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Recent fundamental studies on migratory insertion into metal-carbon bonds

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Contents

Abstract

Numerous unsaturated substrate molecules undergo migratory insertion with metal-carbon bonds. Recent attention has been focused on insertion of CO and alkenes into d^8 metal hydrocarbyl and acyl bonds with the aim of understanding the fundamental steps involved. Knowledge of ligand control over rates and regioselectivity of the insertion reaction would allow the design of highly active and selective catalyst systems for a whole range of carbon-carbon bond forming reactions. Herein are summarised recent advances in delineating the detailed aspects of the insertion mechanism and ligand influences on rates and regioselectivity. Investigations have provided information on the nature of pre- and post-insertion intermediates; the nature of the carbon-carbon bond forming step; ligand control, and advances in theoretical modelling of the details of the intricate insertion reaction.

Keywords: Migratory insertion; d^8 metal complexes; CO; Alkenes; Intermediates and mechanism; Ligand influences

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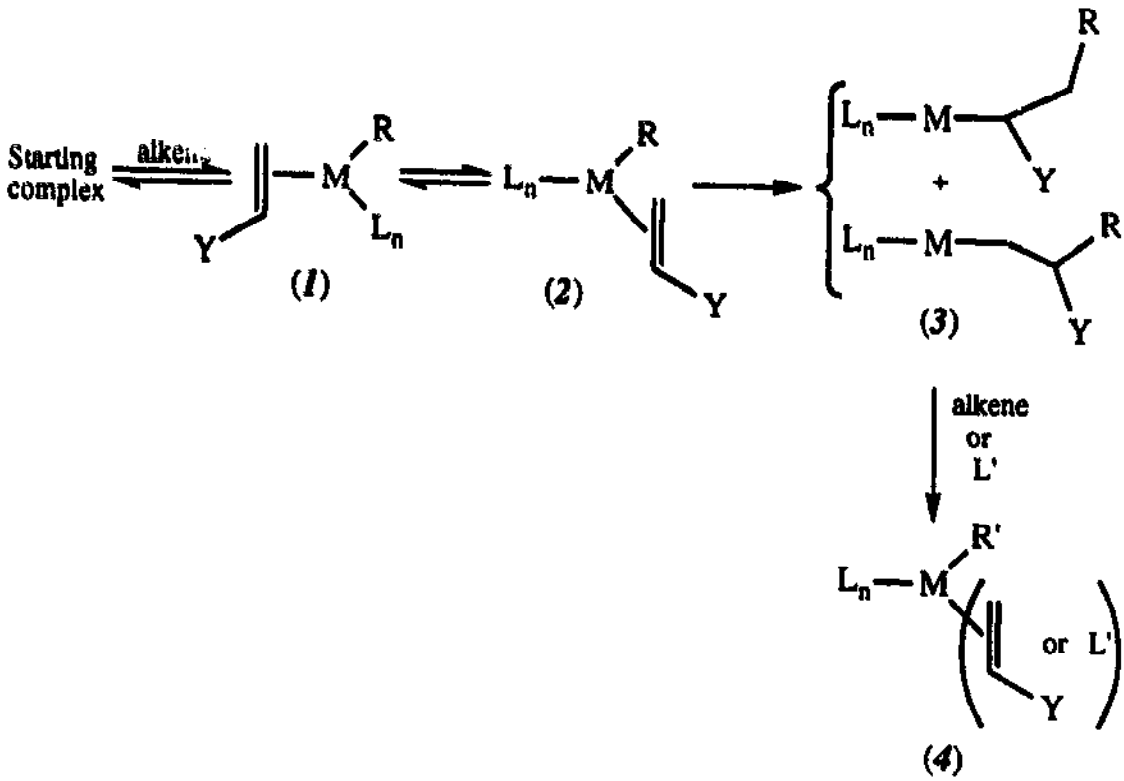
1. Introduction

The migratory insertion of unsaturated molecules into a metal-carbon bond is a fundamental reaction in many important chain growth reactions [1,2]. The recent resurgence of interest in understanding and controlling this process is largely a consequence of major industrial activity, primarily in polyolefin chemistry [3] and in polyketone production [4]. Olefin oligomerisation and co-oligomerisation [5], carbonylation/alkoxycarbonylation of alkenes [6] and alkynes [7] are other examples of important reactions of on-going interest involving migratory insertion. Insertion is generally understood as a reaction involving the incorporation of an unsaturated molecule, such as an alkene, alkyne or CO into a metal-element bond, commonly a metal-carbon bond. The reaction often leads to chain growth.

It is particularly appropriate that a review of the insertion process should appear in a special edition of Coordination Chemistry Reviews recognising the contribution of Professor Kees Vrieze to chemistry. Apart from his other many and varied achievements in chemistry, in recent years Professor Vrieze, his group and collaborators have been leading contributors to a fundamental understanding of processes involving CO and alkene insertion. The work of the Amsterdam group has provided a greatly enhanced understanding of these important reactions.

The generally accepted mechanism for migratory insertion consists of the following broad steps, illustrated for alkenes in Scheme 1: coordination of the unsaturated



Scheme 1.

substrate to the metal centre (*1*); isomerisation, if necessary, of the resulting metal complex to provide an intermediate (*2*) from which migratory insertion can occur (it is believed that the two reacting species on the metal centre are held in mutually cis positions and in energetically favourable orientations); migratory insertion of the *cis*-hydrocarbyl/substrate groups ((*2*)→(*3*))]; stabilisation of the unsaturated complex via complexation with an appropriate liganding group (*4*). The characteristics of ligands in the reacting complex have been shown to have a marked effect on the rate of reaction and the insertion pathway. Furthermore, in a catalytic process the insertion pathway will have a large bearing on the final product distribution. Consequently, a detailed understanding of the insertion reaction and the role of ligands in modifying the reaction is important to the rational development of catalyst systems.

This review is not intended to be a comprehensive evaluation of all literature reports which discuss reactions containing a migration step, as this is clearly beyond the scope of this short article. Discussions will be confined to highlighting very recent developments (principally in the last 5-7 years) in selected reactions involving migratory insertion. There have been many catalytic and stoichiometric reactions reported that include a migratory insertion step at some stage during the process. However, only those accounts will be included here in which the insertion step is specifically discussed. Emphasis will be focused on fundamental studies that enhance the understanding of the insertion process and on ligand influences in modifying the insertion pathway. The majority of recent studies investigating insertion reactions have looked at systems containing Groups 4 and 10 metals. Developments in the application of Group 4 metal complexes as catalysts for polyolefin formation are so diverse and numerous that restraints on the size of the review preclude an adequate discussion of this area, and hence only reactions of Group 10 metals will be highlighted here. Furthermore, many aspects of Group 4 catalysed polyolefin chemistry have been recently and thoroughly reviewed [3].

Complexes of Group 10 metals have been extensively studied as catalysts and as models for the insertion of CO and/or alkenes (and alkynes) into metal-carbon (or metal-alkoxy, etc.) bonds. Attention will be focused on reactions involving alkenes and CO. Whilst insertion may occur with a variety of metal-element bonds (e.g. M-C, M-H, M-O, etc.) only insertion into metal-carbon bonds will be discussed, as the principles covered are in general common to other insertions. A number of important aspects of the reaction have received particular attention; i.e. whether the reaction proceeds via an insertion of the substrate molecule into a metal-ligand bond or whether the σ-co-ordinated group migrates to the olefinic carbon (or carbonyl carbon); whether migratory insertion occurs from a four coordinate species ("dissociative route") or a five coordinate intermediate ("associative route"); the stereochemistry of the migratory insertion step; the role of nonparticipative ligands on rates and stereochemistry of the migratory insertion, are just some of the questions that have been addressed. These aspects of the reaction are considered in separate sections.

