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# Trans-effects in octahedral transition metal complexes

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**Contents**



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**Abstract**

An extensive survey of the occurrences and origins of both structural trans-effects (STEs) and kinetic trans-effects (KTEs) in octahedral d-transition metal complexes is presented. This allows the identification of general STE classes into which the majority of common ligands fit: (a) very large STE ligands (STE vs. $Cl^- >$ ca. 0.20 Å): $SiR_3^-$, $NO^-$, $N^{3-}$, $O^{2-}$, $S^{2-}$, $RC^{3-}$; (b) large STE ligands (ca. 0.20 > STE vs. $Cl^- >$ ca. 0.10 Å): $H^-$, $R^-$, $\eta^1$-alkenyl, $\eta^1$-Ph, $RCO^-$, $RN_2^-$; (c) moderate STE ligands (ca. 0.10 Å > STE vs. $Cl^- >$ 0.00 Å): CO, $CN^-$, CNR, $\eta^1$-acetylide, $R_2C$, $NO_2^-$, $NS^+$, $RN_2^+$, $SO_3^{2-}$, $RSO_2^-$, $PR_3$, $P(OR)_3$, $RNH^-$, $RS^-$, $\eta^1$-thiones. The $NO^+$ ligand best illustrates the *mutual* nature of STEs, since it shows moderate STEs when *trans* to π-acceptor ligands, negligible STEs when *trans* to purely σ-donor ligands, and inverse STEs when *trans* to π-donors. STEs can sometimes show a marked dependency upon the electronic properties of the complexed metal centre, e.g. π-accepting RNC and $PR_3$ ligands generally give moderate STEs, but in $d^0$ complexes their STEs are weaker than that of $Cl^-$. This may be attributed to an absence of π-back-bonding in such complexes. Also, the STEs of π-donating $RN^{2-}$ ligands show an extremely wide variation which partially correlates with the metal d-configuration. The relationship between STEs and KTEs depends upon ligand substitution mechanisms, and because such reactions in octahedral complexes are generally dissociatively activated, there is often a close correlation between STEs and KTEs. For example, $N^{3-}$ causes very large STEs and KTEs, whilst $SO_3^{2-}$ gives moderate STEs and large KTEs. Since both of these ligands cause STEs primarily via powerful electron donation, the ground state destabilisations implied by STEs are likely to be accompanied by stabilisation of the electron-deficient five-co-ordinate transition states. By contrast, π-acceptor ligands such as CO or RNC generally exert

moderate STEs, but cause pronounced delabilisation of *trans* metal–ligand bonds due to destabilisation of transition states. 

*Keywords:* Trans-effects; Octahedral transition metal complexes

## 1. Introduction

It has long been recognised that a co-ordinated ligand can exert a profound influence upon the metal-to-ligand bonding and lability of other ligands within a complex, particularly those in a *trans* position. A 'trans-effect' has been defined as 'the effect of a co-ordinated group on the rate of substitution reactions of ligands *trans* to itself' [1]. This is hence a kinetic phenomenon which depends upon both ground state and transition state factors [2,3], and is distinct from purely ground state properties such as bond length. The term 'trans-influence' was originally used to describe 'the tendency of a ligand to selectively weaken the bond *trans* to itself' [4], and is commonly used to describe ground state phenomena. However, although bond weakening is often assumed to be synonymous with bond lengthening, it should always be remembered that this is not necessarily the case. There is no logical reason why an 'effect' should describe a kinetic property, whilst an 'influence' refers to a thermodynamic property, and ambiguous use of the term 'trans-effect' (TE) is a common source of confusion. We hence use the latter term in a general sense to cover both kinetic and equilibrium phenomena, and adopt the specific expressions 'structural trans-effect' (STE) to refer to the effect of a ligand on the *bond distance* to a *trans* ligand and 'kinetic trans-effect' (KTE) to describe the effect on the *lability* of a *trans* ligand.

The majority of work on TEs has concentrated on square planar complexes and reviews on this subject hence generally pay rather less attention to octahedral complexes [1–3,5–11], with one notable exception [12]. The present objective is to provide an overview of the occurrences and origins of TEs in octahedral complexes, for which no recent review exists. This survey, which covers the years up until and including 1998, is not intended to be entirely comprehensive, but rather attempts to summarise current knowledge and highlight recent developments by using carefully selected examples.

## 2. Historical summary

Over 100 years ago, Werner was the first to recognise that certain complexed ligands have the power to affect the reactions of groups opposite themselves and termed the principle 'trans-elimination' [13]. Some 33 years later, Chernyaev proposed his 'trans-effect rule', i.e. 'the co-ordinated groups in the complex spheres have an effect on one another when they are in *trans* positions to one another' [14]. From studies with square planar Pt(II) complexes, Chernyaev concluded that anions are the strongest trans-labilising ligands.

The earliest theoretical description of TEs was the 'polarisation theory' suggested by Grinberg in 1932 [15]. This states that an easily polarisable donor group induces a build-up of negative charge on the metal, which in turn tends to repel negative charge in the *trans* ligand, thus weakening the *trans* bond. A few years later, Nekrasov made slight modifications to Grinberg's theory by clarifying the picture of dipoles and induced charges [16]. However, although this improved theory had a very sound basis, its essentially electrostatic viewpoint did not explain the observation that metals which display the largest TEs are those which form the most covalent metal–ligand bonds [7]. Therefore, in 1948, Syrkin included hybridisation at the metal, suggesting that opposing metal–ligand bonds will compete for the available s and d orbitals with a strength proportional to their covalent bond character [17]. This model explained TEs in an entirely novel fashion, emphasising cis-stabilisation rather than trans-labilisation.

Although the early theoretical treatments of TEs considered only σ-bonding, they proved adequate to explain the majority of available data. Later attempts to improve the existing theory were made by Chatt et al. in 1955 [18], and by Orgel in 1956 [19] who took the important step of considering metal–ligand π-bonding in order to account for some unexpected behaviour discovered by Gel'man [6]. Gel'man had found that, in contrast to predictions made using the polarisation theory, certain unsaturated ligands (e.g. $C_2H_4$, CO) show strong KTEs. Chatt and Orgel explained this by invoking transition state stabilisation by such π-acceptor ligands. However, by 1961, Basolo et al. had found that this model did not explain the large KTEs of ligands such as $H^-$ and $Me^-$, reaffirming the validity of the simple polarisation theory in cases where π-effects are unimportant [20].

Throughout the 1960s, various workers studied TEs, building on the earlier postulates. For instance, Pidcock et al. [4] considered the strong σ-inductive effects of phosphines and McWeeny et al. developed further theoretical ideas [21] which were applied by Mason and Towl to octahedral complexes [22]. The latter were the first to explicitly address such considerations to other than square planar complexes. A more radical judgement was given by Bright and Ibers in 1969 who invoked steric, rather than electronic arguments to account for the unusually large STEs in octahedral metal nitrido complexes [23]. Their postulate was that the structures of such complexes are strongly affected by the steric repulsion of the *cis* ligands [24].

The only significant theoretical developments in recent years have been those involving MO analyses of octahedral complexes by Shustorovich et al. in 1975 [25] and by Burdett and Albright in 1979 [26]. These indicate that it is energetically unfavourable for *trans* ligands to share the same metal orbital, and if they are forced to do so there will be a differential weakening of one of the metal–ligand bonds. Hence, quantum chemical calculations have served to restate the earlier polarisation theory. Other recent theoretical work includes that of Lyne and Mingos who have employed approximate density functional theory calculations [27,28].

It is now clear that a complete understanding of TEs must account for both electronic effects and also, but generally to a lesser extent, steric factors. The former

require consideration of the σ- and π-bonding properties of both the metal centre and ligands, whilst the latter are usually most important for ligands which form particularly short metal–ligand bonds [23–25].

## 3. Incentives for studying trans-effects in octahedral transition metal complexes

Besides the obvious benefits to theoretical understanding, a primary motivation for studying TEs is that knowledge gained may be useful in synthetic co-ordination chemistry. Indeed, the original discoverers of KTEs quickly appreciated their utility in allowing the controlled syntheses of square planar complexes [13,14]. However, because the structures and substitution reactions of octahedral complexes are inherently more complicated, examples of the application of KTEs in their synthesis have always been limited [2,8,11]. The current level of ability to prepare 'tailor-made' octahedral transition metal complexes by exploiting directed ligand substitutions is remarkably primitive, and the exploitation of KTEs is one means by which this situation may be rectified (Section 5.8).

Another important area in which understanding of TEs is of immediate practical benefit is that of synthetic organic chemistry. Transition metal complexes are increasingly finding applications in this field, particularly as homogeneous catalysts [3,29], and TEs may have dramatic effects on their behaviour in such roles [30]. Of particular interest in this regard are complexes of phosphane ligands. Owing to their wide structural diversity, such ligands are ideal for tuning the electronic and steric properties of complexed metal centres and are generally considered to be the best 'non-participating ligands' for 'tailoring transition metal complexes for their application as homogeneous catalysts' [31].

A number of studies of TEs have also been undertaken with the primary objective of modelling the function of metal-containing biological molecules. For example, investigations involving alkyl cobaloximes [32] or rhodoximes [33,34] have yielded insights which are relevant to the behaviour of the vitamin $B_{12}$ coenzyme (5′-deoxyadenosylcobalamin).

## 4. Structural trans-effects in octahedral metal complexes

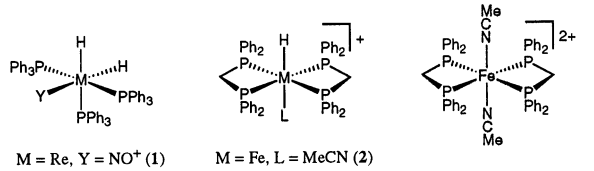
Investigations into ground state TEs have employed a variety of physicochemical techniques, including IR and NMR spectroscopic measurements [6–8]. However, the information obtained from such studies is sometimes ambiguous and has been rendered of less general interest in recent years by the increasing availability of accurate structural data obtained from diffraction methods. The following discussion concentrates almost exclusively on bond distances derived from X-ray crystallography because these provide by far the most extensive and unambiguous information on STEs in octahedral complexes. Coverage is gener-

ally limited to common ligands which show at least moderate STEs when compared to relatively weak STE ligands such as $NH_3$ or $Cl^-$. Ligands are classified according to their electronic bonding properties, and for simplicity we consider predominantly mononuclear complexes, with cluster species being completely excluded.

### 4.1. σ-Donor ligands

#### 4.1.1. Hydride

The hydride ion behaves as a strong σ-donating ligand which can exert pronounced STEs due to polarisation effects. This has been observed experimentally [20] and corroborated by extended Hückel MO calculations for square planar complexes [35]. X-ray crystallographic data for representative octahedral hydride complexes featuring a range of metal ions and *trans* ligands are given in Table 1. Comparisons of the STEs of $H^-$ with those of other ligands are found in subsequent sections.



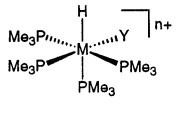
M = Re, Y = $NO^+$ (1)
M = Ir, Y = $H^-$ (10)



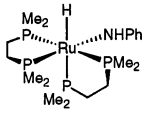
M = Fe, L = MeCN (2)
M = Rh, L = $Cl^-$ (7)



(3)



M = Ru, Y = $OTol^-$, n = 0 (4)
M = Ir, Y = $OH^-$, n = 1 (11)



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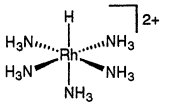
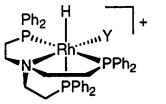
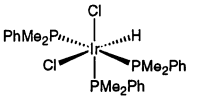


(6)



Y = $CCH^-$ (8), $COMe^-$ (9)



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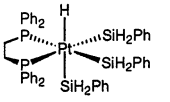


(13)

#### 4.1.2. Alkyl ligands

Alkyl anions, such as $Me^-$, are also strong σ-donor ligands which exert marked STEs in a similar manner to hydride [20]. Early crystallographic evidence for this in octahedral complexes of Pt(IV) and Ir(III) has been reviewed previously [22], and selected data for alkyl complexes which show STEs are given in Table 2.

Table 1
Selected crystallographic data for hydrido complexes

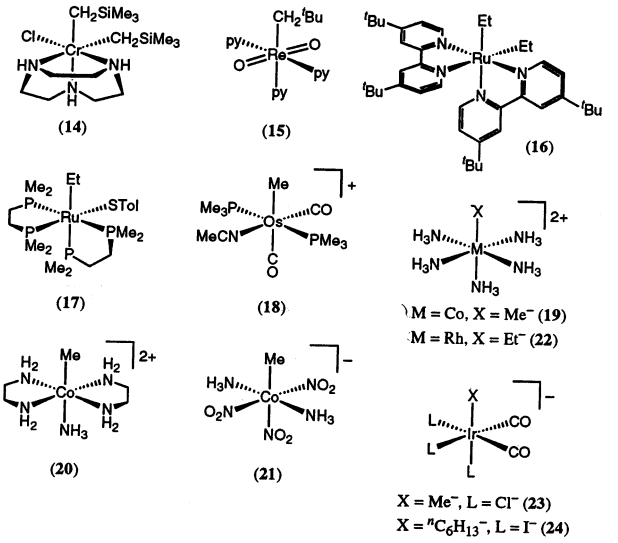
| No. [a] | Compound | L [b] | Bond distances (Å) | | | Δ (Å) [c] | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ [d] | $M–L_{comp}$ [e] | | |
| **1** | *cis*,*mer*-$Re^{I}(H)_2(PPh_3)_3(NO)\cdot 0.5C_6H_6$ | $PPh_3$ | 2.47(1) | 2.39(1) | | 0.08 | [36] |
| **2** | *trans*-$[Fe^{II}H(MeCN)(dppm)_2]BF_4$ | MeCN | 1.927(4) | | 1.87(1) [f] | 0.06 | [38] |
| **4** | *cis*-$Ru^{II}H(OTol)(PMe_3)_4$ | $PMe_3$ | 2.364(2) | 2.328(3) (*trans* P) | | 0.04 | [39] |
| | | | | 2.229(2) (*trans* O) | | 0.14 | [39] |
| **5** | *cis*-$Ru^{II}H(NHPh)(dmpe)_2$ | dmpe | 2.335(3) | 2.286(4) (*trans* P) | | 0.05 | [40] |
| | | | | 2.244(3) (*trans* N) | | 0.09 | [40] |
| **6** | $[Rh^{III}H(NH_3)_5](ClO_4)_2$ | $NH_3$ | 2.24(1) | 2.079(7) | | 0.17 | [41] |
| **7** | *trans*-$[Rh^{III}Cl(H)(dppm)_2]BPh_4$ | $Cl^-$ | 2.465(2) | | 2.365(6) | 0.10 | [42] |
| **8** | $[Rh^{III}(C_2H)H(tdpa)]BPh_4\cdot 1.5thf$ | tdpa | 2.382(4) | 2.309(6) | | 0.07 | [43] |
| **9** | $[Rh^{III}(COMe)H(tdpa)]BPh_4$ | tdpa | 2.414(3) | 2.304(4) | | 0.11 | [44] |
| **10** | *mer*-$Ir^{III}(H)_3(PPh_3)_3\cdot 0.5C_6H_6$ | $PPh_3$ | 2.347(3) | 2.286(4) | | 0.06 | [45] |
| **11** | *cis*-$[Ir^{III}H(OH)(PMe_3)_4]PF_6$ | $PMe_3$ | 2.369(2) | 2.337(1) (*trans* P) | | 0.03 | [46] |
| | | | | 2.259(2) (*trans* O) | | 0.11 | [46] |
| **12** | *cis*,*mer*-$Ir^{III}HCl_2(PMe_2Ph)_3$ (orthorhombic form) | $Cl^-$ | 2.503(1) | 2.449(1) | | 0.05 | [47] |
| **13** | *fac*-$Pt^{IV}H(SiH_2Ph)_3$dppe | $SiH_2Ph^-$ | 2.406(5) | 2.374(7) | | 0.03 | [48] |

[a] Bold numbers refer only to the complex of interest, without any counter-ions or solvent of crystallisation.
[b] *Trans* ligand.
[c] Difference: $(M–L_{trans})-(M–L_{cis})$ or $(M–L_{trans})-(M–L_{comp})$.
[d] In cases where there is more than one *cis* M–L bond, $(M–L_{cis})$ is the average value (excluding bonds *trans* to another strong STE ligand).
[e] A comparable M–L bond distance found in a related complex generally featuring a weak *trans* STE ligand.
[f] Fe–N bond distance in *trans*-$[Fe^{II}(MeCN)_2(dppm)_2][FeI_4]\cdot 2H_2O$ (**3**) [37].

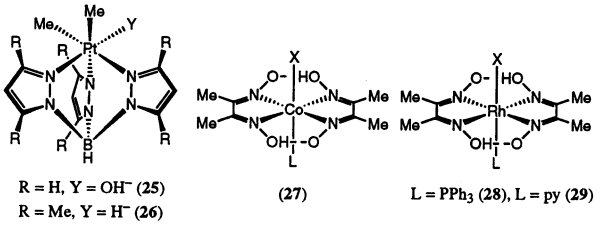
Table 2
Selected crystallographic data for alkyl complexes [a]

| No. | Compound | X [b] | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **14** | $Cr^{III}(CH_2SiMe_3)_2Cl(tacn)\cdot 1.5C_7H_8$ | $CH_2SiMe_3^-$ | tacn | 2.292(4) | 2.181(4) | 0.11 | [49] |
| **15** | *trans*-$Re^{V}O_2Np(py)_3$ | $Np^-$ | py | 2.35(1) | 2.15(2) | 0.20 | [50] |
| **16** | *cis*-$Ru^{II}Et_2(4,4'\text{-}{}^{t}Bu_2bpy)_2$ | $Et^-$ | 4,4′-$^{t}Bu_2$bpy | 2.096(8) | 2.038(7) | 0.06 | [51] |
| **17** | *cis*-$Ru^{II}Et(STol)(dmpe)_2$ | $Et^-$ | dmpe | 2.346(3) | 2.322(4) (*trans* P) | 0.02 | [40] |
| | | | | | 2.270(3) (*trans* S) | 0.08 | [40] |
| **18** | *cis*,*trans*-$[Os^{II}Me(CO)_2(PMe_3)_2(MeCN)]BPh_4$ | $Me^-$ | CO | 1.92(2) | 1.82(1) | 0.10 | [52] |
| **19** | $[Co^{III}Me(NH_3)_5]S_2O_6$ | $Me^-$ | $NH_3$ | 2.105(1) | 1.974(3) | 0.13 | [53] |
| **20** | *trans*-$[Co^{III}Me(en)_2NH_3]S_2O_6$ | $Me^-$ | $NH_3$ | 2.127(2) | 1.966(4) [c] | 0.16 | [53] |
| **21** | *mer*,*trans*-$[Co^{III}Me(NO_2)_3(NH_3)_2]^-$ [d] | $Me^-$ | $NO_2^-$ | 2.027(2) | 1.928(3) | 0.10 | [53] |
| **22** | $[Rh^{III}Et(NH_3)_5]Br_2$ | $Et^-$ | $NH_3$ | 2.256(8) | 2.072(7) | 0.18 | [54] |
| **23** | *fac*-$AsPh_4[Ir^{III}MeCl_3(CO)_2]$ | $Me^-$ | $Cl^-$ | 2.500(2) | 2.376(3) | 0.12 | [55] |
| **24** | *fac*-$AsPh_4[Ir^{III}({}^{n}C_6H_{13})I_3(CO)_2]$ | ${}^{n}C_6H_{13}^-$ | $I^-$ | 2.775(4) | 2.706(6) | 0.07 | [56] |
| **25** | $Pt^{IV}Me_2Tp(OH)$ | $Me^-$ | Tp | 2.151(3) | 2.022(5) | 0.13 | [57] |

[a] Details as for Table 1.
[b] Trans-effecting ligand.
[c] Average of Co–N(en) bond distances.
[d] As salt with $[Co^{II}(NH_3)_6]^{2+}$ and *trans*-$[Co^{III}(NO_2)_4(NH_3)_2]^-$ counter-ions.




The data for **17** [40] show that the STE of an ethyl group is a little larger than that of a dialkyl phosphine, but considerably larger than that of a thiolato ligand. In $Pt^{IV}Me_2(H)Tp^*$ (**26**) [58] the Pt–N bond distance *trans* to $H^-$ [2.169(6) Å] is ca. 0.02 Å longer than the other two [2.145(4) Å], showing that $H^-$ exerts a slightly greater STE than $Me^-$ [58].



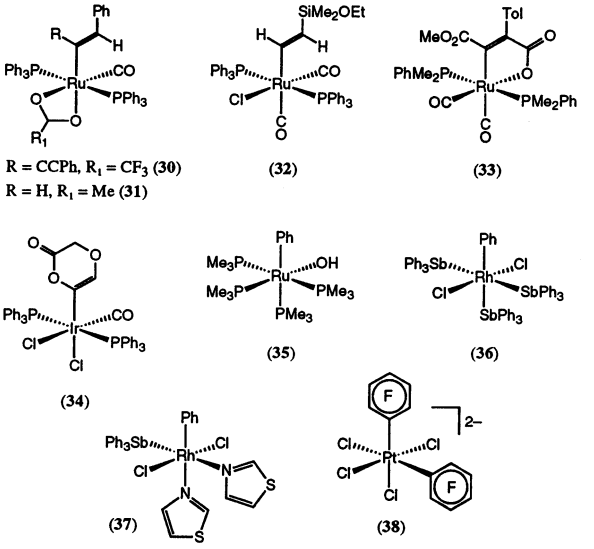

Undoubtedly the most extensive crystallographic investigations into STEs have involved cobaloximes *trans*-$Co^{III}X(dmgH)_2L$ (**27**) which are of interest as models for the $B_{12}$ coenzyme. The results of this work have been reviewed recently [32,59]. The greatest body of data is available for L = py complexes for which the following STE series is observed: $X = CH_2CN^- \leq CH(CN)Cl^- \leq CH_2NO_2^- \leq CH_2CO_2Me^- \leq CH_2CF_3^- \leq CH(Me)CN^- \leq C_2H_4CN^- \leq Bz^- \leq CH(Me)CO_2Me^- \leq Me^- \leq CH_2C(Me)(CO_2Et)_2^- \leq Np^- \leq Et^- \leq CH_2SiMe_3^- \leq {}^iPr^- \leq Ad^-$. However, the use of crystallographic results to derive such series should be treated with caution because the precision of measurement relative to the magnitude of the differences is not great. In fact, in the above series none of the differences between adjacent Co–N(py) bond distances is greater than $3\sigma$ and the total range is only ca. 0.09 Å. Nevertheless, these data do indicate broadly that the STEs of alkyl ligands decrease as their $\sigma$-donating strength diminishes upon attachment of electron-withdrawing substituents. A more useful body of high resolution

crystallographic data is also available for complexes in which L = 1,5,6-trimethylbenzylimidazole which are especially relevant as $B_{12}$ models [60]. This affords the STE series $X = Cl^- < CH(CN)Cl^- \approx CH_2NO_2^- < CH(CN)CH_2CN^- < CHCl_2^- < Me^- < {}^iPr^- < Cy^- < Ad^-$, with a difference between the two extremes of ca. 0.18 Å [60].

The STEs of alkyl ligands on $PPh_3$ or py have also been investigated in rhodoximes. X-ray structural determinations on *trans*-$Rh^{III}X(dmgH)_2PPh_3$ (**28**; $X = Me^-$ [61], $Et^-$ [62], $^iPr^-$ [63], $^tBu^-$ [64]) afford the STE series $X = Me^- \leq Et^- < {}^iPr^- \leq {}^tBu^-$, but with a maximum difference in the Rh–P bond distance of only ca. 0.04 Å. As in the cobaloximes, the STE of X is a function of its σ-donor strength which is increased by electron-donating methyl groups. Crystallographic studies of *trans*-$Rh^{III}X(dmgH)_2py$ complexes (**29**) [33,34] afford the STE series $X = CH_2CF_3^- < CH_2Cl^- \leq {}^nPr^- < Me^- \approx Et^- \leq {}^iPr^-$.

### *4.1.3. η[1]-Alkenyl and phenyl ligands*

When co-ordinated to a metal in a $\eta^1$ fashion, alkenyl and phenyl ligands behave as simple σ-donors with no evidence from M–C bond lengths of π-back-donation. The data in Table 3 demonstrate that the strong σ-donor properties of these groups lead to considerably larger STEs than those caused by CO (**30**, **31**, **34**), $Cl^-$ (**32**), $OH^-$ (**35**) or $SbPh_3$ (**36**, **37**).




