coordinate $\{ReNO\}^8$ species were obtained. As the chemistry of nitroxyl ligand is not fully understood, further study of these species seems to be of high significance.

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