2. Insertion vs. ligand migration

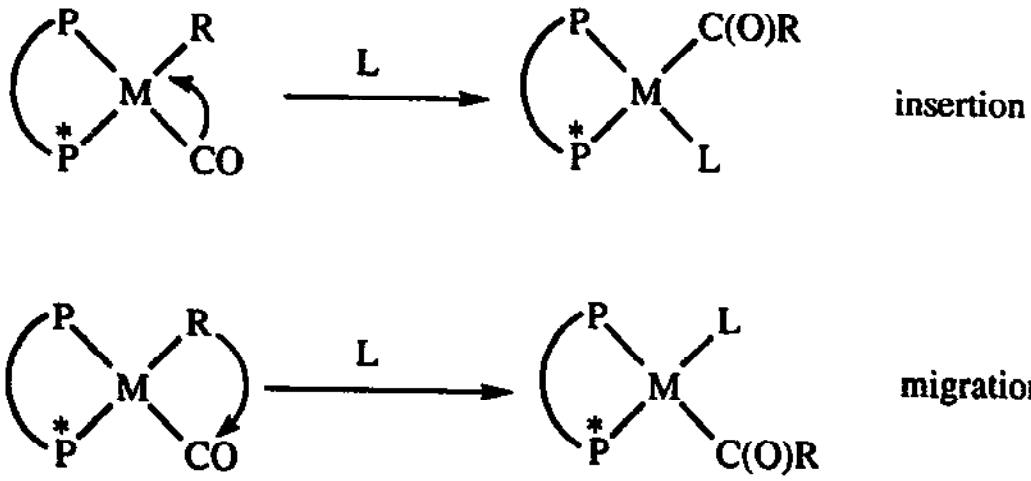
The question of whether the chain-growth process follows a stereochemical pathway in which the *cis*-hydrocarbyl group migrates to the coordinated substrate, or whether the substrate inserts into the metal-carbon bond has been the basis of many studies. Much of the work reported has concentrated on carbonylation processes, i.e. migratory insertion of carbon monoxide to give an acyl complex. Early investigations looking at migratory insertion in methylmanganese carbonyl complexes provided evidence in favour of an alkyl migration process [8–10]. Isotopic labelling was employed to follow the stereochemistry at the metal centre during insertion [8,9]. It was found that the reacting fragments, the carbon monoxide and the hydrocarbyl group, should be cis to each other prior to insertion. A more recent study of carbonylation in the methylmanganese bipyridyl carbonyl complex {*fac*-[$Mn(CO)_3$(bipy)(Me)]}, in the presence of incoming ligand L, was unable to differentiate between possible pathways [11]. However, it was found that, in contrast to the accepted migration mechanism, incoming L occupied a coordination site trans to the resulting acyl group.

Alkyliron carbonyl complexes have also been extensively investigated in attempts to delineate the details of the migratory insertion step for the carbonylation process [12–19]. Investigations involve ligand- [19], solvent- [18] and halide-assisted [17] carbonylation. Whilst studies largely favour an alkyl migration pathway, information is conflicting, or at best ambiguous, and few provide experimental evidence to differentiate between insertion or migration. However, very recent studies by van Leeuwen and coworkers [20,21] on alkylplatinum and palladium complexes containing nonsymmetrical chelating phosphine ligands (P-P*) have provided, for the first time, unambiguous experimental evidence demonstrating that the migratory insertion process occurs via ligand migration for these complexes. ^{31}P NMR was able to clearly differentiate between the individual phosphorus signals of the ligands and follow the complex isomerisation and migratory insertion steps for both CO and alkene reactions (Scheme 2).

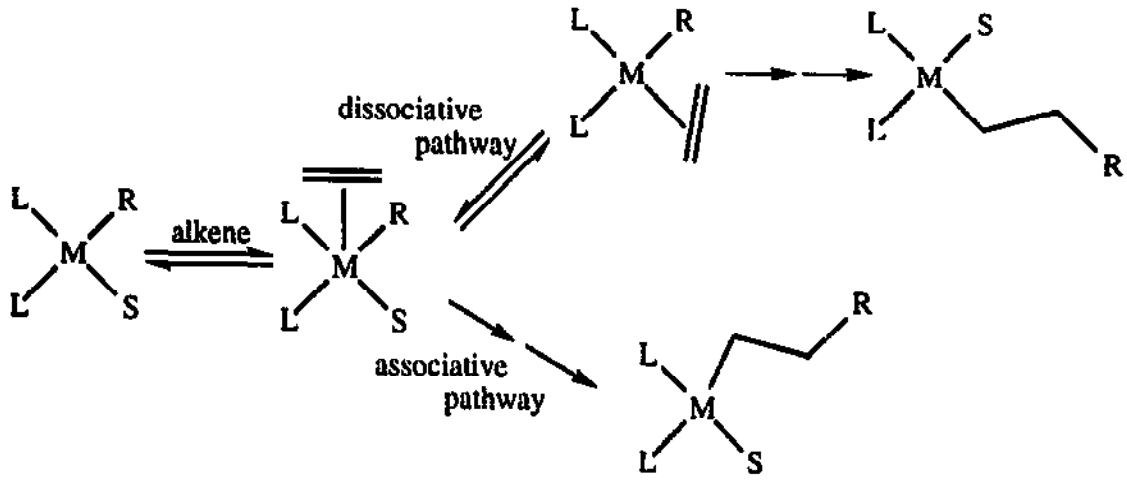
Van Leeuwen et al. also note that in the migration mechanism when a series of migrations occur, i.e. the growing chain alternates between cis sites on the metal centre, it is implied that the fastest catalysts will be those which contain symmetric chelate ligands, e.g. diphosphines or bipyridines [20].

3. Pre-insertion intermediate: four-coordinate or five-coordinate

Another fundamental question regarding migratory insertion that has been extensively studied is whether insertion occurs from a four-coordinate or five-coordinate intermediate, i.e. whether the insertion pathway can be described as an associative or dissociative process (Scheme 3). The terms associative and dissociative are at times somewhat blurred. Even processes that insert from a four-coordinate intermediate may initially form five-coordinate species with the incoming substrate molecule, i.e. for the substrate to obtain a coordination site before inserting a ligand exchange



Scheme 2.



Scheme 3.

process is necessary which may take place via an associative process. Molecular rearrangements (e.g. pseudorotations) to give the required *cis*-alky/substrate intermediate probably also involve five-coordinate intermediates. In the context of this review the term dissociative refers to a pathway in which the migratory insertion occurs from a four-coordinate intermediate, and an associative pathway is one in which the migratory insertion occurs from a five-coordinate indermediate.

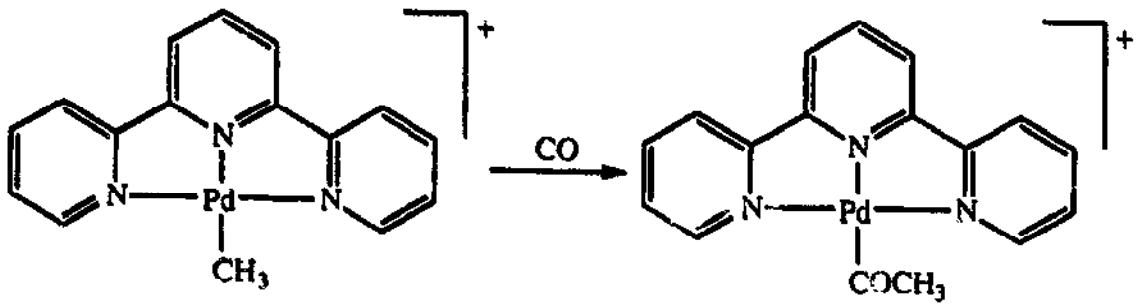
A notable early contribution to this aspect of the mechanism was that of Garrou and Heck [22] who studied the insertion of CO into hydrocarbylmetal (bisphosphine) complexes $[MR(L)_2X]$ (M = Pt, Pd, Ni; R = hydrocarbyl group; L = phosphine; X = halide). Kinetic studies undertaken on the insertion process were interpreted in terms of two possible insertion pathways originating from an initial five-coordinate intermediate $[(MR(CO)(L)_2X]$. The favoured pathway which is inhibited by excess ligand (L) is a dissociative one in which insertion occurs from a four-coordinate complex [MR(CO)LX]. The second, slower route, not inhibited by

excess ligand, is an associative pathway and involves direct insertion from the five-coordinate intermediate. In the presence of sufficient L only the associative route is followed. This study is an important one in that it indicates that either or both pathways may occur depending on the nature of the complex and the reaction conditions. More recent investigations appear to be consistent with the conclusions of Garrou and Heck.