X-ray crystal structures of the cobaloximes *trans*-$Co^{III}X(dmgH)_2py$ (**27**, L = py) yield Co–N(py) bond distances of 2.073(3) Å for $X = CH{=}CH_2^-$ [74] and 2.028(2) Å for $X = cis$-$CCl{=}C(H)Cl^-$ [75], giving a difference of ca. 0.05 Å. The $\eta^1$-1,2-dichlorovinyl ligand hence exerts a rather weaker STE than its unsubstituted counterpart, which can be ascribed to a decrease in basicity caused by the electronegative chlorine atoms. The Co–N(py) bond distance in *trans*-$Co^{III}Me(dmgH)_2py$ is 2.068(3) Å [76], and the Rh–P bond distances in *trans*-

Table 3
Selected crystallographic data for $\eta^1$-alkenyl and $\eta^1$-phenyl complexes [a]

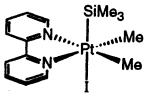
| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **30** | *trans*-$Ru^{II}\{C(C_2Ph)CH(Ph)\}(CF_3CO_2)(CO)(PPh_3)_2$ | $C(C_2Ph)CH(Ph)^-$ | $CF_3CO_2^-$ | 2.352(7) | 2.235(6) | 0.12 | [65] |
| **31** | *trans*-$Ru^{II}\{CHCH(Ph)\}(MeCO_2)(CO)(PPh_3)_2$ | $CHCH(Ph)^-$ | $MeCO_2^-$ | 2.38(1) | 2.26(1) | 0.12 | [66] |
| **32** | *cis*,*trans*-$Ru^{II}\{CHCH(SiMe_2OEt)\}Cl(CO)_2(PPh_3)_2$ | $CHCH(SiMe_2OEt)^-$ | CO | 1.954(7) | 1.846(7) | 0.11 | [67] |
| **33** | *cis*,*trans*-$Ru^{II}\{C(CO_2Me)C(Tol)CO_2\}(CO)_2(PMe_2Ph)_2$ | $C(CO_2Me)C(Tol)CO_2^-$ | CO | 1.913(6) | 1.824(6) | 0.09 | [68] |
| **34** | *cis*,*trans*-$Ir^{III}(C_4H_3O_3)Cl_2(CO)(PPh_3)_2$ | $C_4H_3O_3^-$ | $Cl^-$ | 2.459(4) | 2.391(4) | 0.07 | [69] |
| **35** | *cis*-$Ru^{II}Ph(OH)(PMe_3)_4$ | $Ph^-$ | $PMe_3$ | 2.354(1) | 2.286(1) | 0.07 | [70] |
| **36** | *trans*,*mer*-$Rh^{III}PhCl_2(SbPh_3)_3$ | $Ph^-$ | $SbPh_3$ | 2.706(2) | 2.588(3) | 0.12 | [71] |
| **37** | *trans*,*cis*-$Rh^{III}PhCl_2(thz)_2SbPh_3$ | $Ph^-$ | thz | 2.245(5) | 2.120(5) | 0.13 | [72] |
| **38** | *cis*-$(PEtPh_3)_2[Pt^{IV}(\eta^1\text{-}C_6F_5)_2Cl_4]\cdot 2CH_2Cl_2$ | $C_6F_5^-$ | $Cl^-$ | 2.417(4) | 2.361(1) | 0.06 | [73] |

[a] Details as for Tables 1 and 2.

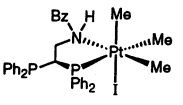
$Rh^{III}X(dmgH)_2PPh_3$ (**28**) are 2.447(1) Å for $X = CH{=}CH_2^-$ [77] and 2.454(1) Å for $X = Me^-$ [61]. The STE of a $\eta^1$-vinyl group is hence very similar to that of a methyl ligand.

*4.1.4. Silyl ligands*

It has long been recognised that the especially powerful σ-donating properties of anionic silyl ligands cause large STEs in square planar Pt(II) complexes. This was originally demonstrated by IR spectroscopic studies [78], and has since been confirmed by crystallographic results for square planar Pt(II) complexes [79,80]. The very limited data available show that silyl ligands also exert large STEs in octahedral complexes. For example, *cis*-$Pt^{IV}Me_2I(SiMe_3)$bpy (**39**) exhibits an exceptionally long Pt–I bond distance of 2.962(2) Å [81], which is ca. 0.11 Å longer than that *trans* to a methyl group in *fac*-$Pt^{IV}Me_3I\{Ph_2PCH(PPh_2)CH_2NHBz\}$ (**40**) [82]. The Ir–P distances in *fac*-$Ir^{III}Me(H)(SiR_3)(PMe_3)_3$ [R = Et (**41**), Ph (**42**)] are 2.300(4) Å (*trans* to C), 2.339(2) Å (*trans* to H), 2.346(3) Å (*trans* to Si in **42**) and 2.359(2) Å (*trans* to Si in **41**) [83]. These data afford the STE order $Me^- < H^- < SiPh_3^- < SiEt_3^-$ [83], the triethyl silyl ligand having a slightly greater σ-donor strength than its phenyl counterpart due to inductive effects [78,83].




(39)

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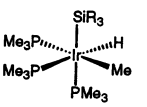



R = Et (41), R = Ph (42)

*4.2. σ-Donor–π-acceptor ligands*

In this section we include ligands which have the potential to exhibit π-acceptor behaviour, but do so to a variable extent depending upon the nature of the complexed metal centre (e.g. $NO_2^-$, $SO_3^{2-}$), together with ligands which apparently act as strong π-acceptors in all of their known complexes (e.g. $NO^+$).

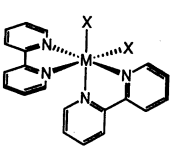
*4.2.1. Carbon monoxide and other chalcocarbonyl ligands*

Carbon monoxide acts as a weak σ-donor ligand, but a strong π-acceptor which exerts moderate STEs in octahedral complexes (Table 4). The difference between the two Ru–N(bpy) bond distances in **53** shows that the STE of CO is somewhat weaker than that of $H^-$ [92]. It is generally, and entirely reasonably, supposed that the STE of CO is a result of its strong π-acceptor ability. However, although the Tc–C bond distance and ν(C=O) value in **46** indicate the

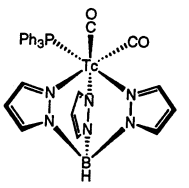
Table 4
Selected crystallographic data for carbonyl complexes [a]

| No. | Compound | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | M–$L_{trans}$ | M–$L_{cis}$ | M–$L_{comp}$ | | |
| **43** | *cis*-$Mo^{0}(CO)_2(bpy)_2$ | bpy | 2.230(7) | 2.149(8) | | 0.08 | [84] |
| **44** | $Tc^{I}Tp(CO)_2PPh_3$ | Tp | 2.217(2) | 2.166(2) | | 0.05 | [85] |
| **45** | $[Tc^{I}(CO)_2(tacn)PPh_3]$ Cl·MeOH | tacn | 2.244(6) | 2.192(3) | | 0.05 | [85] |
| **46** | *mer*,*trans*-$Tc^{III}Cl_3(CO)(PPh_3)_2$ | $Cl^-$ | 2.397(2) | 2.322(2) | | 0.08 | [86] |
| **47** | *cis*-$[Re^{I}(MeCN)_4(CO)_2]_2ReCl_6$ | MeCN | 2.15(1) | 2.06(1) | | 0.08 | [87] |
| **48** | *trans*-$Cs_2[Ru^{II}Cl_4(CO)(H_2O)]$ | $H_2O$ | 2.25(1) | | 2.12(2) [b] | 0.13 | [89] |
| **50** | *trans*,*mer*-$Ru^{II}Cl_2(CO)(pdmp)_3$ | pdmp | 2.411(1) | 2.361(1) | | 0.05 | [90] |
| **51** | *cis*,*cis*-$Ru^{II}Cl_2(CO)_2bpy$ | $Cl^-$ | 2.439(3) | 2.411(4) | | 0.03 | [91] |
| | | | | | 2.391(5) [c] | 0.05 | [91] |
| **53** | *cis*,*cis*-$Ru^{II}H(NCS)(CO)_2(6,6'\text{-}Me_2bpy)$ | bpy | 2.163(3) | 2.225(4) | | −0.06 | [92] |
| | | *N*CS$^-$ | 2.083(4) | | 2.055(5) [d] | 0.03 | [92] |
| **55** | *mer*,*cis*-$Ru^{III}Cl_3(CO)(Me_2SO)_2$ | $Me_2SO$ | 2.124(3) | 2.054(6) | | 0.07 | [94] |

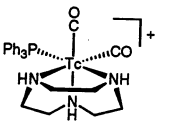
[a] Details as for Tables 1 and 2.
[b] Average Ru–O bond distance in $[Ru^{II}(H_2O)_6](TolSO_3)_2$ (**49**) [88].
[c] Ru–Cl bond distance in *trans*,*cis*-$Ru^{II}Cl_2(CO)_2bpy$ (**52**) [91].
[d] Ru–*N*CS bond distance in *cis*-$Ru^{II}(NCS)_2(bpy)_2$·MeCN (**54**) [93].




M = Mo, X = CO (**43**)
M = Ru, X = NCS$^-$ (**54**)

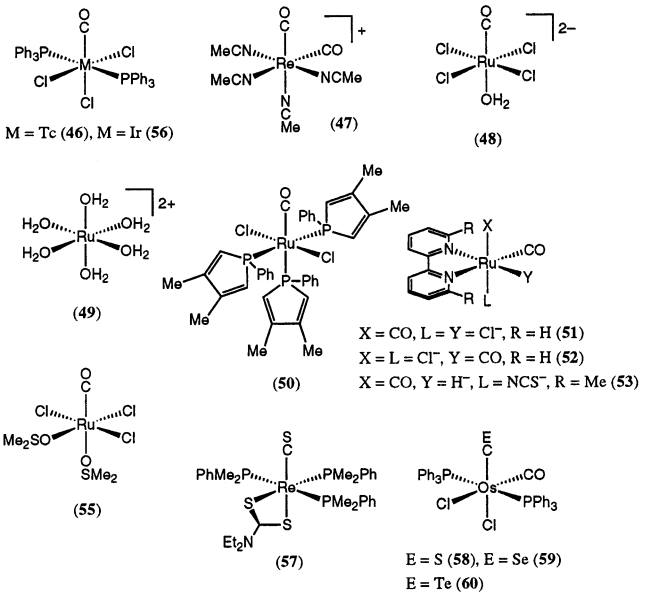



(**44**)




(**45**)

absence of any significant C → $Tc^{III}$ π-back-bonding [86], the observed CO STE is of similar magnitude to those in complexes of low-valent metal centres. The Ru(III) complex **55** also shows a CO STE, but *mer*,*trans*-$Ir^{III}Cl_3(CO)(PPh_3)_2$ (**56**) does not [95].




The chalcocarbonyls CS, CSe and CTe are stronger π-acceptors than CO, and the limited structural data available show that these ligands exert larger STEs than CO. For example, in *mer*-$Re^0(Et_2NCS_2)(PMe_2Ph)_3(CS)$ (**57**) the Re–S bond *trans* to CS [2.580(5) Å] is ca. 0.09 Å longer than that *trans* to the phosphine ligand [2.491(4) Å] [96]. The complete series *cis*,*trans*-$Os^{II}Cl_2(CO)(CE)(PPh_3)_2$ [E = S (**58**), Se (**59**) or Te (**60**)] have been crystallographically characterised [97], and the relative extensions of the Os–Cl bonds *trans* to CE with respect to those *trans* to CO are ca. 0.02 Å (**58**), ca. 0.03 Å (**59**) and ca. 0.06 Å (**60**), affording the STE series CO < CS ≤ CSe < CTe [97].

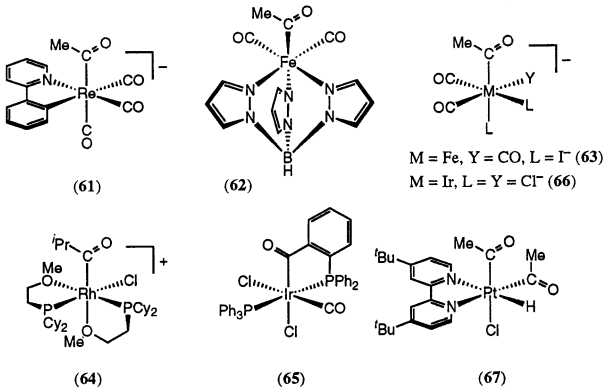
### *4.2.2. η¹-Acyl ligands*

When $\eta^1$-carbon-co-ordinated, acyl ligands act as strong σ-donors with some π-back-bonding capability which exert large STEs (Table 5). The data for complexes **62**, **63**, **65** and **66** show that the STEs of acyl ligands are larger than those of CO [55,99,100,102]. In **62** the Fe–C(O)Me bond distance [1.968(5) Å] is considerably longer than the average Fe–CO bond distance [1.765(9) Å], but still ca. 0.14 Å shorter than an Fe–C single bond [99]. The $MeCO^-$ ligand hence possesses weaker π-acceptor ability than CO, and its larger STE is ascribed to a greater σ-donor strength [99]. The data for complex **64** show that the STE of $^iPrCO^-$ is much greater than that of a trialkyl phosphine ligand, whilst **67** reveals that $MeCO^-$ has a slightly weaker STE than $H^-$. Comparison of the data for **66** with that for **23** shows that the $MeCO^-$ ligand has a somewhat larger STE than a methyl group [55]. Taken together, these observations suggest the following STE order: $PR_3 < CO < R^- < RCO^- < H^-$ (R = alkyl).

Table 5
Selected crystallographic data for $\eta^1$-acyl complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **61** | *fac*-PPN[$Re^{I}$(MeCO)$(CO)_3$(2-Phpy)] | $MeCO^-$ | CO | 2.014(7) | 1.90(1) | 0.11 | [98] |
| **62** | $Fe^{II}$(MeCO)Tp$(CO)_2$ | $MeCO^-$ | Tp | 2.082(4) | 1.996(5) | 0.09 | [99] |
| **63** | *cis*,*mer*-[PPN][$Fe^{II}$(MeCO)$I_2(CO)_3$] | $MeCO^-$ | $I^-$ | 2.683(1) | 2.632(1) | 0.05 | [100] |
| **64** | *cis*-[$Rh^{III}$($^i$PrCO)Cl(medcp)$_2$]$BPh_4$ | $^i$PrCO$^-$ | medcp (O) | 2.385(6) | 2.236(5) | 0.15 | [101] |
| **65** | *cis*-$Ir^{III}$(2-$PPh_2C_6H_4CO$)$Cl_2$(CO)$PPh_3$ | 2-$PPh_2C_6H_4CO^-$ | $Cl^-$ | 2.501(3) | 2.384(3) | 0.12 | [102] |
| **66** | *fac*-$AsPh_4$[$Ir^{III}$(MeCO)$Cl_3(CO)_2$] | $MeCO^-$ | $Cl^-$ | 2.560(2) | 2.369(2) | 0.19 | [55] |
| **67** | *cis*,*cis*-$Pt^{IV}$Cl$(MeCO)_2$H(4,4′-$^t$Bu$_2$bpy) | $MeCO^-$ | bpy | 2.147(6) | 2.172(6) | −0.03 | [103] |

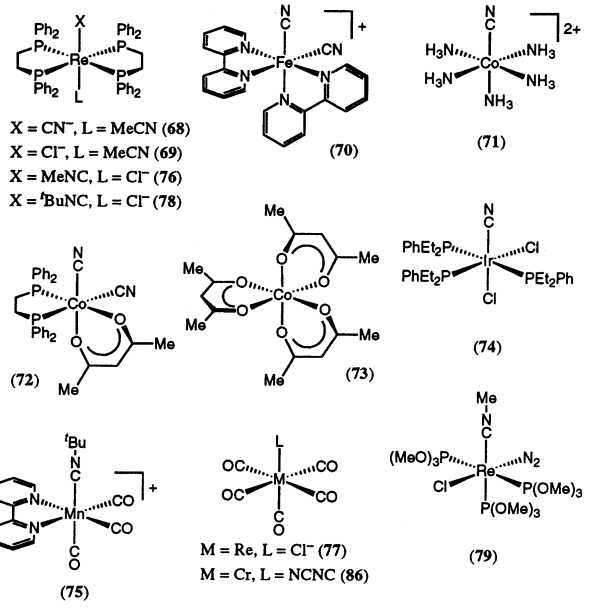
[a] Details as for Tables 1 and 2.




(61) (62) (64) (65) (67)

*4.2.3. Cyanide and isocyanide ligands*

In its common carbon co-ordinated mode, the cyanide anion is a good σ-donor, but a relatively weak π-acceptor ligand. Isocyanides have stronger π-acceptor abilities than $CN^-$, and their bonding properties can be tuned by variation of the *N*-substituent. The order of π-acceptor strength is $CN^- < CNR < CO$ for most R groups. Cyanide ions usually exert only weak STEs, whilst those of isocyanides are generally somewhat larger (Table 6).




(70) (71) (72) (73) (74) (75) (79)

The Re–C bond distance and the ν(C≡N) value in **68** indicate significant $Re^I \rightarrow CN$ π-back-bonding [105] and it is hence likely that $CN^-$ exerts a relatively large STE in this complex by competing with the weaker π-acceptor acetonitrile for π-electron density. In relatively high-valent complexes such as **70**–**74** [106–108,110] $CN^-$ behaves largely as a simple σ-donor. Comparison of the Co–O bond distances

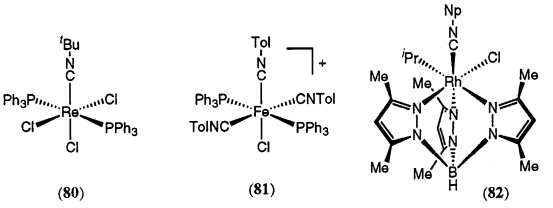
Table 6
Selected crystallographic data for cyanide and isocyanide complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **68** | *trans*-$Re^{I}(CN)(MeCN)(dppe)_2 \cdot {}^{i}PrOH$ | $CN^-$ | MeCN | 2.085(4) | | 1.978(5) [b] | 0.11 | [105] |
| **70** | *cis*-$[Fe^{III}(CN)_2(bpy)_2]ClO_4$ | $CN^-$ | bpy | 1.991(7) | 1.964(6) | | 0.03 | [106] |
| **71** | $[Co^{III}(CN)(NH_3)_5]Cl_2$ | $CN^-$ | $NH_3$ | 1.996(1) | 1.970(5) | | 0.03 | [107] |
| **72** | *cis*-$Co^{III}(CN)_2$(acac)dppe | $CN^-$ | acac | 1.937(3) | 1.955(4) | | −0.02 | [108] |
| | | | | | | 1.888(6) [c] | 0.05 | |
| **74** | *cis*,*mer*-$Ir^{III}Cl_2(CN)(PEt_2Ph)_3$ | $CN^-$ | $Cl^-$ | 2.458(2) | 2.445(2) | | 0.01 | [110] |
| **75** | *fac*-$[Mn^{I}(CN^{t}Bu)(CO)_3phen]ClO_4$ | $CN^{t}Bu$ | CO | 1.846(6) | 1.813(9) | | 0.03 | [111] |
| **76** | *trans*-$Re^{I}Cl(CNMe)(dppe)_2$ | CNMe | $Cl^-$ | 2.607(5) | | 2.515(2) [d] | 0.09 | [113] |
| **78** | *trans*-$Re^{I}Cl(CN^{t}Bu)(dppe)_2 \cdot$thf | $CN^{t}Bu$ | $Cl^-$ | 2.520(2) | | 2.515(2) [d] | 0.01 | [114] |
| **79** | *mer*-$Re^{I}Cl(CNMe)\{P(OMe)_3\}_3(N_2)$ | CNMe | $P(OMe)_3$ | 2.387(4) | 2.357(2) | | 0.03 | [115] |
| **80** | *mer*,*trans*-$Re^{III}Cl_3(CN^{t}Bu)(PPh_3)_2 \cdot CH_2Cl_2$ | $CN^{t}Bu$ | $Cl^-$ | 2.426(2) | 2.339(3) | | 0.09 | [116] |
| **81** | *mer*,*trans*-$[Fe^{II}Cl(CNTol)_3(PPh_3)_2]FeCl_4$ | CNTol | CNTol | 1.867(6) | 1.813(4) | | 0.05 | [117] |
| **82** | $Rh^{III}Cl(^{i}Pr)Tp^*(CNNp)$ | CNNp | Tp* | 2.129(4) | 2.047(4) | | 0.08 | [118] |

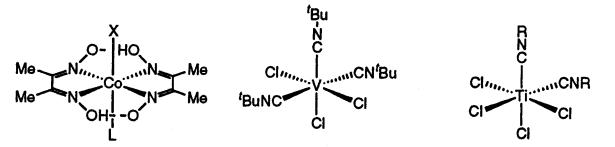
[a] Details as for Tables 1 and 2.
[b] Re–N bond distance in *trans*-$Re^{I}Cl(MeCN)(dppe)_2$ (**69**) [104].
[c] Average Co–O bond distance in $Co^{III}(acac)_3$ (**73**) [109].
[d] Re–Cl bond distance in $Re^{I}Cl(CO)_5$ (**77**) [112].

in **72** with those in **73** [109] shows that the STE of $CN^-$ is a little less than that of a diaryl phosphine, but greater than that of an acac O donor. In **74** $CN^-$ exerts a slightly larger STE than the dialkyl phosphine. Studies on the series *trans*-$Co^{III}X(dmgH)_2\{P(OMe)_3\}$ (**83**; $X = Cl^-$, $CN^-$ or $Me^-$) reveal the STE ordering $Cl^- < CN^- < Me^-$ [119], as shown by the Co–P bond distances 2.188(4) Å ($X = Cl^-$) [120], 2.225(3) Å ($X = CN^-$) [119] and 2.256(4) Å ($X = Me^-$) [119]. Also, the Co–N(py) bond distances in *trans*-$Co^{III}X(dmgH)_2py$ (**84**) of 1.995(2) Å ($X = CN^-$) [121], 1.973(4) Å ($X = N_3^-$) [59] and 2.102(3) Å ($X = Ad^-$) [59] yield the STE order $N_3^- < CN^- < Ad^-$ [121].

Comparison of the Re–Cl bond distances in **76** and in **77** [112] shows that the methylisocyanide ligand has a rather larger STE than CO, which may be attributed to the stronger basicity of the former. However, the greater STE in **76** compared with **78** is associated with more extensive π-back-bonding in **76**, as evidenced by an increase of ca. 0.07 Å in the Re–C bond distance and an increase of ca. 35° in the C–N–C angle on going from **76** to **78** [113,114]. The $CN^tBu$ ligand in the $Re^{III}$ complex **80** acts primarily as a σ-donor but still exerts a STE [116]. The Rh–N bond distance *trans* to the isopropyl group in **82** is 2.250(4) Å, confirming that the STE of an alkyl anion is considerably greater than that of an alkylisocyanide ligand [118]. The cyanoisocyanide ligand is unusual in that its π-acceptor strength exceeds that of CO. CNCN also has the slightly greater STE, as shown by the Cr–C bond distances in $Cr^0(CNCN)(CO)_5$ (**86**) which are 1.883(3) Å (Cr–CNCN), 1.903 (average equatorial Cr–CO distance) and 1.913(4) Å (axial Cr–CO distance) [122].




Although isocyanide ligands produce moderate STEs in $d^4$ or $d^6$ transition metal complexes, the situation is quite different in complexes of less electron-rich metal ions. For example, in the $d^2$ complex *mer*-$V^{III}Cl_3(CN^tBu)_3$ (**87**), the mutually *trans* V–Cl bonds [2.317(2) Å] are ca. 0.03 Å longer than those *trans* to $CN^tBu$ [2.288(4) Å], showing that the isocyanide ligand has a weaker STE than $Cl^-$ in this complex [123]. A similar situation pertains in the $d^0$ complexes *cis*-$Ti^{IV}Cl_4(CN^tBu)_2$ (**88**) [124] and *cis*-$Ti^{IV}Cl_4(CNC_6H_4\text{-}2\text{-}OSiMe_3)_2$ (**89**) [125], the Ti–Cl bond distances being 2.287(3) Å (average, mutually trans) and 2.231(4) Å (average, *trans* to $CN^tBu$) in **88** [124] and 2.275(1) Å (mutually trans) and 2.232(1) Å (*trans* to $CNC_6H_4$-2-$OSiMe_3$) in **89** [125]. As would be expected, the Ti–C distance, Ti–C–N angle and ν(C≡N) value in **89** show that the isocyanide ligand acts exclusively as a σ-donor [125]. It hence appears likely that the STEs of isocyanides in $d^4$ or $d^6$ complexes arise primarily from the relatively strong π-acceptor abilities of these ligands.



X = $CN^-$, $Cl^-$, $Me^-$, L = $P(OMe)_3$ (**83**)
X = $CN^-$, $N_3^-$, $Ad^-$, L = py (**84**)

(**87**)

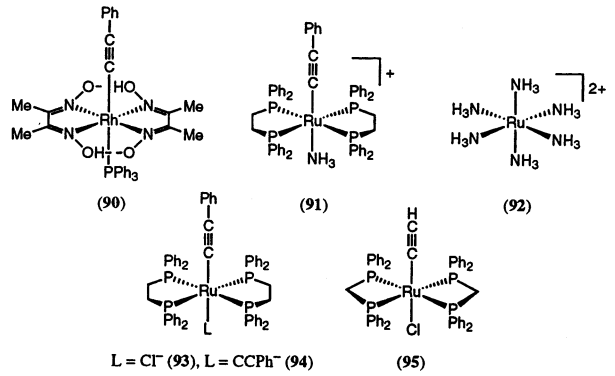
R = $^t$Bu (**88**)
R = $C_6H_4$-2-$OSiMe_3$ (**89**)

### 4.2.4. $\eta^1$-Acetylide ligands

When co-ordinated to a transition metal in a $\eta^1$ fashion, acetylide ligands behave as strong σ-donors which may also engage in π-back-bonding with low-valent metal ions.

