Ligand Substitution Reactions of Square-planar Molecules

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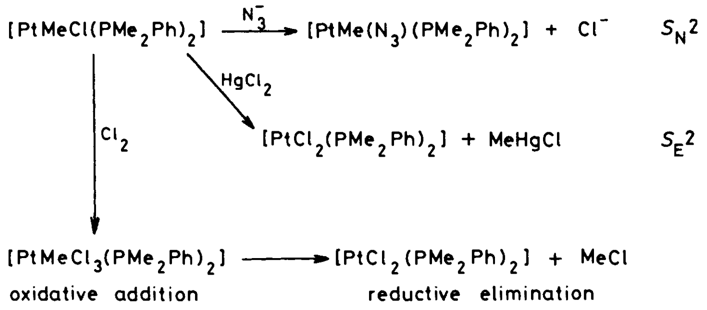
1 Introduction

Ligand exchange reactions of square-planar molecules are usually divided into three main groups—nucleophilic substitutions, electrophilic substitutions, and oxidative additions followed by reductive eliminations. Scheme 1 shows three reactions of one compound which would conventionally be respectively assigned to these types.[1,2]



Scheme 1

The basic features of these three mechanisms have been understood for years.[3-5] Each pathway has generally been considered in isolation however, though to an extent this reflects the nature of the available data. For example, nearly all the mechanistic and kinetic studies on nucleophilic substitutions have been made on compounds of platinum or palladium, and very few on square-planar compounds of iridium or rhodium, whereas the reverse is nearer the truth when applied to oxidative additions. Well-proven examples of electrophilic substitution of square-planar molecules are rare, but many reactions have been assigned to this class on the basis of comparisons with other systems.

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[1] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 1969, 2801, 2989.

[2] R. J. Cross and R. Wardle, *J. Chem. Soc. A*, 1970, 840.

[3] (*a*) F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions' 2nd Edn., Wiley, New York, 1967; (*b*) L. Cattalini, *Prog. Inorg. Chem.*, 1970, **13**, 263.

[4] (*a*) M. H. Abraham, 'Comprehensive Chemical Kinetics', Vol. 12, ed. C. H. Bamford and C. F. H. Tipper, Elsevier, New York, 1973; (*b*) O. A. Reutov, *Tetrahedron*, 1978, **34**, 2827; (*c*) F. R. Jensen and B. Rickborn, 'Electrophilic Substitutions of Organomercurials,' McGraw-Hill, New York, 1968.

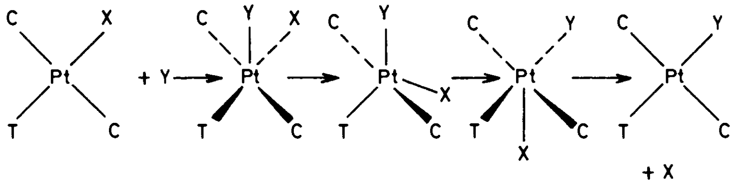
[5] (*a*) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, 1968, **7**, 53. (*b*) J. Halpern, *Acc. Chem. Res.*, 1970, **3**, 386; (*c*) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, 1977, **10**, 434.

Nucleophilic substitutions and oxidative additions have been the subjects of several recent investigations and it now appears that both processes are more complicated and span a wider range in their intimate mechanisms than had previously been supposed. Moreover, there are indications that there are areas of overlap in the operation of these routes, and possibly with the intimate mechanisms of some electrophilic substitutions and dissociative ligand replacements also.

This article summarizes the mechanistic information on these reactions. This now indicates the existence of a broad range of available reaction pathways, and it is concluded that it may well be unrealistic and unhelpful to think in terms of the operation of three basic routes only. Even small changes in reaction conditions, solvents, or the nature of the reactants have the capacity to alter the initial bimolecular interaction, and hence the choice of which pathway a reaction follows. For convenience, the work is divided into three sections, based loosely on nucleophilic substitutions, electrophilic substitutions, and oxidative additions. It should be realized that the labels are formalisms, owing more to traditional ideas than to the true situation.

2 Nucleophilic Ligand Replacements

Thanks to many studies on kinetically inert complexes of platinum(II), ligand replacement at square-planar complexes is one of the best understood of all inorganic reaction mechanisms. There is general agreement that the reactions are associative and involve nucleophilic attack of the entering ligand (Y) at the metal, the 5-co-ordinate adduct passing through square-pyramidal and trigonal-bipyramidal stages (equation 1).[3] A solvolysis step often competes with the direct replacement of equation 1, leading to rate law 2. The subsequent replacement of the co-ordinated solvent molecule by Y is fast.



(1)

$$\text{rate} = (k_1 + k_2[\text{Y}])[\text{complex}] \qquad (2)$$

The trigonal-bipyramidal complex of equation 1 has sometimes been regarded as a reaction intermediate,[3b] with the two square-pyramidal species as transition states. Over the years, however, many 5-co-ordinate complexes of platinum(II) and other d^8 metal ions have been isolated and investigated, and whilst there are indeed trigonal-bipyramidal molecules amongst them,[6] many are closer to square-

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[6] E. A. Jeffery, *Aust. J. Chem.*, 1973, **26**, 219; E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1922; J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1090; A. Gleizes, A. Kerkeni, M. Dartiguenove, Y. Dartiguenove, and H. F. Klein, *Inorg. Chem.*, 1981, **20**, 2372; R. Favez and R. Roulet, *Inorg. Chem.*, 1981, **20**, 1598.

pyramidal geometry,[7] so any or all of the 5-co-ordinate species of equation 1 might be regarded as intermediates. The reaction profile is therefore likely to resemble Figure 1. The pathways of the entering and leaving ligands are probably off-axis,[8] and the relative heights of the energy maxima dictate whether bond-making or bond-breaking determines the rate.

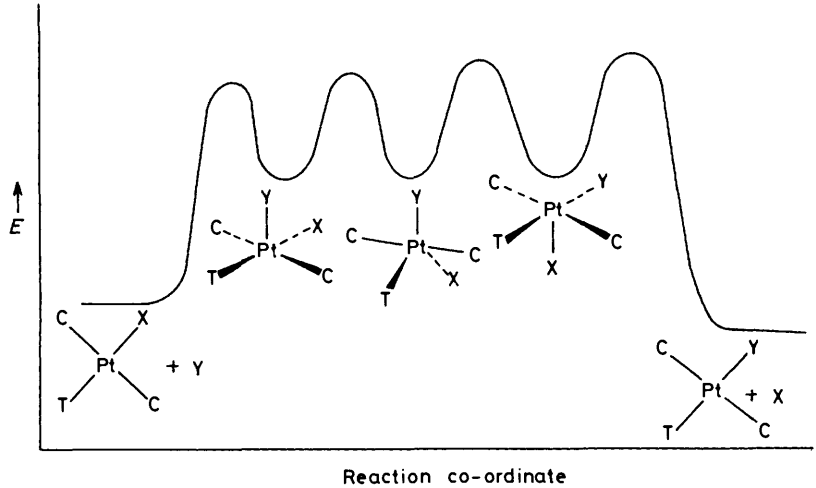

Figure 1

A major complication of these ligand-substitution processes, pseudorotation of the 5-co-ordinate intermediates, first became apparent quite recently from studied of isomerization reactions.[9] The overwhelming majority of substitutions studies to date have been stereospecific [that is, the arrangement of the three other ligands, *trans*, T, and *cis*, C (Figure 1 and equation 1) remained unaltered], and this had been taken as evidence that pseudorotation did not operate during such processes. Isomerization reactions of square-planar molecules, usually catalysed by nucleophiles, are common, however, and the best understood mechanism for such geometry changes, consecutive displacement, simply involves two stereospecific ligand substitutions (equation 3) and no necessity for pseudorotation. Examination of the details of the two steps of equation 3 reveals a potential for the operation of a pseudorotation mechanism: one 5-co-ordinate intermediate is common to both steps (Scheme 2) and the operation or not of pseudorotation steps would depend

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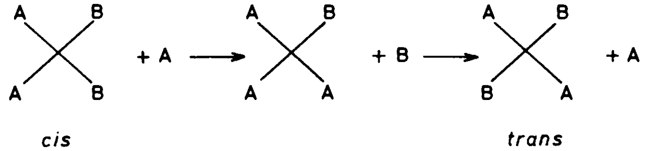
[7] W. J. Louw, D. J. A. de Waal, and G. J. Kruger, *J. Chem. Soc.. Dalton Trans.*, 1976, 2364; K. M. Chui and H. M. Powell, *J. Chem. Soc., Dalton Trans.*, 1974, 1879, 2117; E. C. Alyea and D. W. Meek, *Inorg. Chem.*, 1972, **11**, 1029; N. K. Roberts and S. B. Wild, *Inorg. Chem.*, 1981, **20**, 1892, 1900; G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A.-M. Manotti-Lanfredi, and A. Tiripiccio, *J. Chem. Soc., Dalton Trans.*, 1981, 2280; A. Albinati, P. S. Pregosin, and H. Ruegger, *Angew. Chem., Int. Edn. Engl.*, 1984, **23**, 78.