There is a body of research which indicates that for palladium complexes, at least, the preferred reaction pathway is a dissociative one. One example is the work of Samsel and Norton [23] who provide kinetic and ^{31}P NMR data to show that intramolecular migratory insertion of alkyne and alkene for several palladium complexes occurs via four-coordinate intermediates involving equilibrium displacement of a phosphine ligand by the unsaturated species. In agreement with this result, a very recent study by Cavell and Jin [24] has demonstrated that intramolecular insertion of an alkene in palladium complexes containing chelating anionic ligands probably occurs from four-coordinate intermediates. Kinetic evidence is provided supporting initial coordination of the olefinic species followed by partial dissociation of the chelate ligand prior to insertion. Other recent examples highlighting the generally preferred dissociative mechanism for insertion in palladium complexes are discussed in the following sections describing ligand influences.

Strong evidence has been provided by recent investigations to suggest insertion does occur from five-coordinate intermediates if reaction conditions are appropriate [25–27]. In particular, studies by Vrieze and coworkers [26] seem to provide clear evidence of CO insertion in a palladium complex (1) which almost certainly involves a five-coordinate intermediate. They found that the cationic complex [(σ^3-*N,N'N''*-2,2':6',2''-terpyridyl)methylpalladium(II)] chloride dihydrate rapidly inserts CO into the Pd-Me bond in water or MeOH as solvent (Scheme 4). The inflexibility of the tridentate ligand precludes the formation of a free coordination site by partial dissociation of the ligand. Coordination of CO prior to insertion most likely involves a five-coordinate intermediate. The rigidity of the ligand also prevents de-insertion of CO for the same reason. Boersma and coworkers [27] have also proposed a five coordinate intermediate for CO insertion into a palladium-carbon bond for a complex containing a tridentate ligand.

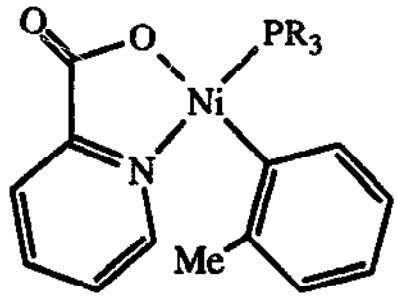
Five-membered intermediates have also been implicated in carbon-carbon bond



(1)

Scheme 4.

forming reactions involving cationic platinum and palladium complexes containing chelating diazabutadiene ligands [28], although insertion may still be occurring from four-coordinate species. Reactions involving nickel complexes often involve five-coordinate species as intermediates or isolable complexes [29], and very recently, for catalytic systems involving hydrocarbylnickel complexes with chelating pyridinecarboxylate ligands (**2**), it has been suggested that insertion occurs from five-coordinate species [30].

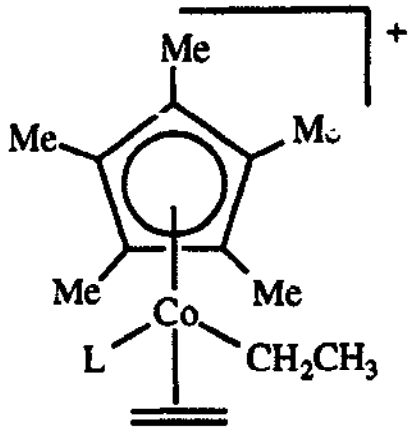


(**2**)

4. Identification of intermediates in migratory insertion reactions

A number of important developments relating to identification and isolation of intermediates formed prior to or during migratory insertion reactions have occurred in recent years. In particular, Brookhart and coworkers have identified examples of *cis*-alkyl/alkene complexes which are active intermediates in catalytic alkene conversion processes [31,32]. Employing high-pressure NMR techniques, the hydrocarbylcobalt intermediates (**3**) and (**4**) were identified during ethylene polymerisation reactions [33]. In a similar study on pentamethylcyclopentadienylrhodium complexes, ^{1}H and ^{13}C NMR spectroscopy was employed to establish the intermediates (**5**) and (**6**) as the resting states in the catalytic dimerisation of ethylene [32].

Of particular relevance to this review are the most recent investigations of Brookhart and coworkers in which the reaction of hydrocarbylpalladium and nickel complexes with CO and ethylene were studied [33,34]. Treatment of the cationic palladium complex [PdMe(1,10-phenanthroline)(OEt_2)]$^+$ (**7**) with slightly less than one equivalent of ethylene at -78 °C gave rise to the *cis*-methyl/ethylene complex [PdMe(C_2H_4)(1,10-phenanthroline)]$^+$ (**8**) [33]. In the presence of excess ethylene the *cis*-ethyl/ethylene complex [PdEt(C_2H_4)(1,10-phenanthroline)]$^+$ (**9**) (and propene) is formed. The latter complex, which is described as the catalyst resting state for the dimerisation of ethylene, was isolated as an unstable solid at -78 °C and separately characterised. Rate constants for ethyl migration were also determined. Treatment of the initial methyl complex (**7**) at -78 °C with CO formed the isolable *cis*-methyl/carbonyl intermediate [PdMe(CO)(1,10-phenanthroline)]$^+$ (**10**) [33].



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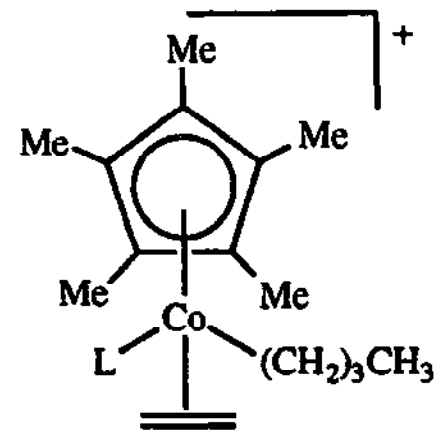
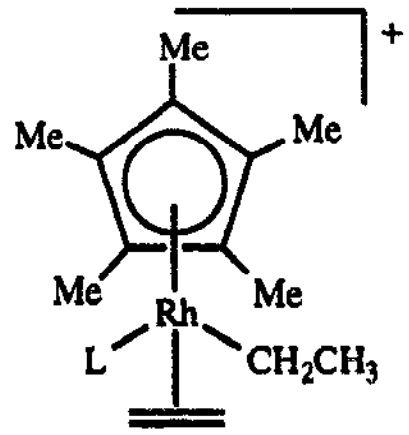


(4)



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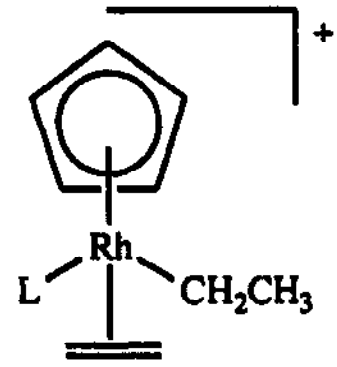


(6)

