Coordination Chemistry Reviews, 26 (1978) 7—32 7
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NITROSYL COMPLEXES OF RUTHENIUM

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(Received 20 January 1978)

CONTENTS

A. INTRODUCTION

It is appropriate that an article on nitrosyl * complexes of ruthenium should appear in a volume dedicated to the memory of Professor A.D. Allen. Although Bert Allen did not, to my knowledge, investigate ruthenium nitrosyls, the topic was very important to his work on dinitrogen complexes of ruthenium. In the early days of the discovery of $[Ru(NH_3)_5N_2]^{2+}$ [1] much discussion took place in his Toronto laboratory of the possibility that $[Ru(NH_3)_5N_2]^{2+}$ might be a nitrosyl; in fact Bert's first attempt to publish the discovery was rejected by one referee because of this possibility. It was also clear that most of the then known ruthenium nitrosyls could be regarded

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* Nitrosyl is the nitrogen mono-oxide ligand, NO.

naively as being complexes of NO^+, which is isoelectronic with N_2. The fact that ruthenium formed more nitrosyls than any other metal [2], and that the {RuNO} group was very robust made the analogy between $[Ru(NH_3)_5N_2]^{2+}$ and $[Ru(NH_3)_5NO]^{3+}$ an attractive way of thinking about the new complex. Such analogies have been extensively pursued; although "a resurgence of interest in nitrosyl chemistry" or "the development of dinitrogen chemistry" are often spoken of, it is probably more true to say that there has been, since about 1965, a general development of the chemistry of small, multiply-bonded, nitrogen containing ligands; N_2, NO, RN_2 and NS being four such ligands. The present article will, however, be restricted to a theme relevant to Bert Allen's work, that of ruthenium nitrosyls; it will also be restricted to developments occurring since about the time of the discovery of $[Ru(NH_3)_5N_2]^{2+}$. Neither of these boundaries are overly restrictive; the time boundary, as has been noted above, corresponds to an active period of investigation. The fact that ruthenium forms more nitrosyls than any other element, even if in the last few years the balance has been somewhat redressed from the point of view of the number of nitrosyls of other elements prepared (though many of the new complexes are of osmium and iridium and are analogues of known ruthenium ones) means that the single element boundary is not restrictive either. New ruthenium complexes have been obtained, new routes to existing complexes found, and, most important, new areas of chemistry of these complexes and new ideas on the nature of their bonding have appeared. Hence, ruthenium nitrosyls probably still occupy the central place in nitrosyl chemistry in general.

General reviews of nitrosyls are available [3—6]; others deal in particular aspects of nitrosyl chemistry or bonding [7—12]. The reader is referred to these articles where appropriate. Recently Enemark and Feltham have proposed circumventing the problem of the non-innocent nature of the nitrosyl ligand by considering nitrosyls as containing $\{MNO\}^n$ groups, where n is the number of d electrons of M plus the number of electrons in the π^* orbitals of NO (or, more conveniently, n is the number of d electrons if the nitrosyl is regarded as being coordinated as NO^+) [8,13]. As a means of classification this scheme has considerable merit. This review is therefore organized into sections on the known $\{RuNO\}^6$, $\{RuNO\}^7$, $\{RuNO\}^8$ and $\{RuNO\}^{10}$ complexes, each type considered under the headings of structure and bonding, and reactions.

B. $\{RuNO\}^6$ COMPLEXES

(i) Structure and bonding

All $\{RuNO\}^6$ complexes so far prepared are mononitrosyl complexes, six-coordinate, and with essentially linear {RuNO} groups. Table 1 gives details of the structural studies illustrating these generalizations. Note that the phrase "essentially linear" hides a potential problem in structural nitrosyl chemistry.

TABLE 1

Structural parameters for 6-coordinate $\{RuNO\}^6$ complexes

Complex	r(Ru–N) (Å) [a]	r(N–O) (Å) [a]	Ru–N–O (°) [a]	r(Ru–*trans*-X) (Å)	r(Ru–*cis*-X) (Å)	Ref.
trans-$[RuOH(NH_3)_4(NO)]Cl_2$	1.735(3)	1.159(5)	173.8(3)	1.961(3)	1.99–2.10 [b]	14
$[Ru(NH_3)_5(NO)]Cl_3$, H_2O	1.770(9) [c]	1.172(14) [c]	172.8(9) [c]	2.017(11) [c]	2.097(8) [d]	14
$(NH_4)_2[RuCl_5(NO)]$	1.738(2)	1.131(3)	176.7(5)	2.357(1)	2.376(1) [e]	15
$K_2[RuCl_5(NO)]$	1.747(6)	1.112(7)	176.8(9)	2.359(2)	2.372(8) [e]	16
trans-$Na_2[RuOH(NO_2)_4(NO)]$, $2H_2O$	1.748(4)	1.127(7)	179.98(55)	1.950(5)	1.99–2.10 [b]	17
$[Ru(sal_2en)(NO_2)(NO)]$ [f]	1.713(–)	1.152(13)	176.9(9)	2.011(–) [g]	2.022(6) [h]	18
$[RuCl_3(CH_3(C_6H_5)_2P)_2(NO)]$	1.744(6)	1.132(6)	176.4(6)	2.357(2) [i]	2.398(7) [d,j]	19
$[RuCl_3((C_6H_5)_3P)_2(NO)]$	1.737(7)	1.142(8)	180.0(0)	2.353(2) [i]	2.394(2) [d,j]	20
$[Ru(S_2CN(C_2H_5)_2)_3(NO)]$	1.72(–)	1.17(–)	170(–)	2.415(–)	2.397(–) [e,k]	21
$[RuBr_3((C_2H_5)_2SO)(NO)]_2$	1.71(2)	1.16(1)	178(1)	2.050(7) [l]	2.142 [m]	22
$[Ru(NO_2)_2(OH)(NH_3)_2(NO)]$	1.76(1)	1.12(2)	177(1)	1.95(1) [n]	1.99–2.10 [b]	23

[a] Standard deviations relating to the least significant figures in brackets.

[b] Calculated from the covalent radius of Ru(II) and O.

[c] Correlation problems make the errors shown unrealistically small.

[d] Average of two values.

[e] Average of four values.

[f] Sal_2en = *N,N'*-ethylenebis(salicylideneiminato).

[g] *Trans*-NO_2, O-bonded.

[h] *Cis*-O of sal_2en ligand.

[i] *Trans*-Cl.

[j] *Cis*-Cl.

[k] Average of 4-*cis*-Ru–S distances; the monodentate $S_2CN(C_2H_5)_2$ ligand is in a *cis*-position.

[l] *Trans*-$(C_2H_5)_2SO$ group, O-bonded.

[m] Calculated from the Ru–O distance of the one O-bonded $(CH_3)_2SO$ group in $[Ru((CH_3)_2SO)_4Cl_2]$ [24].

[n] *Trans*-OH.

Deviations of up to 15° from linearity in the MAB (AB = NO, CO, N_2 or other diatomic ligand) group have been ascribed to crystal packing forces and/or unsymmetrical π-bonding of the metal to the AB ligand [25,26]. For $\{RuNO\}^6$ complexes there is every reason to expect a linear {RuNO} unit [25], and the accurate structures so far determined (Table 1) do show a maximum deviation from linearity of only about 7°. However, with configurations where marked bending may (but not necessarily will) be found there emerges a rather large "grey" area at MAB angles of around 160° where the significance of the bending becomes unclear. The results in Table 1 may indicate that less than about 10° represents minor distortion, and anything over 10° should be regarded as significant bending in accurate structure determinations.

These six-coordinate, linear, $\{RuNO\}^6$ complexes have been regarded historically as complexes between Ru(II) and NO^+. The metal ligand bond was then considered, by analogy with the isoelectronic CO ligand, to be formed by donation of σ-electrons from nitrogen to the metal, and back donation from the filled metal *d* orbitals to π^*(NO) orbitals. The spectra, structures and reactivity (e.g. towards nucleophiles) of the $\{RuNO\}^6$ complexes are in accord with this description, and it has been persuasively pointed out that this naive viewpoint still has considerable power in predicting synthetic routes to, and the geometries and possible reactivity patterns of, nitrosyls, as well as the relation of NO to ligands such as RN_2 (R = aryl) [20,27]. Other workers have used a similar viewpoint to predict reactivity [28,29].