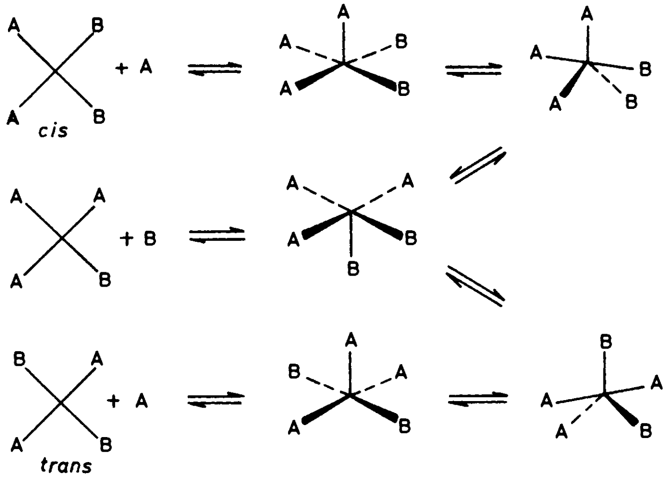
[8] R. G. Pearson, 'Symmetry Rules for Chemical Reactions', Wiley-Interscience, New York, 1976, p. 316.

[9] G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.

only on the relative rates of the steps depicted. Moreover, many 5-co-ordinate d^8 complexes are known to be fluxional.[10] Not surprisingly, then, reports of isomerization by pseudorotation, though few at first and often controversial, are beginning to accrue.[9] Scheme 3 shows a good example.[11] A comparison of the rates of the chloride-catalysed isomerization with those of individual substitution steps revealed that consecutive displacement could not be responsible, and the reaction presumably proceeded *via* pseudorotation. (Interestingly, DMSO also catalysed the isomerization and in this case the kinetics were compatible with consecutive displacement).



(3)



Scheme 2

It follows that pseudorotation could accompany any ligand replacement steps, and at least one clear example of this may already have been described.[12] The ring closure shown in reaction 4 is a replacement of Cl^- by NH_2R. It proceeds without retention of configuration, and pseudorotation of a 5-co-ordinate intermediate is the most likely cause.

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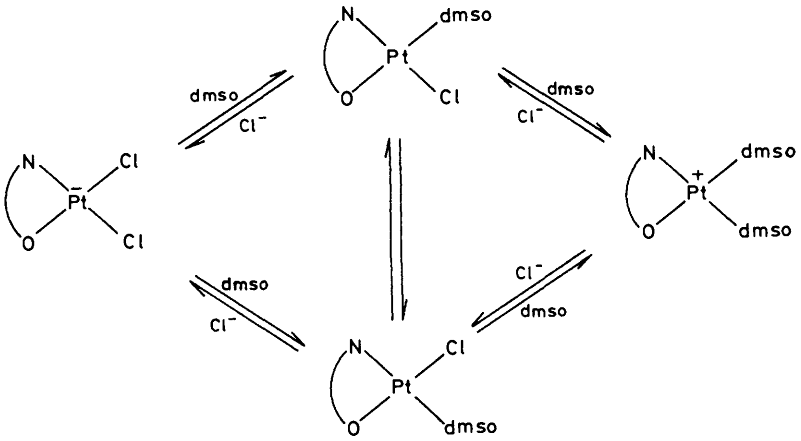
[10] E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, 1975, **14**, 1926; P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, **96**, 5751, 5760; J. J. MacDougall, J. H. Nelson, and F. Mathey, *Inorg. Chem.*, 1982, **21**, 2145.

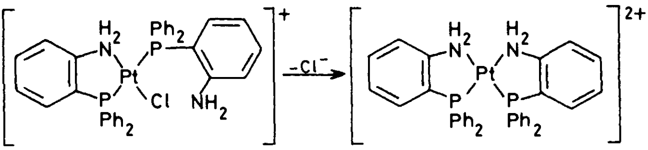
[11] L. F. Erickson, T. A. Ferrett, and L. F. Buhse, *Inorg. Chem.*, 1983, **22**, 1461.

[12] M. K. Cooper and J. M. Downs, *J. Chem. Soc., Chem. Commun.*, 1981, 381.



N⌒O represents glycine, sarcosine, or *N*,*N*-dimethylglycine

Scheme 3

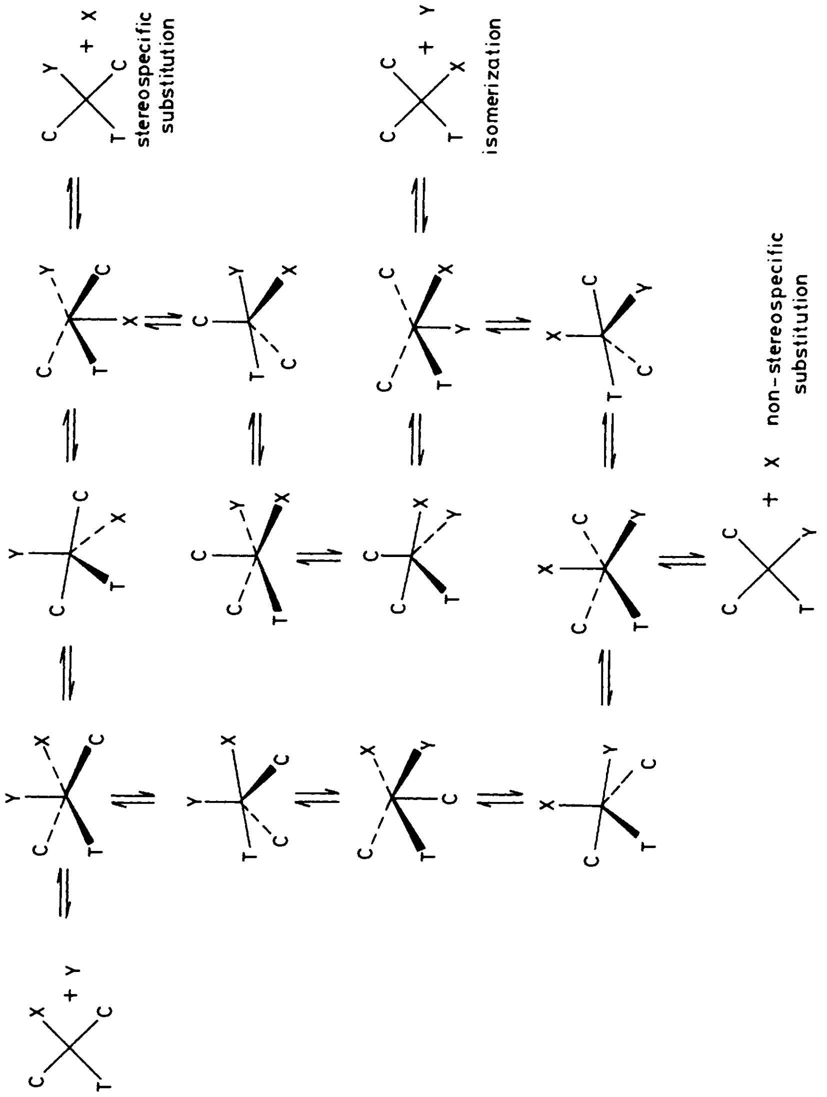


(4)

With 5-co-ordinate d^8 species being commonly fluxional, by pseudorotation or some other mechanism,[13] a question which must be asked is why many more non-stereospecific ligand-replacement reactions of square-planar molecules have not come to light in the past? The answer is almost certainly that the systems studied have been those which, for one reason or another, would suppress such a process. For example, in the interests of simplicity molecules with only one weakly-held ligand for the leaving group, X, are frequently employed; the *trans* ligands, T, are often chosen to assist the departure of X, by further weakening M–X or by having a preference for the trigonal plane of the trigonal bipyramid;[14] and the use of chelating ligands which further cut down the scope for unwanted side-reactions, including isomerizations, is popular. It seems inevitable now, however, that many more examples of ligand replacement without retention of configuration will be discovered. Indeed it has been pointed out that the numerous stereospecific

[13] I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, 1971, **4**, 288.

[14] *Ref.* 8, p. 318.


stereospecific substitution
isomerization
non-stereospecific substitution
C
T
X
Y

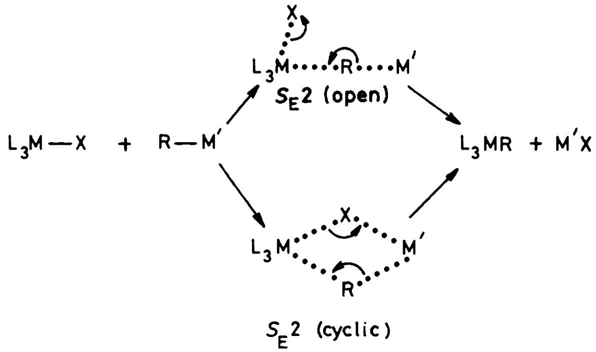
Scheme 4

replacements already described and assumed to conform to a mechanism like that in Figure 1 would be indistinguishable kinetically from more complicated systems involving rapidly fluxional 5-co-ordinate intermediates.[11]

Overall then, the broadest picture of the intimate mechanism of associative nucleophilic ligand replacement at square-planar molecules is one where the resulting 5-co-ordinate species can have a number of energy minima, and may fluctuate between them, affording a choice of pathways before a group is eliminated. Equation 1 should be extended to Scheme 4 in the general case.