The Rh–P bond distance of 2.409(1) Å in *trans*-$Rh^{III}(C_2Ph)(dmgH)_2PPh_3$ (**90**) [126] is rather shorter than those found in the analogous ethyl [2.461(2) Å] [62] or $\eta^1$-vinyl [2.447(1) Å] [77] complexes. The resultant STE sequence alkynyl < alkenyl < alkyl has been ascribed to the lower basicity of the sp hybridised donor orbital on $PhC_2^-$ compared with the $sp^3$ or $sp^2$ donor orbitals of the ethyl or $\eta^1$-vinyl groups, respectively [126]. The phenylacetylide ligand is hence a weaker σ-donor than $Et^-$ or $CH_2{=}CH^-$ and competes less favourably with $PPh_3$ for σ-electron density.

STEs of $\eta^1$-acetylide ligands have also been observed in Ru(II) complexes. For example, the Ru–$NH_3$ bond distance of 2.215(5) Å in *trans*-$[Ru^{II}(C_2Ph)(dppe)_2NH_3]PF_6$ (**91**) [127] is ca. 0.07 Å longer than that found in $[Ru^{II}(NH_3)_6]I_2$ (**92**) [128]. The complex *trans*-$Ru^{II}(C_2Ph)Cl(dppe)_2$ (**93**) exhibits a relatively long Ru–Cl bond [2.479(1) Å] and a Ru–C bond distance of 2.007(5) Å [129]. The latter is considerably shorter than the average Ru–C bond distance [2.063(5) Å] in *trans*-$Ru^{II}(C_2Ph)_2(dppe)_2$ (**94**) [130], which reflects a competition between the *trans* acetylide ligands for π-electron density in **94**. An extremely long Ru–Cl bond distance of 2.628(2) Å is found in *trans*-$Ru^{II}(C_2H)Cl(dppm)_2$ (**95**) [131]. Comparison of this result with the data for **93** demonstrates that $HC_2^-$ exerts a much greater STE than does $PhC_2^-$; this can be attributed to the greater basicity of the former.



(**90**)

(**91**)

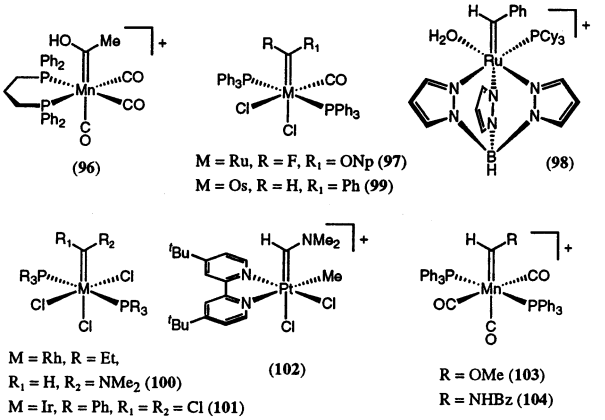
(**92**)

L = $Cl^-$ (**93**), L = $CCPh^-$ (**94**)

(**95**)

*4.2.5. Carbene ligands*

In considering a carbene (*alkylidene*) as a formally neutral ligand, such species are isoelectronic with CO. Carbenes engage in donation of a lone pair on C accompanied by back-donation into an empty C p-orbital, and are generally considered to be stronger σ-donors but weaker π-acceptors than CO. The electronic properties of $CR_2$ ligands are strongly influenced by the nature of their substituents.




A selection of crystallographic data for carbene complexes is given in Table 7. By a comparison of $Rh^{III}$–Cl bond lengths, carbenes have been included in the following STE series: $ROH < Cl^- \approx NH_3 \approx py < AsR_3 \approx \pi$-alkene $< P(OR)_3 < PR_3 < C(H)R < CR_2^* < \eta^1$-phenyl $< \eta^1$-alkyl [136] (* added later [139]). Although in **96**, **97** and **99** the carbene ligands exert larger STEs than CO [132,133,135], this is not always the case. The Mn–C(OH)Me bond distance in **96** is 1.968(4) Å [132]. By contrast, in the closely related *mer*,*trans*-$[Mn^I(CO)_3\{C(H)OMe\}(PPh_3)_2]$-$CF_3SO_3 \cdot 0.8CH_2Cl_2$ (**103**) the Mn–C(H)OMe bond distance is 1.947(4) Å and the carbene ligand exerts no STE [140]. The extent of back-bonding to the carbene moiety is hence greater in **103** than in **96**, and this is accompanied by a reduced STE which is similar to that of CO. However, in *mer*,*trans*-$[Mn^I(CO)_3\{C(H)NHBz\}(PPh_3)_2]CF_3SO_3 \cdot CH_2Cl_2$ (**104**) the Mn–C(H)NHBz bond distance is 2.003(5) Å and the Mn–CO bond *trans* to the carbene ligand is ca. 0.03 Å shorter than those mutually *trans* [140]. Hence, in **104** the greater π-donating power of the amino substituent leads to decreased back-bonding to the carbene moiety (when compared with **96**) and the carbene STE is smaller than that of CO. The resulting STE series $C(H)NHBz < C(H)OMe \approx CO < C(OH)Me$ does not correlate with the π-acceptor strength order $C(H)NHBz < C(OH)Me < C(H)OMe < CO$.

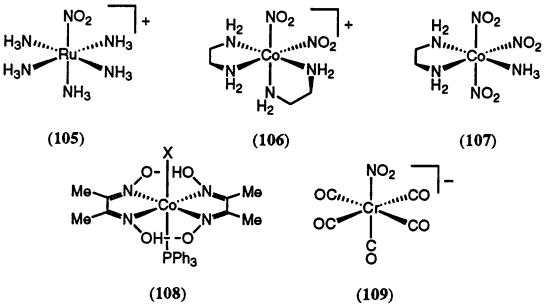
*4.2.6. Nitrite*

The nitrite ion co-ordinates most commonly to transition metals via nitrogen, acting as a good σ-donor which can also exhibit π-acceptor properties. In $[Ru^{II}(NO_2)(NH_3)_5]Cl \cdot H_2O$ (**105**) the Ru–$NO_2$ bond distance is ca. 0.22 Å shorter than the average equatorial Ru–$NH_3$ distance, indicating a significant Ru–$NO_2$ π-interaction [141]. In **105** $NO_2^-$ exerts a relatively large STE, producing a *trans* Ru–$NH_3$ bond length of 2.199(6) Å, ca. 0.07 Å longer than the average equatorial Ru–$NH_3$ distance.

Table 7
Selected crystallographic data for carbene complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **96** | *fac*-$[Mn^{I}(CO)_3\{C(OH)Me\}(dppp)]CF_3SO_3·H_2O$ | C(OH)Me | CO | 1.852(4) | 1.801(8) | 0.05 | [132] |
| **97** | *cis*,*trans*-$Ru^{II}Cl_2(CO)\{C(F)ONp\}(PPh_3)_2$ | C(F)ONp | $Cl^-$ | 2.486(1) | 2.435(1) | 0.05 | [133] |
| **98** | $[Ru^{II}Tp\{C(H)Ph\}(H_2O)(PCy_3)]BF_4·Et_2O·Me_2CO$ | C(H)Ph | Tp | 2.200(4) | 2.129(3) (*trans* P) | 0.07 | [134] |
| | | | | | 2.056(4) (*trans* O) | 0.14 | [134] |
| **99** | *cis*,*trans*-$Os^{II}Cl_2(CO)\{C(H)Ph\}(PPh_3)_2$ | C(H)Ph | $Cl^-$ | 2.550(3) | 2.483(3) | 0.07 | [135] |
| **100** | *mer*,*trans*-$Rh^{III}Cl_3\{C(H)NMe_2\}(PEt_3)_2$ | $C(H)NMe_2$ | $Cl^-$ | 2.445(4) | 2.361(5) | 0.08 | [136] |
| **101** | *mer*,*trans*-$Ir^{III}Cl_3(CCl_2)(PPh_3)_2$ | $CCl_2$ | $Cl^-$ | 2.407(2) | 2.359(1) | 0.05 | [137] |
| **102** | *cis*-$[Pt^{IV}Cl_2Me\{C(H)NMe_2\}(4,4'\text{-}^{t}Bu_2bpy)]Cl·CH_2Cl_2$ | $C(H)NMe_2$ | $Cl^-$ | 2.378(5) | 2.289(5) | 0.09 | [138] |

[a] Details as for Tables 1 and 2.



(105) (106) (107)

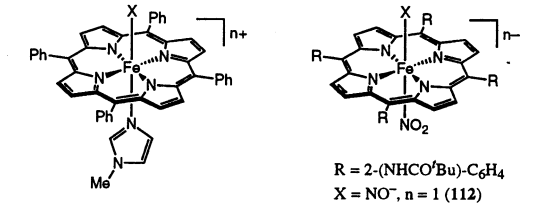
(108) (109)

Small STEs of nitrito ligands are also observed in various Co(III) complexes in which $NO_2^-$ acts primarily as a σ-donor, with little evidence for π-back-bonding. For example, in *cis*-[$Co^{III}(ONO)_2(en)_2$]I (**106**) the Co–en bonds *trans* to $NO_2^-$ are on average ca. 0.05 Å longer than those mutually *trans* [142], and in *mer*-$Co^{III}(ONO)_3(NH_3)(en)$ (**107**) the Co–en bond *trans* to $NO_2^-$ is ca. 0.03 Å longer than that *trans* to $NH_3$ [143]. Comparison of the Co–P bond distances in *trans*-$Co^{III}X(dmgH)_2PPh_3$ (**108**) for $X = NCS^-$ [2.286(8) Å] [144], $X = Cl^-$ [2.327(4) Å] [145], $X = Br^-$ [2.331(4) Å] [146], $X = ONO^-$ [2.392(3) Å] [147] and $X = Me^-$ [2.418(1) Å] [148] affords the STE series $NCS^- < Cl^- \approx Br^- < ONO^- < Me^-$. The equivalence of the five Cr–C bond distances in $(PPh_4)[Cr^0(NO_2)(CO)_5]$ (**109**) [149] shows that in this case the STE of nitrito is similar to that of CO, which may be associated with extensive $Cr \rightarrow NO_2$ π-back-bonding in this low-valent complex.

### *4.2.7. Bent nitrosyl ligands*

Nitric oxide co-ordinates most often as a linearly bonded terminal ligand, but can also adopt a bent bonding mode. When co-ordinated in the latter fashion, NO behaves as '$NO^-$' and is a very strong σ-donor which may also engage in some π-back-bonding. However, caution should be exercised when interpreting crystallographic results for such complexes because disorder of the nitrosyl oxygen atoms can lead to inaccuracies in M–N–O bond angles [150]. We will hence restrict our coverage to cases in which the X-ray structure unambiguously identifies a bent NO ligand (M–N–O ≤ ca. 140°).

Although octahedral bent NO complexes are rare and comparatively little structural information is available, the data in Table 8 clearly show that $NO^-$ has a particularly strong STE on a range of ligands. Although the porphinato complexes **110** and **112** are often described as containing Fe(II) [152,154], we consider their $\{Fe(NO)\}^{2+}$ cores as $Fe^{III}/NO^-$.



X = NO⁻, n = 0 (110), X = mim, n = 1 (111)

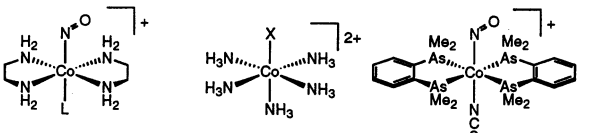
R = 2-(NHCO$^t$Bu)-$C_6H_4$
X = NO⁻, n = 1 (112)
X = im, n = 0 (113)

Table 8
Selected crystallographic data for bent nitrosyl complexes [a]

| No. | Compound | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **110** | $Fe^{III}(TPP)(NO)(mim)$ | mim | 2.180(4) | | 1.974(4) [b] | 0.21 | [152] |
| **112** | $[K(222\text{-}C)][Fe^{III}(TpivPP)(NO)(NO_2)]\cdot(C_5H_{12})_{0.36}(PhCl)_{0.64}$ | $NO_2^-$ | 2.086(8) | | 1.95(1) [c] | 0.14 | [154] |
| **114** | *trans*-$[Co^{III}Cl(NO)(en)_2]ClO_4$ | $Cl^-$ | 2.575(3) | | 2.286(2) [d] | 0.29 | [156] |
| **116** | $[Co^{III}(NO)(NH_3)_5]Cl_2$ | $NH_3$ | 2.220(4) | 1.981(8) | | 0.24 | [157] |
| **117** | *trans*-$[Co^{III}(NCS)(NO)(diars)_2]NCS$ | $NCS^-$ | 2.12(1) | | 1.90(2) [e] | 0.22 | [159] |
| **119** | *trans*-$[Co^{III}(ClO_4)(NO)(en)_2]ClO_4$ | $ClO_4^-$ | 2.360(4) | | 2.320(2) [f] | 0.04 | [161] |
| **121** | *mer*,*trans*-$[Rh^{III}(NO)(MeCN)_3(PPh_3)_2](PF_6)_2$ | MeCN | 2.308(8) | 2.02(1) | | 0.29 | [162] |
| **122** | *mer*,*trans*-$[Ir^{III}(NO)(MeCN)_3(PPh_3)_2](PF_6)_2$ | MeCN | 2.36(3) | 1.94(2) | | 0.42 | [163] |

[a] Details as for Tables 1 and 2.
[b] Average Fe–N(mim) bond distance in $[Fe^{III}(TPP)(mim)_2]ClO_4$ (**111**) [151].
[c] Fe–$NO_2$ bond distance in $Fe^{III}(TpivPP)(NO_2)(im)\cdot PhCl$ (**113**) [153].
[d] Co–Cl bond distance in $[Co^{III}Cl(NH_3)_5]Cl_2$ (**115**) [155].
[e] Co–NCS bond distance in $[Co^{III}(NCS)(NH_3)_5]Cl_2$ (**118**) [158].
[f] Co–O bond distance in *trans*-$[Co^{III}(MeCO)(ClO_4)\{[14]aneN_4\}]ClO_4$ (**120**) (only other $Co^{III}$–$OClO_3$ structure available) [160].

Comparison of the data for **116** with the results for $[Co^{III}(NO_2)(NH_3)_5]Br_2$ [164] ($\Delta = 0$), **71** ($\Delta = 0.03$) [107] and **19** ($\Delta = 0.13$) [53] affords the STE series $NO_2^- < CN^- < Me^- < NO^-$, the STE of $NO^-$ being considerably greater than that of the methyl group. Also, the greater length of the Co–O bond in **119** compared to that in **120** [160] shows that $NO^-$ exerts a greater STE than the acetyl ligand.



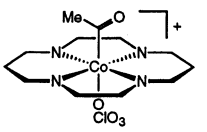
L = Cl⁻ (114)
L = $OClO_3^-$ (119)



X = Cl⁻ (115)
X = $NO^-$ (116), X = $NCS^-$ (118)



(117)



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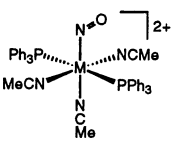


M = Rh (121), M = Ir (122)

*4.2.8. Linear nitrosyl ligands*

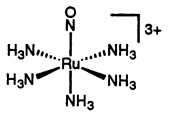
The linearly bonded nitrosyl ligand is a poor σ-donor, but a very strong π-acceptor. The STEs of $NO^+$ are particularly interesting since they depend very much upon the bonding properties of the ligand being affected.

An early low-resolution X-ray crystallographic investigation into $[Ru^{II}(NH_3)_5(NO)]Cl_3{\cdot}H_2O$ (**123**) indicated an STE of the $NO^+$ ligand [165], but a subsequent study was unable to confirm this due to disorder [166]. The Ru–$NH_3$ bond distance of 2.146(4) Å in *trans*-$PPh_4[Ru^{II}(S_4)_2(NH_3)(NO)]$ (**124**) [167] is the same as that in **92** [128], showing that $NO^+$ does not exert a STE in **124**. Furthermore, no significant STEs of $NO^+$ are observed in *mer*-$Ru^{II}Y_3(en)(NO)$ (**125**, $Y = Cl^-$, $Br^-$, $I^-$) [168], *cis*-$[Ru^{II}X(en)_2(NO)](X)PF_6$ (**126**, $X = Cl^-$, $Br^-$) or *cis*-$[Ru^{II}(NCS)(en)_2(NO)]I_2{\cdot}H_2O$ (**127**) [169]. It is hence apparent that $NO^+$ generally exerts little or no STE when opposite a purely σ-donating $NH_3$ or amino ligand. However, the unusual complex $W^{II}O(Me)(^iPr_3tacn)$-$(NO){\cdot}EtOH{\cdot}2H_2O$ (**128**) provides a notable exception, since the W–N($^iPr_3$tacn) bond distances are 2.422(9) Å (*trans* to $O^{2-}$), 2.42(1) Å (*trans* to $NO^+$) and 2.297(8) Å (*trans* to $Me^-$) [170]. In this case, the STE of $NO^+$ on an amine donor is as large as that of an oxo ligand (see Section 4.3.4) and much larger than that of a methyl group.

Table 9
Selected crystallographic data for linear nitrosyl complexes showing STEs [a]

| No. | Compound | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **129** | *trans*-$V^{-I}(CO)_4(PMe_3)(NO)$ | $PMe_3$ | 2.543(1) | | 2.45 | 0.09 | [171] |
| **130** | *mer*-$[Cr^0(CN^tBu)_3(dppm)(NO)]PF_6$ | dppm | 2.478(2) | 2.347(2) | | 0.13 | [172] |
| **131** | *trans*,*mer*-$Cr^I(ONO)_2(py)_3(NO)\cdot py$ | py | 2.17(1) | 2.096(8) | | 0.07 | [173] |
| **132** | $[Co^{III}(en)_3][Cr^I(CN)_5(NO)]\cdot 2H_2O$ | $CN^-$ | 2.08(1) | 2.033(7) | | 0.05 | [174] |
| **133** | *trans*-$Mo^0Cl_2(bpy)(NO)_2$ | bpy | 2.20(1) | | 2.149(8) [b] | 0.05 | [175] |
| **134** | $Mo^{II}I(NHC_5H_{10})Tp^*(NO)$ | Tp* | 2.302(5) | 2.151(5) (*trans* I) | | 0.15 | [176] |
| **135** | $Mo^{II}(NC_4H_4)_2Tp^*(NO)$ | Tp* | 2.246(2) | 2.193(3) | | 0.05 | [177] |
| **136** | *trans*,*mer*-$Tc^IBr_2(CN^tBu)_3(NO)$ | $CN^tBu$ | 2.14(2) | 2.08(2) | | 0.06 | [178] |
| **137** | *cis*-$[Tc^I(phen)_2(NH_3)(NO)](PF_6)_2\cdot Me_2CO$ | phen | 2.16(1) | 2.11(1) | | 0.05 | [179] |
| **138** | *cis*-$(AsPh_4)_2[Re^I(CN)_4(tu)(NO)]$ | $CN^-$ | 2.23(1) | 2.12(1) | | 0.11 | [180] |
| **139** | *trans*-$Et_4N[Re^{II}Cl_4(py)(NO)]$ | py | 2.218(6) | | 2.12 [c] | 0.10 | [182] |

[a] Details as for Tables 1 and 2.
[b] Average of the mutually *trans* Mo–N distances in **43** [84].
[c] Average Re–N distance in *mer*-$Re^{III}X_3(py)_3$ (**140**; $X = Cl^-$, $Br^-$) (best available comparison data) [181].



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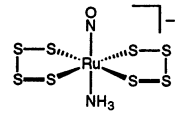
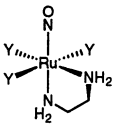
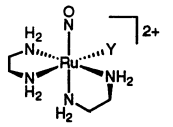


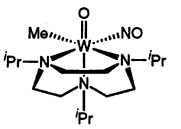
(124)



(125)



Y = $Cl^-$ or $Br^-$ (126)
Y = $NCS^-$ (127)



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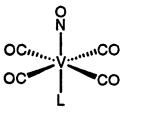
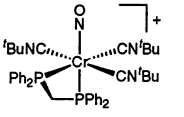


L = $PMe_3$ (129)
L = CO (162)



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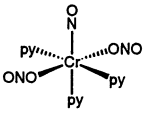

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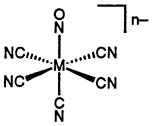
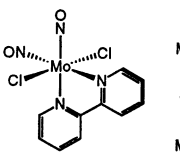
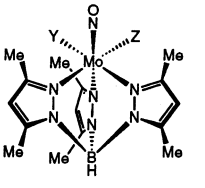


M = Cr, n = 3 (132)
M = Ru, n = 2 (141)

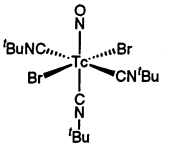
By contrast, when *trans* to another π-acceptor ligand, $NO^+$ does exhibit STEs which vary from small to moderate (Table 9). Although **132** and **138** demonstrate STEs on the weakly π-accepting $CN^-$, certain related complexes such as that in $Na_2[Ru^{II}(CN)_5(NO)]\cdot 2H_2O$ (**141**) do not show such an effect [183]. This may be due to subtle differences in electronic structure and bonding caused by changing the nature of the metal ion. Comparison of the data for **133** with those for **43** indicate that the STE of $NO^+$ on the π-accepting bpy ligand is a little smaller than that of CO.



(133)



Y = $I^-$, Z = $C_5H_{10}NH^-$ (134)
Y = Z = $C_4H_4N^-$ (135)



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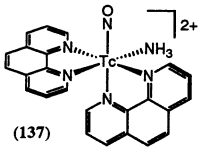

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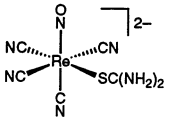

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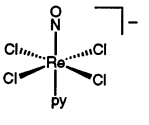


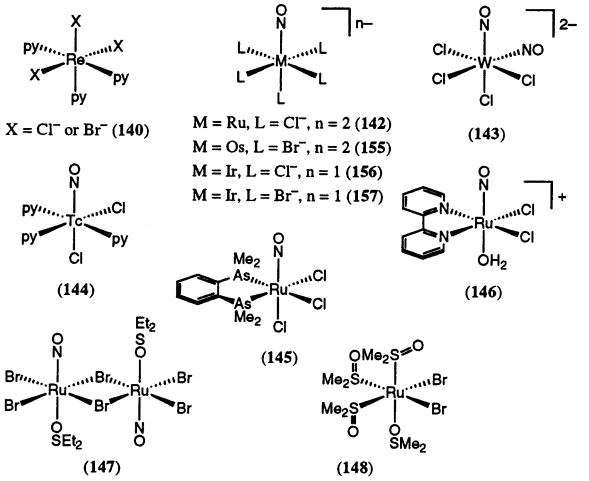
(139)

When opposite a ligand which possesses π-donor ability, $NO^+$ shows unusual 'inverse STEs', i.e. the *trans* bonds are shortened. For example, in $(NH_4)_2[Ru^{II}Cl_5(NO)]$ (**142**) the *trans* Ru–Cl bond distance [2.357(1) Å] is ca. 0.02 Å shorter than the average equatorial Ru–Cl distance [184]. Such effects are observed in many linear nitrosyl complexes, especially those of Ru(II) (Table 10).

Table 10
Selected crystallographic data for linear nitrosyl complexes showing inverse STEs [a]

| No. | Compound | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **143** | *cis*-$(PMePh_3)_2[W^0Cl_4(NO)_2]$ | $Cl^-$ | 2.424(2) | 2.445(2) | | −0.02 | [185] |
| **144** | *cis*,*mer*-$Tc^ICl_2(py)_3(NO)\cdot 2MeCN$ | $Cl^-$ | 2.367(2) | 2.432(1) | | −0.07 | [186] |
| **145** | *fac*-$Ru^{II}Cl_3$(diars)(NO) | $Cl^-$ | 2.420(3) | 2.350(5) | | −0.07 | [187] |
| **146** | *cis*,*trans*-$[Ru^{II}Cl_2(bpy)(H_2O)(NO)]NO_3\cdot H_2O$ | $H_2O$ | 2.044(3) | | 2.12(2) [b] | −0.08 | [188] |
| **147** | *mer*-$[Ru^{II}Br_3(Et_2SO)(NO)]_2$ | $Et_2SO$ | 2.050(7) | | 2.143(5) [c] | −0.09 | [190] |
| **149** | *trans*-$[Ru^{II}(OH)(NH_3)_4(NO)]Cl_2$ | $OH^-$ | 1.961(3) | | 2.168(3) [d] | −0.21 | [166] |
| **150** | *trans*-$[Ru^{II}(OH)(py)_4(NO)](PF_6)_2\cdot H_2O$ | $OH^-$ | 1.910(3) | | 2.168(3) [d] | −0.26 | [191] |
| **151** | *cis*-$Ru^{II}Cl_2(F)$(bpy)(NO) | $F^-$ | 1.942(5) | | 2.011(4) [e] | −0.07 | [193] |
| **153** | *trans*-$[Ru^{II}(NCS)(en)_2(NO)](NCS)_2$ | $NCS^-$ | 1.89(1) | 2.043(8) [f] | | −0.15 | [169] |
| **155** | $(phenH)_2[Os^{II}Br_5(NO)]\cdot 2H_2O$ | $Br^-$ | 2.478(7) | 2.534(3) | | −0.06 | [194] |
| **156** | $K[Ir^{III}Cl_5(NO)]\cdot H_2O$ | $Cl^-$ | 2.286(3) | 2.338(2) | | −0.05 | [195] |
| **157** | $K[Ir^{III}Br_5(NO)]\cdot H_2O$ | $Br^-$ | 2.419(4) | 2.480(3) | | −0.06 | [195] |

[a] Details as for Tables 1 and 2.
[b] Average Ru–O bond distance in **49** [88].
[c] Ru–O bond distance in *cis*,*fac*-$Ru^{II}Br_2(Me_2SO)_3(Me_2SO)$ (**148**) [189].
[d] Ru–OH bond distance in **35** [70].
[e] Ru–F bond distance in *cis*,*cis*-$Ru^{II}F_2(CO)_2(PPh_3)_2$ (**152**) (only other $Ru^{II}$–F structure available) [192].
[f] Ru–NCS bond distance in *cis*-$[Ru^{II}(NCS)(en)_2(NO)]I_2\cdot H_2O$ (**154**) [169].