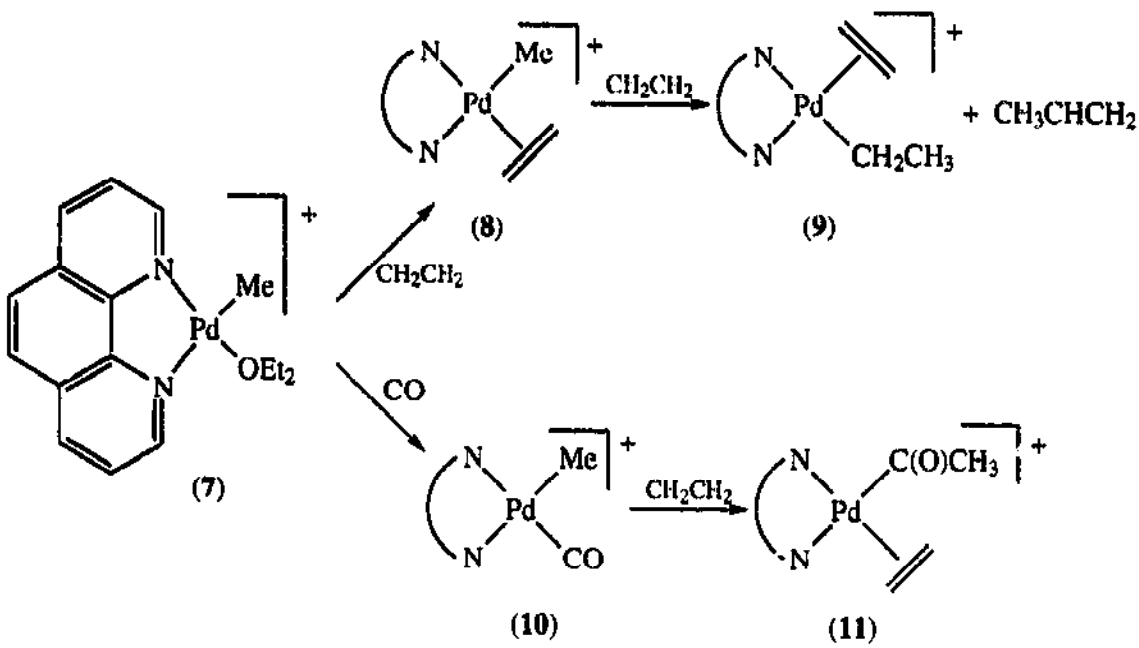
The acyl carbonyl complex [Pd(COMe)(CO)(1,10-phenanthroline)]$^+$ could also be isolated at -50 °C and an X-ray structure obtained. Reaction of the methyl carbonyl complex at -66 °C with ethylene gave the remarkable acyl olefin complex [Pd(COMe)(C_2H_4)(1,10-phenanthroline)]$^+$ (11) and small amounts of complexes resulting from ethylene insertion. The reactions and complexes are outlined in Scheme 5. This represents a unique achievement, in which intermediates linked to three related migratory insertion reactions at the same metal centre have been observed. $\Delta G^{\ddagger}$ values for the insertion reactions were determined and found to increase in the order Me→CO (15.4±0.1 kcal mol; −66 °C)<acyl→C_2H_4 (16.6±0.1; −46 °C)<alkyl→C_2H_4 (~19; −25 °C). Rix and Brookhart [33] argue that the high barrier for alkyl/alkene migratory insertion relative to alkyl/carbonyl migratory insertion may help to explain the alternating nature of the chain growth reaction for these catalysts.

In a further study, Brookhart and coworkers [34] have investigated Pd(II) and Ni(II) catalysts for the polymerisation of α-olefins. The catalyst precursors are cationic methyl complexes which incorporate bulky diimine ligands (**12**). NMR studies established the *cis*-alkyl/alkene complexes as the catalyst resting states. Reaction of the palladium complex with propylene at -30 °C gave the *cis*-propylene/methyl complex (**13**), from which the chain growth could be monitored and the rate of migratory insertion measured (Scheme 6). Significantly, the first insertion enabled the propylene alkyl complex (**14**) to be observed, which indicated a 2,1-regioselectivity for insertion. From these studies, a detailed chain growth mechanism was proposed.

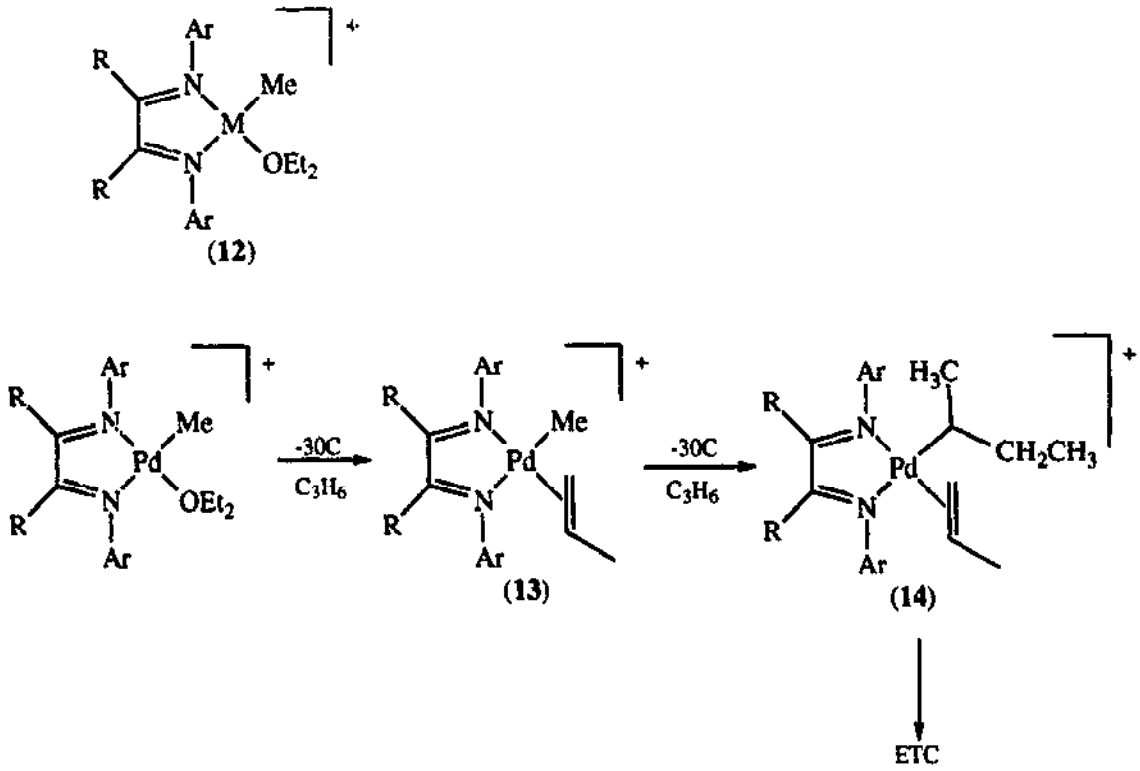
Tóth and Elsevier have investigated the reaction of CO with the palladium complex [Pd(Me){(*S*,*S*)-BDPP}Cl] [where (*S*,*S*)-BDPP=(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane] [35]. Consistent with earlier mechanistic proposals, they identified spectroscopically the square-planar *cis*-alkyl(carbonyl)-transition-metal complex (**15**) containing a chelating diphosphine which they propound is an intermediate in the formation of the acyl complex. The carbonyl complex, which has the *cis*-(CO/Me) and *trans*-(P/Me) configuration is believed to be important for insertion to occur, and subsequent acyl species are thought to be formed in the reaction sequence shown in Scheme 7 [35].

5. Theoretical modelling studies on migratory insertion

Modelling studies have provided valuable information on the nature of the migratory insertion process. From early studies by Berke and Hoffman [36], and later by



Scheme 5.