3 Electrophilic Substitutions and Dissociative Ligand Replacements

When the incoming nucleophile (Y of Figure 1) is an organic group, R, from an organometallic reagent, the ligand replacement process is not normally regarded as a nucleophilic substitution, although if complete charge-separation occurs to form a carbanion, R^-, then clearly it would be. (This may occur with, for example, organolithium compounds.[15]) More commonly, charge separation is believed to be incomplete and a transition state involving a degree of bridging through the organic group is likely. The ligand exchange reactions are usually described as electrophilic substitutions at carbon, and the reaction pathways, S_E2 (open) or S_E2 (cyclic), are shown in Scheme 5. Both involve second-order kinetics. The S_E2 (cyclic) route proceeds with retention of configuration at R, whereas S_E2 (open) can proceed with inversion or retention. The transfer of the organic group from mercury to palladium in reaction 5 proceeds with retention of configuration at carbon,[16a] whereas transfer of an (*S*)-(−)-(α-deuteriobenzyl) group from tin to a similar palladium(II) complex in a polar solvent proceeded with inversion.[16b] Both appear to be electrophilic substitutions.



Scheme 5

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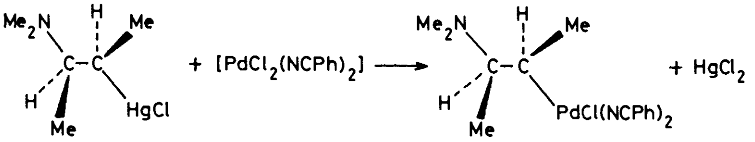
[15] K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1857; F. Ozawa, T. Ito, Y. Nakamoro, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1869.

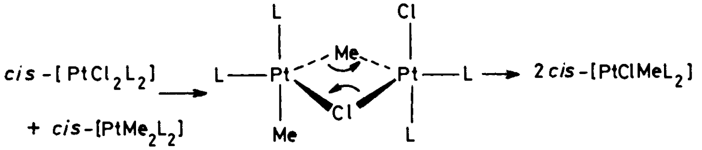
[16] (*a*) J.-E. Bäckvall and B. Åkermark, *J. Chem. Soc., Chem. Commun.*, 1975, 82; (*b*) J. W. Labadie and J. K. Stille, *J. Am. Chem. Soc.*, 1983, **105**, 669.



(5)

The majority of studies on this type of process have been performed on organomercury or organotin compounds,[4] and the consensus is that if an appropriate bridging group is present (X in Scheme 5), some degree of bridging will take place, tending towards a transition state of the S_E2 (cyclic) form. It is this route which is most appropriate to the square-planar complexes under discussion here.

Whilst such electrophilic substitution reactions are rarely considered alongside the ligand-exchange processes described in the previous section, an obvious link exists since electrophilic attack at the carbon atom by a metal ion can equally be regarded as nucleophilic attack at the metal by carbon. An example is the reaction between *cis*-$[PtCl_2(PMe_2Ph)_2]$ and *cis*-$[PtMe_2(PMe_2Ph)_2]$ (see below, reaction 6). This produces, initially, only the *cis* isomer of $[PtClMe(PMe_2Ph)_2]$.[17] The authors postulated a cyclic transition-state, pointing out that retention of configuration at both platinum atoms was entirely consistent with what might be expected from a reaction that can be described as S_E2 with respect to the carbon atoms, and S_N2 with respect to the platinum atoms. Similar reactions showed the expected second order kinetics.[18]



(6)

Many transfers of organic groups from tin to platinum are also believed to follow S_E2 (cyclic) routes (equation 7).[19] The acceleration by electron-releasing substituents on R and retardation by electron-withdrawing groups is consistent with this interpretation (though Wheland intermediates are possible when R is aromatic). Interestingly, trifluoroacetate complexes of platinum are more reactive than chlorides, and six-centre cyclic intermediates could be involved here (equation 8).[20] A recent variation concerns the second order reaction between *cis*-$[PtMe_2(SMe_2)_2]$ and $[PtCl_2(SMe_2)_2]$, leading to *trans*-$[PtMeCl(SMe_2)_2]$.[21] This

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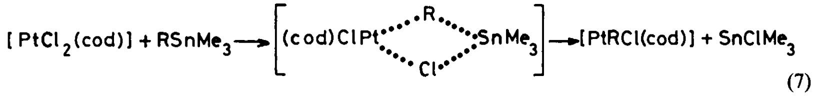
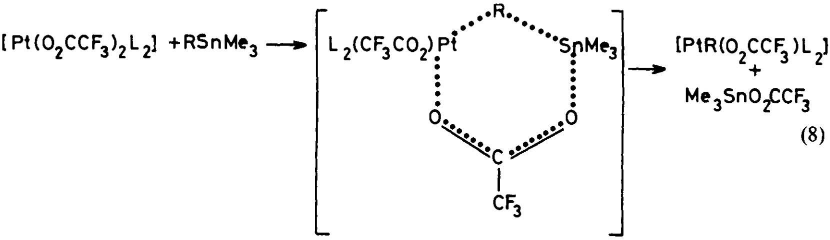
[17] R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1975, 1810.
[18] R. J. Puddephatt and P. J. Thompson, *J. Chem. Soc., Dalton Trans.*, 1977, 1219.
[19] C. Eaborn, K. J. Odell, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1978, 357.
[20] C. Eaborn, K. J. Odell, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1979, 758.
[21] J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.

proceeds after preliminary loss of Me_2S from $[PtMe_2(SMe_2)_2]$. Such ligand losses may not, however, be general requirements. Altogether, a great many reactions involving transfer of organic groups between *e.g.* Pt, Pd, Au, Hg, Ge, Sn, and Pb have been postulated as proceeding by S_E2 (cyclic) routes,[22] though reliable mechanistic evidence is often lacking.



(7)



(8)

If we regard the reactions as nucleophilic displacements at the 4-co-ordinate metal, the potential for geometry change at the intermediate/transition-state presumably exists, as it appears to do in the more conventional nucleophilic displacement reactions discussed in the last section. No clear examples have been pointed out, however, and it is conceivable that the transition state is too short-lived to allow anything other than stereospecific exchange. The steric constraints of two sites being involved in these interactions might further reduce opportunities for rearrangement, though it must be noted that one of the best examples to date of isomerization by pseudorotation of 5-co-ordinate platinum involves chelating ligands,[11] and other geometry-change routes[13] may be less prone to steric constraint than classical pseudorotation.

An added complication may arise from the proximity of the two metal atoms in some of the S_E2 (cyclic) reactions described. A significant interaction is possible,[18,23] and an entire range from S_E2 (cyclic) (no MM′ interaction) through to oxidative addition (complete M–M′ bond formation) can be envisaged. Scheme 6 illustrates this progression. Thus this one type of oxidative addition reaction at least is also mechanistically related to nucleophilic attack at square-planar complexes; reductive elimination (of M′X in Scheme 6) leads to the ligand-exchanged products. It is of interest that a comparative study of organic group-

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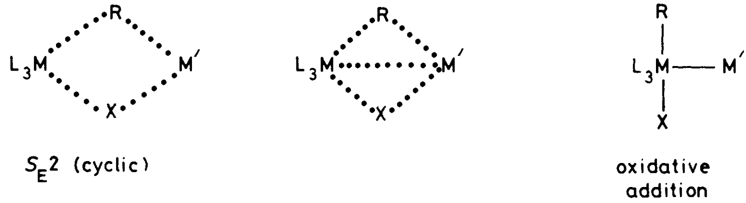
[22] J. P. Visser, W. W. Jago, and C. Masters, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 70; A. Segnitz, E. Kelly, S. H. Taylor, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **124**, 113; C. Eaborn, K. J. Odell, and A. Pidcock, *J. Organomet. Chem.*, 1978, **146**, 17; R. J. Puddephatt and P. J. Thompson, *J. Organomet. Chem.*, 1979, **166**, 251; Z. Dawoodi, C. Eaborn, and A. Pidcock, *J. Organomet. Chem.*, 1979, **170**, 95; C. Eaborn, K. Kundu, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1981, 933; 1223.

[23] R. J. Cross in 'Mechanisms of Inorganic and Organometallic Reactions', Vol. 2, ed. M. V. Twigg, Plenum, New York, 1984, Ch. 5, p. 105.

transfer reactions involving mixed alkyl–aryl complexes of gold(III) and platinum(II) led to the suggestion that aryl groups are more likely to transfer by S_E2 mechanisms, whereas alkyl groups are more likely to exchange by oxidative addition/reductive elimination,[24] a change that may simply reflect the position of the transition-state/intermediate along the 'scale' of Scheme 6. Presumably any degree of metal–metal interaction at the transition state will further reduce opportunities for geometry change to occur concurrently with the ligand exchange, and it seems reasonable to conclude that pseudorotation-type complications at the S_E2 (cyclic) family of reactions are likely to be rare.



Scheme 6

Another variation of S_E2 reaction types is the involvement of nucleophilic catalysis:[4] in the reactions under discussion a nucleophilic agent would approach the metal of the carbon–metal bond in M′R, thus activating the carbon to the electrophilic attack of M. When the catalysing or activating nucleophile is the eventual leaving-group, X, this could clearly lead to the cyclic transition-state already encountered, and would be virtually indistinguishable from cases where the interaction of M and R was synchronous or primary. A second pathway in the *abstraction* of the group X by M′ is available however (Scheme 7). There is growing evidence that a preliminary electrophilic attack by a metal ion at, for example, a co-ordinated halide can lead directly to its abstraction. An example is the action on $[FeI(CO)_2(C_5H_5)]$ of $AgBF_4$, which produces first an adduct $[Fe(IAg)(CO)_2(C_5H_5)]^+$, before AgI is eliminated.[25] With square-planar platinum complexes also, several reactions involve silver(I) or mercury(II) co-ordinating to ligand halide ions leading to their abstraction.[26] Other electrophilic agents such as boron halides,[27] $[Me_3O]BF_4$,[28] or $MeSO_3F$[29] act in a similar manner. (These last

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[24] J. K. Jawad, R. J. Puddephatt, and M. A. Staltori, *Inorg. Chem.*, 1982, **21**, 332.