X = $Cl^-$ or $Br^-$ (140)

M = Ru, L = $Cl^-$, n = 2 (142)
M = Os, L = $Br^-$, n = 2 (155)
M = Ir, L = $Cl^-$, n = 1 (156)
M = Ir, L = $Br^-$, n = 1 (157)

(143)

(144)

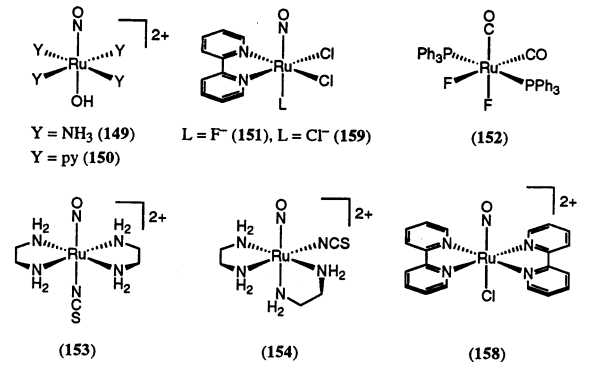
(145)

(146)

(147)

(148)

The shortening of *trans* M–L bonds by $NO^+$ is accompanied by shortening of the M–NO bonds. An extreme example is *trans*-$[Ru^{II}Cl(bpy)_2(NO)](ClO_4)_2$ (**158**), in which the Ru–Cl bond distance is 2.306(2) Å and the Ru–NO bond distance is 1.751(6) Å [196]. The structures of **151** and of *fac*-$Ru^{II}Cl_3(bpy)(NO)$ (**159**) [197] allow a comparison of the behaviour of chloride and fluoride *trans* to $NO^+$.



Y = $NH_3$ (149)
Y = py (150)

L = $F^-$ (151), L = $Cl^-$ (159)

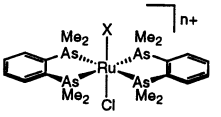
(152)

(153)

(154)

(158)

The Ru–NO bond distance in **151** of 1.706(7) Å [193] is ca. 0.05 Å shorter than that in *fac*-$Ru^{II}Cl_3(bpy)(NO)$ [1.754(3) Å], showing that $F^-$ has the greater inverse STE on $NO^+$. This is perhaps surprising, given that both the σ- and π-donor abilities of $Cl^-$ are greater than those of $F^-$. The Ru–Cl bond length in *trans*-$[Ru^{II}Cl(diars)_2(NO)](PF_6)_2$ (**160**) [2.199(4) Å] is ca. 0.25 Å shorter than that in *trans*-$Ru^{II}Cl(NO_2)(diars)_2$ (**161**) [2.448(9) Å], providing an illustration of the dramatic difference in STEs between the $NO^+$ and $NO_2^-$ ligands [198].



X = $NO^+$, n = 2 (160)
X = $NO_2^-$, n = 0 (161)

$NO^+$ is unusual in being the only ligand known to exhibit such a range of STEs which clearly correlates with the nature of the *trans* ligand (Fig. 1). It was originally suggested [184] that the widespread inverse STEs occur because $NO^+$ is such a weak σ-donor that it does not compete with *trans* ligands for σ-electron density. However, a later MO treatment indicated that π-donation from the *trans* ligand is also important [199,200]. This is consistent with the absence of any STEs with $NH_3$ or amines [169] and the inverse STEs with ligands such as $Cl^-$ or $OH^-$. The extremely strong π-acceptor nature of $NO^+$ enhances π-donation by *trans* ligands, forming particularly stable structures. Although it has been claimed that $NO^+$ will always cause inverse STEs [201], this is clearly not the case: bonds to π-acceptor ligands are lengthened (Table 9) due to competition for π-electron density. This may explain the instability of complexes featuring $NO^+$ *trans* to itself or to other strong π-acceptor ligands such as CO, e.g. $V(CO)_5(NO)$ (**162**) [202].

Although comparison of the data in Tables 9 and 10 with those in Table 4 clearly shows that the relative STEs of the closely related $NO^+$ and CO ligands generally differ greatly (e.g. the difference between the $Ru^{II}$–$OH_2$ bond distances in **48** and **146** is ca. 0.21 Å), in certain mixed carbonyl/nitrosyl complexes this contrast is much less pronounced. For example, in *trans*-$W^0(\eta^2\text{-}MeCO_2)(CO)(PPh_3)_2(NO)$ (**163**) the W–O bond distances are 2.217(5) Å (*trans* to $NO^+$) and 2.249(5) Å (*trans* to CO), a difference of only ca. 0.03 Å [203]. A similar situation pertains in $[Re^I(CO)tacn(NH_3)(NO)]Br_2$ (**164**) where the Re–N(tacn) bond distances are 2.149(6) Å (*trans* to $NO^+$), 2.154(6) Å (*trans* to $NH_3$) and 2.169(6) Å (*trans* to CO) [204].

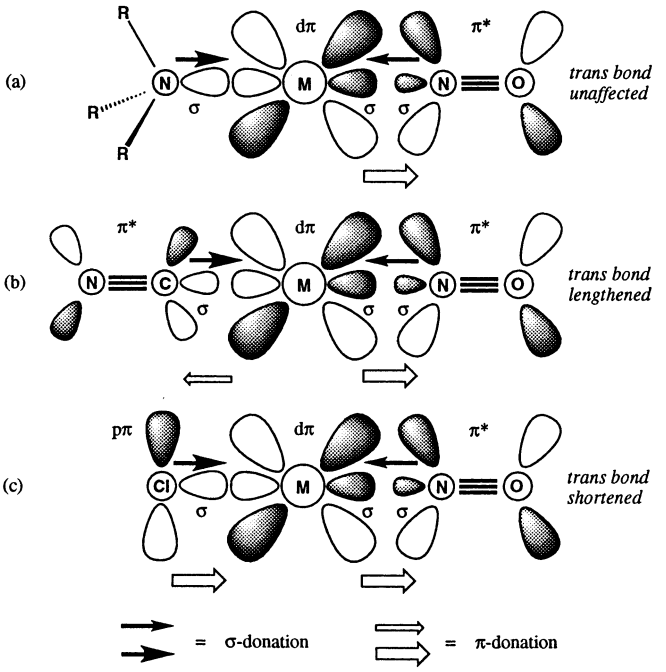
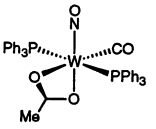
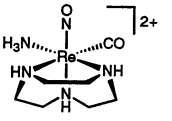



Fig. 1. Simplified orbital representations of the bonding in linear metal nitrosyl complexes with different types of *trans* ligand. (a) σ-Donor $NH_3/NR_3$ ligand; (b) σ-donor–π-acceptor $CN^-$ ligand; (c) σ-donor–π-donor $Cl^-$ ligand.



(163)

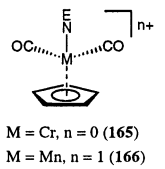


(164)

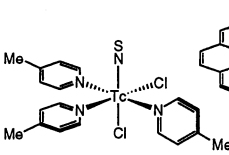
*4.2.9. Linear thionitrosyl ligands*

Given the peculiar inverse STEs of $NO^+$, some comparison with thionitrosyl complexes is deemed appropriate. UVPE spectroscopy and MO calculations indicate that the $NS^+$ ligand is both a better σ-donor and a better π-acceptor than $NO^+$ in $Cr^0Cp(CO)_2(NE)$ (**165**, E = O or S) [205], whilst $NO^+$ is the better acceptor in $[Mn^ICp(CO)_2(NE)]AsF_6$ (**166**) and in $[Fe^{II}Cp(CO)_2(NE)](AsF_6)_2$ (**167**) [206]. It is hence apparent that the comparative acceptor abilities of the linear nitrosyl and thionitrosyl ligands depend on the nature of the metal centre.

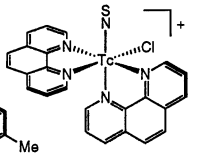
X-ray structural data for a selection of linear thionitrosyl complexes (Table 11) reveal negligible-to-moderate STEs. The $Re^I$–Cl bond in **172** is ca. 0.11 Å shorter than that in **77** [112] and the $Ru^{II}$–$OH_2$ bond in **176** is ca. 0.14 Å shorter than that in **48** [89], showing that $NS^+$ exerts a rather smaller STE than CO. The absence of inverse STEs with π-donor ligands such as $Cl^-$ suggests that $NS^+$ generally behaves as a weaker π-acceptor than $NO^+$. **171** and **178** allow comparison of the STEs of $NS^+$ and the related bromothionitrosyl (NSBr) and chlorothionitrosyl (NSCl) ligands. The latter are also strong π-acceptors and co-ordinate to metals in a pseudo-linear fashion. In **171** $NS^+$ and NSBr produce identical trans-lengthenings of the Re–Br bonds, but NSCl has a slightly smaller STE than $NS^+$ on the Os–Cl bond in **178**. However, in $[N(SCl)_2][Mo^{IV}Cl_5(NSCl)]$ (**179**) the *trans* Mo–Cl bond of 2.468(4) Å is 0.12 Å longer than the average of the *cis* Mo–Cl distances [217].



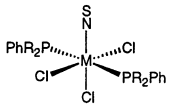
M = Cr, n = 0 (**165**)
M = Mn, n = 1 (**166**)
M = Fe, n = 2 (**167**)



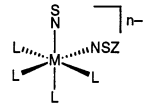
(**168**)



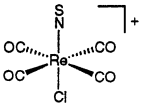
(**169**)



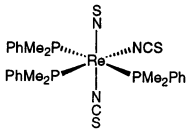
M = Tc, R = Me (**170**)
M = Re, R = Me (**175**)
M = Os, R = Ph (**177**)



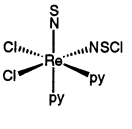
M = Re, L = $Br^-$, Z = Br, n = 2 (**171**)
M = Os, L = $Cl^-$, Z = Cl, n = 1 (**178**)



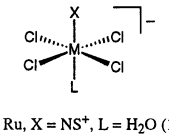
(**172**)



(**173**)



(**174**)



M = Ru, X = $NS^+$, L = $H_2O$ (**176**)
M = Mo, X = NSCl, L = $Cl^-$ (**179**)

Table 11
Selected crystallographic data for linear thionitrosyl complexes [a]

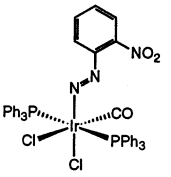
| No. | Compound | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **168** | *cis*,*mer*-$Tc^{I}Cl_2(pic)_3(NS)\cdot CHCl_3$ | $Cl^-$ | 2.443(1) | 2.430(2) | | 0.01 | [207] |
| **169** | *cis*-$[Tc^{I}Cl(phen)_2(NS)]PF_6$ | phen | 2.179(4) | 2.130(4) (*trans* Cl) | | 0.05 | [179] |
| **170** | *mer*,*trans*-$Tc^{II}Cl_3(PMe_2Ph)_2(NS)$ | $Cl^-$ | 2.432(1) | 2.351(1) | | 0.08 | [208] |
| **171** | *cis*-$(PPh_4)_2[Re^{I}Br_4(NSBr)(NS)]\cdot CH_2Br_2$ | $Br^-$ | 2.592(2) | 2.541(3) | | 0.05 | [209] |
| **172** | *trans*-$[Re^{I}Cl(CO)_4(NS)]AsF_6$ | $Cl^-$ | 2.410(5) | | 2.380(2) [b] | 0.03 | [210] |
| **173** | *cis*,*mer*-$Re^{I}(NCS)_2(PMe_2Ph)_3(NS)$ | $NCS^-$ | 2.08(2) | 2.07(1) | | 0.01 | [211] |
| **174** | *cis*,*cis*,*cis*-$Re^{I}Cl_2(py)_2(NSCl)(NS)$ | py | 2.234(4) | 2.136(4) | | 0.10 | [212] |
| **175** | *mer*,*trans*-$Re^{II}Cl_3(PMe_2Ph)_2(NS)$ | $Cl^-$ | 2.424(1) | 2.352(1) | | 0.07 | [213] |
| **176** | *trans*-$PPh_4[Ru^{II}Cl_4(H_2O)(NS)]$ | $H_2O$ | 2.112(3) | | 2.12(2) [c] | −0.01 | [214] |
| **177** | *mer*,*trans*-$Os^{II}Cl_3(PPh_3)_2(NS)$ | $Cl^-$ | 2.399(3) | 2.387(3) | | 0.01 | [215] |
| **178** | *cis*-$AsPh_4[Os^{II}Cl_4(NSCl)(NS)]$ | $Cl^-$ | 2.380(2) | 2.364(3) | | 0.02 | [216] |

[a] Details as for Tables 1 and 2.
[b] Re–Cl bond distance *trans* to py in **174** [212].
[c] Average Ru–O bond distance in **49** [88].

*4.2.10. Diazenido ligands*

Diazenido ligands can form terminal bonds to metal ions in several bonding modes. By far the most common is the 'singly bent' co-ordination featuring a linear M–N=N unit in which the ligand is formally considered as '$RN_2^+$' (a *diazonium* complex). An $RN_2^+$ ligand is isoelectronic with $NO^+$, but the latter is a stronger π-acceptor due to the greater electronegativity of oxygen compared with nitrogen. An alternative co-ordination mode is the 'doubly bent' geometry which contains a '$RN_2^-$' ligand. This is analogous to the bent nitrosyl formalism, $RN_2^-$ being a stronger σ-donor, but a weaker π-acceptor than $RN_2^+$.

The few crystallographic studies on complexes of $RN_2^-$ ligands show that such species exert large STEs. For example, in *cis*,*trans*-$Ir^{III}Cl_2(N_2\text{-}2\text{-}NO_2\text{-}C_6H_4)(CO)(PPh_3)_2$ (**180**) the Ir–Cl bond *trans* to the diazenido ligand [2.48(1) Å] is ca. 0.11 Å longer than that *trans* to CO [2.37(1) Å] [218]. By contrast, $RN_2^+$ ligands generally exert very little STE on various ligands [219]. However, a recent study on *mer*,*trans*-$Re^{II}Br_3(PPh_3)_2(N_2Ph)$ **181** shows that the diazenido ligand is present in the singly bent mode, but nevertheless exerts a moderate STE, the *trans* Re–Br distance [2.564(2) Å] being ca. 0.08 Å longer than the average *cis* Re–Br distance [2486(3) Å] [220].

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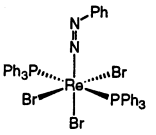
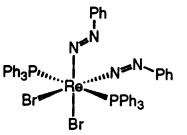



(181)




(182)

The related complex *cis*,*trans*-$Re^{II}Br_2(N_2Ph)(PPh_3)_2(N_2Ph)$ (**182**) is unusual in containing both $PhN_2^+$ and $PhN_2^-$ ligands, allowing a direct comparison of their bonding and STEs [221]. The Re–N distance, Re–N–N angle and *trans* Re–Br distance (Δ vs. average *cis* Re–Br distance in **181**) for the $PhN_2^+$ ligand are as follows: 1.827(9) Å, 130.6(6)° and 2.563(2) Å (ca. 0.08 Å), respectively, whilst those for the $PhN_2^-$ moiety are 1.908(7) Å, 171.2(7)°, and 2.596(1) Å (ca. 0.11 Å), respectively. These data confirm the presence of greater π-back-bonding to the $PhN_2^+$ ligand, and show that both ligands exert a STE, although that of the $PhN_2^-$ group is slightly larger [221].

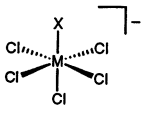
*4.2.11. Phosphanes and related ligands*

Tertiary phosphanes and related ligands possess a wide range of σ-donor/π-acceptor properties and their STEs are hence variable. Selected data for phosphine complexes (Table 12) reveal moderate STEs in the range 0.04–0.11 Å. Comparison of the data for the analogous complexes **187**, **190** and **194** indicates that the STE of $PMe_2Ph$ decreases slightly as the metal d-configuration increases from $d^4$ to $d^6$ [226].

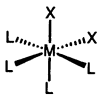
Table 12
Selected crystallographic data for phosphine complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **183** | $(PMe_2PhH)[Nb^{IV}Cl_5(PMe_2Ph)]$ | $PMe_2Ph$ | $Cl^-$ | 2.405(5) | 2.363(2) | 0.04 | [222] |
| **184** | *cis*-$Ta^{IV}Br_4(PMe_2Ph)_2$ (monoclinic form) | $PMe_2Ph$ | $Br^-$ | 2.536(2) | 2.468(1) | 0.07 | [223] |
| **185** | *mer*-$[Tc^{III}Cl_3(PMe_3)_3][(PhNCO)_3]$ | $PMe_3$ | $Cl^-$ | 2.440(1) | 2.361(1) | 0.08 | [224] |
| **186** | *trans,mer*-$[Tc^{III}Cl_2(py)_3(PPh_3)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5C_6H_{14}$ | $PPh_3$ | py | 2.218(5) | 2.166(5) | 0.05 | [225] |
| **187** | *mer*-$Re^{III}Cl_3(PMe_2Ph)_3$ | $PMe_2Ph$ | $Cl^-$ | 2.454(6) | 2.353(6) | 0.10 | [226] |
| **188** | *trans,mer*-$Ru^{II}Cl_2(thz)_3(PPh_3)$ | $PPh_3$ | thz | 2.183(5) | 2.094(7) | 0.09 | [227] |
| **189** | *cis*-$Os^{II}Cl_2(dppm)_2$ | dppm | dppm | 2.339(2) | 2.302(3) | 0.04 | [228] |
| **190** | *mer*-$Os^{III}Cl_3(PMe_2Ph)_3$ | $PMe_2Ph$ | $Cl^-$ | 2.439(6) | 2.347(6) | 0.09 | [226] |
| **191** | *cis*-$[Co^{III}(acac)_2(PMe_3)_2]PF_6$ | $PMe_3$ | acac | 1.934(4) | 1.896(3) | 0.04 | [229] |
| **192** | *cis*-$[Co^{III}(acac)_2(PEt_3)_2]PF_6$ | $PEt_3$ | acac | 1.886(9) | 1.951(8) | 0.07 | [229] |
| **193** | $[Rh^{III}I_2(PPh_3)ttcn]ClO_4$ | $PPh_3$ | ttcn | 2.358(2) | 2.298(2) | 0.06 | [230] |
| **194** | *mer*-$Ir^{III}Cl_3(PMe_2Ph)_3$ | $PMe_2Ph$ | $Cl^-$ | 2.429(6) | 2.361(6) | 0.07 | [226] |
| **195** | *cis*-$Pt^{IV}Cl_4(PEt_3)_2$ | $PEt_3$ | $Cl^-$ | 2.321(3) | 2.394(3) | 0.07 | [231] |
| **196** | $[2,5\text{-}Me_2\text{–}C_4H_3N_2][Pt^{IV}Cl_5(PEt_3)]$ | $PEt_3$ | $Cl^-$ | 2.425(4) | 2.316(4) | 0.11 | [232] |

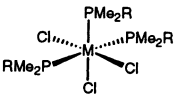
[a] Details as for Tables 1 and 2.



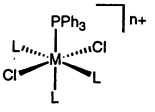
M = Nb, X = $PMe_2Ph$ (**183**)
M = Pt, X = $PEt_3$ (**196**)



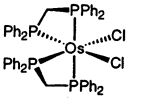
M = Ta, L = $Br^-$,
X = $PMe_2Ph$ (**184**)
M = Pt, L = $Cl^-$,
X = $PEt_3$ (**195**)



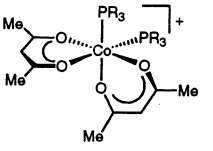
M = Tc, R = Me (**185**)
M = Re, R = Ph (**187**)
M = Os, R = Ph (**190**)
M = Ir, R = Ph (**194**)



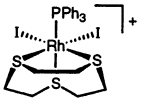
M = Tc, L = py, n = 1 (**186**)
M = Ru, L = thz, n = 0 (**188**)



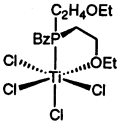
(**189**)



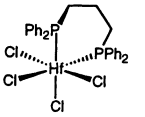
R = Me (**191**), R = Et (**192**)



(**193**)

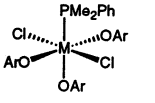


(**197**)

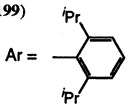


(**198**)

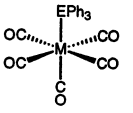
Although the $d^1$ complexes **183** and **184** show typical phosphine STEs, crystallographic studies with $d^0$ complexes show greatly reduced STEs, which may be traced to an absence of M→P π-back-bonding. For example, in $Ti^{IV}Cl_4\{EtOC_2H_4P(C_2H_4OEt)Bz\}$ (**197**) the mutually *trans* Ti–Cl distances [average 2.296(3) Å] are ca. 0.02 Å longer than that *trans* to the phosphorus atom [2.280(2) Å], showing that the phosphine ligand has a smaller STE than $Cl^-$ [233]. In $Hf^{IV}Cl_4$(dppp) (**198**) the mutually *trans* Hf–Cl distances of 2.398(5) Å are ca. 0.05 Å longer than those *trans* to the phosphine ligand [average 2.347(9) Å] [234], and relative shortenings of ca. 0.04 Å are found in the M–O distances *trans* to $PMe_2Ph$ in *trans,mer*-$M^VCl_2(Odipp)_3(PMe_2Ph)$ (**199**; M = Nb or Ta) [235]. This variation of phosphine STEs is reminiscent of the situation with isocyanide ligands for which the extent of π-back-bonding is also strongly dependent upon the metal d-configuration (see Section 4.2.3).



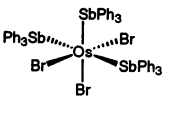
(**199**)



Structural studies with the complete series of nine complexes $M^0(CO)_5(EPh_3)$ (**200**; M = Cr, Mo, W; E = P, As, Sb) reveal that the *trans* M–CO bonds are shorter than their *cis* counterparts by ca. 0.03–0.07 Å [236]. This is because the $EPh_3$ ligands are weaker π-acceptors than CO and so compete less effectively for π-electron density



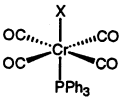

(200)




(201)

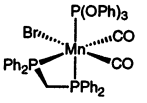
[236]. No clear periodic trends between the three metals or three donor atoms are evident within this body of data. Due to the predominance of *trans*-bis structures, very little further structural evidence exists to illustrate the STEs of tertiary arsine or stibine ligands. In *mer*-$Os^{III}Br_3(SbPh_3)_3$ (**201**) the Os–Br bond distance *trans* to antimony is 2.522(2) Å, only ca. 0.01 Å longer than the average of the mutually *trans* Os–Br distances [237], indicating that the STE of $SbPh_3$ is similar to that of $Br^-$.

Direct structural evidence for STEs of phosphite ligands is also scarce. However, X-ray studies on complexes *trans*-$Cr^0(CO)_4(PPh_3)X$ [X = $P(^nBu)_3$ (**202**), $P(OMe)_3$ (**203**), $P(OPh)_3$ (**204**), CO (**205**)] have afforded the bond distance data given in




**X = $P(^nBu)_3$ (202), X = $P(OMe)_3$ (203)**
**X = $P(OPh)_3$ (204), X = CO (205)**

Table 13. These show that the Cr–$PPh_3$ bond lengthens steadily as the π-acceptor strength of X increases in the order $P(^nBu)_3 < P(OMe)_3 < P(OPh)_3 < CO$, the difference between the strong σ-donor $P(^nBu)_3$ and the strong π-acceptor CO being ca. 0.07 Å [238]. In keeping with the competitive π-bonding theory, the Cr–X bond is strengthened and shortened at the expense of the *trans* Cr–$PPh_3$ bond [238]. In *cis*,*cis*-$Mn^IBr(CO)_2$dppm{$P(OPh)_3$} (**206**) the Mn–P(dppm) bond *trans* to CO [2.362(2) Å] is ca. 0.06 Å longer than that *trans* to $P(OPh)_3$ [2.302(2) Å] [240], confirming the weaker STE of the phosphite ligand.