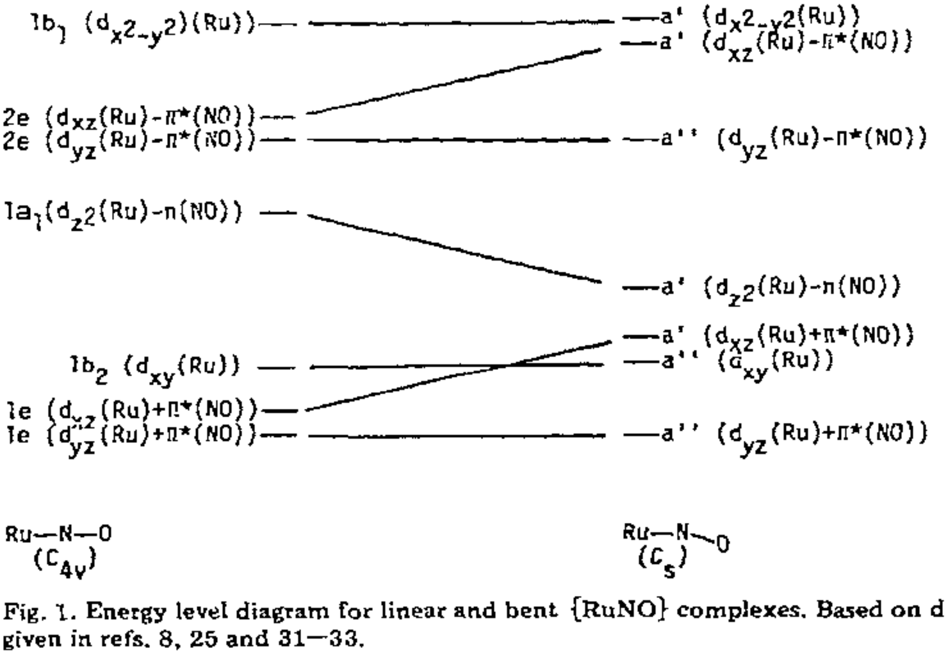

Fig. 1. Energy level diagram for linear and bent {RuNO} complexes. Based on diagrams given in refs. 8, 25 and 31—33.

The molecular orbital approach, while presently lacking this simple gross predictive power, has rationalized a large number of seeming contradictions, and provided a very unified view of nitrosyl chemistry. In this approach the description six-coordinate, linear, $\{RuNO\}^6$ implies that the $d_{xz}(Ru) + \pi^*(NO)$, $d_{yz}(Ru) + \pi^*(NO)$ and $d_{xy}(Ru)$ orbitals are filled, with the antibonding $d_{z^2}(Ru) - n(NO)$, $d_{yz}(Ru) - \pi^*(NO)$, $d_{xz}(Ru) - \pi^*(NO)$, and $d_{x^2-y^2}(Ru)$ orbitals empty (Fig. 1) [8,25,30—35]. Note that the precise ordering of $1a_1$ and 2e is very dependent on the complex under discussion, but the overall picture is not altered if $2e < 1a_1$ (see the description of the electronic spectra of $\{RuNO\}^6$ complexes below, and sections C and D(i)). This approach stresses the extremely important role of the $\pi^*(NO)$ orbital in transferring charge from Ru to NO, and thus its role in the metal—ligand bond. One other interesting result emerges: that the π-orbitals on the NO ligand are now polarized such that there is an increase in electron density at the O rather than the N atom [25]. As with the simple $Ru(II)—NO^+$ approach, potential electrophilic behaviour at N and nucleophilic at O is anticipated.

The importance of the d_{xz}, $d_{yz}(Ru) + \pi^*(NO)$ interaction to the bonding in $\{RuNO\}^6$ complexes is also illustrated by the data on the Ru—L ligand distances *cis* and *trans* to the NO ligand given in Table 1. It is seen, for L ligands which are not themselves π-acceptors, that the *trans*-Ru—L distances are significantly shorter than the *cis*-Ru—L *. Such results are found only for NO; no other analogous ligand (e.g. N_2, CO, RN_2) shows such a *trans* shortening. The results can be explained by the overriding importance of the d_{xz}, $d_{yz}(Ru) + \pi^*(NO)$ interaction to the M—NO bond. In these linear RuNO complexes the NO is such a good π-acceptor and poor σ-donor that rather than a competition between NO and the *trans*-L ligand for the same orbitals, there is mutual reinforcement when L is a good σ-donor and poor π-acceptor, e.g. Cl or OH. Mutually short Ru—NO and Ru—*trans*-L bond distances result. A more sophisticated treatment, based on molecular orbital calculations, indicates that the Ru—*trans*-Cl π-bonding in $[RuCl_5(NO)]^{2-}$ (Cl acting as a π-donor) is greater than the Ru—*cis*-Cl π-bonding, because of withdrawal of π-electron density from Ru into NO. Hence the Ru—*trans*-Cl bond is strengthened, relative to the *cis*, by both σ and π effects [38], though the σ effect is the most important [39]. This approach suggests that the difference between *cis* and *trans*-Ru-NH_3 bonds in $[Ru(NH_3)_5(NO)]^{3+}$ may not be so marked because the π-bonding effect is impossible with the NH_3 ligand [38]. This suggestion cannot really be tested because of technical problems with the structure [14]. A further interesting result of this approach is that because no ligand is likely to be a weaker σ-donor than a linear NO, NO will always

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* This conclusion may be incorrect for $[Ru(S_2CN(C_2H_5)_2)_3(NO)]$, though the structure would bear careful re-examination. Two other structures are not listed in Table 1; $[RuCl(Ph_3P)_2(SO_4)(NO)]$ [36] because it is disordered and nothing meaningful can be said about the metal—ligand bond distances; and "$(NH_4)_2[RuCl_4(H_2O)(NO)]Cl, H_2O$" because the data are not accurate [37].

have a *trans*-strengthening effect in six-coordinate linear $\{MNO\}^6$ complexes, even in, for example, $[Ru(CN)_5(NO)]^{2-}$, in which the π-acceptor ligand CN^- is *trans* to NO [39]. Note that the structure of $[Fe(CN)_5(NO)]^{2-}$ does show a slight shortening of the *trans*-Fe—C bond compared to the *cis*, but the errors are large in this early structure determination [40]; the structure is presently being redetermined. A redetermination of the structure of $[Ru(S_2CN(C_2H_5)_2)_3(NO)]$ is also required, since the work of Nikol'skii et al. [38,39] requires this, too, to have a short *trans*-Ru—S bond, despite the π-acceptor capabilities of dithiolate ligands.

The degree of Ru—NO shortening, and the strength of the Ru—NO bond, may also be gauged by comparing the average Ru—NO distance, 1.739 Å, from Table 1, with the average $Ru—NH_3$ single bond distance from $[Ru(NH_3)_5(NO)]Cl_3$, H_2O and $[RuOH(NH_3)_4(NO)]Cl_2$, which is 2.100 Å [14]. This latter distance is already much shorter than the 2.144 Å in $[Ru(NH_3)_6]I_2$, and similar to the 2.104 Å of $[Ru(NH_3)_6](BF_4)_3$ [41], again illustrating the withdrawal of electron density from Ru by NO. Finally, the Ru—N distances in the formally very similar singly bent RuNNR group (1.784 Å, in $[RuCl_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2]$, CH_2Cl_2 [20] and in the RuN_2 group (1.894 Å in $[RuN_3(en)_2N_2]PF_6$ [42]) are much longer than the Ru—NO distance above, again illustrating the relative strength of the Ru—NO bond.

The vibrational spectra of $\{RuNO\}^6$ complexes have continued to attract attention on two levels of sophistication. At the lower level, there is the continuing problem of the non-innocence of the NO ligand, which may form linear or bent MNO complexes. Despite the success of molecular orbital theory in explaining and correlating the MNO angle with the electronic state of the complex, there remains the need for a simple diagnostic tool for prediction of structure and reactivity. The frequency of $\nu(NO)$ in the infrared spectra of nitrosyls has previously been this tool, and recent work has been devoted to sharpening it. Haymore et al. have refined the previous ideas of a high $\nu(NO)$ indicating a linear nitrosyl and a low $\nu(NO)$ a bent one by making empirical corrections for charge and the other ligands of the nitrosyl complex, and concluded that the corrected frequency, $\nu'(NO)$, of linear nitrosyls (such as $\{RuNO\}^6$ complexes) will be greater than 1620 cm^{-1} and of bent nitrosyls less than 1610 cm^{-1} [20,43]. Suggestions that linear $\{MNO\}^6$ nitrosyls with $\nu(NO)$ greater than 1886 cm^{-1} [29], or greater than about 1850 cm^{-1} [44,45], will be susceptible to nucleophilic attack have also been made. These rules, treated with the normal caution required of such empirical conclusions, are certain to prove increasingly useful as the chemistry of metal nitrosyls develops.

At a more sophisticated level, the complete assignment of the vibrational spectra of $\{RuNO\}^6$ complexes has been undertaken, and in a number of very thorough analyses this has been achieved [46—54]. Previous controversies on the assignment of $\nu(RuNO)$ and $\delta(RuNO)$ have been settled, the former being assigned to a band (weak in the i.r., strong in the Raman) around 600 cm^{-1}, the latter to an absorption (weak in the Raman, strong in the i.r.) at somewhat lower frequency *. Force constant calculations using various approximations show, at least for the cases where other ligands are heavier than N or O, that a simple three-body {RuNO} approximation is quite adequate for discussing the bonding and vibrations of the {RuNO} unit [49,51,54]. The results are interpreted in terms of a considerable degree of π-bonding between Ru and NO, and indicate that the degree of π-bonding is in the order $N_2 < CO < NO$ in analogous $\{RuAB\}^6$ complexes of these ligands [48,49,53]. The metal—ligand vibrations of $[RuX_5(NO)]^{2-}$ (X = Cl, Br or I) have also been reassigned in the light of recent results on the relative strengths of *cis* and *trans*-Ru—X bonds [55]; it is probable that reassignment of the spectra of some other complexes is also necessary on the same basis.