[25] B. M. Mattson and W. A. G. Graham, *Inorg. Chem.*, 1981, **20**, 3186.

[26] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. A*, 1970, 545; K. R. Dixon and D. J. Hauke, *Can. J. Chem.*, 1971, **49**, 3252; R. J. Cross and I. G. Phillips, *J. Chem. Soc., Dalton Trans.*, 1982, 2261; R. G. Goel and R. C. Srivastava, *Can. J. Chem.*, 1983, **61**, 1352; Z.-Y. Yang and G. B. Young, *J. Chem. Soc., Dalton Trans.*, 1984, 2019.

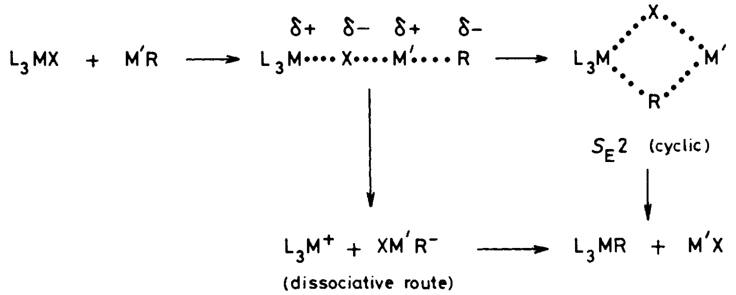
[27] P. M. Druce, M. F. Lappert, and P. N. K. Riley, *J. Chem. Soc., Dalton Trans.*, 1972, 438; H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, 1968, **90**, 2259; H. C. Clark and K. R. Dixon, *J. Am. Chem. Soc.*, 1969, **91**, 596.

[28] P. M. Treichel, K. P. Wagner, and W. J. Knebel, *Inorg. Chim. Acta*, 1972, **6**, 674.

[29] C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1976, 58.

reactions provide interesting contrasts with some oxidative addition reactions of the same reagents discussed in the next section.)

Loss of a ligand from 4-co-ordinate square-planar complexes produces a reactive



Scheme 7

14-electron species. These tend rapidly to add another group (possibly after isomerization of the T-shaped intermediate), producing the ligand exchange. Whilst proposals of such mechanisms have for some years been regarded as somewhat controversial,[9] many possible examples have accumulated,[30] and evidence presented for some recent examples at least is strong.[31]

$$cis\text{-}[\mathrm{PtCl}(m\text{-tol})(\mathrm{PEt_3})_2] \xrightarrow{-\mathrm{Cl}^-} [\mathrm{Pt}(m\text{-tol})(\mathrm{PEt_3})_2] \xrightarrow[\text{then Cl}^-]{\text{isomerization}} trans\text{-}[\mathrm{PtCl}(m\text{-tol})(\mathrm{PEt_3})_2] \quad (9)$$

Many of these reactions proceed without the agency of obvious electrophiles like Ag^+, and loss of a halide has been regarded as more-or-less spontaneous. The leaving group will certainly be solvated once free, however, and prior co-ordination to solvent is likely. This type of interaction (of the co-ordinated halide) with solvent is closely related to electrophilic attack by a metal ion: the solvent molecules take the abstracting role of M′R in Scheme 7. Thus whilst this comparatively rare route to ligand exchange at square-planar complexes seems far removed from the 'traditional' routes of nucleophilic attack, the relationship to catalysed S_E2 processes establishes a pattern of gradually changing reaction pathways which encompass all these types. Scheme 8 shows the scope of the initial interactions leading, by degrees, through the well-recognized ligand-exchange pathways of nucleophilic substitution, S_E2 (cyclic), oxidative addition/reductive elimination, and the dissociative routes. Combined with the possible variations following nucleophilic attack (Scheme 4), the overall picture is already rich in choice.

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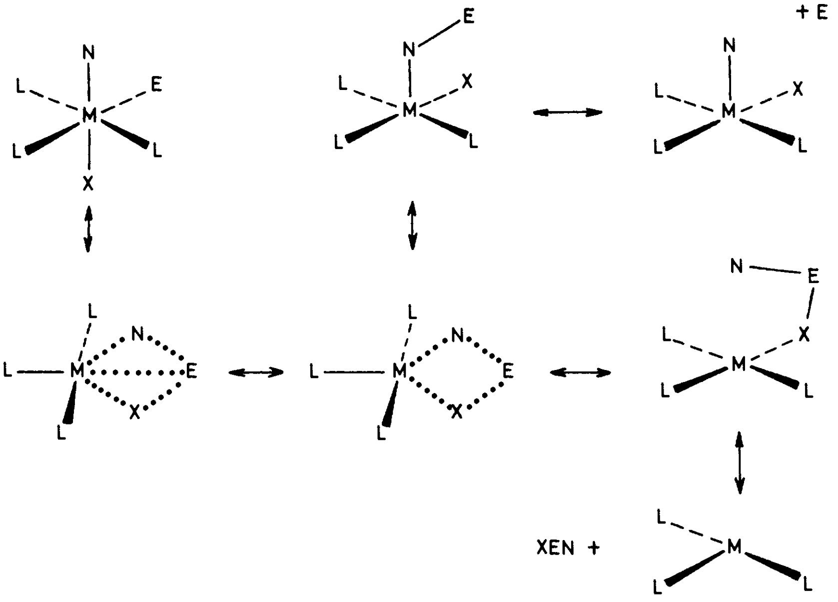
[30] R. J. Mureinik, *Coord. Chem. Rev.*, 1978, **25**, 1.

[31] M. J. Blandamer, J. Burgess, and R. Romeo, *Inorg. Chim. Acta*, 1982, **65**, L179; M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1982, **54**, 2285.



Scheme 8 *Relationships between the primary interactions of* E–N (E *and* N *are electrophile and nucleophile, respectively) with square-planar* MXL_3, *which can lead subsequently to replacement of* X *by another ligand*

4 Oxidative Addition Reactions

The ligand substitution is effected by the operation both of an oxidative addition step and a reductive elimination step, as in equation 10.[32] Since it is the modes of

$$[PtMe_2(PEt_3)_2] + I_2 \longrightarrow [PtI_2Me_2(PEt_3)_2] \longrightarrow [PtMeI(PEt_3)_2] + MeI \qquad (10)$$

interaction of the reacting molecules which are being compared here, we concentrate on the oxidative addition step. Although one type of oxidative addition reaction has already been related to the nucleophilic and electrophilic substitutions discussed in the last sections, the mechanistic variations available to reactions thus described are truly vast and further extend the range of interactions encountered.

$$L_4M + AB \longrightarrow L_4MAB \qquad (11)$$

Represented in general terms by equation 11, oxidative addition reactions have usually been classified into one of three types; concerted, S_N2 two-step, or free radical.[5,33] The free-radical mechanism is quite distinct from the paired-electron

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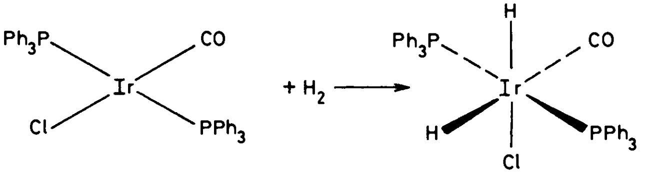
[32] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[33] *Ref.* 8, p. 408.

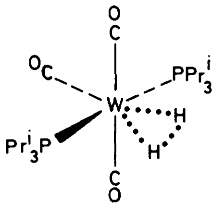
processes being compared here and will not be discussed further (though it is worth noting that it can sometimes be difficult in practice to distinguish between the operation of this route and the S_N2 two-step mechanism [5c,8]).

Concerted oxidative-addition leads to products with (initially) *cis* entering groups. It is typified by H_2 addition to Vaska's compound (equation 12), and had



(12)

been likened to O_2 or C_2H_4 additions. This similarity has recently been amplified by the description of an 'H₂ complex', (1), which probably resembles an intermediate stage in a reaction like 12.[34] Whereas concerted *trans* addition is a symmetry-forbidden proces,[8,35] *cis* addition is allowed. Often described in terms of overlap of a filled d_{xz} or d_{yz} orbital of the metal and an empty σ^* orbital of the adding molecule (Figure 2),[8] this would be essentially an electrophilic attack at the metal and such concerted oxidative additions have usually been referred to as this.[5] As Saillard and Hoffmann have pointed out,[36] however, an overlap of a filled σ orbital of A–B with an empty metal acceptor-orbital must also be involved, representing a transfer of charge in the other direction, from A–B to the metal. (Both interactions weaken A–B and strengthen M–A and M–B, see Figure 2). These authors also suggest, because of the experimental requirements of co-ordinative unsaturation, that *initial* flow of electron density from AB to M might be more important than the reverse. In this description, then, the concerted oxidative addition, of, for example, H_2 to a square-planar molecule resembles *nucleophilic* attack at the metal, at least in the early stages. The formal similarity between simple addition of an η^1 ligand and concerted oxidative addition has been emphasized previously,[35] though if two *trans* ligands of the metal are bent away from the entering group(s), the energy of the interaction appears to be greatly reduced.[36]



(1)

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[34] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451.

[35] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

[36] J.-Y. Saillard and R. Hoffman, *J. Am. Chem. Soc.*, 1984, **106**, 2006.