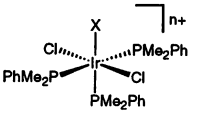

(206)

A number of complexes *trans*,*mer*-$[Ir^{III}Cl_2X(PMe_2Ph)_3]^{n+}$ ($n = 0$ or 1) have been crystallographically characterised (**207**–**213**) [241–244], and selected data which

Table 13
Selected crystallographic data for complexes *trans*-$Cr^0(CO)_4(PPh_3)X$

| No. | X | Cr–$PPh_3$ (Å) | Cr–P(X) (Å) | Ref. |
|---|---|---|---|---|
| **202** | $P(^nBu)_3$ | 2.349(4) | 2.344(4) | [238] |
| **203** | $P(OMe)_3$ | 2.364(6) | 2.261(6) | [238] |
| **204** | $P(OPh)_3$ | 2.395(2) | 2.228(2) | [238] |
| **205** | CO | 2.422(1) | | [239] |

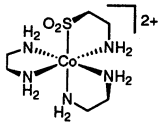
allow comparison of the STEs of X on $PMe_2Ph$ are shown in Table 14. It has been suggested that the differences in the *cis* Ir–P distances within this series are due to conformational effects (i.e. the relative orientations of the three phenyl substituents), and a direct comparison of the *trans* Ir–P distances was used to derive the STE sequence $H_2O < Cl^- < SH^- \leq NH_3 < H^- < PH_2^- < PH_3$ [242]. However, use of the $\Delta$ parameters affords the slightly different STE ordering $H_2O < NH_3 \leq Cl^- < SH^- < PH_2^- < H^- < PH_3$, which reflects more closely the established series for square planar complexes.



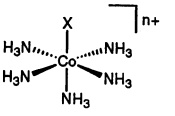
**X = $H_2O$, n = 1 (207)**
**X = $NH_3$, n = 1 (208)**
**X = $Cl^-$, n = 0 (209)**
**X = $SH^-$, n = 0 (210)**
**X = $PH_2^-$, n = 0 (211)**
**X = $H^-$, n = 0 (212)**
**X = $PH_3$, n = 1 (213)**

### *4.2.12. S-Bonded sulfinato, sulfito and sulfoxide ligands*

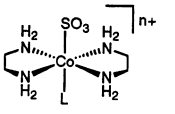
Sulfur-co-ordinated, sulfinato and sulfito anions are good σ-donors which have the potential to engage in π-back-bonding. The crystal structures of a number of Co(III) complexes containing such ligands reveal moderate STEs (Table 15).



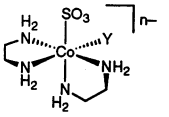
**(214)**



**X = $PhSO_2^-$, n = 2 (215)**
**X = $TolSO_2^-$, n = 2 (216)**
**X = $SO_3^{2-}$, n = 1 (217)**
**X = $H_2O$, n = 3 (219)**
**X = $S_2O_3^{2-}$, n = 1 (226)**



**L = $H_2O$, n = 1 (218)**
**L = $Cl^-$, n = 0 (220)**
**L = $NCS^-$, n = 0 (221)**
**L = $SO_3^{2-}$, n = –1 (222)**
**L = $NH_3$, n = 1 (223)**



**Y = $NO_2^-$, n = 0 (224)**
**Y = $S_2O_3^{2-}$, n = 1 (225)**

Table 14
Selected crystallographic data for complexes *trans,mer*-$[Ir^{III}Cl_2X(PMe_2Ph)_3]^{n+}$ ($n = 0$ or 1)

| No. | Compound | X | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|
| | | | Ir–$P_{trans}$ | Ir–$P_{cis}$ | | |
| **207** | *trans,mer*-$[Ir^{III}Cl_2(H_2O)(PMe_2Ph)_3]ClO_4$ | $H_2O$ | 2.249(3) | 2.379(4) | −0.13 | [241] |
| **208** | *trans,mer*-$[Ir^{III}Cl_2(NH_3)(PMe_2Ph)_3]ClO_4$ | $NH_3$ | 2.302(5) | 2.400(7) | −0.10 | [242] |
| **209** | *mer*-$Ir^{III}Cl_3(PMe_2Ph)_3$ | $Cl^-$ | 2.280(1) | 2.373(2) | −0.09 | [243] |
| **210** | *trans,mer*-$Ir^{III}Cl_2(SH)(PMe_2Ph)_3$ | $SH^-$ | 2.296(2) | 2.361(3) | −0.07 | [242] |
| **211** | *trans,mer*-$Ir^{III}Cl_2(PH_2)(PMe_2Ph)_3$ | $PH_2^-$ | 2.378(3) | 2.365(4) | 0.01 | [242] |
| **212** | *trans,mer*-$Ir^{III}Cl_2(H)(PMe_2Ph)_3$ | $H^-$ | 2.363(2) | 2.329(3) | 0.03 | [244] |
| **213** | *trans,mer*-$[Ir^{III}Cl_2(PH_3)(PMe_2Ph)_3]ClO_4$ | $PH_3$ | 2.46(1) | 2.397(6) | 0.06 | [242] |

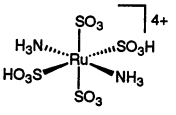
Table 15
Selected crystallographic data for Co(III) sulfinato and sulfito complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | $M–L_{comp}$ | | |
| **214** | *cis*-$[Co^{III}(H_2NC_2H_4SO_2)(en)_2](ClO_4)(NO_3)$ | $H_2NC_2H_4SO_2^-$ | en | 2.027(4) | 1.978(3) | | 0.05 | [245] |
| **215** | $[Co^{III}(PhSO_2)(NH_3)_5][Cl_3SnOClO_3]$ | $PhSO_2^-$ | $NH_3$ | 2.020(4) | 1.960(5) | | 0.06 | [246] |
| **216** | $[Co^{III}(TolSO_2)(NH_3)_5](ClO_4)_2·H_2O$ | $TolSO_2^-$ | $NH_3$ | 2.023(4) | 1.97(1) | | 0.05 | [247] |
| **217** | $[Co^{III}(SO_3)(NH_3)_5]Cl·H_2O$ | $SO_3^{2-}$ | $NH_3$ | 2.055(2) | 1.966(2) | | 0.09 | [247] |
| **218** | *trans*-$[Co^{III}(SO_3)(en)_2(H_2O)]ClO_4·H_2O$ | $SO_3^{2-}$ | $H_2O$ | 2.037(7) | | 1.954(1) [b] | 0.08 | [249] |
| **220** | *trans*-$Co^{III}Cl(SO_3)(en)_2·H_2O$ | $SO_3^{2-}$ | $Cl^-$ | 2.377(2) | | 2.286(2) [c] | 0.09 | [250] |
| **221** | *trans*-$Co^{III}(NCS)(SO_3)(en)_2·2H_2O$ | $SO_3^{2-}$ | $NCS^-$ | 1.97(2) | | 1.90(2) [d] | 0.07 | [251] |
| **222** | *trans*-$Na[Co^{III}(SO_3)_2(en)_2]·3H_2O$ | $SO_3^{2-}$ | $SO_3^{2-}$ | 2.267(2) | | 2.218(1) [e] | 0.05 | [252] |
| **223** | *trans*-$[Co^{III}(SO_3)(en)_2(NH_3)]ClO_4$ | $SO_3^{2-}$ | $NH_3$ | 2.070(3) | | 1.966(2) [f] | 0.10 | [253] |
| **224** | *cis*-$Co^{III}(NO_2)(SO_3)(en)_2·H_2O$ | $SO_3^{2-}$ | en | 2.019(3) | 1.960(3) (*trans* $NO_2$) | | 0.06 | [254] |
| | | | | | 1.951(3) (*trans* en) | | 0.07 | [254] |

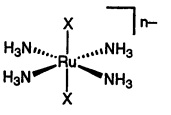
[a] Details as for Tables 1 and 2.
[b] Co–O bond distance in $[Co^{III}(NH_3)_5(H_2O)](S_2O_6)_{1.5}·H_2O$ (**219**) [248].
[c] Co–Cl bond distance in **115** [155].
[d] Co–*N*CS bond distance in **118** [158].
[e] Co–S bond distance in **217** [247].
[f] Co–N(eq) bond distance in **217** [247].

In **224** the sulfito ligand has a considerably larger STE than $NO_2^-$ [254], and the Co–N bond distances in *cis*-$NH_4[Co^{III}(SO_3)(S_2O_3)(en)_2]\cdot 3H_2O$ (**225**) reveal that the STE of the S-bound thiosulfato ligand is almost as large as that of $SO_3^{2-}$ [254]. By contrast, the relative *trans* Co–$NH_3$ bond lengthening in $[Co^{III}(S_2O_3)(NH_3)_5]Cl\cdot H_2O$ (**226**) is only ca. 0.02 Å [255], rather smaller than that in **217** [247]. Since π-back-bonding is unlikely to be extensive with Co(III), such STEs can be ascribed primarily to strong σ-donation.

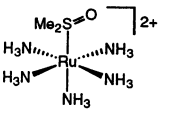
In sulfito/sulfinato complexes with low-valent metal ions more extensive M → S π-back-bonding can be expected, but little crystallographic data is available to probe how this may affect the STEs of such ligands. In *trans*,*trans*-$Na_4[Ru^{II}(SO_3)_2(SO_3H)_2(NH_3)_2]\cdot 6H_2O$ (**227**) the Ru–$SO_3$ distances are unusually long for $Ru^{II}$–S bonds [2.333(1) Å] [256], and the Ru–$SO_3$ distance in *trans*-$(NH_4)_2[Ru^{II}(SO_3)_2(NH_3)_4]\cdot 4H_2O$ (**228**) is 2.305(1) Å [257]. Comparison of the latter with the Ru–S distance in *trans*-$Ru^{II}(SO_3H)_2(NH_3)_4$ (**229**) [2.276(1) Å] [258] shows that protonation of the sulfito ligand causes a reduction in STE which is ascribed to a decrease in basicity [257].




(227)




X = $SO_3^{2-}$, n = 2 (228)
X = $SO_3H^-$, n = 0 (229)




(230)

Neutral S-bonded sulfoxide ligands possess weak π-acceptor properties and display small STEs. Structural data for Ru(II) and Rh(III) complexes have been reviewed recently [259]. For example, the Ru–S and S–O bond distances in $[Ru^{II}(Me_2SO)(NH_3)_5](PF_6)_2$ (**230**) provide evidence for significant $Ru^{II} \rightarrow S$ π-bonding [260] and this is accompanied by a differential *trans* Ru–N bond lengthening of ca. 0.04 Å.

### *4.3. σ-Donor–π-donor ligands*

Although many types of ligand are capable of acting as π-donors, including halides and pseudohalides, pronounced STEs are caused only by species which form double or triple bonds to transition metals, e.g. oxo, nitrido and imido ligands. In fact, such species are the strongest STE ligands known [24,25].

#### *4.3.1. Carbyne ligands*

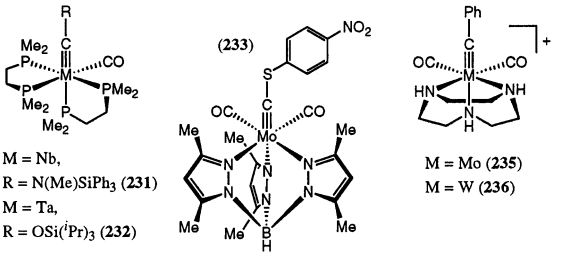
Here we adopt the tradition of considering a carbyne (*alkylidyne*) as a '$CR^{3-}$' ligand co-ordinated to metals in high formal oxidation states. In this case a carbyne moiety acts as a strong, 6-electron σ/π-donor, forming M≡C triple bonds.

The selected crystallographic information for carbyne complexes collected in Table 16 show a considerable variation in STE. The bond distance data for **231** and **232** [261,262] demonstrate the STE order phosphine < CO < carbyne.

Table 16
Selected crystallographic data for carbyne complexes [a]

| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **231** | *cis*-$Nb^{III}\{CN(Me)SiPh_3\}(CO)(dmpe)_2\cdot 0.5Et_2O$ | $CN(Me)SiPh_3^{3-}$ | dmpe | 2.661(3) | 2.604(3) (*trans* CO) | 0.06 | [261] |
| | | | | | 2.542(3) (*trans* P) | 0.12 | [261] |
| **232** | *cis*-$Ta^{III}\{COSi(^iPr)_3\}(CO)(dmpe)_2$ | $COSi(^iPr)_3^{3-}$ | dmpe | 2.636(4) | 2.538(4) (*trans* CO) | 0.10 | [262] |
| | | | | | 2.498(6) (*trans* P) | 0.14 | [262] |
| **233** | $Mo^{IV}(CSC_6H_4\text{-}4\text{-}NO_2)Tp^*(CO)_2$ | $CSC_6H_4\text{-}4\text{-}NO_2^{3-}$ | Tp* | 2.290(4) | 2.216(4) | 0.07 | [263] |
| **234** | *mer*-$[Mo^{IV}(CNEt_2)I(CO)_3]_2$ | $CNEt_2^{3-}$ | $\mu\text{-}I^-$ | 2.943(2) | 2.883(2) | 0.05 | [264] |
| **235** | $[Mo^{IV}(CPh)(CO)_2tacn]BPh_4$ | $CPh^{3-}$ | tacn | 2.351(4) | 2.278(6) | 0.07 | [265] |
| **236** | $[W^{IV}(CPh)(CO)_2tacn]BPh_4$ | $CPh^{3-}$ | tacn | 2.316(5) | 2.265(7) | 0.05 | [265] |
| **237** | *mer*-$[W^{IV}(CNEt_2)(SPh)(CO)_3]_2$ | $CNEt_2^{3-}$ | $\mu\text{-}SPh^-$ | 2.610(9) | 2.547(8) | 0.06 | [264] |
| **238** | *cis*,*trans*-$W^{VI}(C^tBu)Cl_2PHPh(PEt_3)_2$ | $C^tBu^{3-}$ | $Cl^-$ | 2.578(2) | 2.456(2) | 0.12 | [266] |
| **239** | $W^{VI}(CSMe)Tp(SMe)_2$ | $CSMe^{3-}$ | Tp | 2.288(5) | 2.209(8) | 0.08 | [267] |
| **240** | *mer*-$[W^{VI}(CEt)(O^iPr)_3(Me_2NH)]_2$ | $CEt^{3-}$ | $\mu\text{-}O^iPr^-$ | 2.360(7) | 2.035(6) | 0.33 | [268] |
| **241** | *trans*,*cis*-$Re^V(C^tBu)I_2\{C(H)^tBu\}(py)_2$ | $C^tBu^{3-}$ | py | 2.415(6) | 2.369(6) | 0.05 | [269] |
| **242** | *cis*-$[Re^V(C^tBu)Cl_2\{C(H)^tBu\}(XylNH_2)]_2$ | $C^tBu^{3-}$ | $\mu\text{-}Cl^-$ | 2.619(3) | 2.673(4) (*trans* C) | −0.05 | [270] |
| | | | | | 2.397(4) (*trans* N) | 0.22 | [270] |
| **243** | $[Os^{VI}(CPh)(NH_3)_5](CF_3SO_3)_3\cdot 1.5Me_2CO$ | $CPh^{3-}$ | $NH_3$ | 2.245(8) | 2.13(2) | 0.12 | [271] |
| **244** | $Os^{VI}(C^tBu)Np_2Tp$ | $C^tBu^{3-}$ | Tp | 2.30(2) | 2.19(3) | 0.11 | [272] |

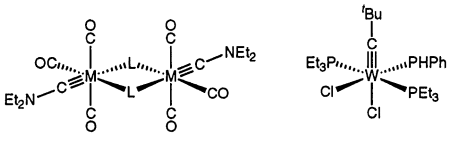
[a] Details as for Tables 1 and 2.



M = Nb,
R = N(Me)SiPh$_3$ (**231**)
M = Ta,
R = OSi($^i$Pr)$_3$ (**232**)

(**233**)

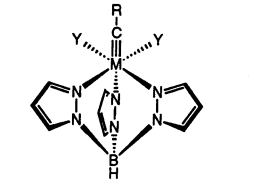
M = Mo (**235**)
M = W (**236**)



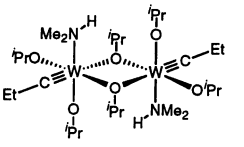
M = Mo, L = I$^-$ (**234**)
M = W, L = SPh$^-$ (**237**)

(**238**)

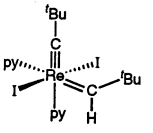
As with carbene ligands, the electronic properties of carbynes are strongly influenced by substituent effects, and it has been suggested that π-donating heteratom groups compete with the metal for a C p-orbital, decreasing the extent of π-donation to the metal centre [261]. The smaller STE of the carbyne in **231** with respect to that in **232** may then be ascribed to the lower electronegativity of the N(Me)SiPh$_3$ substituent compared to OSi($^i$Pr)$_3$. Taken as a whole, the data in Table 16 provide further support for the aforementioned hypothesis since they indicate that alkyl carbynes exert the largest STEs of this type of ligand. For example, the C$^t$Bu$^{3-}$ ligand in **244** has a much larger STE than Np$^-$, which is in keeping with the greater overall electron-donating ability of a carbyne compared with an alkyl group. Also, an extremely large STE is caused by the CEt$^{3-}$ ligand in **240**. Somewhat surprisingly, in **241** the C$^t$Bu$^{3-}$ ligand has a somewhat larger STE that the C(H)$^t$Bu group, whilst in the isoelectronic complex **242** this situation is reversed.



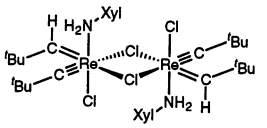
M = W, R = SMe, Y = SMe$^-$ (**239**)
M = Os, R = $^t$Bu, Y = Np$^-$ (**244**)



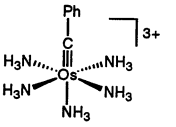
(**240**)



(**241**)



(**242**)



(**243**)

*4.3.2. Nitride*

Co-ordinated nitrogen ions are isoelectronic with carbyne ligands, and form M≡N bonds to high-oxidation-state transition metal ions. N$^{3-}$ units invariably exert unusually large STEs, as has been reviewed previously [273], and the existence

of many square pyramidal complexes such as $[M^{VI}NX_4]^-$ (M = Mo, W, Re, Ru, Os; X = halide) can be viewed as an extreme result of this phenomenon.

In $K_2[Os^{VI}NCl_5]$ (**245**), the Os–Cl bond distance *trans* to $N^{3-}$ [2.605(4) Å] is ca. 0.24 Å longer than the average *cis* Os–Cl distance [23]. Because the *cis* Os–Cl bonds are distorted away from the nitrido ligand by ca. 5–8°, it was originally suggested that the observed STE is largely steric in origin, i.e. due to the shortness of the Os≡N bond, the *cis* Os–Cl bonds bend away in order to relieve non-bonded interactions. This causes the *trans* $Cl^-$ to be forced out, lengthening the *trans* Os–Cl bond [23]. However, a recent MO study indicates that electronic effects are more important than steric factors in **245** [28]. The electronic origin of the TEs of nitrido ligands can be explained as arising from highly effective competition for both σ- and π-orbitals with other ligands which are invariably considerably weaker donors. The distortion of the *cis* bonds away from the M≡N unit, as observed in **245**, is a characteristic feature of nitrido complexes.

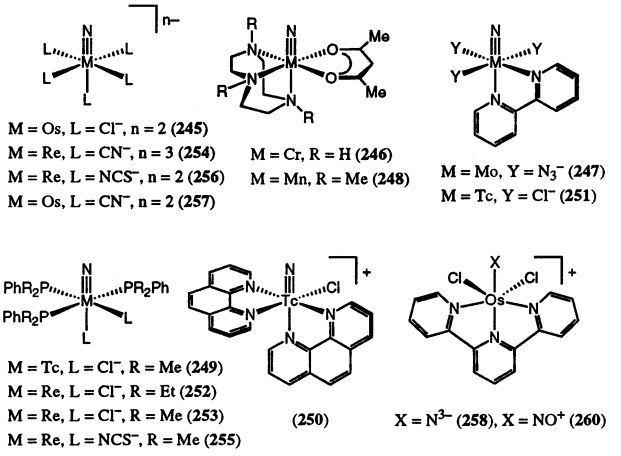


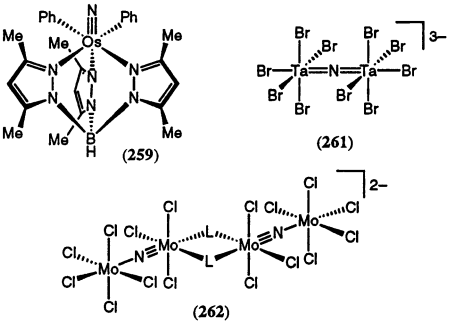

Table 17
Selected crystallographic data for nitrido complexes [a]

| No. | Compound | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **246** | $Cr^{V}N(acac)tacn$ | tacn | 2.35(1) | 2.069(9) | 0.28 | [274] |
| **247** | *mer*-$Mo^{VI}N(N_3)_3bpy$) | bpy | 2.419(5) | 2.240(4) | 0.18 | [275] |
| **248** | $Mn^{V}N(acac)(Me_3tacn)$ | $Me_3tacn$ | 2.301(4) | 2.064(7) | 0.24 | [274] |
| **249** | *cis,mer*-$Tc^{V}NCl_2(PMe_2Ph)_3$ | $Cl^-$ | 2.665(1) | 2.441(1) | 0.22 | [276] |
| **250** | *cis*-$[Tc^{V}NCl(phen)_2]Cl·H_2O$ | phen | 2.399(5) | 2.123(5) (*trans* Cl) | 0.28 | [277] |
| **251** | *mer*-$Tc^{V}NCl_3bpy$ | bpy | 2.371(4) | 2.136(5) | 0.24 | [278] |
| **252** | *cis,mer*-$Re^{V}NCl_2(PEt_2Ph)_3$ | $Cl^-$ | 2.563(4) | 2.454(4) | 0.11 | [279] |
| **253** | *cis,mer*-$Re^{V}NCl_2(PMe_2Ph)_3$ | $Cl^-$ | 2.633(2) | 2.442(2) | 0.19 | [280] |
| **254** | $(PPh_4)_3[Re^{V}N(CN)_5]·7H_2O$ | $CN^-$ | 2.39(1) | 2.12(2) | 0.27 | [281] |
| **255** | *cis,mer*-$Re^{V}N(NCS)_2(PMe_2Ph)_3$ | $NCS^-$ | 2.257(6) | 2.074(8) | 0.18 | [282] |
| **256** | $(AsPh_4)_2[Re^{VI}N(NCS)_5]$ | $NCS^-$ | 2.31(1) | 2.02(2) | 0.29 | [283] |
| **257** | $(AsPh_4)_2[Os^{VI}N(CN)_5]$ | $CN^-$ | 2.353(8) | 2.08(2) | 0.27 | [284] |
| **258** | *trans*-$[Os^{VI}NCl_2tpy]Cl$ | tpy | 2.162(4) | 2.080(6) | 0.08 | [285] |
| **259** | $Os^{VI}N(Ph)_2Tp^*$ | $Tp^*$ | 2.352(3) | 2.152(4) | 0.20 | [286] |

[a] Details as for Tables 1 and 2.

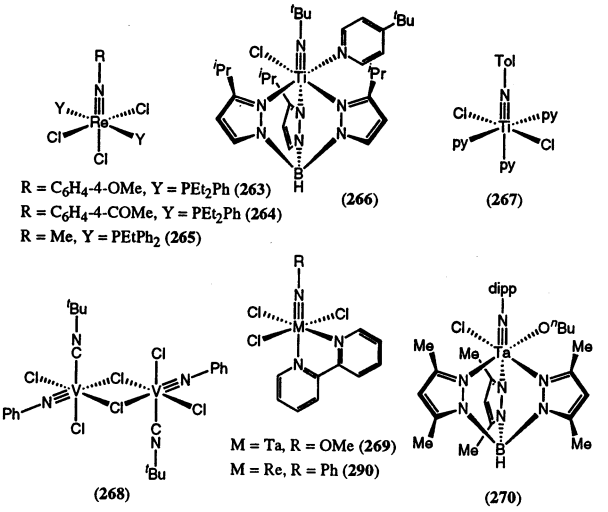
Crystallographic data for a selection of octahedral nitrido complexes are given in Table 17. The relatively small apparent STE in **258** [285] is undoubtedly a result of the bis-chelating nature of the tpy ligand which restricts elongation of the Os–N bond to the central pyridyl ring. An interesting comparison is provided by *trans*-$[Os^{II}Cl_2(tpy)(NO)]BF_4$ (**260**) in which the mutually *trans* Os–N(tpy) bonds are on average ca. 0.05 Å longer than that *trans* to $NO^+$ [287]. The data for **259** show that the STE of $N^{3-}$ is much larger than that of a $\eta^1$-phenyl ligand, which itself exerts relatively large STEs (Section 4.1.3). Complexes **246** and **248** are rare examples of octahedral nitrido complexes of first-row transition metals which are stabilised by the chelating ligands tacn or $Me_3$tacn [274].

Nitrido ligands also exert large STEs when adopting a bridging co-ordination mode. For example, $(NH_4)_3[Ta_2^VNBr_{10}]$ (**261**) features a $\{Ta{=}N{=}Ta\}^{7+}$ core, and the axial Ta–Br bond distance [2.738(6) Å] is ca. 0.22 Å longer than the corresponding equatorial distance [288]. An even larger STE is observed in $(PPh_4)_2[Mo_2NCl_9]_2$ (**262**) which contains two $\{Cl_4Mo^{VI}{\equiv}N{-}Mo^{V}Cl_5\}^+$ units; the average $Mo{-}Cl_{bridge}$ distances are 2.427(2) Å (*trans* to $Cl^-$) and 2.866(2) Å (*trans* to N), giving a difference of ca. 0.44 Å [289].