In contrast to vibrational spectra there has been relatively little consideration of the electronic spectra of $\{RuNO\}^6$ species. The assignments of the observed absorption bands are presently controversial, and the arguments are unlikely to be resolved until more detailed spectra (such as low temperature polarized single crystal spectra) become available. By extrapolation from previous general energy level diagrams for {MNO} complexes, or by approximate calculations of the orbital energy levels in the individual complexes, the electronic spectra of $[Ru(CN)_5(NO)]^{2-}$ [58,60], $[RuCl_5(NO)]^{2-}$ [58,61,62], $[RuX(NH_3)_4(NO)]^{n+}$ ($X = NH_3$ for $n = 3$ [56—59,62], X = Cl [56,62], Br, CH_3COO, OH, NCO and N_3 for $n = 2$ [56]) have been assigned. Both Danon and co-workers [58] (for $[RuCN)_5(NO)]^{2-}$, $[RuCl_5(NO)]^{2-}$ and $[Ru(NH_3)_5(NO)^{3+})$ and Schreiner and co-workers [56] (for $[RuX(NH_3)_4(NO)]^{n+}$) assigned the weak low energy bands to $d_\pi(Ru) \rightarrow \pi^*(NO)$ transitions (e.g. $1b_2 \rightarrow 2e$ (see Fig. 1)), with a $d \rightarrow d$ component also included. The medium intensity, medium energy bands were assigned to mainly $d \rightarrow d$ transitions (e.g. $1b_2 \rightarrow 1b_1$, $1e \rightarrow 1b_1$ etc.) and the high energy bands to ligand (Cl, π(NO) etc.) to metal charge transfer. Nikol'skii and co-workers [63] (for $[RuCl_5(NO)]^{2-}$, $[Ru(NH_3)_5(NO)]^{3+}$ and $[RuCl(NH_3)_4(NO)]^{2+}$) considered, however, the lowest energy bands to be $d \rightarrow d$ ($1e \rightarrow 1b_1$) with, where appropriate, the occupied metal orbital having some Cl character. The medium energy bands were assigned to $d_\pi(Ru) \rightarrow \pi^*(NO)$ transitions. Evidence for this assignment was the intensity of the bands and the fact that irradiation of aqueous solutions of $[RuCl_5(NO)]^{2-}$ in the low energy absorption region produces no photochemical reaction; irradiation in the medium energy region, on the other hand, leads to replacement of NO by H_2O [62,63], implying that transitions involving NO lie there.

The technically difficult method of ^{99}Ru Mössbauer spectroscopy has been increasingly applied to provide information on the bonding in $\{RuNO\}^6$ complexes. To date, investigations of $[Ru(NH_3)_5(NO)]^{3+}$ [58,64—67], $[Ru(CN)_5(NO)]^{2-}$ [58,64—68], $[RuCl_5(NO)]^{2-}$ [64,65,67], $[Ru(NCS)_5(NO)]^{2-}$ [64,65], $[RuBr_5(NO)]^{2-}$ [64,65] and *trans*-

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* Except, apparently, for $[Ru(NH_3)_5(NO)]Cl_3$ for which δ(RuNO) is 608 and ν(RuN) 597 cm^{-1}; see Table 2 of ref. 48. For $[Os(NH_3)_5(NO)]Cl_3$ δ(OsNO) is at lower frequency [53]. Reversal (i.e. $\delta(IrNO) > \nu(IrN)$) occurs for $K[IrCl_5(NO)]$ also [50].

$[RuOH(NH_3)_4(NO)]^{2+}$ [67] have been made. Negative isomer shifts, indicating increased *s*-electron density at the ruthenium, are observed when a ligand in $[RuX_6]^{m+}$ is replaced by NO. These could be caused by both increased σ-electron donation to Ru and/or increased d_π-electron back donation to the NO ligand, though with NO the π-component must be much more important than the σ [64—66]. Comparison of $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_5(NO)]^{3+}$ indicates a charge difference at the ruthenium of about two units, i.e. in the {RuNO} complex the ruthenium has an isomer shift in the region found for Ru(IV) complexes with no π-acceptor ligands [66,67]. An analysis of quadrupole splittings leads to a similar conclusion on the π-bonding ability of NO in these complexes. The partial quadrupole splitting, which becomes more positive with increasing π and decreasing σ bonding is +0.02 mm s^{-1} for linearly bonded NO, the only positive value for any ligand [64,69].

As with Mössbauer spectroscopy, ESCA measurements of N 1*s* and O 1*s* binding energies provide information on the electron density in the {MNO} group. Complexes studied, including $\{RuNO\}^6$ examples, all have N 1*s* binding energies close to 400 eV (38 500 kJ mol^{-1}); those known to have a low electron density (i.e. greater positive charge) on the NO nitrogen atom show higher binding energies, and there is a correlation between ν(NO) (a measure of the electron density transferred to the NO ligand) and the N 1*s* binding energy for complexes which have large ν(NO) ($\simeq$200 cm^{-1}) and large N 1*s* binding energy ($\simeq$2 eV) differences. However more detailed information cannot be extracted [70]. It has been suggested that the difference between the N 1*s* and O 1*s* binding energies of the NO ligand can be used to distinguish between linear ((N 1*s*)—(O 1*s*) $\simeq$132 eV) and bent ((N 1*s*)—(O 1*s*) $\simeq$129 eV) groups [71]. Because of sample preparation difficulties, and the relatively few complexes studied so far (which makes the boundary limit rather wide) this interesting technique is unlikely to supplant the simple infrared method of deciding between linear and bent nitrosyls.

(ii) Reactions

1. Substitution reactions. When present in the $\{RuNO\}^6$ grouping, NO does not undergo ligand substitution in the normal fashion. However, it has now been established that photolyses of $[RuX_5(NO)]^{2-}$ (X = Cl, Br, I) in aqueous solution, and of $[RuCl(bipy)_2(NO)]^{2+}$ (bipy = 2,2′-bipyridine) in acetonitrile solution proceed via the primary photochemical processes [63,72,73]

$$[RuX_5(NO)]^{2-} + H_2O \overset{h\nu}{\rightleftharpoons} [RuX_5(H_2O)]^{2-} + NO \qquad (1)$$

$$[RuCl(bipy)_2(NO)]^{2+} + CH_3CN \overset{h\nu}{\rightleftharpoons} [RuCl(bipy)_2(CH_3CN)]^{2+} + NO$$

In deoxygenated solution, at neutral pH, the simple reaction (1) was essentially the only reaction for X = Cl or Br (halide substitution did occur, but at a slower rate than the photolysis). In the presence of O_2 or $HClO_4$, oxidation of both $[RuCl_5(H_2O)]^{2-}$ and NO occurred, and in alkaline solution ligand substitution reactions of the initial products were rapid. When X = I complications due to the lability of the I^- ligand were found [63]. For reaction (2) the final reaction products in the presence of argon were a mixture of $[Ru(CH_3CN)(bipy)_2Cl]^+$ and $[Ru(CH_3CN)(bipy)_2Cl]^{2+}$. In the presence of dioxygen, or under vacuum, $[Ru(CH_3CN)(bipy)_2Cl]^{2+}$ was the only product. The difference in behaviour under vacuum or under argon can probably be explained by the secondary reaction

$$NO + [Ru(CH_3CN)(bipy)_2Cl]^{2+} \rightarrow [Ru(CH_3CN)(bipy)_2Cl]^+ + NO^+ \qquad (3)$$

which can occur unless NO is removed under vacuum [73]. It is somewhat surprising that photochemical substitution of NO has not been more extensively investigated in view of earlier problems with the stability of the $\{RuNO\}^6$ group towards substitution.

Previous ideas on the substitution of other ligands in six-coordinate $\{RuNO\}^6$ complexes require modification in the light of the crystallographic and theoretical results which show very clearly that the bond *trans* to NO is thermodynamically strengthened, not weakened, by the NO ligand (see B(i) above). It has previously been stated that NO in $\{RuNO\}^6$ complexes is a good *trans* ligand (i.e. *trans* directing ligand; see, for instance, refs. 74—76). This view was understandable when the following evidence is considered. (1) Until the recent preparation of *cis*-$[RuX(NH_3)_4(NO)]^{2+}$ (X = Cl, Br, OH) [77] by reaction of NO with a preformed *cis* complex, all known complexes of type $[RuXL_4(NO)]^{n+}$ were *trans* isomers (e.g. the extensive $[RuX(NH_3)_4(NO)]^{2+}$ series [78]); complexes of type $[RuX_3L_2(NO)]$ (X = Cl, Br or I; L = ammonia, tertiary phosphine, arsine or stibine, or secondary sulphide or selenide) invariably had X *trans* to NO [76,79—83]. (2) Substitution reactions of $[RuL_5(NO)]^{n+}$ were relatively facile and invariably gave *trans* products [75]. (3) Replacement of the X ligand in complexes of type $[RuX_3L_2(NO)]$ were relatively facile [80,82], and in some cases complexes of type $[RuXY_2L_2(NO)]$ could be isolated, in which X, the ligand of weakest *trans* influence, was *trans* to NO [76].