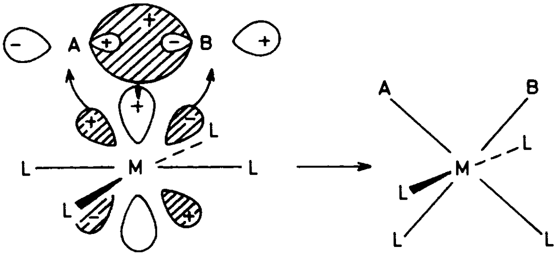


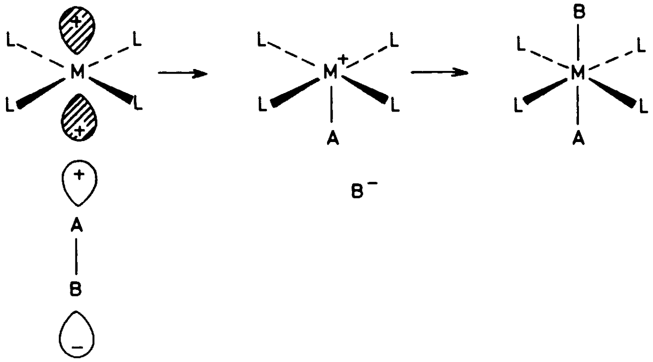
Figure 2

The S_N2 two-step route is probably the most difficult of the mechanisms to assess. Represented by Scheme 9, it can apply to the addition of dipolar molecules such as MeI or HCl, and involves *electrophilic* attack at the metal atom.[5,8] Clearly the initial interaction is exactly opposite to the processes we have examined so far, all of which can be related to nucleophilic attack at the metal. Though uncommon, there are precedents for the same atom of a molecule acting as both electrophile and nucleophile in different reactions. Equation 13, for example, shows PCl_3 acting as a nucleophile,[37] whilst equation 14 involves the same P atom in an acceptor role.[38]

$$[Ni(CO)_4] + 4PCl_3 \longrightarrow [Ni(PCl_3)_4] + 4CO \qquad (13)$$

$$PCl_3 + NMe_3 \rightleftharpoons Cl_3PNMe_3 \qquad (14)$$

The case of square-planar molecules is somewhat different, however, in that the donor orbital (presumably the filled d_{z^2}) and acceptor orbital (p_z) have the same symmetry with respect to the entering group along the z-axis. Evidence for the operation of this S_N2 two-step process is clearly worthy of close scrutiny to



Scheme 9

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[37] W. C. Smith, *Inorg. Synth.*, 1960, **6**, 20.
[38] R. H. Holmes and R. P. Wagner, *Inorg. Chem.*, 1963, **2**, 384.

establish whether or not it can be regarded as established, so we shall examine the evidence in greater detail than in the previous sections.

Many possible examples have been shown to be first order in both reagents.[39–48] Examples include methyl iodide addition to Vaska's complex,[39,43] and related iridium,[41,46] rhodium, [40] or platinum compounds,[44,48] and similar addition reactions of other polar molecules.[41,47] The order of reaction is not very helpful in itself in establishing the mechanism operating here, however, since it does not distinguish between two-step mechanisms like Scheme 9 (where the initial step is rate-determining) and concerted processes like Figure 2, or indeed some compromise between the two.

Scheme 9 implicates a *trans* geometry of addition, but this can be misleading. Geometry change at intermediate cationic complexes, $[ML_4A]^+$, is a possible fast process, and examples are known.[49] Thus 16-electron 5-co-ordinate species seem at least as likely to undergo complicating isomerizations as the 18-electron analogues met in the first section following nucleophilic interactions. Some octahedral platinum(IV) complexes, products of oxidative additions to square-planar Pt^{II} species, were found to isomerize readily by ligand loss to form 5-co-ordinate cations.[48] (It should be noted also that free-radical addition routes can lead to *trans* products.[8]) Clearly, then, product geometry is not definitive in establishing the mechanistic route. In practice many examples of *trans* addition of polar molecules have been detected[45,50–56] (equation 15 is an example[50]) including some where chelating ligands would make geometry change unlikely.[45,51,53] Examples of *cis* addition of polar molecules, including hydrogen halides and cases where neighbouring group participation (*vide infra*) is important, are, however, also recorded.[57–60]

Observation of the stereochemistry at A or B (Scheme 9 and Figure 2) should

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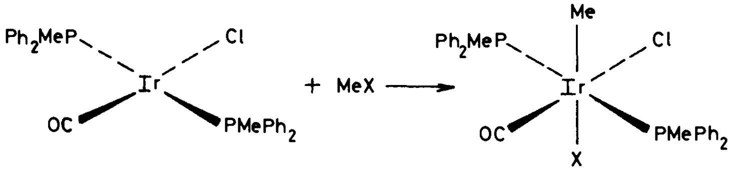
[39] P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1966, **88**, 3511.
[40] I. Douek and G. Wilkinson, *J. Chem. Soc. A*, 1969, 2604.
[41] R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Am. Chem. Soc.*, 1972, **94**, 7364.
[42] M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, 1973, **7**, 195.
[43] H. Stieger and K. Kelm, *J. Phys. Chem.*, 1973, 290.
[44] J. K. Jawad and R. J. Puddephatt, *J. Organomet. Chem.*, 1976, **117**, 297.
[45] J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, 1974, **96**, 3019.
[46] W. H. Thompson and C. T. Sears, *Inorg. Chem.*, 1977, **16**, 769.
[47] J. Burgess, M. J. Hacker, and R. D. W. Kemmitt, *J. Organomet. Chem.*, 1974, **72**, 121.
[48] T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organomet. Chem.*, 1974, **65**, 275.
[49] P. Meakin, R. A. Schunn, and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, **96**, 277; A. D. English, P. Meakin, and J. P. Jesson, *J. Am. Chem. Soc.*, 1976, **98**, 422.
[50] J. P. Collman and C. R. Sears, *Inorg. Chem.*, 1968, **7**, 27.
[51] J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Am. Chem. Soc.*, 1973, **95**, 2687.
[52] A. Morarskiy and J. K. Stille, *J. Am. Chem. Soc.*, 1981, **103**, 4182.
[53] J. L. Paterson, I. T. E. Nappier, and D. W. Meek, *J. Am. Chem. Soc.*, 1973, **95**, 8195.
[54] D. Strope and D. F. Shriver, *Inorg. Chem.*, 1974, **13**, 2652.
[55] F. M. Miller and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1974, 480.
[56] R. G. Pearson and C. T. Kresge, *Inorg. Chem.*, 1981, **20**, 1878.
[57] E. M. Hyde and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1975, 765.
[58] L. Vaska, *J. Am. Chem. Soc.*, 1966, **88**, 5325.
[59] H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 1968, 2516.
[60] D. M. Blake and M. Kubota, *Inorg. Chem.*, 1970, **9**, 989.



(15)

afford a means of distinguishing between the operation of concerted or two-step ionic routes. Concerted addition should involve retention of configuration, whereas the S_N2 two-step mechanism would require inversion. (Free-radical processes should lead to racemization). In practice the few studies that have been made with optically active organic halides[61,62] have led to no clear conclusions.[63–65] One problem is the potential involvement of free-radical processes, either intrinsically or *via* exposure to oxygen.[64] As a general caveat, it should be noted that a comparative study of several oxidative addition reactions led to the conclusion that free-radical paths were often almost competitive with other routes.[66]

Operation of the S_N2 two-step mechanism in the presence of other anionic species should be expected to lead to the incorporation of these into the product. Scheme 10 depicts a clear example of this.[45] When the reaction with butyl bromide was performed in the presence of Cl^-, the chlororhodium complex was isolated (subsequent halogen exchange was not responsible.) Acetonitrile solvates resulted from methyl tosylate reactions. On the other hand, addition of MeI to $[Ir(SCN)(CO)L_2]$ (L = PPh_3 or $PMePh_2$) in the presence of excess SCN^- in dichloroethane, or to $[IrCl(CO)L_2]$ in the presence of Cl^-, resulted in no incorporation of the free anions in the products,[61] and the addition of MeI to Vaska's complex in the presence of $^{131}I^-$ involved no uptake of radioactive iodine,[67] though the geometry of these additions is believed to be *trans*.[50] Either a one-step route must operate under these conditions, or intimate ion-pairs must be retained throughout.

To complete the preliminary general view of the requirements of the S_N2 two-step mechanism, solvent effects must be considered. Obviously polar solvents should favour and accelerate this ionic route, and this appears to be the case. The magnitude of solvent effect on, for example, H_2 or O_2 additions is less than on RX or HX additions, which might be expected to conform to Scheme 9.[39–41,43,44,47,52,68]

Inevitably the effects are not straightforward, as the choice of solvent can affect the *course* of the reactions by differentially altering the rates of competing paths.

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[61] R. G. Pearson and W. R. Muir, *J. Am. Chem. Soc.*, 1970, **92**, 5519.

[62] J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1970, 612.

[63] G. M. Whitesides and D. J. Boschetto, *J. Am. Chem. Soc.*, 1971, **93**, 1529.