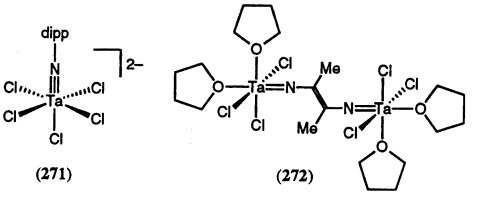



*4.3.3. Imido ligands*

Imido ligands usually bind to transition metals in a pseudo-linear fashion, which can generally be understood as involving an sp-hybridized nitrogen atom in a M≡N–R bonding arrangement [290]. $RN^{2-}$ groups hence act as 6-electron donors and are sometimes referred to as *nitrenes* [273].



The extent of the STEs caused by imido ligands varies greatly. Early crystallographic studies on the $d^2$ complexes *mer*,*trans*-$Re^{V}(NR)Cl_3(PEt_2Ph)_2$ (R = $C_6H_4$-4-OMe **263** or $C_6H_4$-4-COMe **264**) [291] and *mer*,*trans*-$Re^{V}(NMe)Cl_3(PEtPh_2)_2$ (**265**) [292] revealed no significant STEs, but many subsequent investigations have detected pronounced effects. A comparison of results available in 1986 suggested a correlation with the d-configuration of the complexed metal ion, i.e. 'the magnitude of the STE exerted by organoimido ligands in pseudo-octahedral species... decreases as follows: 16-electron, $d^0$ (ca. 0.20–0.25 Å) > 17-electron, $d^1$ (ca. 0.06–0.10 Å) > 18-electron, $d^2$ (ca. 0.00 Å)' [293]. Since this time, many more imido complexes have been structurally characterised, and selected data are given in Table 18.



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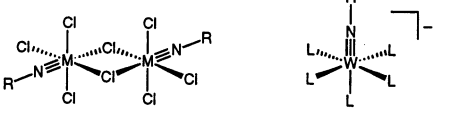
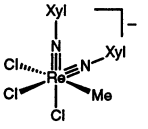


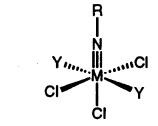
M = Mo, R = $^t$Bu (273)
M = W, R = $^i$Pr (274)



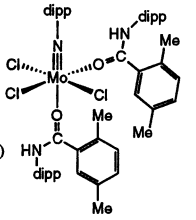
R = $^i$Pr, L = $Cl^-$ (275)
R = $CBr_3$, L = $Br^-$ (276)
R = Tol, L = $Cl^-$ (277)



(278)



M = Mo, R = Tol, Y = $PEtPh_2$ (279)
M = W, R = Ph, Y = $PPh_3$ (281)
M = W, R = $^i$Pr, Y = $H_2N^iPr$ (282)
M = W, R = dipp, Y = $PMe_3$ (284)
M = Tc, R = Ph, Y = $PPh_3$ (288)
M = Re, R = Ph, Y = $PPh_3$ (289)



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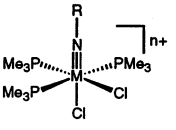
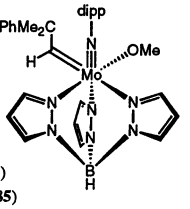
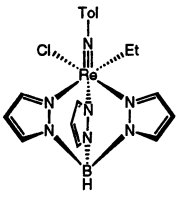


M = W, R = Cy, n = 1 (283)
M = Mo, R = $^t$Bu, n = 0 (285)
M = W, R = Cy, n = 0 (287)



(286)



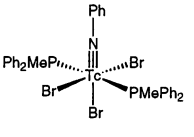
(291)

Table 18
Selected crystallographic data for imido complexes [a]

| No. | Compound | $n$ [b] | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **266** | $Ti^{IV}(N^tBu)Cl(^iPr_3Tp)(4\text{-}^tBupy)$ | 0 | $N^tBu^{2-}$ | $^iPr_3Tp$ | 2.417(6) | 2.208(6) (*trans* Cl) | 0.21 | [294] |
| | | | | | | 2.176(7) (*trans* N) | 0.24 | [294] |
| **267** | *trans,mer*-$Ti^{IV}(NTol)Cl_2(py)_3$ | 0 | $NTol^{2-}$ | py | 2.428(4) | 2.227(2) | 0.20 | [295] |
| **268** | $[V^V(NPh)Cl_3(CN^tBu)]_2$ | 0 | $NPh^{2-}$ | μ-$Cl^-$ | 2.681(1) | 2.351(1) | 0.33 | [124] |
| **269** | *mer*-$Ta^V(NOMe)Cl_3(bpy)$ | 0 | $NOMe^{2-}$ | bpy | 2.299(3) | 2.229(3) | 0.07 | [296] |
| **270** | $Ta^V(Ndipp)Cl(Tp^*)(O^nBu)$ | 0 | $Ndipp^{2-}$ | Tp* | 2.377(7) | 2.267(6) (*trans* O) | 0.11 | [297] |
| | | | | | | 2.198(6) (*trans* Cl) | 0.18 | [297] |
| **271** | $(^tBu\text{-}pyH)_2[Ta^V(Ndipp)Cl_5]$ | 0 | $Ndipp^{2-}$ | $Cl^-$ | 2.695(3) | 2.419(6) | 0.28 | [298] |
| **272** | *cis,mer*-$[Ta^VCl_3(thf)_2]_2(\mu\text{-}NC_4H_6N)$ | 0 | μ-$NC_4H_6N^{4-}$ | thf | 2.356(6) | 2.151(5) | 0.21 | [299] |
| **273** | $[Mo^{VI}(N^tBu)Cl_4]_2$ | 0 | $N^tBu^{2-}$ | μ-$Cl^-$ | 2.727(1) | 2.456(1) | 0.27 | [300] |
| **274** | $[W^{VI}(N^iPr)Cl_4]_2{\cdot}C_6H_6$ | 0 | $N^iPr^{2-}$ | μ-$Cl^-$ | 2.736(5) | 2.418(4) | 0.32 | [301] |
| **275** | $(NEt_4)[W^{VI}(N^iPr)Cl_5]$ | 0 | $N^iPr^{2-}$ | $Cl^-$ | 2.462(5) | 2.346(3) | 0.11 | [301] |
| **276** | $(PMePh_3)[W^{VI}(NCBr_3)Br_5]$ | 0 | $NCBr_3^{2-}$ | $Br^-$ | 2.601(3) | 2.483(5) | 0.12 | [302] |
| **277** | $(PBzPh_3)[W^{VI}(NTol)Cl_5]$ | 0 | $NTol^{2-}$ | $Cl^-$ | 2.451(2) | 2.347(2) | 0.10 | [303] |
| **278** | *cis,fac*-$(XylNH_3)[Re^{VII}(NXyl)_2Cl_3(Me)]$ | 0 | $NXyl^{2-}$ | $Cl^-$ | 2.545(3) | 2.447(1) | 0.10 | [304] |
| **279** | *mer,trans*-$Mo^V(NTol)Cl_3(PEtPh_2)_2$ | 1 | $NTol^{2-}$ | $Cl^-$ | 2.486(2) | 2.387(3) | 0.10 | [293] |
| **280** | *mer,cis*-$Mo^V(Ndipp)Cl_3(dippdb)_2$ | 1 | $Ndipp^{2-}$ | dippdb | 2.239(5) | 2.102(5) | 0.14 | [305] |
| **281** | *mer,trans*-$W^V(NPh)Cl_3(PPh_3)_2$ | 1 | $NPh^{2-}$ | $Cl^-$ | 2.443(3) | 2.387(4) | 0.06 | [306] |
| **282** | *mer,trans*-$W^V(N^iPr)Cl_3(H_2N^iPr)_2$ | 1 | $N^iPr^{2-}$ | $Cl^-$ | 2.473(2) | 2.407(1) | 0.07 | [307] |
| **283** | *cis,mer*-$[W^V(NCy)Cl_2(PMe_3)_3]CF_3SO_3$ | 1 | $NCy^{2-}$ | $Cl^-$ | 2.480(4) | 2.411(6) | 0.07 | [308] |
| **284** | *mer,trans*-$W^V(Ndipp)Cl_3(PMe_3)_2$ | 1 | $Ndipp^{2-}$ | $Cl^-$ | 2.490(2) | 2.385(4) | 0.11 | [309] |
| **285** | *cis,mer*-$Mo^{IV}(N^tBu)Cl_2(PMe_3)_3$ | 2 | $N^tBu^{2-}$ | $Cl^-$ | 2.552(2) | 2.508(2) | 0.04 | [310] |
| **286** | $Mo^{IV}(Ndipp)Tp(OMe)\{C(H)CMe_2Ph\}$ | 2 | $Ndipp^{2-}$ | Tp | 2.33(1) | 2.295(8) (*trans* C) | 0.03 | [311] |
| | | | | | | 2.232(8) (*trans* O) | 0.10 | [311] |
| **287** | *cis,mer*-$W^{IV}(NCy)Cl_2(PMe_3)_3$ | 2 | $NCy^{2-}$ | $Cl^-$ | 2.507(6) | 2.522(6) | −0.02 | [308] |
| **288** | *mer,trans*-$Tc^V(NPh)Cl_3(PPh_3)_2{\cdot}CH_2Cl_2$ | 2 | $NPh^{2-}$ | $Cl^-$ | 2.414(2) | 2.410(3) | 0.00 | [312] |
| **289** | *mer,trans*-$Re^V(NPh)Cl_3(PPh_3)_2{\cdot}0.5CHCl_3$ | 2 | $NPh^{2-}$ | $Cl^-$ | 2.411(2) | 2.411(2) | 0.00 | [313] |
| **290** | *mer*-$Re^V(NPh)Cl_3(bpy)$ | 2 | $NPh^{2-}$ | bpy | 2.243(9) | 2.087(8) | 0.16 | [314] |
| **291** | $Re^V(NTol)(Et)Cl(Tp)$ | 2 | $NTol^{2-}$ | Tp | 2.248(4) | 2.146(4) (*trans* C) | 0.10 | [315] |
| | | | | | | 2.111(4) (*trans* Cl) | 0.14 | [315] |

[a] Details as for Tables 1 and 2.
[b] $n$ = formal d-count of metal ion.

It can be seen that although some $d^0$ imido complexes show very large STEs, the aforementioned apparent trend is only partially true. In particular, the largest effects are found in $d^0$ binuclear chloride-bridged complexes (e.g. **268**, **273**, **274**), and mononuclear $d^0$ complexes generally show smaller STEs. Comparison of the W–N bond distances indicates that the smaller STE in **275** with respect to its binuclear analogue **274** is associated with a decrease in W–N π-bonding. Although $d^2$ complexes often show little or no imido STE, in others the effects are of similar magnitude to those observed in $d^1$ or $d^0$ complexes. However, in certain $d^2$ complexes, the imido STE is found to be even weaker than that of a halide ion. For example, in *mer*,*trans*-$Tc^{V}(NPh)Br_3(PMePh_2)_2$ (**292**) the Tc–Br bond *trans* to the $NPh^{2-}$ group [2.498(4) Å] is ca. 0.08 Å shorter than the average of the mutually *trans* Tc–Br bond distances [2.573(4) Å] [316]. A recent approximate density functional theory study on the series *mer*,*trans*-$[Mo(NH)Cl_3(PR_3)_2]^{n+}$ (**293**, R = H, Me or F; $n = 0, \pm 1$) suggests that the STE of the $NH^{2-}$ ligand is unaffected by the molybdenum oxidation state, but is obscured in the $d^2$ Mo(IV) complex by a concomitant lengthening of the equatorial Mo–Cl bonds [27].

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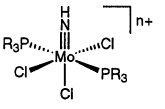


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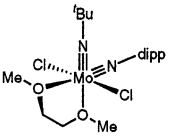



(294)

Limited studies have been carried out to assess the effect of the imido substituent on bonding properties. The Mo–O bonds in *cis*,*trans*-$Mo^{VI}(N^tBu)(Ndipp)Cl_2(dme)$ (**294**) of 2.392(1) Å (*trans* to $N^tBu^{2-}$) and 2.330(2) Å (*trans* to $Ndipp^{2-}$) show that the *t*-butylimido ligand exerts the stronger STE [317]. By contrast, in the series *trans*,*mer*-$Ti^{IV}(NR)Cl_2(py)_3$ [R = $^t$Bu, Ph, Tol (**267**), $C_6H_4$-4-$NO_2$], the STE of the imido ligand shows little dependence on R, and relative extensions of the *trans* Ti–N(py) bonds compared with the *cis* Ti–N(py) bonds are in the range ca. 0.18–0.20 Å [295].

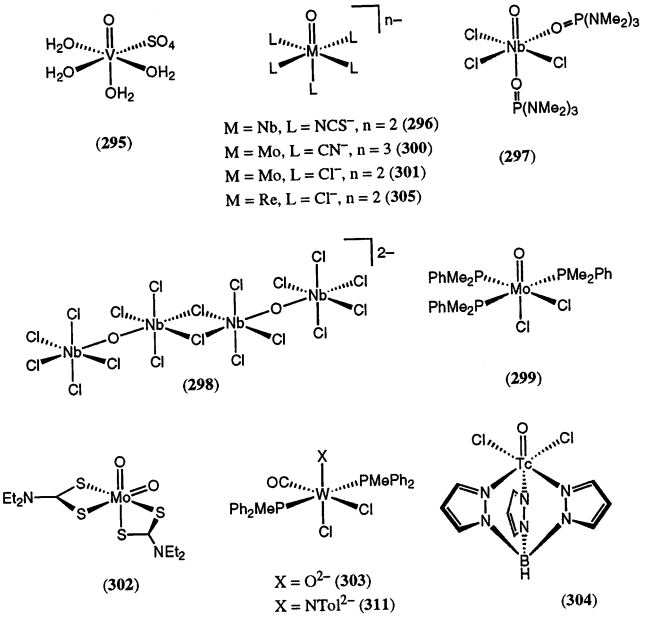
### 4.3.4. Oxide

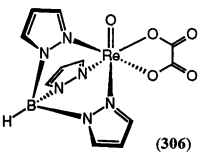
Oxygen ions are isoelectronic with $CR^{3-}$, $N^{3-}$, and $RN^{2-}$ and form formal triple bonds to transition metal ions. However, electron donation from the more electronegative $O^{2-}$ is less extensive than that from the other ligands, and the bonding is hence usually depicted as 'M=O'. The large STEs of oxo ligands were first noted in 1964 [318], and since then many cases have been documented. As with $N^{3-}$, the *cis* bonds are invariably distorted away from the M=O unit, and the pronounced STEs of $O^{2-}$ explain the existence of many square pyramidal oxo complexes [319]. Crystallographic data for selected octahedral oxo complexes are given in Table 19.

Table 19
Selected crystallographic data for oxo complexes [a]

| No. | Compound | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **295** | *cis*-$V^{IV}O(SO_4)(H_2O)_4·H_2O$ | $H_2O$ | 2.223(5) | 2.040(9) | 0.18 | [320] |
| **296** | $(AsPh_4)_2[Nb^{V}O(NCS)_5]$ | $NCS^-$ | 2.27(4) | 2.09(8) | 0.18 | [321] |
| **297** | *mer*,*cis*-$Nb^{V}OCl_3(hmpa)_2$ | hmpa | 2.243(4) | 2.048(5) | 0.20 | [322] |
| **298** | $(C_4Ph_4Cl)_2[Nb_2^{V}OCl_9]_2$ | $Cl^-$ | 2.697(2) | 2.483(2) | 0.21 | [323] |
| **299** | *cis*,*mer*-$Mo^{IV}OCl_2(PMe_2Ph)_3$ | $Cl^-$ | 2.551(3) | 2.464(3) | 0.09 | [324] |
| **300** | $(PPh_4)_3[Mo^{IV}O(CN)_5]·7H_2O$ | $CN^-$ | 2.373(6) | 2.18(1) | 0.19 | [325] |
| **301** | $K_2[Mo^{V}OCl_5]$ | $Cl^-$ | 2.63 | 2.40 | 0.23 | [326] |
| **302** | *cis*-$Mo^{VI}O_2(dedtc)_2$ | dedtc | 2.639(1) | 2.450(1) | 0.19 | [327] |
| **303** | *cis*,*trans*-$W^{IV}OCl_2(CO)(PMePh_2)_2$ | $Cl^-$ | 2.504(2) | 2.411(3) | 0.09 | [328] |
| **304** | $Tc^{V}OCl_2Tp$ | Tp | 2.259(4) | 2.087(4) | 0.17 | [329] |
| **305** | $K_2[Re^{V}OCl_5]$ | $Cl^-$ | 2.47 | 2.39 | 0.08 | [25] |
| **306** | $Re^{V}O(Tp)(\eta^2\text{-}C_2O_4)·0.5C_6H_6$ | Tp | 2.258(7) | 2.064(7) | 0.19 | [330] |
| **307** | *cis*-$NEt_4[Re^{VII}O_2(OTeF_5)_4]$ | $OTeF_5^-$ | 2.05(1) | 1.94(1) | 0.11 | [331] |
| **308** | $[Ru^{VI}O_2(CF_3CO_2)(Me_3tacn)]ClO_4$ | $Me_3tacn$ | 2.21(3) | 2.097(9) | 0.11 | [332] |

[a] Details as for Tables 1 and 2.





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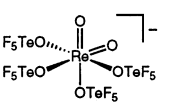

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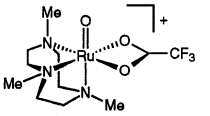
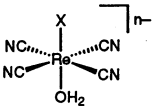


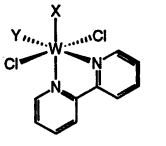
(308)

The STE order imido < oxo < nitrido has been proposed [25], but this was based upon limited structural data, particularly for nitrido and imido complexes. Whilst $N^{3-}$ ligands clearly cause larger STEs than $O^{2-}$, e.g. the Re–$OH_2$ bond distance in *trans*-$(AsPh_4)_2[Re^{V}N(CN)_4(H_2O)]\cdot 5H_2O$ (**309**) [2.496(7) Å] [333] is much longer than that in *trans*-$NEt_4[Re^{V}O(CN)_4(H_2O)]\cdot 2H_2O$ (**310**) [2.142(7) Å] [334], analysis of recent results (Section 4.3.3) indicates that the STEs of imido ligands are often of similar magnitude or even slightly larger than those of $O^{2-}$.

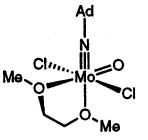


X = $N^{3-}$, n = 2 (**309**)
X = $O^{2-}$, n = 1 (**310**)

In the tolylimido analogue of **303**, *cis*,*trans*-$W^{IV}(NTol)Cl_2(CO)(PMePh_2)_2$ (**311**) the W–Cl bond distance *trans* to $NTol^{2-}$ is 2.476(2) Å, whilst that *trans* to CO is 2.455(2) Å, indicating the STE order $CO < NTol^{2-} < O^{2-}$ [328]. However, in the mixed oxo-imido complex *cis*,*trans*-$W^{VI}(N^{t}Bu)OCl_2bpy$ (**312**), the W–N(bpy) bond distances are 2.313(5) Å (*trans* to O) and 2.335(5) Å (*trans* to N) [335]. Furthermore, the average W–N(bpy) bond distance in *cis*,*trans*-$W^{VI}(N^{t}Bu)_2Cl_2bpy$ (**313**) is 2.372(7) Å [335], whilst that in *cis*,*trans*-$W^{VI}O_2Cl_2(bpy)$ (**314**) is 2.276(4) Å [336]. These data clearly indicate that $N^{t}Bu^{2-}$ exerts a greater STE than $O^{2-}$, although it has been suggested that the donor ability of the oxo ligand in such complexes may be reduced by hydrogen-bonding [335]. However, further evidence for the greater STE of alkylimido ligands is found in *cis*,*trans*-$Mo^{VI}(NAd)OCl_2dme$ (**315**) in which the Mo–O bond distances are 2.346(1) Å (*trans* to O) and 2.356(1) Å (*trans* to N) [317]. Taking these results, together with the observation that the STE of $N^{t}Bu^{2-}$ is considerably larger than that of $Ndipp^{2-}$ in **294** [317], suggests the STE order $NAr^{2-} < O^{2-} < NR^{2-}$ (Ar = aryl, R = alkyl).



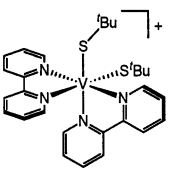
X = $N^{t}Bu^{2-}$, Y = $O^{2-}$ (**312**)
X = Y = $N^{t}Bu^{2-}$ (**313**)
X = Y = $O^{2-}$ (**314**)



(315)

*4.3.5. Sulfide*

Sulfide ions co-ordinate to high-oxidation-state transition metal ions in analogous fashion to oxide ions, forming M=S 'double' bonds. Although relatively little structural data for such complexes is available, and in a number of cases disorder between $S^{2-}$ and $Cl^{-}$ prevents the determination of accurate bond lengths, sulfido ligands clearly cause large STEs (Table 20). In common with related strong π-donor ligands, $S^{2-}$ causes distortion of the *cis* bonds away from the M=S unit.

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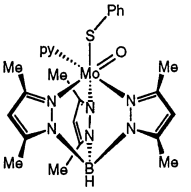


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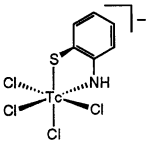


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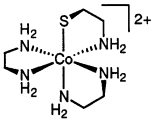


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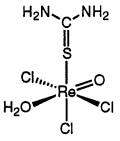


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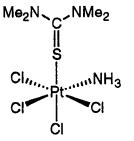



(337)

Complexes **321** and **324** allow direct comparisons of the STEs of the $S^{2-}$ and $O^{2-}$ ligands. In **321** the W–N bond *trans* to oxo of 2.31(2) Å is possibly longer than that *trans* to sulfido [342], indicating that the latter exerts a slightly weaker STE on the $W^{IV}$–N(Tp*) bond. By contrast, the sulfido group perhaps has a slightly larger

Table 20
Selected crystallographic data for sulfido complexes [a]

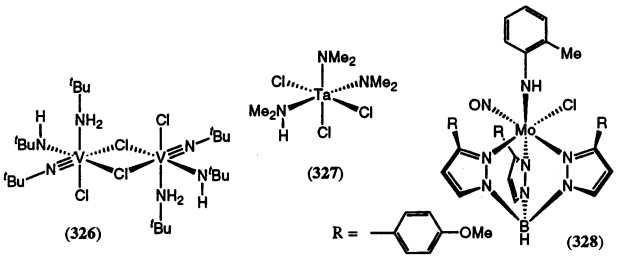
| No. | Compound | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|
| | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **316** | *mer*,*cis*-$Nb^{V}SBr_3(tht)_2$ | tht | 2.84(2) | 2.69(2) | 0.15 | [337] |
| **317** | *mer*-$Ta^{V}SCl_3$bpte | bpte | 2.836(4) | 2.705(5) | 0.13 | [338] |
| **318** | $Mo^{IV}S$(Tp*)($\eta^2$-$S_2CNEt_2$)·$CH_2Cl_2$ | Tp* | 2.435(5) | 2.181(6) | 0.25 | [339] |
| **319** | $W^{IV}S$(Tp*)($\eta^2$-$S_2CNEt_2$) | Tp* | 2.408(6) | 2.186(9) | 0.22 | [340] |
| **320** | $W^{IV}S$(Tp*)(CO){*S*P(S)$Ph_2$} | Tp* | 2.29(1) | 2.18(1) (*trans* C) | 0.11 | [341] |
| **321** | $W^{IV}O$(S)(Tp*)men | Tp* | 2.26(1) | 2.18(1) (*trans* men) | 0.08 | [342] |
| **322** | *mer*-$W^{V}SCl_3$bmte | bmte | 2.668(9) | 2.560(6) | 0.11 | [343] |
| **323** | ($PPh_3Bz$)[$W^{VI}SCl_5$] | $Cl^{-}$ | 2.46(1) | 2.30(2) | 0.16 | [344] |
| **324** | *cis*-($PPh_4$)$_2$[$W^{VI}$O(S)(*N*CS)$_4$]·MeCN | *N*CS$^{-}$ | 2.211(6) | 2.189(8) (*trans* O) | 0.02 | [345] |
| | | | | 2.07(1) (*trans* N) | 0.14 | [345] |
| **325** | PPN[$W^{VI}SF_5$]·MeCN | $F^{-}$ | 1.963(3) | 1.873(5) | 0.09 | [346] |

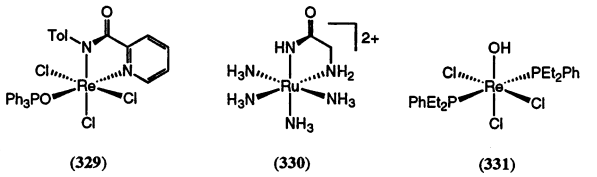
[a] Details as for Tables 1 and 2.

STE on the $W^{VI}$–NCS bond in **324** [345]. It is hence apparant that the STEs of these closely related ligands are very similar and their relative magnitudes may depend upon the nature of the metal centre and the ligand being affected.

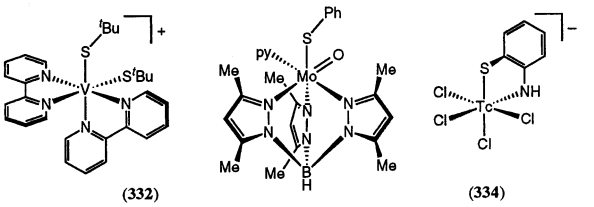
*4.3.6. Miscellaneous π-donor ligands*

Various other species such as amido ($HNR^-$), hydroxo ($OH^-$), thiolato ($SR^-$) and thione ($S{=}CR_2$) ligands are capable of acting as π-donors and can exert moderate STEs in high-oxidation-state complexes (Table 21).