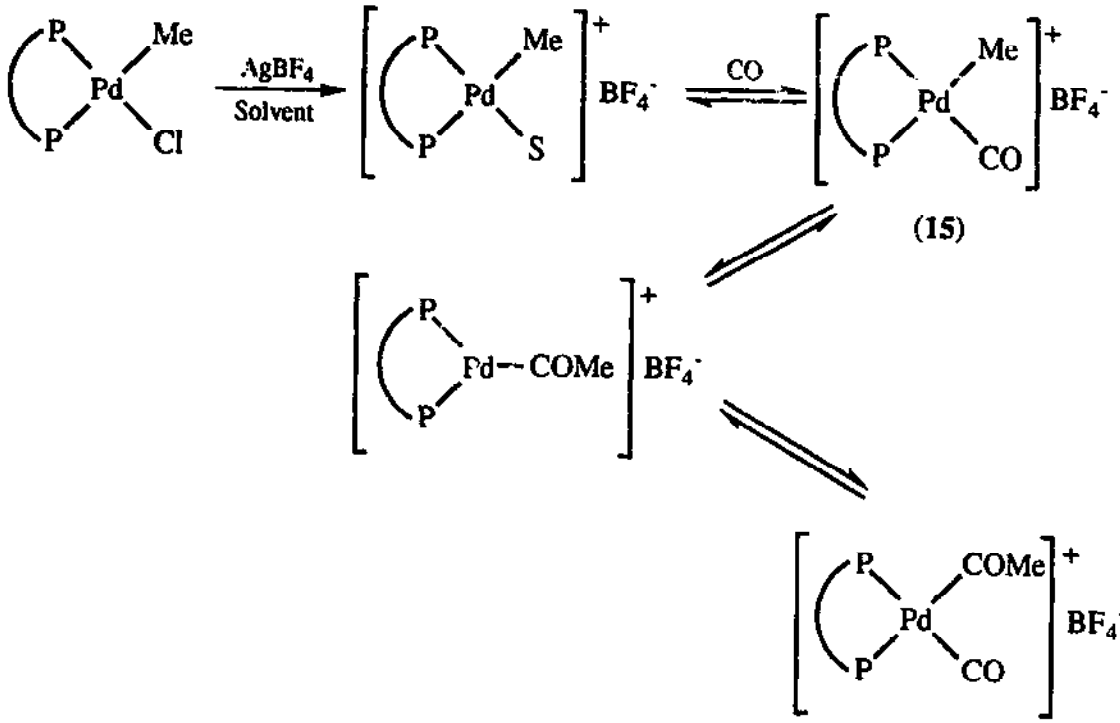


Scheme 6.

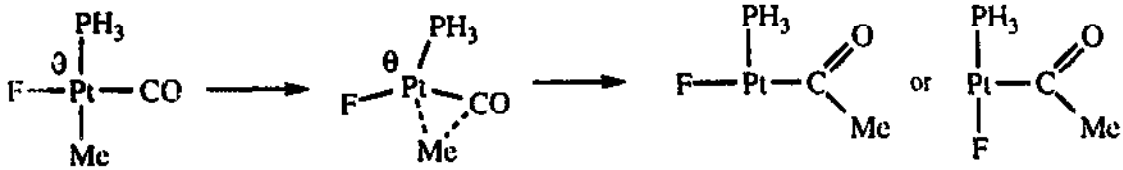
Sakaki et al. [37], using extended Hückel and ab initio calculations it was found that the activation energy for migratory insertion is lowered when the angle θ between the non-participatory ligands is increased in complexes of the type M(L)(L')(Me)(CO). In particular, Sakaki et al. looked at the reaction $Pt(F)(Me)(CO)(PH_3) \rightarrow Pt(F)(COMe)(PH_3)$ along three different reaction pathways: methyl migration, carbonyl migration or simultaneous migration with opening of the F-Pt-P angle. Results indicated that methyl migration and opening of the F-Pt-P angle would give the lowest energy pathway (Scheme 8).

Further studies by Koga and Morokuma [38] have investigated a similar model, $M(Me)(H)(CO)(PH_3)$ (in which M = Pd and Pt). The carbonylation reaction which is shown as a methyl migration proceeds via a three-centre transition state. The transition state is composed of a hybrid three-centre orbital stabilised by interaction between metal (d + p) orbitals, the carbonyl π* orbital and a methyl sp^3-like orbital (Scheme 9). This proposal is in agreement with a previous suggestion [39] that ligands which tend to provide the alkyl group with partial negative charge and the CO with partial positive charge will increase the reaction rate. These studies also indicate that the energy of migration of the methyl group can also be lowered by using ligands with a large trans influence in the position trans to the migrating alkyl group.

A number of more recent studies by Morokuma and coworkers [40,41] have employed extended Hückel and ab initio methods to analyse the migratory

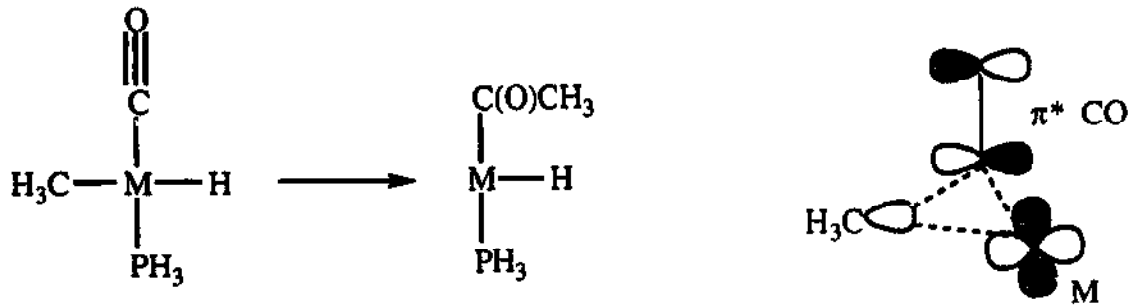


Scheme 7.



Scheme 8.

insertion of ethylene into the platinum-hydride bond in the complex *cis*-Pt(H)(C_2H_4)(PH_3)$_2$. Consistent with the CO insertion investigations, they found that the opening of the P-Pt-P angle concurrently with insertion provides a lower energy pathway. The importance of cis coordination of the ethylene to the hydride and coplanarity of the reacting groups was reconfirmed. Employing the previous



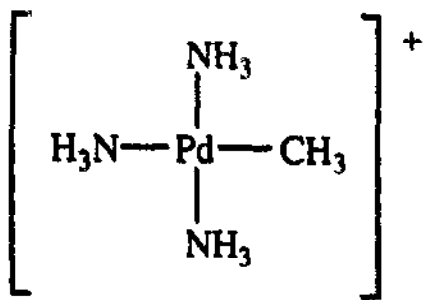
Scheme 9.

model system, $Pd(Me)(H)(CO)(PH_3)$, a comparison of methyl and hydride migration has been reported [41]. The authors conclude that while the hydride migratory insertion reaction is more endothermic than the methyl reaction, due to the stronger Pd-H bond, the three-centred transition state for hydride migratory insertion is more stable than the methyl counterpart (the hydrogen ls orbital is more appropriate for the three-centred interaction than the more directional carbon sp^3 hybrid orbital of the methyl group) [41]. Despite little experimental evidence for the reaction, based on the model systems studied it was believed that hydride migratory insertion can take place relatively easily.

A variety of studies involving CO insertion into transition metal-hydrogen and metal-carbon bonds have been undertaken in recent years [42,43]. These studies, however, involve scandium and magnesium complexes and hence fall outside the scope of this review and will not be considered further. The insertion of CO into metal-hydrogen and metal-methyl bonds for the second row transition metal atoms has been appraised by Blomberg et al [43].

Very recently, Markies [44] undertook extensive ab initio studies on the carbonylation of the cationic complex $[Pd(CH_3)(NH_3)_3]^+$ **(16)**. This complex models the actual complexes **(17)** that were prepared to experimentally investigate the insertion process. Both the formal dissociative and the associative routes for CO insertion were investigated at the restricted Hartree-Fock level (RHF).

Calculations on the dissociative route indicate that for such a pathway the rate determining step appears to be the dissociation of the NH_3 ligand. From these calculations the authors also propose an alternative explanation for the enhanced catalytic reactivity of cationic complexes, compared with closely related neutral species. Previously, it has been proposed that cationic metal centres possess an enhanced coordinating ability for nucleophilic reagents which lowers the transition state energy. Markies [44] suggested that it is not the energy of the transition state that is lowered but rather that of the final product. There is a much larger energy gain in going from the transition state to the final acyl complex for the cationic species.