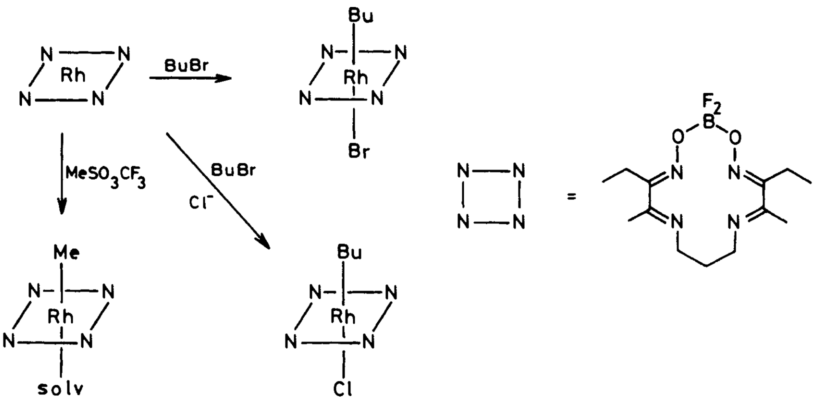
[64] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Am. Chem. Soc.*, 1972, **94**, 4043; J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Am. Chem. Soc.*, 1973, **95**, 7908.

[65] F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, 1971, **93**, 6339.

[66] R. G. Pearson and P. E. Figidore, *J. Am. Chem. Soc.*, 1980, **102**, 1541.

[67] P. B. Chock and J. Halpern, *Proc. 10th Int. Conf. Coord. Chem.*, 1967, 135.

[68] K. Walper and H. Z. Kelm, *Z. Phys. Chem. (Neue Folge)*, 1978, **113**, 207.

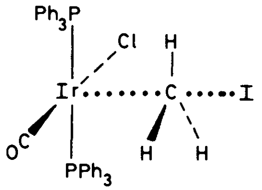


Scheme 10

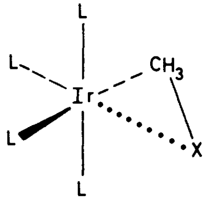
For example, *cis* addition of HX to Vaska-type complexes was found in benzene[60] or toluene,[68] but some *trans* addition is also apparent in MeOH, MeCN, H_2O, or DMF.[60] Moreover, some solvents may exert other effects: DMF reacts with MeI leading to a 20-fold increase in conductivity,[40] and casting some doubt on the suitability of this solvent for kinetic investigation.

Already then it can be seen that there is not a clear-cut class of reactions adhering simply to the S_N2 two-step route, although a few systems do show strong evidence for the operation of an ionic mechanism compatible with Scheme 9. Further consideration of specific cases is needed to identify the intimate interactions involved.

The suggestion that these oxidative addition reactions of organic halides and similar molecules proceed by nucleophilic attack at carbon originated in the first instance from the similarity of the activation parameters (particularly the large negative value of $\Delta S^\ddagger$) for MeI and $[IrX(CO)(PPh_3)_2]$ [39] to those for the reactions of alkyl halides and tertiary amines. These latter reactions are well established as proceeding *via* linear S_N2 displacements at carbon, so a transition state like (2) seemed plausible. Later studies on related oxidative additions, however, revealed that the marked solvent effects on rate did not exactly parallel the change in solvent polarity, and the substituent effects on rates of addition of *para* substituted benzyl halides did not resemble those of their reactions with pyridine.[41] The authors concluded that an asymmetric transition-state like (3) was more likely than a linear one, and explained the large negative $\Delta S^\ddagger$ and solvent effects by the marked deformations of the iridium complexes from planarity. A greater degree of Ir–C bond making than of C–X bond breaking was necessary to account for observed electronic effects (*vide infra*), and the variable degree of Ir ••• X bond formation could usefully account for the previously mentioned ambiguities over retention or inversion of configuration at carbon.



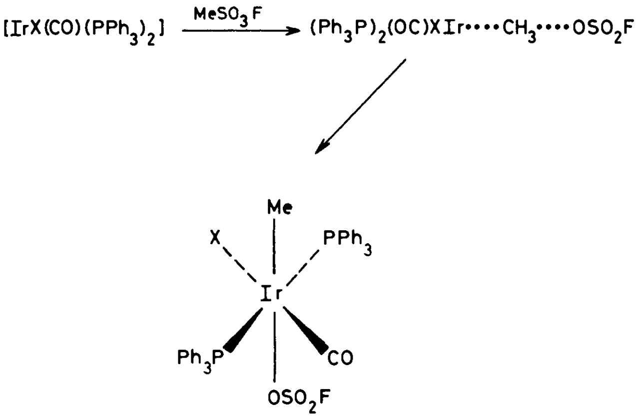
(2)



(3)

Activation volume measurements of the addition of MeI or O_2 to Vaska's complex in several solvents provided more information.[43] $\Delta V^{\ddagger}$ are negative, in keeping with a bond-making associative rate-determining step. The values for MeI were not as great as for the Menschutkin reaction between MeI and pyridine, and the authors considered that they fitted a linear transition-state such as (2) better than simultaneous formation of two bonds as in (3) (interestingly, they pointed out that $Ir \cdots I \cdots CH_3$ bond making would fit the data as well as $Ir \cdots CH_3 \cdots I$).

The reactions of $MeSO_3F$ or $MeSO_3CF_3$ with Vaska's complex[47,53,54,69] or $[RhCl(Ph_2PC_3H_6PPhC_3H_6PPh_2)]$[53] were also found to be in keeping with nucleophilic displacement of SO_3F^- or $SO_3CF_3^-$ from carbon, and with a linear transition-state as in equation 16. The reactions were more rapid than with MeI, probably because SO_3F^- is a better leaving group. Altogether, then, the evidence in favour of operation of the S_N2 two-step route in *some* examples is quite compelling, though a gradation of intermediate configurations ranging from (2) to (3) seems likely. Further comparative studies of such reactions both strengthen the case for this mechanism (Scheme 9) and add interesting extra detail.



(16)

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[69] D. Strope and D. F. Shriver, *J. Am. Chem. Soc.*, 1973, **95**, 8197.

Several studies of oxidative additions to iridium or rhodium complexes, [MX(CO)L_2], found consistently that more basic or electron-donating ligands, L, (usually tertiary phosphines) increased the reaction rate.[39–42,46,68] This is entirely consistent with increased electron-density on the metal atom enhancing nucleophilic attack by the metal on the substrate. The rates of reaction generally parallel the basicity of the metal atom, as determined from the *extent* of protonation by benzoic acid.[70] (It should be noted that tertiary phosphines exert a steric effect also:[41,46] indeed when L is P(*o*-tol)$_3$, oxidative additions to [IrX(CO)L_2] do not proceed at all.[46])

The effects of varying the halide, X, of [MX(CO)L_2] are less easy to explain. For additions of H_2, O_2,[39] and hydrogen halides (which usually undergo *cis* additions)[68] rates increase in the order of $X = Cl < Br < I$. Paralleling increasing basicity at the metal,[70] this could again be interpreted in terms of electrophilic attack at the metal. The order for the addition of organic halides, however, is $X = F \gg Cl > Br > I$, the reverse of that observed above.[39,42,47] The basis of an explanation may lie in the fact that the ligands L are usually *trans* in both the reactants and products, and probably do not change position during the course of reactions. X and CO on the other hand, are in the plane of entering H_2, O_2, or (*cis*)HX, and are displaced as the new bonds form. This is presumably also the case with transition states resembling (3) for organic halide addition,[68] and it is quite conceivable that CO and X bend towards a trigonal-bipyramidal geometry even with a linear transition-state. If so it would be quite reasonable for L_2 and CO,X to exert their electronic effects in different ways, as is observed. It should be noted that the apparent conformality of the halogen effect in the H_2 or O_2 additions could be misleading since, as we have seen, these interactions could well be nucleophilic. The relative effects on rate of altering the halide are not as great as those brought about by changing L.

Changing the halide of the adding molecule RX has a relatively small effect,[41,47] but when R is aryl, it is found that electron-withdrawing substituents increase the reaction rate.[71–73] This, too, is indicative of electrophilic attack by carbon on the metal, though a three-centre transition-state like (3) could still operate.[72] CF_3I fails to add to [RhX(CO)$(PPh_3)_2$], whereas MeI reacts readily.[40] Reversal of the polarity of the C–I bond might explain this, and would lend support to the S_N2 two-step route as the general mechanism for organic halide addition, but steric or other factors could be involved.

In some cases ligand loss from the square-planar molecules prior to the oxidative addition step has been shown not to occur,[43,73] and this is presumed to be so with the majority of reactions described above. A few examples have been described, however, where L is lost from [RhClL_3][74] or [IrX(CO)L_2] prior to addition. The increased lability of rhodium compounds or high temperatures in the iridium cases

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[70] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1969, 1802.

[71] J. Blum, M. Weitzberg, and R. J. Mureinik, *J. Organomet. Chem.*, 1976, **122**, 261.

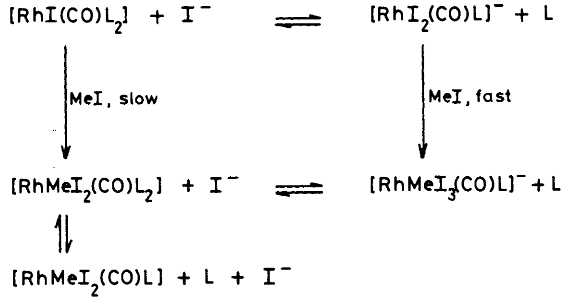
[72] R. J. Mureinik, M. Weitzberg, and J. Blum, *Inorg. Chem.*, 1979, **18**, 915.

[73] D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, 1979, **101**, 4992.