The binuclear $d^0$ complex **326** is an interesting example of a complex containing amino, amido and imido ligands, and hence allows a comparison of the relative bonding properties and STEs of these three groups. The V–N bond distances and V–N–C bond angles in **326** are as follows: 2.163(3) Å and 130.6(2)° (to amino ligand); 1.842(2) Å and 143.6(3)° (to amido ligand); 1.624(3) Å and 164.2(3)° (to imido ligand) [347]. The decreasing V–N bond distances and increasing V–N–C bond angles confirm expectations that the extent of $N \rightarrow V^V$ π-donation increases in the order $H_2N^tBu < HN^tBu^- < N^tBu^{2-}$, and the STE increases accordingly.



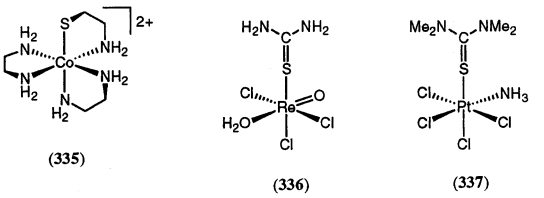



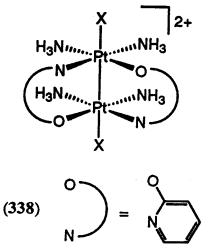
Table 21
Selected crystallographic data for complexes of amido, hydroxo, thiolato and thione ligands [a]

| No. | Compound | X | L | Bond distances (Å) | | Δ (Å) | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | $M–L_{trans}$ | $M–L_{cis}$ | | |
| **326** | *cis*-$[V^{V}(N^{t}Bu)Cl_2(HN^{t}Bu)(H_2N^{t}Bu)]_2$·2MeCN | $HN^{t}Bu^{-}$ | $Cl^{-}$ | 2.533(1) | 2.681(1) (*trans* $N^{t}Bu$) | −0.15 | [347] |
| | | | | | 2.393(1) (*trans* $H_2N^{t}Bu$) | 0.14 | [347] |
| **327** | *mer*,*cis*-$Ta^{V}Cl_3(NMe_2)_2(HNMe_2)$ | $NMe_2^{-}$ | $Cl^{-}$ | 2.450(2) | 2.400(3) | 0.05 | [348] |
| **328** | $Mo^{II}Cl(Mp_3Tp)mpa(NO)$ | $mpa^{-}$ | $Mp_3Tp$ | 2.259(9) | 2.201(7) (*trans* Cl) | 0.06 | [349] |
| **329** | *mer*-$Re^{IV}Cl_3(tamp)(OPPh_3)$·$0.5C_6H_6$ | $tamp^{-}$ | $Cl^{-}$ | 2.385(3) | 2.325(4) | 0.06 | [350] |
| **330** | $[Ru^{III}(glyca)(NH_3)_4](PF_6)_2$ | $glyca^{-}$ | $NH_3$ | 2.161(5) | 2.120(9) | 0.04 | [351] |
| **331** | *mer*,*trans*-$Re^{IV}Cl_3(OH)(PEt_2Ph)_2$ | $OH^{-}$ | $Cl^{-}$ | 2.428(2) | 2.377(3) | 0.05 | [352] |
| **332** | *cis*-$[V^{III}(S^{t}Bu)_2(bpy)_2][V^{III}(S^{t}Bu)_4]$·$C_6H_6$ | $S^{t}Bu^{-}$ | bpy | 2.20(2) | 2.13(2) | 0.07 | [353] |
| **333** | $Mo^{IV}O(Tp^{*})(SPh)py$·0.6MeOH | $SPh^{-}$ | $Tp^{*}$ | 2.194(7) | 2.144(6) (*trans* py) | 0.05 | [354] |
| **334** | $N(^{n}Bu)_4[Tc^{V}Cl_4abt]$ | $abt^{-}$(S) | $Cl^{-}$ | 2.390(2) | 2.323(3) | 0.07 | [355] |
| **335** | *cis*-$[Co^{III}(H_2NC_2H_4S)(en)_2](SCN)_2$ | $H_2NCH_2S^{-}$ | en | 2.001(5) | 1.960(9) | 0.04 | [356] |
| **336** | *mer*,*trans*-$Re^{V}OCl_3(H_2O)tu$ | tu | $Cl^{-}$ | 2.425(7) | 2.366(9) | 0.06 | [357] |
| **337** | *cis*-$Pt^{IV}Cl_4(NH_3)tmtu$ | tmtu | $Cl^{-}$ | 2.370(1) | 2.312(2) | 0.06 | [358] |

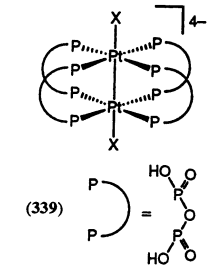
[a] Details as for Tables 1 and 2.

### 4.4. STEs in metal–metal bonded complexes

Since the presence of a quadruple Re–Re bond in $[Re_2^{III}Cl_8]^{2-}$ was recognised in 1964, numerous complexes containing metal–metal bonds have been studied, many of which feature two (or three) octahedrally co-ordinated metal ions [359,360]. A number of the structural studies on such complexes have featured a consideration of STEs, both those of the axial ligands and those of the metal–metal bonded units themselves. For example, the Pt–Pt single bond distances in the compounds $[Pt_2^{III}X_2(pyd)_2(NH_3)_4](NO_3)_2{\cdot}nH_2O$ (**338**) are as follows: 2.547(1) Å ($X = ONO_2^-$, $n = 0.5$) [361], 2.568(1) Å ($X = Cl^-$, $n = 0$) [362], 2.576(1) ($X = NO_2^-$, $n = 0.5$) [362] and 2.582(1) ($X = Br^-$, $n = 0.5$) [362].




These data afford the STE series $X = ONO_2^- < Cl^- < NO_2^- \leq Br^-$ [362], which parallels the established order for these ligands in square planar Pt(II) complexes. Furthermore, the axial Pt–X bonds in these complexes are ca. 0.10–0.15 Å longer than the expected values, showing that the $\{Pt_2\}^{6+}$ unit exerts a large STE on the axial ligands [362]. Crystallographic studies on the pyrophosphito complex salts $Y_4[Pt_2^{III}(P_2O_5H_2)_4X_2]$ (**339**) afford the Pt–Pt distances 2.695(1) Å ($Y = K^+$, $X = Cl^-$), 2.716(1) Å ($Y = {}^nBu_4N^+$, $X = Br^-$) and 2.754(1) Å ($Y = K^+$, $X = I^-$), giving the STE series $X = Cl^- < Br^- < I^-$ which follows increasing σ-donor strength [363]. From IR data it was estimated that the STE of the $\{Pt_2\}^{6+}$ unit is greater than those of halide ions, but weaker than those of $H^-$, $Me^-$ or $Ph^-$ ligands [363]. Further structural studies with such complexes allow extension of this STE series to $X = Cl^- < Br^- < im^- < I^- = NO_2^- \leq SCN^- < Me^-/I^-$ [364].



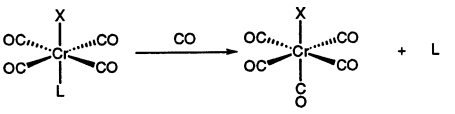
## 5. Kinetic trans-effects in octahedral metal complexes

Although a STE destabilises a complex in the ground state, this will enhance reactivity towards ligand substitutions only if there is no effect on the energy of the transition state. This is sometimes the case for dissociatively activated substitutions, and the STE and KTE ligand series of a particular complex will then be similar. However, if the transition state energy is affected by the ligand in question, then there may be no correlation between STEs and KTEs. This is commonly observed in substitution reactions of square planar complexes which react via associative mechanisms [2,3]. A general KTE sequence for such complexes has been established as follows: $H_2O < OH^- < NH_3 \approx RNH_2 < py < Cl^- < Br^- < I^- \approx SCN^- \approx NO_2^- < SO_3H^- < PR_3 \approx SR_2 \approx tu \approx Me^- < NO^- \approx \eta^2\text{-}C_2H_4 \approx CO \approx CN^-$ [11].

Kinetic data for ligand substitution reactions are most often obtained via spectrophotometric methods, but NMR and other techniques may also be used. Substantial studies of KTEs in octahedral complexes are relatively scarce by comparison with reports concerning STEs. This is largely because ground state phenomena are more readily understood, and the complete explanation of kinetic properties requires knowledge of ligand substitution reaction mechanisms. Early work on KTEs in octahedral Co(III) and Pt(IV) complexes has been reviewed previously [1,12].

### 5.1. Chromium(0) complexes

The first-order kinetics and activation parameters for the reactions shown in Scheme 1 indicate that dissociation of L is the rate determining step [365]. Comparison of $k_1$ (the first-order rate constant for ligand dissociation) values yields the following KTE series for loss of either $PPh_3$ or $P(OPh)_3$: $CO < P(OMe)_3 \approx P(OPh)_3 < P(^nBu)_3 < PPh_3$. In the case of $L = P(OPh)_3$ the relative rate enhancement moving from $X = CO$ to $X = PPh_3$ is ca. $2 \times 10^4$. It was suggested that these widely differing KTEs arise from electronic rather than steric factors [365]. As discussed earlier (Section 4.2.11), X-ray crystallographic data for *trans*-$Cr^0(CO)_4(PPh_3)X$ [$X = P(^nBu)_3$ (**202**), $P(OMe)_3$ (**203**), $P(OPh)_3$ (**204**), CO (**205**)] afford the STE order $P(^nBu)_3 < P(OMe)_3 < P(OPh)_3 < CO$, which was ascribed to competitive π-acceptance [238]. Since this order is almost the reverse of that found for KTEs, the dissociation rate acceleration caused by the phosphine ligands must arise from a transition state stabilisation effect [365]. The postulate is that a



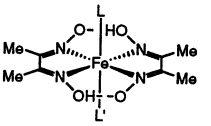

**X = $PPh_3$, $P(^nBu)_3$, $P(OMe)_3$, $P(OPh)_3$, CO**
**L = $PPh_3$, $P(OPh)_3$,**

Scheme 1.

σ-donor ligand stabilises the five-co-ordinate transition state and hence favours dissociation of a *trans* ligand [366]. However, although $P(^nBu)_3$ is clearly the strongest σ-donor of the ligands investigated, $PPh_3$ actually exerts the larger KTE [366]. This apparent anomaly is accounted for by the fact that $P(^nBu)_3$ also causes a large ground state stabilisation of the *trans* Cr–P bond which offsets the effect of the accompanying transition state stabilisation [366].

### 5.2. Iron(II) complexes

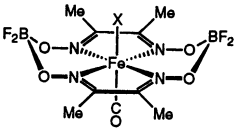
It has been known for some time that low-spin Fe(II) complexes of TPP and related ligands undergo ligand substitutions via a dissociative mechanism and that CO exerts a trans-delabilising effect on ligands such as im [367,368]. This is in stark contrast with square planar Pt(II) complexes in which CO exerts a marked KTE [11]. Kinetic studies with Fe(II) complexes of other tetraazamacrocylic ligands have also shown that both CO and benzylisocyanide (BzNC) have a trans-delabilising effect on MeCN [369]. Extensive axial ligand substitution experiments with complexes *trans*-$Fe^{II}(dmgH)_2L(L')$ [**340**; L, L′ = mim, py, $P(^nBu)_3$, $P(O^nBu)_3$, BzNC, $TosCH_2NC$, CO] confirm the existence of a dissociative mechanism and yield the general KTE order $CO < TosCH_2NC \leq BzNC < P(O^nBu)_3 < P(^nBu)_3 < mim < py$ (no dissociation observed *trans* to CO) [370].




**(340)**

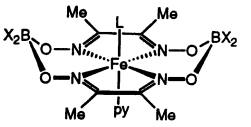
For loss of either py or mim, this KTE sequence correlates with decreasing energy of the $Fe^{II} \rightarrow \pi^*$(dmgH) MLCT band, which is an indicator of the π-acceptor ability of the axial ligands [370]. Hence, the KTE of L/L′ increases as π-acceptor ability decreases. The KTEs of substituted pyridines depend upon the nature of the leaving group. For loss of the weakly π-accepting py, the strongly σ-donating 4-$Me_2$Npy is trans-labilising compared to 4-CNpy, but the situation is reversed for the strong π-acceptor CO which is less labile *trans* to 4-$Me_2$Npy [370]. Similar results have been obtained with related complexes of other dioximato ligands [371].

Subsequent studies in this area have focused on flash-photolysis kinetic studies of borylated Fe(II) bis(dioximato) complexes. For example, experiments involving CO dissociation from complexes *trans*-$Fe^{II}(dmgBF_2)_2X(CO)$ (**341**) afford the KTE order $X = mim < CN^- < py < MeCN \approx 2\text{-mim} < Cl^- \approx Br^-$ [372], and for loss of MeCN the order is $CN^- < NCS^- < Cl^- < Br^-$, which correlates with increasing π-donor capacity [373].




**(341)**

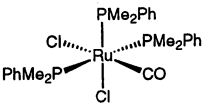
As expected for complexes of π-acceptor ligands, the KTEs in these complexes do not correlate with STEs observed crystallographically. For example, the Fe–N(py) bond distances in *trans*-$Fe^{II}(dmgBX_2)_2(py)_2$ (**342**) are 2.048(5) Å (X = F) and 2.051(5) Å (X = Ph) [374], whilst those in *trans*-$Fe^{II}(dmgBX_2)_2(CO)py$ (**343**) are 2.055(5) Å (X = F) and 2.067(8) Å (X = Ph) [375]. Although CO does not cause any shortening of the Fe–N(py) bonds, py is at least $10^6$ times less labile when *trans* to CO than when *trans* to itself [375].



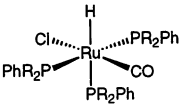

**L = py (342), L = CO (343)**

*5.3. Ruthenium(II) complexes*

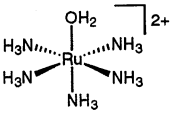
Early reactivity studies between the complex *cis*,*mer*-$Ru^{II}Cl_2(CO)(PMe_2Ph)_3$ (**344**) and $I^-$ showed that the chloride ligand *trans* to $PMe_2Ph$ is replaced much more rapidly than is that *trans* to CO [376]. The greater KTE of the phosphine ligand was ascribed to its stronger σ-donor strength when compared to the very weakly basic CO [376]. The ease of selective substitution by phosphane or arsine ligands of the $PR_2Ph$ ligand *trans* to $H^-$ in the complexes *cis*,*mer*-$Ru^{II}Cl(H)(CO)(PR_2Ph)_3$ (**345**; R = Et, $^n$Pr, $^n$Bu) provides clear evidence for the pronounced KTE of the strongly σ-donating hydrido ligand [377].




**(344)**

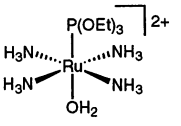



**(345)**




**(346)**

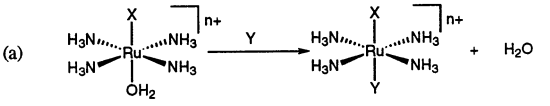
A number of detailed kinetic studies have been carried out with Ru(II) ammine complexes. An early investigation into the reactions of $[Ru^{II}(NH_3)_5(H_2O)]^{2+}$ (**346**) in aqueous solution showed that the aquo substitution rates and activation parameters are essentially constant for a variety of neutral unhindered *N*-ligands, indicating a dissociative mechanism [378]. Sterically hindered ligands yield slower reaction rates, whilst anions react much faster [378]. Subsequent studies have confirmed that the mechanistic details of such reactions are influenced by the nature of the incoming ligand, and a recent volume-profile analysis of the aquo-substitution reactions of *trans*-$[Ru^{II}(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$ (**347**) [379] agrees with an earlier suggestion [380] that a dissociative interchange ($I_d$) mechanism is operative.



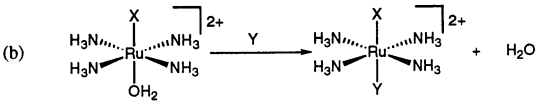

**(347)**

Investigations into the reactions shown in Scheme 2(a) revealed that the sulfito complex reacts ca. 250–300 times faster than **346** [381], showing that $SO_3^{2-}$ exerts a much larger KTE than does $NH_3$. Furthermore, the KTE series $X = SO_2 < SO_3H^- < SO_3^{2-}$ was apparent, although the rate differences are not large. This ordering was ascribed to the increasing σ-donor ability of X [381]. These kinetic experiments were subsequently extended to encompass a wide range of ligands, affording the following KTE series with isn as the incoming ligand: $CO \approx N_2 <$ isn < py < imN < $NH_3 < OH^- < P(OEt)_3 < CN^- < SO_3^{2-} <$ imC. The difference between the substitution rates with *trans* CO and *trans* imC is at least a factor of $2 \times 10^7$ [380,382]. As would be expected, the pronounced trans-delabilising effect of CO in these complexes, parallels that found in related Fe(II) complexes (Section 5.2). It was suggested that the first half of this series (i.e. that preceding $NH_3$) can be explained on the basis of π-back-bonding effects, i.e. the KTE of X on $H_2O$ increases with decreasing π-acceptor strength [380,382].

Later kinetic studies with Ru(II) ammine complexes have featured a strong emphasis on phosphane ligands, due in part to the importance of such ligands in tuning the properties of homogeneous catalysts. The results of this work have been reviewed recently [383]. Extensive measurements of $k_1$ for the substitution reactions shown in Scheme 2(b) afford the following KTE order for Y = pyz: $SbPh_3 < AsPh_3$ < etpb ≈ $P(OPh)_3$ < pta < $P(OC_2H_4Cl)_3 \approx PPh_3$ < dppe ≈ $H_2PCy < P(OMe)_3$ < $P(OEt)_3$ < pdmp < $P(O^tBu)_3 \approx P(O^iPr)_3 < P(O^nBu)_3 < P(OH)(OEt)_2 \approx P(OH)_3$ < $P(^nBu)_3 < PEt_3 < P(OH)_2O^- < P(OEt)_2O^-$ [31,383], and a similar but less extensive series was found for Y = isn [31]. For the phosphane ligands a good inverse linear correlation is observed between $k_1$ and the $Ru^{III/II}$ reduction potentials, i.e. the aquo substitution rate decreases as the potential becomes more positive. Hence, the KTE of L is determined primarily by electronic effects and decreases as the metal centre becomes less electron-rich. This corresponds to an




X = $SO_2$, n = 2; X = $SO_3H^-$, n = 1; X = $SO_3^{2-}$, n = 0
Y = pyz, isn



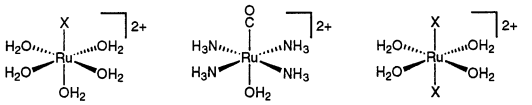

X = phosphane or related ligand
Y = pyz, isn

Scheme 2.

increase in π-acceptor strength accompanied by a decrease in σ-donor strength [31], and is in agreement with the earlier results obtained with other types of neutral ligands [380,382]. Therefore, the more strongly π-accepting phosphites always exhibit a smaller KTE than the corresponding phosphines, e.g. the $PEt_3$ complex reacts some 13 times faster than its $P(OEt)_3$ analogue. These studies have recently been extended to include im as the entering ligand [384], affording the KTE series $SbPh_3 < AsPh_3 < P(^nBu)_3 <$ dppe $\approx PPh_3 < P(OMe)_3 < P(OEt)_3 < P(O^nBu)_3 < P(O^iPr)_3$, which follows that found for entering pyz or isn, with the unexplained exception of $P(^nBu)_3$.

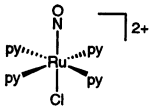
In summary, the available data show that the KTEs of π-acceptor ligands upon $H_2O$ in Ru(II) ammine complexes increase as π-acceptor strength decreases and as σ-donor strength increases. It is likely that the large KTEs of ligands such as as $P(OH)_2O^-$ or $SO_3^{2-}$ are due to their powerful σ-donating properties.

A very recent report concerns the kinetics of water exchange in $[Ru^{II}(H_2O)_5X]^{2+}$ complexes (**348**; X = various neutral ligands) [385]. As with other ligand substitutions at Ru(II) centres, the exchange process is dissociatively activated and values for $k_{ax}$ and $k_{eq}$ (the first-order rate constants for exchange of axial and equatorial $H_2O$, respectively) were determined by using $^{17}O$-NMR. These afford the KTE series MeCN (0.3) < $H_2O$ (1) < CO (2.5) < $Me_2SO$ (45) where the numbers in parentheses represent the ratios $k_{ax}/k_{eq}$ [385]. In contrast to the situation with *trans*-$\{Ru^{II}(NH_3)_4\}^{2+}$ phosphane complexes [31], this KTE series shows no correlation with the $Ru^{III/II}$ redox potentials. Furthermore, the slight trans-labilising effect of CO on $H_2O$ is in marked contrast with the strong trans-delabilisation caused by CO in *trans*-$[Ru^{II}(CO)(NH_3)_4(H_2O)]^{2+}$ (**349**) [383]. Despite attempts using DFT calculations, this apparently anomalous behaviour has not been satisfactorily explained [385]. A subsequent report shows that the rate determining step in the ligand exchange processes in **348** is rupture of the *trans* Ru–$OH_2$ bond which generates *trans*-$[Ru^{II}(H_2O)_4X_2]^{2+}$ intermediates (**350**) [386]. Due to the KTEs of the π-acceptor ligands CO and dmso, these exchange reactions are faster than the reactions to form the complexes **348** from **49** [386].



(348) (349) (350)

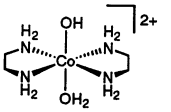
Various studies have shown that the unusual inverse STEs of $NO^+$ are accompanied by trans-delabilising effects. For example, **145** features a relative axial Ru–Cl bond shortening of ca. 0.07 Å (Table 10), and this complex readily reacts with Ag(I) salts to give selective substitution of the equatorial $Cl^-$ ligands [187]. Also, *trans*-$[Ru^{II}Cl(py)_4(NO)](PF_6)_2 \cdot 0.5H_2O$ (**351**) exhibits a short Ru–Cl bond distance of 2.314(1) Å [387], and is inert to chloride substitution without decomposition of the complex [388]. However, replacement of the nitrosyl ligand in **351** by neutral *N*-donors leads to complexes with longer Ru–Cl bonds which readily undergo $Cl^-$ substitutions [388].



(351)

### 5.4. Cobalt(III) complexes

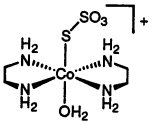
It has long been recognised that sulfito ligands exert large KTEs in Co(III) complexes. For example, the release of $H_2O$ from **218** is 3700 times faster than that from *trans*-$[Co^{III}(OH)(en)_2(H_2O)]^{2+}$ (**352**) [389].



(352)

In the absence of structural data, it was originally suggested that this arises purely from stabilisation of the transition state in a dissociative substitution mechanism [389]. Subsequent kinetic studies with **218** have shown that the rate of aquo substitution depends strongly on the nature and concentration of the incoming ligand, implicating an $I_d$ mechanism [390], and the KTE of $SO_3^{2-}$ is clearly in accord with the long Co–$OH_2$ bond distance in **218** found by X-ray diffraction [249].

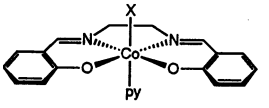
Kinetic studies involving the substitution reactions shown in Scheme 3(a) have revealed that the KTE of $SO_3^{2-}$ upon $NH_3$ is more than 100 times greater than those of the arylsulfinato ligands [247]. Since crystallographic data show the same trend for STEs in such complexes (Section 4.2.12) [246,247], it is clear that the marked KTEs of these sulfur-donor ligands arise primarily from ground state destabilisation due to their strong σ-donating properties [247]. Experiments with *trans*-$[Co^{III}(S_2O_3)(en)_2(H_2O)]^+$ (**353**) have shown that the KTE of the S-co-ordinated thiosulfato ligand upon $H_2O$ is ca. $2 \times 10^4$ times greater than that of $NH_3$ in **219** [391], but ca. $5 \times 10^{-3}$ times less than that of $SO_3^{2-}$ in **218** [390].



(353)

Comparison of these data with those obtained previously for the related ammine complexes [247] affords the KTE series $S_2O_3^{2-} < ArSO_2^- < SO_3^{2-}$. The weaker KTE of $S_2O_3^{2-}$ is consistent with the fact that this ligand exerts the smallest STE of the three types studied [391].

Investigations into the solid-state reaction kinetics of complexes $Co^{III}X$(salen)py (**354**) have shown that the rate of py loss at 400°C increases with the σ-donating strength of the *trans* alkyl group to give the KTE order $X = Me^-$ (2.85) $< Et^-$ (1.52) $< {}^iBu^-$ (1.17) $< {}^nPr^-$ (1.06) $< {}^nBu^-$ (0.45) $< {}^iPr^-$ (0.20), where the numbers in parentheses are the $-\log k_{400}$ values [392].