The above evidence can be viewed differently in the light of recent results; the following are alternative explanations, together with additional evidence [154]. (1) Syntheses of $[RuX_3L_2(NO)]$ complexes generally begin with $[RuCl_3(NO)]$ [80—83]; the Cl ligands are invariably retained. Although replacement of Cl by I or Br can sometimes be effected, it usually requires forcing conditions, e.g. refluxing in ethanol; in several cases such metathetical reactions do not proceed at all [76,83]. (2) $[Ru(NH_3)_5(NO)]^{3+}$ was inert to substitution in acid solution [14]; substitution only occurred in alkaline solution, where $[RuNH_2(NH_3)_4(NO)]^{2+}$ and $[Ru(NH_3)_5(NO_2)]^+$ were also present [84] (the NO_2 ligand in the latter is thermodynamically *trans* weakening [85]). (3) All preparations of $[RuX(NH_3)_4(NO)]^{2+}$ involve either substitution reactions of $[Ru(NH_3)_5(NO)]^{3+}$ in alkaline solution [84] or prolonged refluxing of $[Ru(OH)(NH_3)_4(NO)]^{2+}$ in HX [75,78]. (4) Hydrolysis of the Cl ligand in *cis*-

$[\mathrm{RuCl(NH_3)_4(NO)}]^{2+}$ was faster than the corresponding hydrolysis in *trans*-$[\mathrm{RuCl(NH_3)_4(NO)}]^{2+}$ [86], and *cis* to *trans*, but not *trans* to *cis*, isomerisation occurred in such systems; there was no evidence for substitution of the *trans*-$\mathrm{NH_3}$ in *cis*-$[\mathrm{RuCl(NH_3)_4(NO)}]^{2+}$ [77,86]. (5) An n.m.r. study of aqueous solutions of $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ showed the *trans*-$\mathrm{NH_3}$ protons exchanged faster than the *cis* [87]; the $[\mathrm{RuNH_2(NH_3)_4(NO)}]^{2+}$ which can be isolated from such solutions appeared to be the *trans* isomer (formation of an amido ligand in aqueous solution is an interesting consequence of the remarkable electron-withdrawing ability of NO, which will be more effective along the $\{\mathrm{NH_3RuNO}\}$ axis [84]). (6) Even in the case of the hydrolysis of $[\mathrm{RuCl_5(NO)}]^{2-}$, for which kinetic data are available [74,88,89], the stereochemistry of the initial substitution product is unknown; it is noteworthy that this substitution required temperatures of 50° and that $[\mathrm{RuCl}_n(\mathrm{H_2O})_{4-n}(\mathrm{NO})]^{m-}$ species for $n = 1$—4, but not for $n = 0$, were identified in aqueous solutions of chloronitrosylruthenium [90].

In summary, there is now considerable experimental and theoretical evidence for a thermodynamic *trans* strengthening effect of NO in $\{\mathrm{RuNO}\}^6$ complexes. There is also ample evidence that substitution reactions of such complexes often result in changes at the ligand *trans* to NO, and essentially never in the *cis* position. At least two explanations of this apparent contradiction deserve consideration. First, it is possible that all substitution reactions occur in the *cis* position, with subsequent *cis* to *trans* isomerisation. While there is no direct evidence against such a mechanism, it does not readily explain the preponderance of *trans*-$[\mathrm{RuXL_4(NO)}]^{n+}$, (with a variety of interchangeable X ligands) and $[\mathrm{RuX_3L_2(NO)}]$ amongst $\{\mathrm{RuNO}\}^6$ complexes; examples of the various possible geometrical isomers of $[\mathrm{RuX}_n\mathrm{L}_{5-n}(\mathrm{NO})]^{m+}$ ($n = 0$ to 5) should be obtainable. A second explanation is that NO may exert a kinetic *trans* effect. This possibility requires a mechanistic pathway, and two such may be suggested. In the first the $\{\mathrm{RuNO}\}^6$ unit may become bent in a seven-coordinate transition state, i.e. the addition of a sixth ligand causes a pair of electrons to enter the $d_{z^2}(\mathrm{Ru}) - n(\mathrm{NO})$ orbital, with the resultant interaction between this and $d_{xz} - \pi^*(\mathrm{NO})$ causing $\{\mathrm{RuNO}\}^6$ bending (Fig. 1) (see also D(i) below). This is an example of the stereochemical control of valence [30]. The resultant "$\mathrm{NO^-}$" ligand would be *trans* weakening. Such a possibility was suggested in the oxidation of $\mathrm{Ph_3P}$ by $[\mathrm{Ru(NO)(NCS)(Ph_3P)_2(O_2)}]$ via the bent $\{\mathrm{RuNO}\}^6$ intermediate $[\mathrm{Ru(NO)(NCS)(Ph_3P)_3(O_2)}]$ [91], although the evidence, particularly in the light of the recent proof that the presumed seven-coordinate $[\mathrm{RuCl_2(Ph_3As)_3)_3(O_2)}]$ does not exist [92], is tenuous, and alternative mechanisms may be suggested (see D(ii)1 below and ref. 93). In the second mechanistic pathway, substitution could occur directly at the *trans* position via equilibrium amounts of a *trans* labilizing intermediate produced by nucleophilic addition at $\{\mathrm{RuNO}\}$, e.g. for $\mathrm{OH^-}$

$$\{\mathrm{RuNO}\} + 2\,\mathrm{OH^-} \rightleftharpoons \{\mathrm{RuNO_2}\} + \mathrm{H_2O} \qquad (4)$$

Such an explanation would readily account for *trans* substitution in

$[Ru(NH_3)_5(NO)]^{3+}$. It would also explain the otherwise mysterious increase in the rate of hydrolysis of $[RuCl_5(NO)]^{2-}$ with increasing pH [74], though here purposeful attempts to prepare $[RuCl_5(NO_2)]^{4-}$ have failed [29]. Finally, a brief note indicates that on one-electron reduction $[Ru(NH_3)_5(NO)]^{3+}$ rapidly loses a *trans*-NH_3, and the resultant aquo species reduces $[Ru(NH_3)_5(NO)]^{3+}$. This opens the possibility of a redox-induced catalytic substitution reaction [94]

$$[Ru(NH_3)_5(NO)]^{3+} + e \rightleftharpoons [Ru(NH_3)_5(NO)]^{2+} \qquad (5)$$

$$[Ru(NH_3)_5(NO)]^{2+} + H_2O \rightarrow trans\text{-}[Ru(NH_3)_4(H_2O)(NO)]^{2+} + NH_3 \qquad (6)$$

$$trans\text{-}[Ru(NH_3)_4(H_2O)(NO)]^{2+} + [Ru(NH_3)_5(NO)]^{3+} \rightarrow trans\text{-}[Ru(NH_3)_4(OH)(NO)]^{2+} + [Ru(NH_3)_5(NO)]^{2+} + H^+ \qquad (7)$$

It is of course possible that all the above mechanisms, as well as simple bimolecular substitution, occur in different circumstances. Careful mechanistic studies on these nitrosyls are much needed.

2. *Reactions at the nitrosyl ligand.* Two types of reaction at the NO ligand of $\{RuNO\}^6$ complexes have been observed: reduction in one electron steps and nucleophilic attack at the nitrogen atom. The former type of reaction is conveniently discussed under $\{RuNO\}^7$ complexes (C, below). The latter type of reaction has been extensively investigated for $\{RuNO\}^6$ complexes having high ν(NO) frequencies ($>$1880 cm^{-1}), particularly $[Ru(NH_3)_5(NO)]^{3+}$, $[RuCl(bipy)_2(NO)]^{2+}$ and $[RuCl(pdma)_2(NO)]^{2+}$ (bipy = 2,2'-bipyridine; pdma = *o*-phenylenebis(dimethylarsine)). The subject of the electrophilic behaviour of coordinated nitrosyl has very recently been reviewed in depth, and will not be repeated here [9,95].