[74] Y. Ohtani, M. Fujimoto, and A. Yamagishi, *Bull. Chem. Soc., Jpn.*, 1977, **50**, 1453.

were probably responsible. Though described as ligand loss, the process is most likely one of ligand displacement by solvent. The solvated species formed appear to undergo oxidative additions by the same type of mechanisms as described, though at different rates to their precursors.[72,74]

An interesting variation is the iodide-catalysed methyl iodide addition to [RhI(CO)L_2].[75] When L is Ph_3As or Ph_3Sb (but not Ph_3P), it is displaced by iodide and the anionic complex formed adds MeI much faster than the neutral parent compound (Scheme 11), as might be anticipated for electrophilic attack at the metal. Whilst this type of system does not appear to be common, it can have profound effects when it operates. For example, dissociated triaryl-phosphine from [RhCl(CO)L_2] reacts with MeI to form [PAr_3Me]I, and this iodide in turn co-ordinates to rhodium forming $[RhClI(CO)L]^-$, which reacts much more rapidly than the original complex.[76] An induction period sometimes observed for such reactions might be thus explained.[40,76]



Scheme 11

Iodide catalysis of a different kind has been reported by Louw and co-workers.[77,78] Rather than displace a ligand, I^- *adds* to $[Ir(cod)(phen)]^+$, and the 5-co-ordinate [IrI(cod)(phen)] reacts oxidatively more rapidly with MeI (Scheme 12)[77] or O_2[78] than does the square-planar cation. (Indeed an earlier report indicated that MeI would not react at all in the absence of I^-.[79]) Activation parameters for the iodide-catalysed k_2 step resemble those for the k_1 step indicating the same type of transition-state configuration; reasonably S_N2 displacement of I^- from carbon. Nucleophile catalysis of this sort has also been established for the addition of hydrogen halides to several square-planar iridium complexes.[56,79–81] Co-ordination of polar solvent molecules as well as halide ions enhance the

[75] D. Forster, *J. Am. Chem. Soc.*, 1975, **97**, 951.

[76] S. Franks, F. R. Hartley, and J. R. Chipperfield, *Inorg. Chem.*, 1981, **20**, 3238.

[77] D. J. A. de Waal, T. I. A. Gerber, and W. J. Louw, *Inorg. Chem.*, 1982, **21**, 1259.

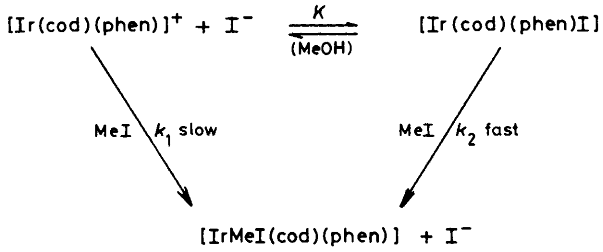
[78] W. J. Louw, T. I. A. Gerber, and D. J. A. de Waal, *J. Chem. Soc., Chem. Commun.*, 1980, 760.

[79] G. Mestroni, A. Camus, and G. Zassinovich, *J. Organomet. Chem.*, 1974, **73**, 119.

[80] J. E. Chapman, D. J. A. de Waal, and W. J. Louw, *J. Chem. Soc., Chem. Commun.*, 1977, 845.

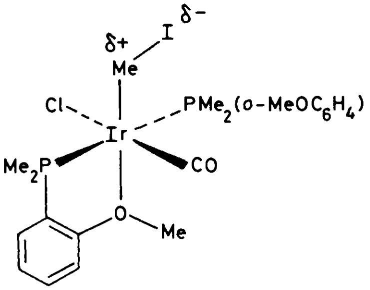
[81] T. V. Ashworth, J. E. Singleton, D. J. A. de Waal, W. J. Louw, E. Singleton, and E. Van der Stok, *J. Chem. Soc., Dalton Trans.*, 1978, 340.

abstraction of H^+ from HX, and it is interesting to speculate to what extent this effect might account for the acceleration of S_N2 two-step mechanisms by polar media.



Scheme 12

The possible importance of polar-solvent co-ordination in promoting two-step oxidative additions is given more emphasis by the discovery by Shaw and co-workers of neighbouring group participation in some systems. Oxidative additions of HCl, MeCl, MeBr, MeI, CCl_4, Cl_2, and PhCOCl to phosphine complexes of Rh^I, Ir^I, or Pt^{II} are all enhanced when the phosphine is $PMe_2(o\text{-}MeOC_6H_4)$, compared to PMe_2Ph, and nucleophilic attack by ligand oxygen at the metal, making it in turn more nucleophilic, is proposed as the explanation [See structure (4)].[55,82,83] Interestingly, no activating effect of these *ortho*-methoxy groups was found for H_2 addition to $[IrCl(CO)L_2]$, and although a low polarity transition-state could be the explanation,[57] the view that H_2 approach actually resembles *nucleophilic* attack[36] is a reasonable alternative.



(4)

Taking account of nucleophilic catalysis in oxidative addition reactions both weakens and strengthens the case to be made for the S_N2 two-step route. When nucleophilic catalysis operates, even by solvent co-ordination, the species being

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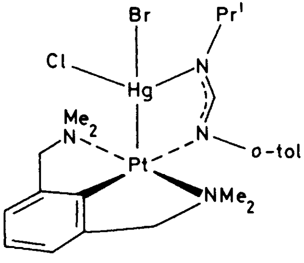
[82] H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1974, 1980.
[83] A. G. Constable, C. R. Langrick, B. Shabanzadeh, and B. L. Shaw, *Inorg. Chim. Acta*, 1982, **65**, L151.

attacked by the electrophile is an 18-electron 5-co-ordinate molecule, and not the 16-electron square-planar complex under scrutiny. There are many examples of electrophilic attack at 18-electron species, and the process can be regarded as well established.[84–87] It seems probable that some apparent examples of the S_N2 two-step route will be, in reality, assignable to this 18-electron route, thus reducing the number of authentic examples. On the other hand it seems clear that many can not be. Some proceed in non-polar solvents, where a significant solvent intereaction seems unlikely. In other cases no change has been noted, and no incorporation observed, when (potentially catalytic) anions have been present. Since there is good reason for believing that 18-electron species undergo closely related processes to these 16-electron molecules,[66,77] the case for electrophilic attack at least at some square-planar molecules is strengthened by the comparison. To this evidence we should now add the isolation of a number of compounds which can be described as $L_4M \longrightarrow E$. These correspond to the transition state following electrophilic attack in the oxidative addition sequences described above. Examples include adducts of Vaska's complex and related molecules with BF_3 or $B(C_6F_5)_3$, which are described in terms of $Ir \longrightarrow B$ co-ordinate bonding.[88] Also, there is evidence to indicate that many metal–metal bonded complexes containing 5-co-ordinate platinum or palladium should be described as electron-pair donation from the Pt or Pd atoms.[89–92] Compound (5) is an example. Clearly it is not only simple species like H^+ or $CH_3{}^+$ which behave as electrophiles to square-planar molecules.



(5)

With the establishment (finally!) of the electrophilic attack route, we now have the curious situation that a square-planar molecule might undergo oxidative addition by a nucleophilic attack followed by electrophilic attack, or *vice versa*! With the potential at intermediate stages for geometry change, and for gradations

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[84] J. P. Collman and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1966, 244.

[85] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1970, 3356.

[86] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.

[87] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.

[88] R. N. Scott, D. F. Shriver, and D. Lehman, *Inorg. Chim. Acta*, 1970, **4**, 73.

[89] A. F. M. J. van der Ploeg, G. van Koten, and K. Vrieze, *J. Organomet. Chem.*, 1982, **226**, 93.

[90] A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, and A. J. M. Duisenberg, *Organometallics*, 1982, **1**, 1066.

[91] A. F. M. J. van der Ploeg, G. van Koten, K. Vrieze, and A. L. Spek, *Inorg. Chem.*, 1982, **21**, 2014.

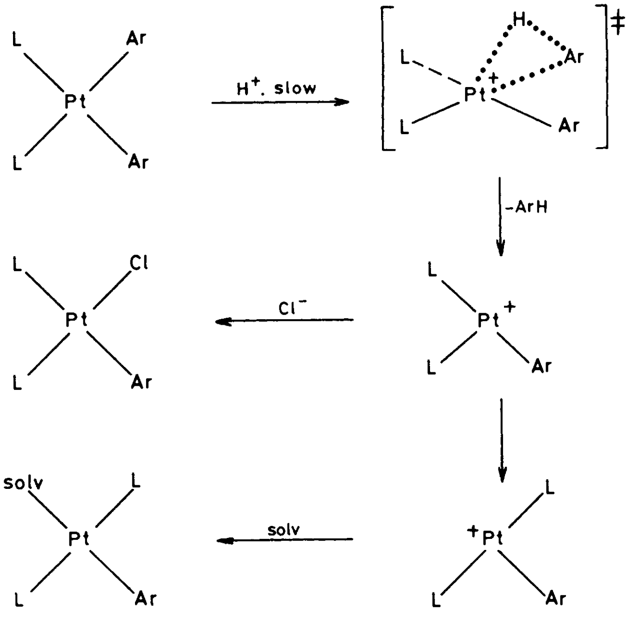
[92] A. F. M. J. van der Ploeg, G. van Koten, and C. Brevard, *Inorg. Chem.*, 1982, **21**, 2878.

away from these classical extremes, the number of possible reaction pathways is again dramatically extended. One more variation needs now to be explored.