Model complex

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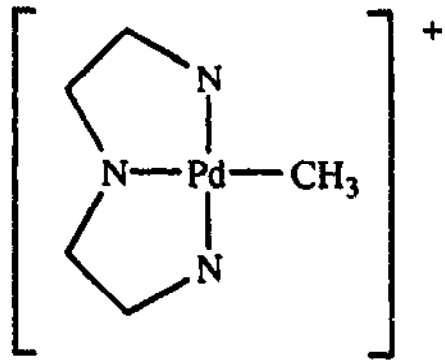


Real complex type

(17)

On consideration of the associative pathway Markies [44] found that formation

of either a square pyramidal or trigonal bipyramidal (TBP) structure is not favourable. A possible scenario is that as the CO enters the coordination sphere of the palladium to form a TBP structure one of the N-ligands (the ligand trans to the large trans influence methyl group) is forced out of the coordination plane, i.e. a CO induced/promoted ligand dissociation [42,43], leading to insertion from a four coordinate intermediate. The authors conclude that a purely dissociative mechanism is not likely, and similarly a purely associative mechanism is energetically unfavourable in the chosen model system. However, they propose that five-coordinate complexes may occur as transition states in the ligand exchange of NH_3 by CO, insertion then occurring from a four-coordinate intermediate.

An analysis of ab initio and non-local density functional calculations employing large basis sets have been performed on the model systems PdCO and $PdPH_3$ by Yates and coworkers [45]. These studies have been carried out in order to assess the influence of the basis set and electron correlation on properties of the Pd-C and Pd-P bonds, and to attempt to select current optimal methods for investigation of insertion steps in "real" catalytic systems.

6. Ligand influences on migratory insertion

6.1. CO insertion: monodentate ligands

Insertion of CO has been the most widely studied of the insertion processes, and most of the early investigations have concentrated on organo-metal complexes with monodentate ligands (primarily phosphines). It was found that the insertion pathway, whether associative or dissociative, was dependent on the basicity of the phosphine. Strongly basic phosphines favour an associative route while less basic phosphines favour a dissociative route [46]. Garrou and Heck have provided evidence that insertion may proceed via either an associative or dissociative route depending on the presence or absence of excess phosphine [22] (see Section 3). These early pioneering studies have been extensively reviewed [46,47] and hence will not be commented on further here. Most recent investigations on complexes with monodentate ligands have concentrated on hitherto less common carbonylation processes (see for example Refs. [48–54] and references cited therein) such as insertion of CO into metalallyl bonds (h^3 and h^1) [49,50], carbonylation of hydrocarbyl halides [48,52] and double carbonylation reactions [51]. In these studies little or no discussion of the insertion pathway is provided. Furthermore, aspects of these reactions have recently been reviewed [2,53,54]; consequently, no additional discussion of these reactions will be provided here.

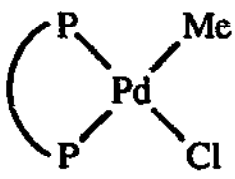
6.2. CO insertion: polydentate ligands

Much less is known about the insertion behaviour of organo-metal complexes containing polydentate ligands, and it is only in recent years that

substantial investigations into the behaviour of systems with chelating ligands have been undertaken. Chelate ligands may be expected to limit the likelihood of a dissociative process occurring, and consequently favour a five-coordinate pre-insertion intermediate. However, early studies looking at P-P, P-N and P-S ligand systems suggested that dissociation of one of the chelate donor atoms may occur to provide a vacant site for CO coordination [55]. It was found for a series of neutral platinum complexes, [PtClPh(P-Y)] (P–Y = 1,2-bis(diphenylphosphino)ethane (dppe), 1-(diphenylphosphino)-2-(diphenylarsino)ethane (appe), 1,3-bis(diphenylphosphino)propane (dppp), 1-(diphenylphosphino)-2-(dimethylamino)ethane (PC_2N) and 1-(diphenylphosphino)-2-(dimethylthio)ethane (PC_2S)), that the rate of carbonylation decreased in the order dppp > PC_2S > PC_2N ≫ appe, dppe [55]. Hence, hemilability of the chelate ligand was considered important. More recent investigations have examined complexes containing neutral bidentate P-P [56,57], P-N [58], N-N [59–66], N-O [67] ligands, and tridentate N-N-N [26,27,68], P-N-N [69] and P-O-N [67] ligands. Anionic, bidentate O-O, S-O β-diketonate-type ligands [70], N-O [71–74], and S-S [75] ligands have been studied.

Anderson and Lumetta [55] reported that the large rate differences for the carbonylation of platinum complexes [PtClPh(P-P)] (P–P = dppe, 1,3-dppp) were due to the higher flexibility of the dppp backbone, which lead to lower barriers to the conformational rearrangements necessary for migratory insertion. It has been shown that for the ligands dppp and 1,4-bis(diphenylphosphino)butane (dppb) the ligand backbone is bent out of the coordination plane and the phosphine phenyl groups can bend away from the other two coordination sites in the square planar complex [76]. More recently Vrieze and coworkers [57] have investigated CO insertion into Me-Pd bonds for a number of neutral (**18**) and ionic (**19**) methylpalladium complexes containing chelating phosphines. The rate of CO insertion was found to decrease in the order dppb ≈ dppp > dppf ≫ dppe, with the rate for the cationic complexes being at least ten times greater than those of the analogous neutral complexes. (It perhaps should be noted here that the insertion process may consist of a number of separate steps, e.g. CO coordination, ligand displacement and migratory insertion. In general it is not possible to separate these steps. When comparing rates this limitation should be kept in mind.)

In a consideration of ligand effects on the rate of carbonylation the authors found that the bite angle of the chelating phosphine and ligand backbone flexibility both strongly influence the rate of migratory insertion of CO in methylpalladium complexes [57]. It is argued that a large P-Pd-P angle will push the methyl group toward the coordinated CO molecule, possibly lowering the activation energy for migration. Flexible ligands can be expected to facilitate pseudorotations within intermediates formed during the carbonylation process, allowing configurations in which the CO and methyl group are cis to each other and in which the large trans influence phosphine is trans to the alkyl group, thus promoting migration. The authors point out that facilitation of complex rearrangements will be particularly important where the exchange of CO for other ligands takes place via an associative process.



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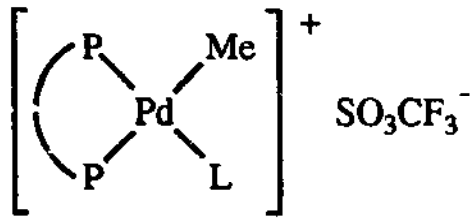


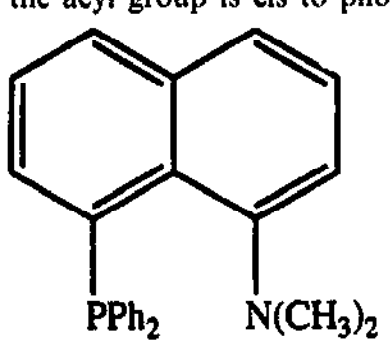
(19)

In terms of the remaining ligand, L (CH_3CN or PPh_3) or Cl^-, the rate of CO insertion follows the same trend as the ease of replacement of the coordinating anion and/or neutral ligand by CO and increases in the order $Cl^- < PPh_3 < CH_3CN$ [57]. This behaviour suggests that the carbonylation rate is largely dependent on the strength of coordination of the anion or L, and hence on the accessibility of a coordination site on the palladium centre

In a further study by Vrieze and coworkers [58], the CO insertion behaviour of methyl complexes of palladium- and platinum-containing chelating P-N ligands have also been investigated, and the influence of the chelate ligand was found to be somewhat more subtle [55,58]. The authors prepared a number of neutral and cationic complexes of the type [MCl(Me)(P-N)], $[(PN)M(Me)]^+Y^-$, $[M(Me)(P\text{-}N)CH_3CN]^+Y^-$, (where M = Pd or Pt; P–N = the rigid ligand 1-(dimethylamino-8-(diphenylphosphino)naphthalene (PAN) (**20**) or the more flexible 1-(dimethylamino)-3-(diphenylphosphino)propane (PC_3N) (**21**); $Y^- = Cl^-$, $SO_3CF_3^-$,BF_4^-) and studied their carbonylation behaviour.