C. $\{RuNO\}^7$ COMPLEXES

The only known route to $\{RuNO\}^7$ is one-electron reduction of $\{RuNO\}^6$ complexes, and two studies have been made of this approach. The most complete is on the reversible electrolytic or chemical (by I^-) reduction of $[RuX(bipy)_2(NO)]^{n+}$ (X = Cl, N_3 or NO_2^- for n = 2; X = pyridine, CH_3CN or NH_3 for n = 3) to give the corresponding $\{RuNO\}^7$ $[RuX(bipy)_2(NO)]^{(n-1)+}$ complexes, of which $[RuCl(bipy)_2(NO)]I$ and $[Ru(CH_3CN)(bipy)_2(NO)](PF_6)_2$ were isolated as solids [73,96]. The most interesting result of this work is that while all physical measurements (i.r., e.s.r., ESCA, Mössbauer, electronic spectroscopy and electrochemistry) indicated extensive $d_\pi(Ru) - \pi^*(NO)$ overlap in both the $\{RuNO\}^6$ and $\{RuNO\}^7$ complexes, they also indicated that the added electron entered a molecular orbital mainly located on the NO ligand. Following the molecular orbital schemes discussed earlier (see Fig. 1) this must be the $d_{xz}(Ru) - \pi^*(NO)$ or

$d_{yz}(\mathrm{Ru}) - \pi^*(\mathrm{NO})$ antibonding orbital, which must be of lower energy than $d_{z^2}(\mathrm{Ru}) - n(\mathrm{NO})$. The chemical behaviour of $[\mathrm{RuX(bipy)_2(NO)}]^{n+}$ towards nucleophiles indicates that relative to other $\{\mathrm{RuNO}\}^6$ complexes the ruthenium *d* orbitals contribute relatively little to these molecular orbitals, and they can therefore be considered as largely $\pi^*(\mathrm{NO})$ in character. As is apparent from molecular orbital arguments, addition of the extra electron to the $d_{xz}(\mathrm{Ru}) - \pi^*(\mathrm{NO})$ or $d_{yz}(\mathrm{Ru}) - \pi^*(\mathrm{NO})$ orbitals should result in significant bending of the $\{\mathrm{RuNO}\}$ group (though the degree will depend on the relative contributions of the ruthenium *d* and $\pi^*(\mathrm{NO})$ orbitals to the molecular orbital). A structural study of one of these $\{\mathrm{RuNO}\}^7$ complexes is not yet available but would be of considerable interest. It is possible to further reduce $[\mathrm{Ru(CH_3CN)(bipy)_2(NO)}]^{2+}$ by one-electron, one of the products being $[\mathrm{Ru(CH_3CN)(bipy)_2(NO_2)}]^+$, but the reduction is irreversible and complicated. With O_2, $[\mathrm{Ru(CH_3CN)(bipy)_2(NO)}]^{2+}$ gave $[\mathrm{Ru(CH_3CN)(bipy)_2(NO_2)}]^+$, an interesting reaction previously observed for $[\mathrm{Co(en)_2(NO)}]^{2+}$ which is presumed to have a bent $\{\mathrm{CoNO}\}^8$ grouping [97].

The one-electron reduction of $[\mathrm{Ru(NH_3)_5NO}]^{3+}$ is also possible, but here the $\{\mathrm{RuNO}\}^7$ product decomposes very rapidly (cyclic voltammograms with scan rates of greater than 0.1 V s^{-1} are necessary for reversible redox behaviour) [94,98]. The estimated standard reduction potential of $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ is more negative than for $[\mathrm{Ru^{III}(NH_3)_6}]^{3+}$, indicating a more difficult reduction process [98]. In contrast, the estimated E° for $[\mathrm{RuX(bipy)_2(NO)}]^{n+}$ was comparable to other $[\mathrm{Ru^{III}X(bipy)_2Y}]^{n+}$ complexes [73]. This may indicate a different site of reduction in the two cases; in fact the observation that $[\mathrm{Ru(NH_3)_5(NO)}]^{2+}$ rapidly loses a *trans*-NH_3 [94], indicates that the electron enters the $d_{z^2} - n(\mathrm{NO})$ orbital (which must have some σ-NH_3 character) of Fig. 1 i.e. $d_{z^2}(\mathrm{Ru}) - n(\mathrm{NO})$ is here lower in energy than $d_{xz}, d_{yz}(\mathrm{Ru}) - \pi^*(\mathrm{NO})$.

$[\mathrm{Ru(NH_3)_5(NO)}]^{2+}$ reacted rapidly with the $\mathrm{CH_2C(CH_3)_2OH}$ radical (both radicals produced by radiolysis of aqueous solutions of $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ in the presence of $\mathrm{Bu^tOH}$) to give a complex formulated as $[\mathrm{Ru(NH_3)_5(N(O)CH_2C(CH_3)_2OH)}]^{2+}$. Such a product would also result from the hypothetical electrophile—nucleophile reaction

$$[\mathrm{Ru(NH_3)_5(NO)}]^{3+} + (\mathrm{CH_2C(CH_3)_2OH})^- \rightarrow$$
$$\rightarrow [\mathrm{Ru(NH_3)_5(N(O)CH_2C(CH_3)_2OH)}]^{2+} \qquad (8)$$

although the infrared spectrum of the product is said to favour the tautomeric structure involving Ru(III) and a nitroxide ligand [99]. Facile reduction of $[\mathrm{Ru(NH_3)_5(NO)}]^{3+}$ by $\mathrm{Cr^{2+}}$, via $[\mathrm{Ru(NH_3)_5(NO)}]^{2+}$, to $[\mathrm{Ru(NH_3)_6}]^{2+}$, was observed [100]. The reverse of this, oxidation of NH_3 to NO on ruthenium by perchloric acid, has also been reported without details [145].

Reduction of $[\mathrm{RuCl_5(NO)}]^{2-}$ with $\mathrm{SnCl_2/HCl}$ ultimately gave $[\mathrm{Ru_2(N)Cl_8(H_2O)_2}]^{3-}$ [101]. The initial product of the reaction was not $[\mathrm{RuCl_5(NO)}]^{2-}$ but a substitution product, $[\mathrm{RuCl_3(SnCl_3)_2(NO)}]^{2-}$. A more reduced product has been formulated as the nitrosyl bridged complex $[Ru_2Cl_6(SnCl_3)_2(NO)_2]$ (ν(NO) 1566 cm^{-1}) [102].

D. $\{RuNO\}^8$ COMPLEXES

(i) Structure and bonding

According to the molecular orbital diagram given earlier, the two electrons added to $\{RuNO\}^6$ to form a $\{RuNO\}^8$ complex will enter either the $d_{z^2} - n(NO)$ or $d_{xz} - \pi^*(NO)$ antibonding orbital. Since the interaction between these two (σ—π mixing) is strong at significant bending angles, and $d_{z^2}(Ru) - n(NO)$ decreases in energy as $d_{xz}(Ru) - \pi^*(NO)$ increases, it is immaterial into which orbital the electrons are initially placed (see Fig. 1) [25]. The consequences of the addition of two electrons depend on other factors. (1) If the $\{RuNO\}^8$ complex is six-coordinate, bending would be strongly favoured [8,30,33]. This effect is the stereochemical control of valence referred to in discussing possible mechanisms of $\{RuNO\}^6$ reactions above; in fact, no six-coordinate $\{RuNO\}^8$ complexes are definitely known. (2) if the $\{RuNO\}^8$ complex is five-coordinate (much more likely than (1), since $d_{z^2}(Ru) - n(NO)$ is stabilized by loss of the sixth ligand) the geometry of the $\{RuNO\}$ unit will depend on the coordination geometry of the complex and the nature of the other ligands [8,31—33]. Stating here only those possibilities applicable to known $\{RuNO\}^8$ complexes, analysis of the energy level diagram for the various coordination geometries shows: (a) nitrosyl groups in basal sites in a square pyramid (SP) and axial sites in a trigonal bipyramid (TBP) prefer linear coordination; (b) if the other ligands are strong π-acceptors a trigonal bipyramid with an equatorial NO will be preferred; (c) a bent NO will prefer the apical site of a square pyramid to the equatorial position of a trigonal bipyramid [33].

Before discussing the structures of $\{RuNO\}^8$ complexes the interesting paper by Haymore and Ibers should again be noted [27]. While noting that the energy and symmetry arguments of molecular orbital theory are fundamental in nature, which empirical generalizations are not, the authors point out that generalizations about the geometry of nitrosyls can be made if some simple assumptions are accepted. (1) The "normal" coordination geometry of NO is linear. (2) In five-coordinate 18-electron (i.e. $\{MNO\}^8$) complexes, TBP geometry is associated with linear NO and SP with bent. (3) Because the energy differences between TBP and SP are small, subtle differences may decide the geometry of both the complex and the $\{MNO\}$ group. (4) Any electrons beyond the "magic number" of 18 must be located on easily reduced ligands (such as NO), not on the metal. Combining these assumptions with empirical rules of stereochemistry (e.g. in 5-coordinate systems bulky ligands will occupy equatorial positions of a TBP and basal of an SP; and, because of their restricted bite angle, small bidentate ligands will span basal positions of an SP or one axial and one equatorial position of a TBP) and

TABLE 2

Structural parameters for 5-coordinate $\{RuNO\}^8$ complexes

Complex	r(Ru—N) (Å) [a]	r(N—O) (Å) [a]	Ru—N—O (°) [a]	Comments	Ref.
$[Ru(diphos)_2(NO)](BPh_4), ((CH_3)_2CO)$ [b]	1.74(1)	1.20(1)	174(1)	TBP with equatorial NO	103
$[RuH((C_6H_5)_3P)_3(NO)]$	1.792(11)	1.183(11)	176(1)	TBP with axial NO *trans* to H	104
$[RuI(CO)((C_6H_5)_3P)_2(NO)]$	1.80(4) [c]	1.15(5) [c]	159(2) [c]	TBP with axial Ph_3P; severe disorder (see text)	105
$[RuCl((C_6H_5)_3P)_2(NO)_2](PF_6), (C_6H_6)$	1.743(20) 1.863(19)	1.158(19) 1.662(20)	178(2) 138(2)	Distorted SP with linear NO in basal, bent in axial position	106

[a] Standard deviations, relating to the least significant figure(s), in brackets. [b] Diphos = 1,2-bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$. [c] Disordered; the RuNO and RuCO distances and angles are combined.

electronic effects (e.g. that neither two strong π-acceptor nor two strong σ-donor ligands will prefer to be *trans* to one another), it is possible to predict much of the structural geometry of metal nitrosyls. Such an approach is not to be underestimated.