Methanolic hydrogen chloride reacts with organoplatinum complexes to cleave R-groups, as in equation 17. Early studies indicated that the mechanism involved

$$[PtR_2L_2] \xrightarrow[-RH]{HCl} [PtRClL_2] \xrightarrow[-RH]{HCl} [PtCl_2L_2] \quad (17)$$

oxidative addition of HCl to Pt (*via* H^+ attack at the metal) followed by reductive elimination of RH.[93] More recent studies on arylplatinum compounds found the reactions to be first order in $[H^+]$ and zero order in $[Cl^-]$. The reaction rate was increased by electron-donating aryl substituents.[94] The authors considered that Scheme 13 best accounted for their observations, the rate-determining step being proton attack *at the Pt–C bond*, a step consistent with the very high deuterium kinetic isotope effects observed. The 3-co-ordinate intermediates could well be solvated, but prior co-ordination of solvent or anion seems unlikely since the reactions are kinetically independent of $[Cl^-]$. Direct attack of $[H^+]$ at the carbon atom, in these cases leading to Wheland-type intermediates (6), offers an alternative pathway, and we have now reached a situation identical to the elimination



Scheme 13

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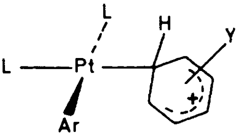
[93] U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.*, 1967, **89**, 6494.

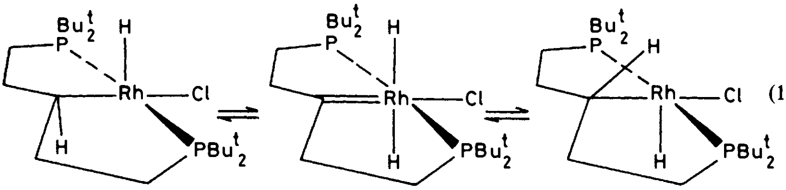
[94] R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chem.*, 1978, **17**, 2813.

pathways already depicted in Schemes 7 and 8, resultant on electrophilic attack at a co-ordinated ligand.

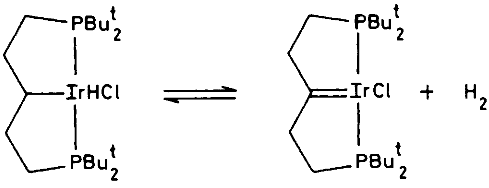


(6)

Since electrophilic attack might take place at either the metal atom, ligand atom, or metal–ligand bond, it seems reasonable that migration of the attacking electrophile across this bond might occur in some cases. This would be difficult to prove, though a theoretical study has indicated that such migrations are feasible,[95] (though more facile at 5-co-ordinate 18-electron species), and hydrogen migrations from carbon to metal (α-eliminations) are common,[96] though not always complete. Equations 18 and 19[97] show two equilibria which appear to involve such migrations.



(18)



(19)

The base-catalysed rearrangement shown in equation 20 may proceed *via* migration of I and PMe_3 across a Rh–C bond,[98] and several similar reactions of platinum complexes could well be related.[99]

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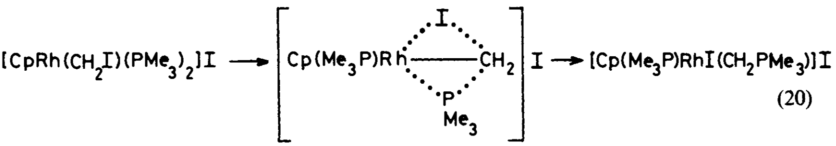
[95] J. V. Ortiz, Z. Havlas, and R. Hoffman, *Helv. Chim. Acta*, 1984, **67**, 1.

[96] R. J. Cross in 'The Chemistry of the Metal–Carbon Bond', ed. F. R. Hartley and S. Patai, John Wiley & Sons, New York, 1985, Vol. 2, p. 559.

[97] (*a*) C. Crocker, R. J. Errington, R. Markham, C. J. Moulton, K. J. Odell, and B. L. Shaw, *J. Am. Chem. Soc.*, 1980, **102**, 4373; (*b*) H. D. Empsall, E. M. Hyde, R. Markham, W. S. McDonald, M. C. Norton, B. L. Shaw, and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 1977, 589.

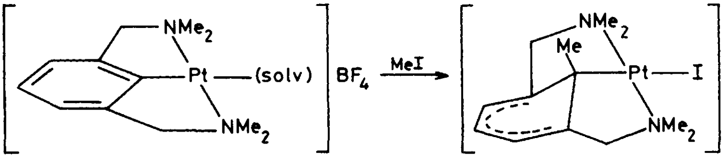
[98] R. Feser and H. Werner, *Angew. Chem., Int. Edn. Engl.*, 1980, **19**, 940.

[99] (*a*) N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White, and J. Holton, *J. Organomet. Chem.*, 1982, **228**, C71; (*b*) J. R. Moss and J. C. Spiers, *J. Organomet. Chem.*, 1979, **182**, C20; (*c*) N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White, and J. Holton, *J. Chem. Soc., Chem. Commun.*, 1981, 698.



(20)

Finally, the unusual oxidative addition of MeI to a square-planar platinum complex (equation 21) might also involve migration across the Pt–C bond.[100] The possibility of these migrations, like the potential for geometry change at the various 5-co-ordinate intermediates we have met, all indicate caution in inferring mechanistic detail from product geometry.



(21)

5 Concluding Remarks

Though this survey is far from comprehensive and takes but a superficial look at some of the reaction types discussed, it is clear that a relationship between many types of reaction mechanism can be demonstrated, ranging gradually right from nucleophilic attack to electrophilic attack at the metal, and encompassing nucleophilic substitution, S_E2 (cyclic) interactions, oxidative additions, dissociative ligand exchange, and even some reactions of co-ordinated ligands. These descriptions must therefore be regarded as extremes and attempting to classify reactions simply as one of these types may be misleading. Scheme 14 summarizes the main pathways in stylized manner. Ligand X of $[MXL_3]$ is replaced by nucleophile, N (which can also be part of N–E or N^- and E^+).

Evidence exists for the operation of all the pathways described in Scheme 14, though the number of choices will depend on the complexity of the interacting systems (*e.g.* L_3 could be three different ligands, creating divergence of some of the pathways and increasing the number of stereochemical options: a choice of leaving groups would lead to yet more variations). Exactly which pathway(s) any individual system follows may be difficult to predict, since it will depend on the nature of all the variables shown in Scheme 14, as well as on the hidden ones such as solvent (which can interact with the attacking species as well as the square-planar

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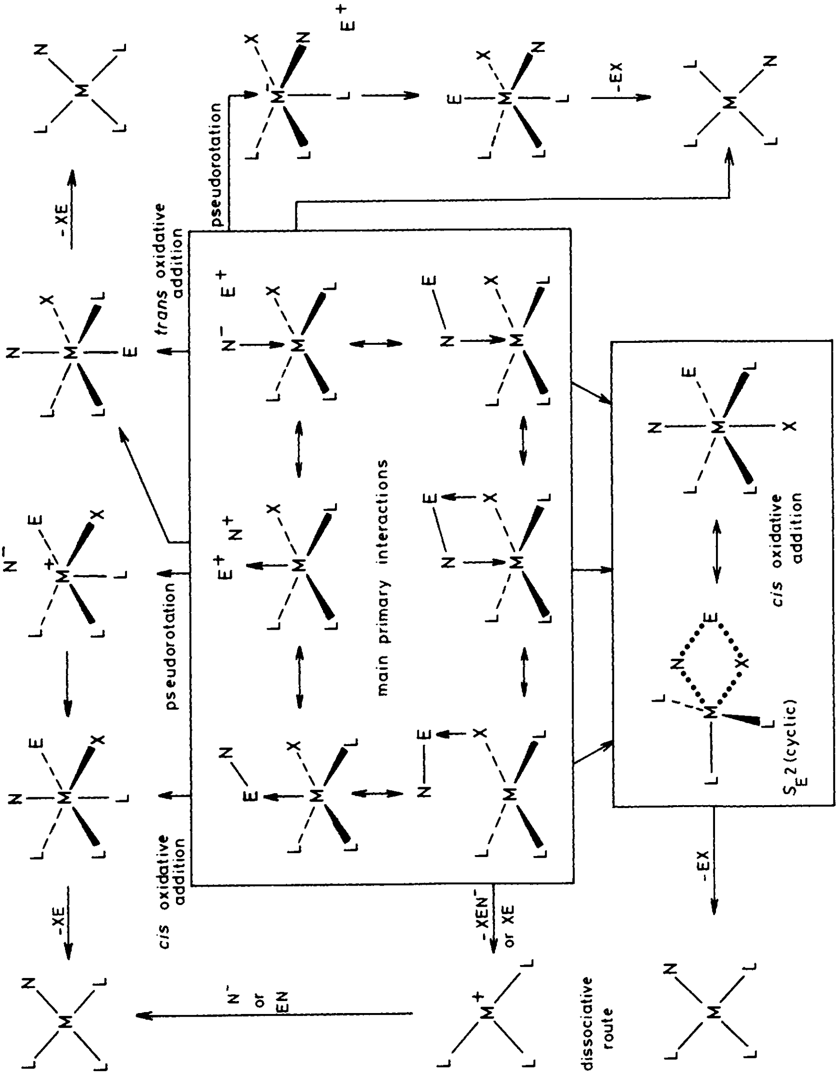
[100] D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek, and H. C. Ubbels, *J. Am. Chem. Soc.*, 1982, **104**, 6609.



Scheme 14 *Interactions of* E–N (*or* E^+ *and* N^-) *with* $[ML_3X]$, *leading to replacement of* X *by* N

molecule). At present it would seem that much more work is needed before predictions of the reaction pathways followed by square-planar molecules can be made confidently, though an understanding of the range of available options is at least a step in the right direction.