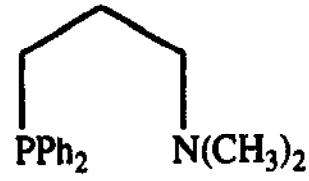
In the reaction of CO with the platinum complexes $[(PC_3N)Pt(Me)Cl]$, intermediates with a terminal CO in which the P-N is monodentate were identified at subambient temperatures [58]. On warming, subsequent insertion of the CO to give the acyl complex $[(PC_3N)Pt(C(O)Me)Cl]$ was observed, where the P-N ligand is again chelating. The proposed reaction sequence is provided in Scheme 10.

During the carbonylation of the cationic palladium complexes $[(PAN)Pd(Me)]^+Y^-$ and $[(PAN)Pd(Me)(CH_3CN)]^+Y^-$ the intermediate $[(PAN)PdMe(CO)]^+Y^-$ (Me cis to P) with the P-N ligand in the chelating form was identified [58]. Insertion then proceeded giving the appropriate acyl complex in which the acyl group is cis to phosphorus. As previously noted [57], insertion



PAN

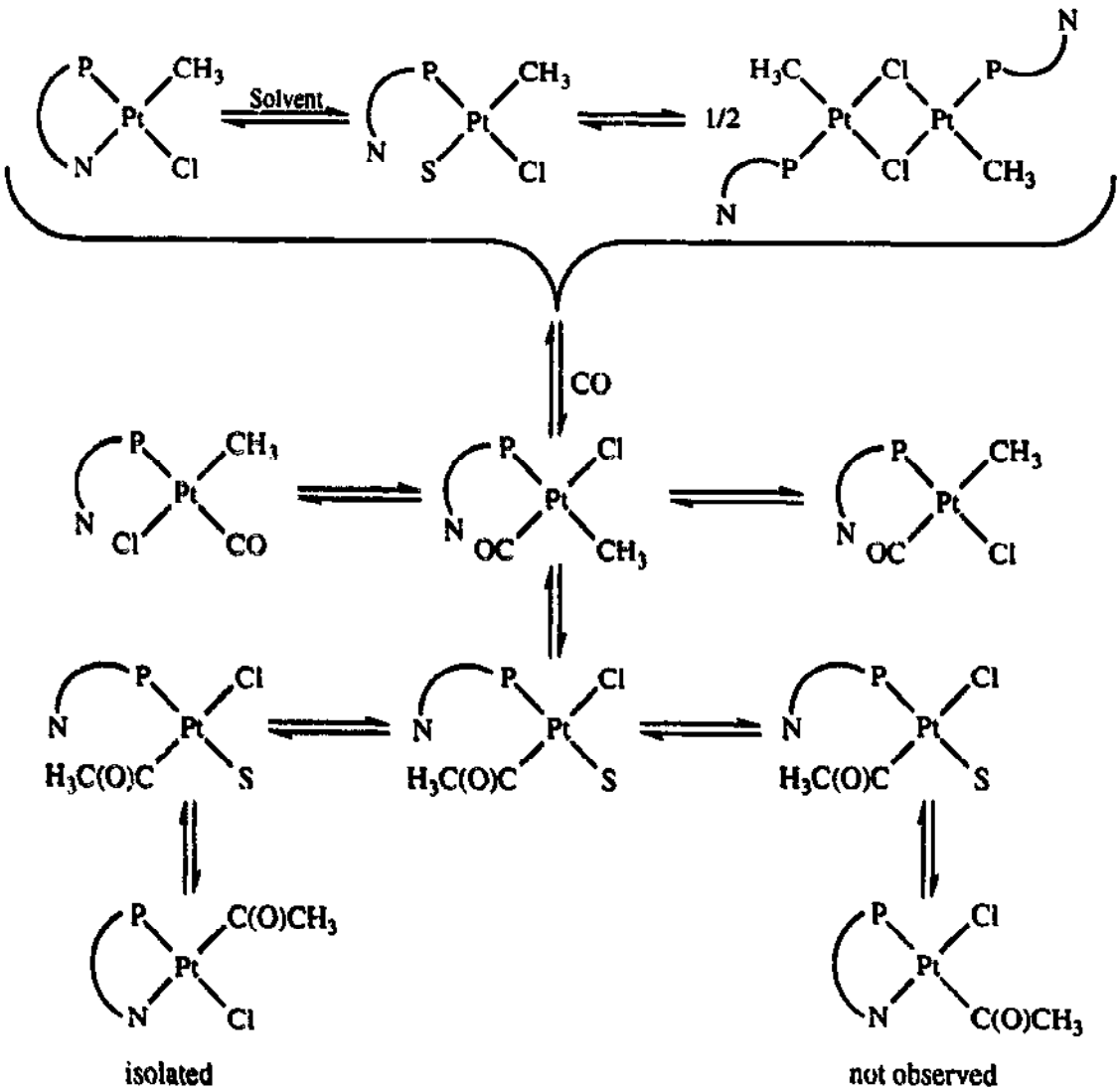
(20)



PC_3N

(21)

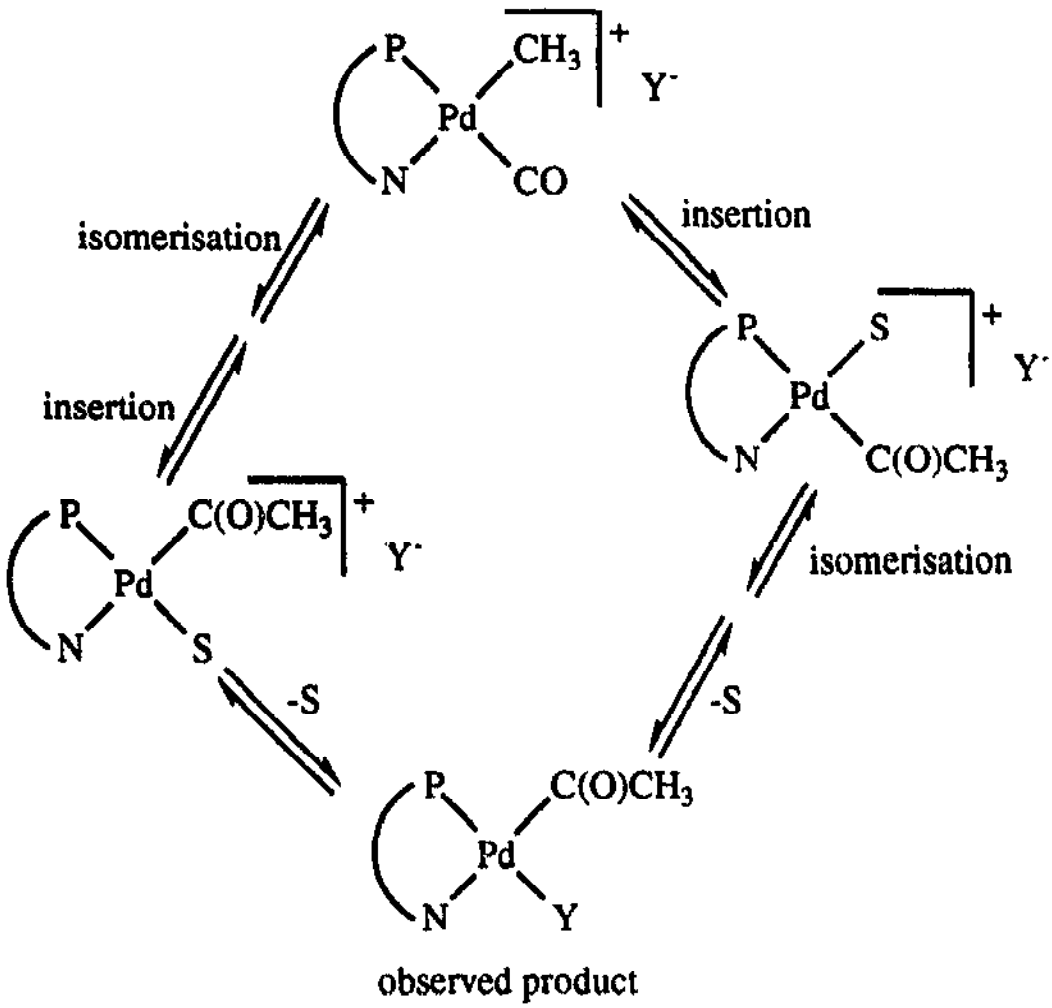
rates were faster with weakly coordinating ligands and/or anions. Rates were also dependent on the metal centre (Pd > Pt). A comparison of carbonylation rates for complexes containing N-N, P-P and P-N chelate ligands (N–N > P–P > P–N) showed that the effect of the chelate ligand on rates was complex and trends varied with different complexes [58]. It was proposed that observed trends were in part a function of the trans influence of the chelate donor atom on the re ments. As previously proposed [38,39], to facilitate migratory insertion the alkyl group should carry a partial negative charge (nucleophilic) and the CO a partial positive charge (electrophilic). The Me group trans to a P atom will be more nucleophilic than one trans to a N atom due to the higher trans influence of the P. However, the CO group trans to a N atom will be more electrophilic than one trans to a P. It is suggested that the electrophilic character of the carbonyl carbon is more important than the nucleophilic character of the alkyl carbon. In the case of P-N ligands, either