Table 2 summarizes the known $\{RuNO\}^8$ structures. All complexes have π-acceptor phosphine groups as co-ligands, and the two mononitrosyls for which accurate data are available have essentially linear {RuNO} groups and TBP geometry. In $[Ru(diphos)_2(NO)]^+$ the NO group is equatorial (the bite angle of diphos being small) [103], in $[RuH(Ph_3P)_3(NO)]$ axial and *trans* to the good σ-donor H ligand [104]. Considerable doubt must be attached to $[RuI(CO)(Ph_3P)_2(NO)]$ whose severely disordered structure has been interpreted to be TBP with axial Ph_3P and disordered CO and NO equatorial ligands with a RuAO (A = N, C) angle of 159° [105]. The high final *R* value of 0.137 perhaps indicates something more serious than a simple two-fold rotation disorder, and at present one should not regard this complex as being the exception to all rules and rationalizations. The single $\{Ru(NO)_2\}^8$ complex, $[RuCl(Ph_3P)_2(NO)_2]^+$, is SP with the linear {RuNO} group in the basal plane and the bent {RuNO} group apical, rotated so as to be above the linear {RuNO} [106]. It has been predicted from molecular orbital calculations that in SP geometry with an apical bent {MNO}, the NO will bend in the plane of the poorest σ-donor [33]. The shorter Ru—NO distance to the linear NO is indicative of much better Ru—NO π-bonding. It may also be noted that because of the close similarity in physical and chemical properties between $[Ru(CO)_2(Ph_3P)_2(NO)]^+$ and its osmium analogue whose structure is known [107], this complex is almost certainly TBP with an equatorial linear NO group [108]. It has been reported that $[RuCl(Ph_3P)_2(O_2)(NO)]$, which can be regarded as a $\{RuNO\}^8$ complex [92], has *trans* axial Ph_3P groups and a linear equatorial NO (see ref. 91). However, there are serious disorder problems [113]. Finally in discussing structures of $\{RuNO\}^8$ complexes, the four-coordinate $[RuCl(Ph_3P)_2(NO)]$ [109], which is closely related to the well-known $[IrCl(Ph_3P)_2(CO)]$, is almost certainly square planar with a linear {RuNO} group. No structural information is available, and ν(NO), at 1670 cm^{-1}, is low (though the corrected value is within the range proposed for linear MNO complexes [20]), but the reactions of this complex (see below) are those expected of a formally d^8, 4-coordinate, square planar complex [110—112].

(ii) Reactions

With three exceptions all reactions of $\{RuNO\}^8$ complexes leave the {RuNO} group intact. However, there is evidence that this group does not necessarily remain stereochemically unchanged on reaction, even when it is retained. It has been suggested, that the infrared spectra of $[RuCl(Ph_3P)_2(NO)_2]^+$ containing one ^{15}NO labelled NO, indicate intramolecular exchange of the basal and apical NO groups, with consequent bending or straightening of the appropriate {RuNO} [114]. Enemark and Feltham [8] have noted that these spectra can also be explained by different orientations of the bent NO with respect to the {$Ru(Ph_3P)_2$} or {RuCl(NO)} basal planes, or from initial (i.e. in the preparation of [$RuCl(Ph_3P)_2(^{14}NO)(^{15}NO)]^+$) formation of isomers having ^{15}NO in the bent and linear positions, with a high energy barrier to interconversion of the isomers. Unequivocal evidence for the conversion of linear into bent NO is known only for the reactions

$$[Co(pdma)_2(NO)]^{2+} + NCS^- \rightarrow [Co(pdma)_2(NCS)(NO)]^+ \tag{9}$$

in which the CoNO angle changes from 179 to 135° [115], and

$$[Fe(pdma)_2(NO)]^{2+} + NCS^- \rightarrow [Fe(pdma)_2(NCS)(NO)]^+ \tag{10}$$

in which the FeNO angle changes from 173 to 159° [116]. Creation of a vacant coordination site (i.e. increasing the coordination number on converting an 18-electron complex to a 16) by moving a pair of electrons from the metal to the NO ligand, as in (9) has been suggested as a general possibility [117—119], and has been proposed in particular in the mechanism of the catalytic oxidation of Ph_3P to Ph_3PO by [$Ru(NCS)(Ph_3P)_2(O_2)NO$] [91] (see below), and in the conversion of [$RuCl(Ph_3P)_2(O_2)(NO)$] into [$RuCl(NO_3)(CO)_2(Ph_3P)_2$] [120]. It also appears that the intramolecular rearrangement of [$Ru(diphos)_2(NO)]^+$ (TBP with a linear equatorial {RuNO}) probably proceeded via a Berry pseudorotation with an SP (bent apical {RuNO}) transition state [121].

1. Reactions of five-coordinate complexes. The series of complexes [$RuX(CO)(PPh_3)_2(NO)$] (X = Cl, Br, I, OH, N_3, NCO, NCS and HCO_2) were obtained by simple metathetical substitution of X for Cl in the parent [$RuCl(CO)(Ph_3P)_2(NO)$] [122]. According to the criteria developed by Haymore and Ibers, all the products should have a bent {RuNO} group, and therefore be SP, except X = I; the severely disordered structure of [$RuI(CO)(Ph_3P)_2(NO)$] has been interpreted as showing a TBP structure with equatorial, but partially bent, {RuNO} [105]. The chloro complex is so labile that in the presence of a precipitating anion and CO, [$Ru(CO)_2(PPh_3)_2(NO)]^+$ was obtained; again one CO is extremely labile, being readily replaced by donor solvents, Cl^- or phosphines [123]. The extreme lability of the chloride ligand is not easily understood even if a bent NO acts as a labilizing ligand as anticipated; the carbonyl is presumably labile because of the inability of the ruthenium to donate sufficient electron density to two π-acceptor ligands as well as NO. No evidence for NO substitution was found [123].

These 5-coordinate {RuNO}^{8} complexes undergo oxidative addition reactions with complete loss of CO. For example, starting from [$RuCl(CO)(Ph_3P)_2(NO)$], the halogens Br_2 and I_2 gave [$RuClX_2(Ph_3P)_2(NO)$] (with *trans*-phosphines) [122] and O_2 gave [$RuCl(Ph_3P)_2(O_2)(NO)$] [124]. Remarkably both [$Ru(CO)_2(Ph_3P)_2(NO)]^+$ and [$RuCl(CO)(Ph_3P)_2(NO)$] reacted with

Cl_2 to give minor products containing no NO (e.g. *cis*-$[RuCl_2(CO)_2(Ph_3P)_2]$), as well as the expected $[RuCl_3(Ph_3P)_2(NO)]$ [122,123]. The fate of NO is unknown, but is of considerable interest in view of the normal stability of the mononitrosyl {RuNO} unit towards substitution. A search for NOCl might be productive, because of the known reaction of $[RuCl(Ph_3P)_2(O_2)(NO)]$ with CO to give $[RuCl(NO_3)(CO)_2(Ph_3P)_2]$ (see below) [120]. The possibility of simple Cl^- substitution for NO cannot be discounted either, in view of the reaction [125]

$$[RuCl(Ph_3P)_2(NO)_2]^+ + \underset{\text{excess}}{Cl^-} \rightarrow [RuCl_3(Ph_3P)_2(NO)] \qquad (11)$$

The fate of the NO was again not stated.

Some 5-coordinate $\{RuNO\}^8$ complexes are catalytically active. Styrene was catalytically hydrogenated and hex-1-ene isomerised by $[Ru(H)L_3(NO)]$ ($L = Ph_3P, Ph_2Pr^iP, Ph_2(C_6H_{11})P$) but $[Ru(H)(Ph_2MeP)_3(NO)]$ was much less active as a catalyst. N.m.r. studies in solution showed the complexes with $L = Ph_3P$ had the TBP structure with the *trans* axial NO and H geometry also found in the solid state [104]; for $L = Ph_2Pr^iP$ and $Ph_2(C_6H_{11})P$ the TBP and another isomer were rapidly interconverting at room temperature; and for $L = Ph_2MeP$ only the other isomer was observed. It appeared, therefore, that only the TBP complex with an axial linear NO was catalytically active [119], and that the other isomer has the SP geometry.