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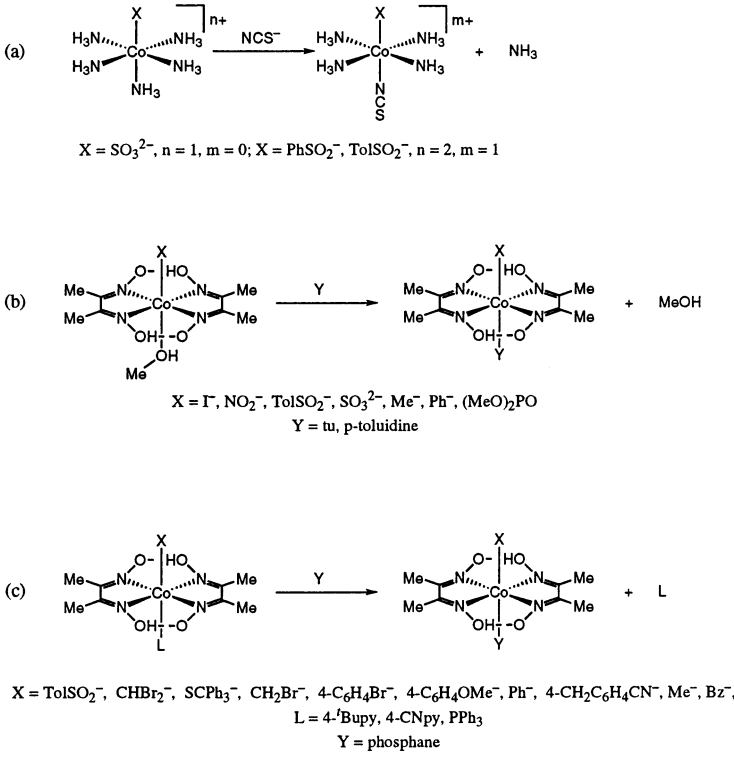



Scheme 3.

Extensive ligand-substitution kinetic studies have been carried out with cobaloximes, and since these have been reviewed recently [32,59], we will discuss only selected highlights of this work. Alkylcobaloximes have received particular attention, largely because they are of interest as models for the vitamin $B_{12}$ coenzyme. It is now well established that such complexes undergo axial ligand substitutions via a dissociative mechanism [59]. Early experiments involving substitution of $H_2O$ by $N_3^-$ or $NCS^-$ in **27** ($L = H_2O$) in aqueous solution afforded the KTE series $X = Me^- < Et^- < {}^iPr^-$ [393] which was attributed to increasing σ-donor strength of the alkyl ligands, possibly acting in conjunction with steric factors.

Investigations have also been carried out involving the reactions shown in Scheme 3(b) and $k_1$ values yield the KTE order $X = I^- \approx NO_2^- < TolSO_2^- < SO_3^{2-} < Me^-$ [394]. This has subsequently been extended to $X = TolSO_2^-$ (1) < $(MeO)_2PO$ (50) < $SO_3^{2-}$ (100) < $Ph^-$ (300) < $Me^-$ (900), where the numbers in parentheses represent the relative dissociation rates [395]. As expected for a

dissociatively activated substitution process, this KTE series follows the σ-donating power of $X^-$, as measured by the Hammett substituent parameter $\sigma_p$ [395].

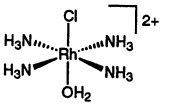
Other studies with a wide range of complexes **27** [Scheme 3(c)] yield the KTE series $X = TolSO_2^- < CHBr_2^- \leq SCPh_3^- < CH_2Br^- < 4\text{-}C_6H_4Br^- < 4\text{-}C_6H_4OMe^- < Ph^- < 4\text{-}CH_2C_6H_4CN^- < Me^- < Bz^- < Et^-$, the relative difference in $k_1$ between the extremes of this series for substitution of 4-CNpy by $P(^nBu)_3$ being ca. $10^4$ [396]. Later experiments have allowed the addition of further ligands to these series, confirming that the rate of ligand dissociation increases with increasing σ-electron-donating ability of X [59]. For example, the rate of substitution of 4-CNpy by $P(OMe)_3$ increases by a factor of $7 \times 10^6$ on replacing $CH(CN)Cl^-$ [397] with the much more basic $CHEt_2^-$ ligand [59]. Furthermore, dissociation rates also generally increase as the basicity and/or steric bulk of the leaving ligand decrease. These KTE series parallel the extensive STE series established for cobaloximes by crystallographic studies [32,59], but the relative differences in the former series are much larger.

Recent studies have also aimed to assess the KTEs of phosphine ligands by studying the rates of $H_2O$ substitution by $SO_3^{2-}$ in complexes *trans*-$[Co^{III}(dmgH)_2(PR_3)(H_2O)]^+$. Phosphines exert a relatively small KTE in cobaloximes, and the trans-labilising ability follows the order $NO_2^- < PR_3 < SO_3^{2-} < R^-$ [398]. The following KTE series was derived: $PMePh_2 < PPh_3 < PEtPh_2 < PEt_2Ph < PEt_3 < P(^nBu)_3 < P(^iPr)_3 < PCy_3$, although the difference between the two extremes is only a factor of ca. 55 [398]. This sequence broadly reflects the order of increasing σ-donor ability, but no correlation exists between $k_1$ and the steric bulk of the phosphine [398], as assessed by Tolman's cone angles [399]. It was therefore suggested that the KTEs of phosphine ligands in cobaloximes are primarily determined by electronic factors [398]. However, a relatively poor correlation is found between $\log k_1$ and the $pK_a$ values for deprotonation of the aquo ligands, which is taken as an indication of the Co–O bond strength [398]. The relationship between KTEs and STEs in these phosphine complexes is hence rather less clear than that in cobaloximes containing other types of ligands, and it seems likely that this is due to the widely variable σ-donor–π-acceptor co-ordinating properties of phosphines. This is in keeping with the fact that the STEs of such ligands are not simply determined by their σ-donor strength (Section 4.2.11).

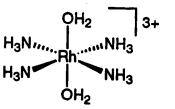
### *5.5. Rhodium(III) and iridium(III) complexes*

A number of studies have addressed the ligand substitution kinetics of Rh(III) penta- and tetra-ammine complexes. For example, investigations into water exchange processes in $^{18}O$-labelled Rh(III) and Ir(III) aquo-ammine complexes afford the KTE series $H_2O << NH_3 < Cl^-$ [400,401], which is the same as that found in square planar Pt(II) complexes [11]. The rate of $H_2O$ exchange in *trans*-$[Rh^{III}Cl(NH_3)_4(H_2O)]^{2+}$ (**355**) is ca. $5 \times 10^3$ times faster than that in *trans*-$[Rh^{III}(NH_3)_4(H_2O)_2]^{3+}$ (**356**) [400], whilst the comparable difference for the analogous Ir(III) complexes is ca. $4 \times 10^4$ [401]. Although the KTE order is

constant, the relative differences in KTE between $H_2O$, $NH_3$ and $Cl^-$ become larger in the order Cr(III) < Rh(III) < Ir(III) [401]. This trend has been rationalised as arising from differences in crystal field stabilisation energies between the metal ions [401].




(355)

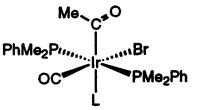



(356)

Rhodoximes undergo ligand substitutions by a mechanism similar to that of cobaloximes [33,402], and $k_1$ measurements for the substitution of $PPh_3$ in **28** by py yield the KTE series $X = CH_2CF_3^- < CH_2Cl^- < Me^- < Et^- < {}^nPr^- < {}^iPr^-$ [33,34], the rate difference between the two extremes being ca. $5 \times 10^5$ [34]. Again, this sequence follows the increasing σ-donating power of $X^-$, as estimated by $^1$H-NMR data [34], and generally parallels the crystallographically-derived STE ordering for these complexes (Section 4.1.2). The same KTE series was determined previously for reactions of cobaloximes [32].

### *5.6. KTEs of η¹-acyl ligands*

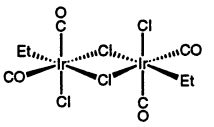
It has been recognised for many years that $\eta^1$-acyl ligands exert marked KTEs in octahedral complexes. For example, *cis*,*trans*-$Ir^{III}BrCl(COMe)(CO)(PMe_2Ph)_2$ (**357**) reacts with LiBr in refluxing ethanol to afford *cis*,*trans*-$Ir^{III}Br_2(COMe)(CO)(PMe_2Ph)_2$ (**358**) whilst the isomeric form of **357** in which $Cl^-$ is *trans* to CO is inert under identical conditions [403].



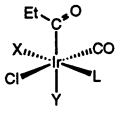

L = Cl⁻ (357)
L = Br⁻ (358)

These results clearly demonstrate that $MeCO^-$ causes a much larger KTE than does CO in Ir(III) complexes. Although CO exerts moderate STEs in a variety of octahedral complexes, it is generally strongly trans-delabilising in octahedral complexes of Cr(0), Fe(II) or Ru(II) (Sections 5.1, 5.2 and 5.3). Furthermore, no STE is observed in **56** (Section 4.2.1) [95]. By contrast, the more strongly σ-donating $\eta^1$-acyl groups show large STEs in all cases (Section 4.2.2), which are accompanied by a pronounced KTE on $Cl^-$ ligands in Ir(III) complexes. Similar KTEs of $H^-$ on phosphine ligands have also been observed [404].

The stereochemistry of migratory CO 'insertion' reactions is determined by the KTEs of $\eta^1$-acyl ligands. The dinuclear complex *cis*-$[Ir^{III}Cl_2Et(CO)_2]_2$ (**359**) reacts with tertiary phosphane or arsine ligands (L) to give the kinetic products **360** which rearrange to form the thermodynamically favoured **361** [405,406].

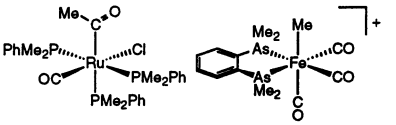


(359)



X = Cl⁻, Y = L (360)
X = L, Y = Cl⁻ (361)

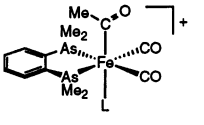
This occurs because the most stable five-co-ordinate intermediate features a vacant co-ordination site *trans* to the most strongly trans-directing ligand, i.e. the $\eta^1$-propionyl group [405,406]. Marked KTEs have also been observed in $\eta^1$-acyl complexes of other metal ions such as *mer*-$Ru^{II}Cl(COMe)(CO)(PMe_2Ph)_3$ (**362**) which shows preferential exchange of the phosphine ligand *trans* to $MeCO^-$ [407]. The kinetic products of the migratory CO insertion reactions of *fac*-$[Fe^{II}Me(diars)(CO)_3]^+$ (**363**) with phosphanes are *cis*-$[Fe^{II}(COMe)(diars)(CO)_2L]^+$ [**364**; $L = PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$, $P(OPh)_3$] which arise from the generation of a vacant co-ordination site *trans* to the $\eta^1$-acetyl ligand [408]. Also, $^{13}CO$ labelling studies show that *fac*-$[Fe^{II}(COMe)(diars)(CO)_3]^+$ (**365**) undergoes selective decarbonylation in the position *trans* to $MeCO^-$ [408].



(362)



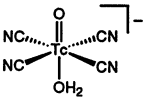
(363)



L = phosphane (364)
L = CO (365)

## 5.7. KTEs of multiply bonded π-donor ligands

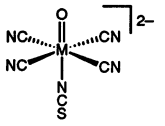
As discussed previously (Section 4.3), nitrido groups and related ligands give rise to especially large STEs due to their strong σ-π-electron donating abilities. This favours dissociative substitution mechanisms for such complexes, a fact confirmed by kinetic studies with octahedral tetracyano nitrido/oxo complexes which also show that $N^{3-}$ and $O^{2-}$ exert marked KTEs [409]. The latter can be rationalised as arising from ground state destabilisation, together with stabilisation of the five-co-ordinate intermediates by these powerfully electron-donating ligands [410]. At 25°C the rate of substitution of the aquo ligand in *trans*-$[Tc^{V}O(CN_4)(H_2O)]^-$ (**366**) by $NCS^-$ ions ($k_1 = 22.2\ M^{-1}\ s^{-1}$) [411] is ca. $6 \times 10^3$ times faster than the analogous reaction of **310** ($k_1 = 3.5 \times 10^{-3}\ M^{-1}\ s^{-1}$) [412].



(366)

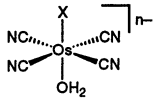
Given the occurrence of a dissociative mechanism [409], this observation is in accord with the larger STE in the Tc(V) product *trans*-$[M^{V}O(CN_4)(NCS)]^{2-}$

compared with its Re(V) analogue ($M^{V}$–*N*CS bond distances: 2.162(9) Å (M = Tc, **367**) [411] and 2.12(1) Å (M = Re, **368**) [413]).



**M = Tc (367)**
**M = Re (368)**

In keeping with the markedly larger STEs of nitrido compared to oxo ligands (Section 4.3.4), the KTEs of $N^{3-}$ are also much larger than those of $O^{2-}$. For example, at 25°C the rate of the reaction of **309** with $CN^{-}$ ($k_1 = 7.2 \times 10^{3}$ $M^{-1}$ $s^{-1}$) [410] is ca. $2 \times 10^{6}$ times faster than that of **310** with $NCS^{-}$ [412]. These data are compatible given that the rates of dissociative substitution reactions generally show little dependence upon the nature of the incoming ligand [409]. A related study also indicates a large KTE in the reaction of *trans*-$[Os^{VI}N(CN_4)(H_2O)]^{-}$ (**369**) with $N_3^{-}$ ions [414], but a comparison with *trans*-$Os^{VI}O(CN_4)(H_2O)$ (**370**) is not possible because the latter complex is synthetically inaccessible [415].

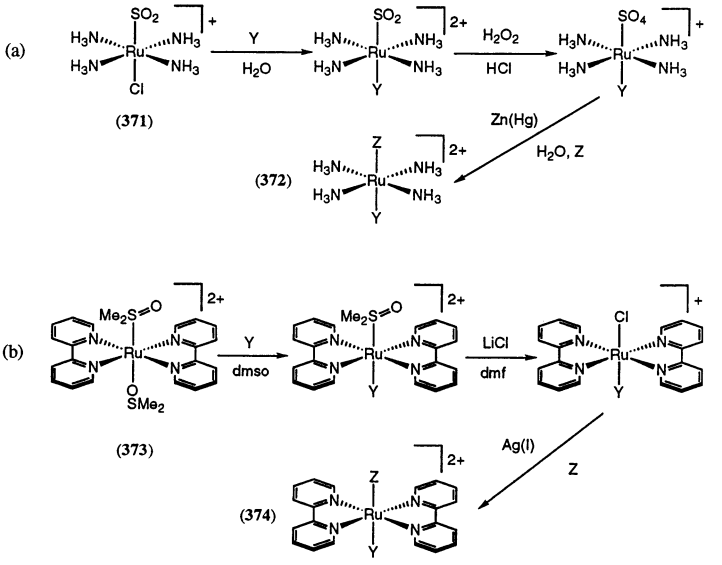


**X = $N^{3-}$, n = 1 (369)**
**X = $O^{2-}$, n = 0 (370)**

### *5.8. The exploitation of KTEs in the controlled synthesis of octahedral complexes*

By contrast with square planar complexes [11], there has been very little work involving the deliberate use of KTEs as a means to achieve directed ligand substitutions in octahedral complexes, particularly in multi-step synthetic procedures. This is obviously due in part at least to the greater complexity of six-co-ordinate systems.

A rare case in which KTEs have been exploited is in the preparation of asymmetric axially substituted Ru(II) tetraammine complexes derived from the precursor *trans*-$[Ru^{II}Cl(NH_3)_4(SO_2)]Cl$ (**371**) [416,417]. Although the Ru–Cl bond distance in **371** [2.415(3) Å] is not unusually long [418], the π-accepting $SO_2$ ligand exerts a marked KTE which allows facile $Cl^{-}$ substitution by various neutral ligands (Y) in aqueous solution [419]. Oxidation of the resulting Ru(II)–$SO_2$ complexes to produce Ru(III)–$SO_4$ analogues [420], followed by reduction in aqueous solution and treatment with a second neutral ligand (Z) affords the di-substituted products **372** [416,417] (Scheme 4(a)). This elegant co-ordination chemistry has been used to synthesise many *trans*-$\{Ru^{II}(NH_3)_4\}^{2+}$ complexes, including pyrazine-bridged polynuclear species [421] and donor/acceptor complexes which exhibit very large nonlinear optical responses [422].




Scheme 4.

Another example of a multi-step ligand substitution scheme in which KTEs play a key role involves complexes based upon *trans*-$\{Ru^{II}(bpy)_2\}^{2+}$ centres. The precursor *trans*-$[Ru^{II}(bpy)_2(dmso)_2]^{2+}$ (**373**) reacts quantitatively with an excess of a pyridyl ligand (Y) to give mono-substituted derivatives [423]. Substitution of the remaining dmso by $Cl^-$, followed by reaction with an Ag(I) salt in the presence of a second pyridyl ligand (Z) affords di-substituted products **374** (Scheme 4(b)) [423]. It is likely that the first step in these syntheses involves replacement by Y of an O-bound dmso ligand *trans* to an S-bound dmso, and the reactions stop cleanly at the monosubstitution stage because S-bound dmso exerts a KTE on O-bound dmso, whilst Y does not exert a KTE on S-bound dmso [423]. This chemistry has been used to prepare functionalised assemblies designed to exhibit photo-induced charge-separation behaviour [424].

The development of further strategies for controlled ligand substitutions in octahedral complexes is of great interest for academic reasons, but also as a means to prepare functionalised derivatives possessing novel properties. It can be expected that developments in this area will hinge to a significant extent upon efforts to understand and exploit KTEs.

## 6. Summary and conclusions

Having analysed a great deal of crystallographic data, it is tempting to propose a universal STE series for ligands in octahedral complexes. However, we are reluctant to attempt this for the following reasons:

1. STEs are always *mutual* effects, i.e. the STE of a given ligand depends upon the bonding properties of the ligand being affected, sometimes to a dramatic extent. This is best exemplified by the linear nitrosyl ligand ($NO^+$) which shows moderate STEs when *trans* to π-acceptor ligands, negligible STEs when *trans* to purely σ-donor ligands, and inverse STEs when *trans* to π-donors.
2. Because they arise primarily from electronic factors which are mediated via a metal atom/ion, STEs can show a marked dependency upon the electronic properties of the complexed metal centre. For example, π-accepting isocyanide and phosphine ligands generally give moderate STEs, but in $d^0$ complexes their STEs are weaker than those of chloride. This is likely to result from an absence of π-back-bonding in such complexes. Also, the STEs of π-donating imido ligands show an extremely wide variation which correlates to some extent with the metal d-configuration.

The above considerations notwithstanding, it is clear that broad, general STE classes can be identified into which the majority of common ligands fit:

1. Very large STE ligands (STE vs. $Cl^- >$ ca. 0.20 Å): $SiR_3^-$, $NO^-$, $N^{3-}$, $O^{2-}$, $S^{2-}$, $RC^{3-}$. These all have very strong σ-, and in most cases π-, electron-donating abilities which act to decrease the ability of a co-ordinated metal centre to form bonds to *trans* ligands. Steric factors also contribute to the STEs of the strong π-donor ligands which form metal–ligand multiple bonds.
2. Large STE ligands (ca. 0.20 > STE vs. $Cl^-$ > ca. 0.10 Å): $H^-$, $R^-$, $\eta^1$-alkenyl, $\eta^1$-Ph, $RCO^-$, $RN_2^-$. These are primarily strong σ-donors which cause STEs for similar electronic reasons to the ligands in category 1: it is clearly logical to expect larger STEs from ligands which also possess π-donating properties.
3. Moderate STE ligands (ca. 0.10 Å > STE vs. $Cl^-$ > 0.00 Å): CO, $CN^-$, CNR, $\eta^1$-acetylide, $R_2C$, $NO_2^-$, $NS^+$, $RN_2^+$, $SO_3^{2-}$, $RSO_2^-$, $PR_3$, $P(OR)_3$, $RNH^-$, $RS^-$, $\eta^1$-thiones. These are a broad mixture of ligands which generally possess either π-acceptor or moderate π-donor properties.

The relationship between STEs and KTEs depends very much upon the mechanisms of ligand substitution reactions. Square planar complexes generally react via associative mechanisms [2,3] and a ligand which causes a STE may not produce an accompanying KTE [11]. However, because ligand substitutions in octahedral complexes are generally dissociatively activated, there is often a close correlation between STEs and KTEs. For example, nitrido ligands give very large STEs and KTEs, whilst sulfito groups give moderate STEs and large KTEs. Since both of these ligands cause STEs primarily via powerful electron donation, the ground state destabilisations implied by STEs are likely to be accompanied by stabilisation of the electron-deficient five-co-ordinate transition states [3]. By contrast, π-acceptor ligands such as CO or isocyanides generally exert moderate STEs but cause pronounced delabilisation of *trans* metal–ligand bonds. This is likely to arise from transition state destabilisation by such ligands, i.e. π-acceptor ligands act to further deplete the electron density at the metal centre in an already electron-deficient transition state [3]. Similar reasoning has been used to rationalise cis-labilisation effects in octahedral metal tetracarbonyl complexes [366].

**Acknowledgements**

We acknowledge extensive use of the Cambridge Crystallographic Database for the location of structural data, and are grateful to Dr Emma M. Coe for checking the manuscript.

## Appendix. Abbreviations

| | |
|---|---|
| acac | acetylacetonato |
| Ad | adamantyl |
| abt | 2-aminobenzenethiolato |
| Bz | benzyl |
| bpy | 2,2′-bipyridine |
| diars | 1,2-bis(dimethylarsino)benzene |
| dmpe | 1,2-bis(dimethylphospino)ethane |
| dppe | 1,2-bis(diphenylphospino)ethane |
| dppm | 1,2-bis(diphenylphospino)methane |
| dppp | 1,2-bis(diphenylphospino)propane |
| bmte | 1,2-bis(methylthio)ethane |
| bpte | 1,2-bis(phenylthio)ethane |
| salen | *N*,*N*′-bis(salicylidene)ethylenediaminato |
| PPN | bis(triphenylphosporanylidene)ammonium |
| $^{n}$Bu | *n*-butyl |
| $^{t}$Bu | *t*-butyl |
| 222-C | 2,2,2-cryptand |
| Cy | cyclohexyl |
| Cp | $\eta^5$-cyclopentadienyl |
| DFT | density functional theory |
| en | 1,2-diaminoethane |
| dedtc | diethyldithiocarbamato |
| dipp | 2,6-di(isopropyl)phenyl |
| dippdb | 2′,6′-di(isopropyl)phenyl-2,5-dimethyl benzamide |
| dme | 1,2-dimethoxyethane |
| dmgH | dimethylglyoximato |
| $dmgBF_2$ | (dimethylglyoximato)difluoroborate |
| dmf | dimethylformamide |
| dmso | dimethylsulfoxide |
| Et | ethyl |
| etpb | 4-ethyl-2,6,7-trioxo-1-phospha-bicyclo-[2,2,2]-octane |
| glyca | *N*,*N*′-glycinamido |
| hmpa | hexamethylphosphoramide |
| im | imidazole |
| imC | imidazole (C-co-ordinated) |
| imN | imidazole (N-co-ordinated) |

| | |
|---|---|
| isn | isonicotinamide |
| $^{i}$Pr | isopropyl |
| KTE | kinetic trans-effect |
| men | (−)-mentholato |
| MLCT | metal-to-ligand charge-transfer |
| medcp | (2-methoxyethyl)dicyclohexylphosphine |
| Me | methyl |
| mim | 1-methylimidazole |
| 2-mim | 2-methylimidazole |
| mpa | 2-methylphenylamido |
| MO | molecular orbital |
| Np | neopentyl |
| phen | 1,10-phenanthroline |
| Ph | phenyl |
| pdmp | 1-phenyl-3,4-dimethylphosphole |
| pic | 4-picoline |
| $^{n}$Pr | *n*-propyl |
| py | pyridine |
| pyd | α-pyridonato |
| pyz | pyrazine |
| STE | structural trans-effect |
| tpy | 2,2′:6′,2″-terpyridine |
| [14]ane$N_4$ | 1,4,8,11-tetraazacyclotetradecane |
| thf | tetrahydrofuran |
| tht | tetrahydrothiophene |
| TpivPP | α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinato |
| tmtu | tetramethylthiourea |
| TPP | *meso*-tetraphenylporphinato |
| thz | 1,3-thiazole |
| tu | thiourea |
| Tos | *para*-toluenesulfonate |
| Tol | *para*-tolyl |
| tamp | 2-(*N*-*para*-tolylamido)pyridine |
| TE | trans-effect |
| tacn | 1,4,7-triazacyclononane |
| pta | 1,3,5-triaza-7-phosphoadamantane |
| $Me_3$tacn | *N*,*N*′,*N*″-trimethyltriazacyclononane |
| $^{i}Pr_3$tacn | *N*,*N*′,*N*″-tri(isopropyl)triazacyclononane |
| tdpa | tris(diphenylphospinoethyl)amine |
| Tp | tris(pyrazol-1-yl)hydroborato |
| Tp* | tris(3,5-dimethyl-pyrazol-1-yl)hydroborato |
| $^{i}Pr_3$Tp | tris(3-isopropyl-pyrazol-1-yl)hydroborato |
| $Mp_3$Tp | tris(3-*para*-methoxyphenyl-pyrazol-1-yl)hydroborato |
| ttcn | 1,4,9-trithiacyclononane |
| Xyl | 2,6-xylyl |

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