The oxidation of Ph_3P to Ph_3PO was catalysed by $[Ru(NCS)(Ph_3P)_2(O_2)(NO)]$. On the basis of kinetic data it was suggested that the mechanism was (RuL_2 representing $Ru(NCS)(Ph_3P)$)

$$\begin{tikzcd}
{\underset{\mathrm{I}}{[RuL_2(Ph_3P)(O_2)(NO)]}} \arrow[r, shift left, "Ph_3P"] & {\underset{\mathrm{II}}{[RuL_2(Ph_3P)_2(O_2)(NO)]}} \arrow[l, shift left, "K_1"] \arrow[d, "k_1", "\text{slow}"'] \\
{[RuL_2(Ph_3P)(NO)]} \arrow[u, "O_2"] & {[RuL_2(Ph_3PO)_2(NO)]} \arrow[l, "+Ph_3P", "-2Ph_3PO"']
\end{tikzcd} \qquad (12)$$

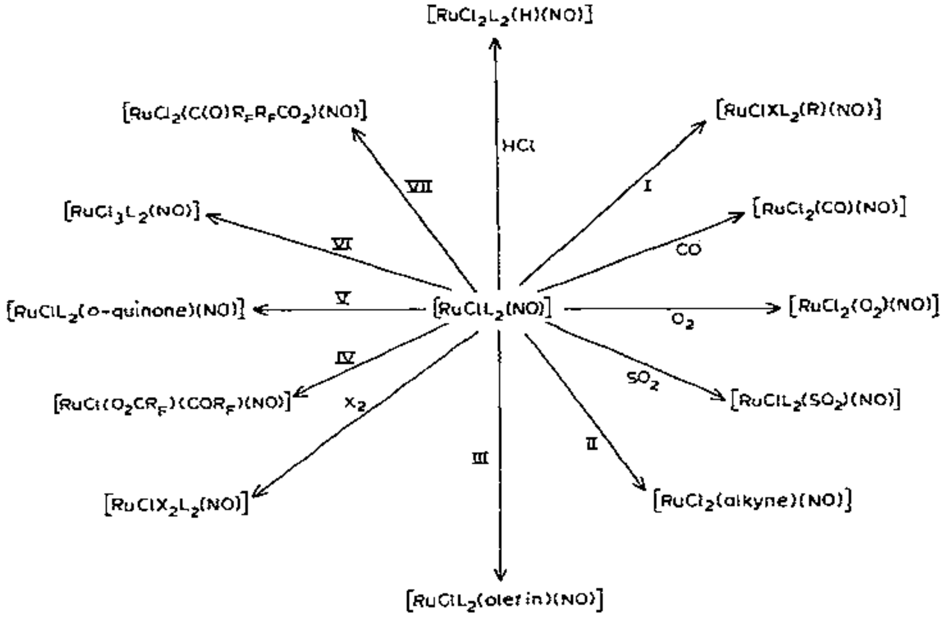
Since I is a coordinatively saturated 18-electron complex, it was proposed that addition of Ph_3P results in bending of the {RuNO} (i.e. two electrons moving from the metal to the NO) [91]. An apparent precedent for the 7-coordinate Ru(II) dioxygen complex II was $[RuCl_2(Ph_3As)_3(O_2)]$ [126], but this has now been shown not to exist [92]. The rate law for the above mechanism is $-d[Ph_3P]/dt = k_1K_1[I][Ph_3P]/(1 + K_1[Ph_3P])$ which reduces to $-d[Ph_3P]/dt = k_1[I]$ at high $[Ph_3P]$, where II should be detectable [127]. This test of the mechanism has not yet been applied, and other mechanisms may prove to be correct. In fact it has been suggested very recently that the reaction proceeds via formation of peroxide [93].

The chlorine oxidation of $[Ru(CO)_2(Ph_3P)_2(NO)]^+$ or $[RuCl(CO)(Ph_3P)_2(NO)]$ to give non-nitrosyl products has been mentioned earlier. One other reaction is known in which the NO ligand itself is involved. This is the remarkable reaction [120]

$$[\mathrm{RuCl(Ph_3P)_2(O_2)(NO)}] + 2\ \mathrm{CO} \rightarrow [\mathrm{RuCl(NO_3)(CO)_2(Ph_3P)_2}] \qquad (13)$$

Since the starting complex very probably has a linear {RuNO} group (ν(NO) 1765 cm^{-1} [124]; see also the structural information in ref. 91), and the NO in such complexes reacts, if at all, as an electrophile, [9], it seems possible that CO addition causes {RuNO} bending, with resultant nucleophilic behaviour of NO towards O_2 (bent {MNO} groups are oxidized by O_2 [97,128]).

2. *Reactions of four-coordinate complexes.* The presumably *trans*, square planar, linear $\{\mathrm{RuNO}\}^8$ complex, [$\mathrm{RuClL_2(NO)}$] (L = tertiary phosphine) underwent oxidative addition reactions [109—112], as expected from its similarity to [$\mathrm{MClL_2(CO)}$] (M = Rh, Ir) and [$\mathrm{IrClL_2(NO)}]^+$, though it is more reactive than these analogues [111]. The reactions are summarized in Scheme 1. In most cases the stereochemistry of the additions was such that the L groups remained *trans* in the final six-coordinate product (though n.m.r. data indicated addition of C_2F_3Cl and $CF_3CF{=}CF_2$ gave products with *cis*-L groups



Scheme 1. L = Ph_3P in all cases; for additions III, IV and for I_2 L may be $MePh_2P$ or Me_2PhP as well.
I: RCOCl, R = Ph, Me; II: alkyne = hexafluorobut-2-yne; III: olefin = tetracyanoethylene, fumaronitrile, tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoropropene; IV: $(R_F CO)_2O$, R_F = CF_3, C_2F_5; V: *o*-quinone, = tetrachloro-1,2-benzoquinone, tetrabromo-1,2-benzoquinone, and 9,10-phenanthrenoquinone; VI: tosylchloride.
Refs.: HCl, CO, SO_2 [109]; O_2 [109,124]; I [110,111]; II [112]; III [110—112]; X_2 [109,112]; IV [110]; V [110,111]; VI [111]; VII [111].

[112]), and the Cl and NO groups were *cis* (I_2 initially added *trans*, producing *trans* Cl and NO groups, but then isomerised; C_2F_3Cl and $CF_3CF{=}CF_2$ gave products having *trans* NO and Cl [112]).

E. {RuNO}^{10} COMPLEXES

(i) Structure and bonding

There are only two examples of {RuNO}^{10} complexes. One is the dinitrosyl $[Ru(Ph_3P)_2(NO)_2]$, first reported by Levison and Robinson [129], and since then prepared by several different methods by other groups [130—134], including a very interesting inter-ligand oxygen transfer reaction [131]

$$[Ru(CO)_2(Ph_3P)_2(NO_2)_2] \rightarrow [Ru(Ph_3P)_2(NO)_2] + CO + CO_2 + Ph_3PO \qquad (14)$$

The second {RuNO}^{10} complex is the closely related $[Ru(\eta^3\text{-}C_3H_5)(Ph_3P)_2(NO)]$ [153].

Two independent structure determinations showed $[Ru(Ph_3P)_2(NO)_2]$ to have distorted tetrahedral geometry (P—Ru—P = 104°, N—Ru—N = 139°) with essentially linear {RuNO} groups [132,135]. As such $[Ru(Ph_3P)_2(NO)_2]$ is one of a series of $[ML_2(NO)_2]$ (M = Fe, Ru, Os, Ir^+, L = tertiary phosphine) complexes of basically similar geometry (see ref. 27 for a complete list with full structural details). Although the distortion from idealized geometry in these complexes has been interpreted in terms of the metal—ligand π-bonding (increased π-donation by the metal should cause a bending of {MNO} and an opening of the {NMN} angle because of the increased repulsion between NO groups) there are still considerable difficulties in explaining the details (e.g. that the Os and Ru complexes have essentially indistinguishable geometries) [27]. For $[Ru(\eta^3\text{-}C_3H_5)(Ph_3P)_2(NO)]$, Ru—N—O is 173.8° and P—Ru—P 104.8 [153].

(ii) Reactions

$[Ru(Ph_3P)_2(NO)_2]$ is an extremely reactive species and undergoes substitution and NO transfer reactions

$$[Ru(Ph_3P)_2(NO)_2] + [RuCl_2(Ph_3P)_3] \xrightarrow{Zn} 2[RuCl(Ph_3P)_2(NO)] + Ph_3P \qquad (15)$$

$$[Ru(Ph_3P)_2(NO)_2] + 3[CoClD_2(Ph_3P)] \rightarrow [RuCl_3(Ph_3P)_2(NO)] + [CoD_2(NO)] + 2\ CoD_2 + 3Ph_3P \qquad (16)$$

(D = dimethylglyoximato) [133]. These nitrosyl transfer reactions probably proceeded via a bridging NO group. With dioxygen, $[Ru(NO_3)(Ph_3P)_2(O_2)(NO)]$ was formed by an unknown mechanism. This latter reacted further with CO to give $[Ru(NO_2)_2(CO)_2(Ph_3P)_2]$, as described above for $[RuCl(Ph_3P)_2(O_2)(NO)]$. With strong acids in the presence of O_2, [Ru(OH)-

$(Ph_3P)_2(NO)_2]^+$ was formed [131]. The mechanisms of the above oxygenation reactions would be of considerable interest. With Cl_2 the initial product was $[RuCl(Ph_3P)_2(NO)]$ (an oxidative addition reaction for which the fate of the lost NO was again not ascertained) which underwent a second oxidative addition, as described above, giving $[RuCl_3(Ph_3P)_2(NO)]$ [109]. With R_FCOOH (R_F = perfluoralkyl group) $[Ru(OCOR_F)_3(Ph_3P)_2(NO)]$ complexes were formed, probably by initial protonation of a nitrosyl group [136], as was observed for $[Os(Ph_3P)_2(NO)_2]$ [137]. Since $[Ru(OCOR_F)_3(Ph_3P)_2(NO)]$ is the first neutral complex with a high $\nu(NO)$ (1905 cm^{-1}) it may be of use in C—N bond formation by nucleophilic attack of {RuNO} in non-polar solvents [9]. Formation of C—N bonds did occur in the reactions of $[Ru(Ph_3P)_2(NO)_2]$ with $PhCH_2Br$ in hot toluene under CO; initially $[RuBr(CO)(Ph_3P)_2(NO)]$ was formed, which was slowly converted to $[RuBr_2(Ph_3P)_2(CO)_2]$. The organic products were (after 48 h) $PhCONH_2$ (77%), PhCN (17%), PhCH=NOH (9%) and PhCHO (5%). Under N_2 or C_2H_4 only $[RuBr_3(Ph_3P)_2(NO)]$ and $[RuBr_2(NCPh)_2(Ph_3P)_2]$ were formed [138]. A plausible mechanism for the reaction involves initial formation of the $\{RuN(O)CH_2Ph\}$ group [138], the product which one might expect from attack of $PhCH_2^-$ on {RuNO}. That a radical reaction was not involved was shown by the lack of effect of the radical scavenger dibenzoyl peroxide [138]. Finally $[Ru(Ph_3P)_2(NO)_2]$ was a converter (though rather inefficient by comparison to its Rh and Ir analogues [125,139]) of NO and CO into N_2O and CO_2 via the reaction [139]

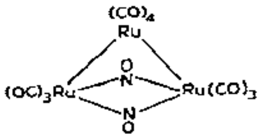
$$[Ru(Ph_3P)_2(NO)_2] \xrightarrow[\text{or CO, } h\nu]{\text{CO, 100 atm, 24 h}} [Ru(CO)_4(Ph_3P)] + CO_2 + N_2O \qquad (17)$$

It has been postulated that this reaction occurred by initial coupling of the two NO groups to form a hyponitrite (N_2O_2) type of ligand. Such a coupling could well be the first stage in reactions of $[Ru(Ph_3P)_2(NO)_2]$ with dioxygen, in which the NO group is oxidized by the electrophile O_2.

When treated with CO in benzene solution, $[Ru(\eta^3\text{-}C_3H_5)(Ph_3P)_2(NO)]$ gave an equilibrium mixture of $[Ru(\eta^3\text{-}C_3H_5)(CO)(Ph_3P)(NO)]$ and $[Ru(C_3H_5)(CO)(Ph_3P)_2(NO)]$. From n.m.r. and i.r. spectra the latter has retained the $\eta^3\text{-}C_3H_5$ (i.e. the allyl ligand acts as a three-electron donor) and is an 18-electron five-coordinate complex. The {RuNO} group must therefore be bent, the first example of bending of a {RuNO} group on reaction (stereochemical control of valence) in a four-coordinate complex [153].

F. BRIDGING NITROSYL COMPLEXES

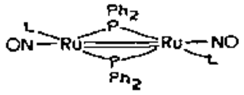
Complexes in which NO bridges two metal centres are, in comparison to their CO analogues, rather rare. For ruthenium the only well characterized complex is $[Ru_3(CO)_{10}(NO)_2]$ obtained from $[Ru_3(CO)_{12}]$ and NO [140] (though bridging complexes are very probably intermediates in nitrosyl transfer reactions [133]). The structure of this complex is similar to that of $Fe_3(CO)_{12}$ without one metal—metal bond but with an essentially symme-



trical double NO bridge between the same two ruthenium atoms. The non-bridged Ru—Ru distances are 2.865 Å, the bridged 3.15 Å [140]. This structure remains the same in solution and at low temperature [140,141]. In solution 2 CO groups, one on each Ru bridged by NO, can be replaced by Ph_3P in an essentially pure S_N1 reaction [142].

G. MISCELLANEOUS COMPLEXES AND REACTIONS

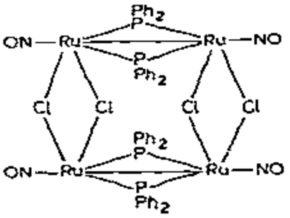
Two cluster complexes of ruthenium nitrosyls have been synthesized and their structures determined. These are



and

III

L = $(CH_3)Ph_2P$ or Ph_3P



IV

Both complexes were obtained in low yield from reduction of $[RuCl_3L_2(NO)]$ in the presence of excess Ph_3P [143,144]. Complex III has essentially linear {RuNO} groups and a distorted tetrahedral arrangement of ligands (excluding the neighbouring Ru) about each ruthenium [144]; complex IV has RuNO angles of 160°, and square pyramidal coordination (neglecting the Ru neighbours) about each ruthenium; the NO is in the apical position [143]. If one ignores Ru—Ru bonding, the complex is formally an $\{RuNO\}^9$ complex. However, for both III and IV neither the molecular orbital schemes discussed above nor simple electron counting can be used to predict geometry or reactivity.

One other topic of interest is the formation of coordinated N_2 from NO and NH_3 on ruthenium. This topic brings us back to the interests of Bert Allen, since the simple reaction

$$[Ru(NH_3)_6]^{3+} + NO + OH^- \rightarrow [Ru(NH_3)_5(N_2)]^{2+} + 2\ H_2O \qquad (18)$$

is perhaps one of the simplest and yet most surprising methods of making

$[Ru(NH_3)_5(N_2)]^{2+}$ [145—147]. The reaction apparently proceeds via formation of a coordinated amide and intramolecular combination of coordinated NO and NH_2 to form N_2 [147]; an intermolecular version of the same process has also been described [86]. Even C—N bonds can be cleaved in a similar reaction [148], illustrating the great stability of the Ru—N_2 bond

$$[Ru(en)_3]^{3+} + NO + OH^- \rightarrow [Ru(en)_2OH(N_2)]^+ \tag{19}$$

H. REACTIONS OF NITRIC OXIDE OVER RUTHENIUM METAL CATALYSTS

In recent years considerable interest in the conversion of NO into less reactive products has arisen. This interest has been stimulated by environmental considerations, though the bond rearrangements necessary for reactions such as

$$2\,NO + CO \rightarrow N_2O + CO_2 \tag{20}$$

have their own intrinsic mechanistic interest. Because present automative catalytic converters for removal of noxious exhaust products use Group VIII metals, there have been investigations of the reactions of NO and CO over ruthenium catalysts at temperatures of 300—600°. Considerable problems are attached to the use of ruthenium since under the oxidising conditions which prevail in the warm-up of an automobile engine the ruthenium metal can be oxidised to volatile RuO_4. Some success has been achieved by the use of non-volatile barium ruthenates as catalysts; these are reduced, in part, to ruthenium metal [149,150]. Ruthenium differs from other catalysts for NO/CO reactions in that NO is more strongly adsorbed than CO; there is therefore a greater chance of NO being adsorbed on adjacent sites and subsequently combining to form N_2. Hence, ruthenium is an efficient catalyst for conversion of NO into N_2 [151]. One of the most interesting aspects of mechanistic work on these systems (which is by no means complete) is the intermediate formation of NCO^- on the surface, and subsequent production of cyanides [151, 152]. Such NCO^- bond formation does not readily occur on ruthenium catalysts, since it requires formation of adsorbed atomic N; as noted, the strong adsorption of NO on ruthenium tends to produce molecular nitrogen. However, C≡N bond formation is even more surprising than N_2O or CO_2 formation in terms of the bond rearrangements necessary, and it would be of considerable interest if such species could be found in low temperature homogeneous catalytic reactions of ruthenium complexes.

ACKNOWLEDGEMENTS

I wish to thank Professors A.C. Skapski, J.A. Ibers and B.R. James for providing material prior to publication, and Professor James for helpful discussions on oxygenation reactions. The National Research Council of Canada is thanked for financial support, and Johnson Matthey provided generous loans of ruthenium for our own researches on ruthenium nitrosyls.

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