Scheme 10.

isomerisation of the initial carbonyl intermediate must occur to give the preferred pre-insertion intermediate (P trans Me and N trans CO), or the final acyl complex must isomerise to give the thermodynamically preferred product (Scheme 11) [58]. For complexes with N-N or P-P ligands no isomerisation need take place, indicating, in agreement with the recent conclusion of van Leeuwen et al [20], that symmetrical ligands may give faster insertion rates.

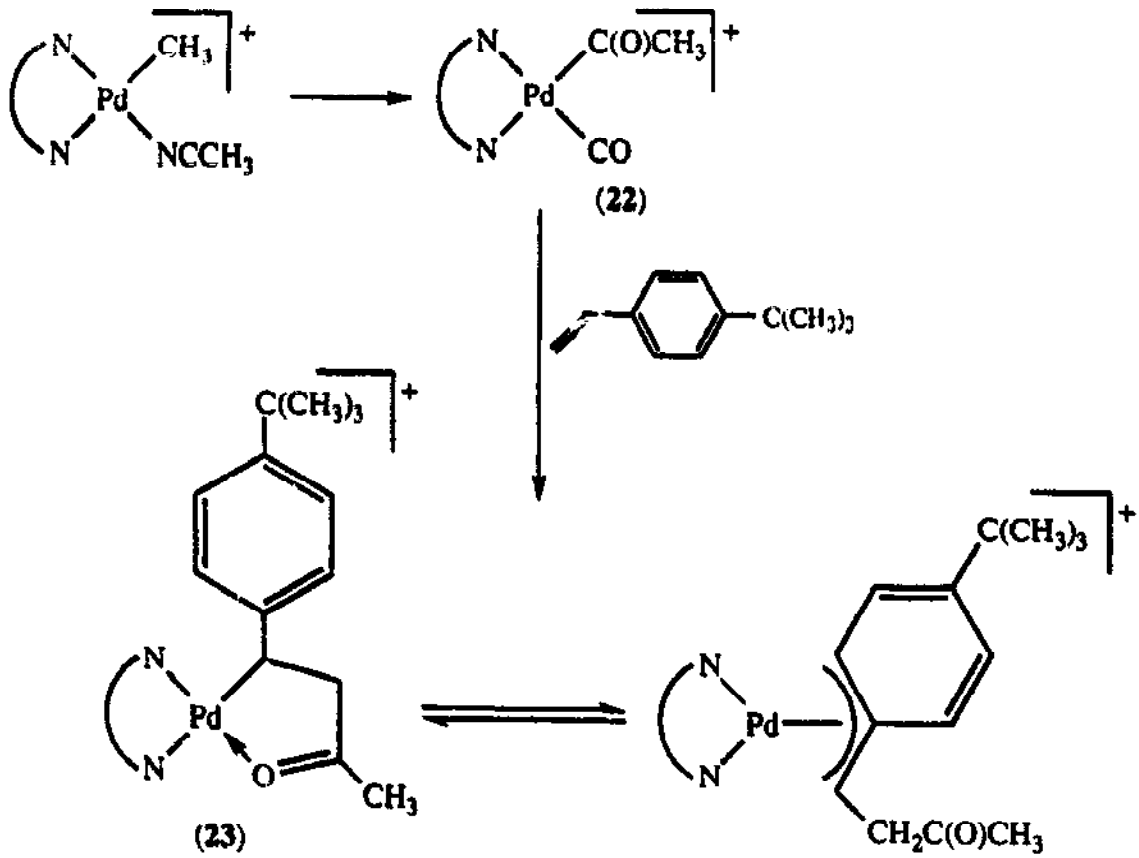
Studies investigating the migratory insertion of CO in systems containing N-N and N-N-N chelating ligands have been reported [26,27,59–66,68]. In an notable study, Brookhart and coworkers have demonstrated the stepwise insertion of CO and alkenes into palladium-carbon bonds, generating a living catalyst for the copolymerisation of CO and alkenes [61]. Starting from the cationic complexes $[Pd(Me)(N\text{-}N)(CH_3CN)]^+$ (N–N = bpy, 1,10-phenanthroline (phen)) the stepwise insertion of CO and alkene (4-*tert*-butylstyrene) was followed spectroscopically. Intermediates in the reaction scheme have been identified (Scheme 12) and the carbonyl acyl complex (**22**) was described as the resting state of the stepwise insertion



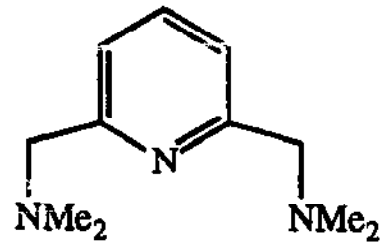
Scheme 11.

process. The olefin insertion step was found to be the slow step in the reaction. The resulting insertion product (**23**) was stabilised against β-elimination by the formation of a chelating alkyl-carbonyl species. Chelation via the carbonyl oxygen had been observed previously in manganese complexes [77]. A second leading study by the Brookhart group [33] investigating intermediates formed in the co-reaction of CO and ethylene with Pd(Me)(phen) complexes was discussed in Section 4.

Following on from the work of Brookhart et al., Elsevier and coworkers [63,65] isolated and fully characterised a number of complexes resulting from the successive stoichiometric insertion of CO and strained olefins, such as norbornadiene. The sequential reaction of CO and then alkene with the complexes [Pd(Me)Cl(N-N)] and [Pd(Me)(MeCN)(N-N)]SO_3CF_3 (where N-N is a rigid bidentate nitrogen ligand Ar-bian = bis-(arylamino)acenaphthene) resulted in isolable insertion products (Scheme 13), the stability of which is thought to be due to the rigid chelate ligand Ar-bian preventing a facile route for decarbonylation. Similar enhanced stability to de-insertion of CO was previously noted by Vrieze's group [26] for a system containing a rigid tridentate nitrogen ligand, whereas complexes containing the more flexible ligand, 2,6-$(Me_2NCH_2)_2$-C_5H_3N (**24**), readily decarbonylate [27].



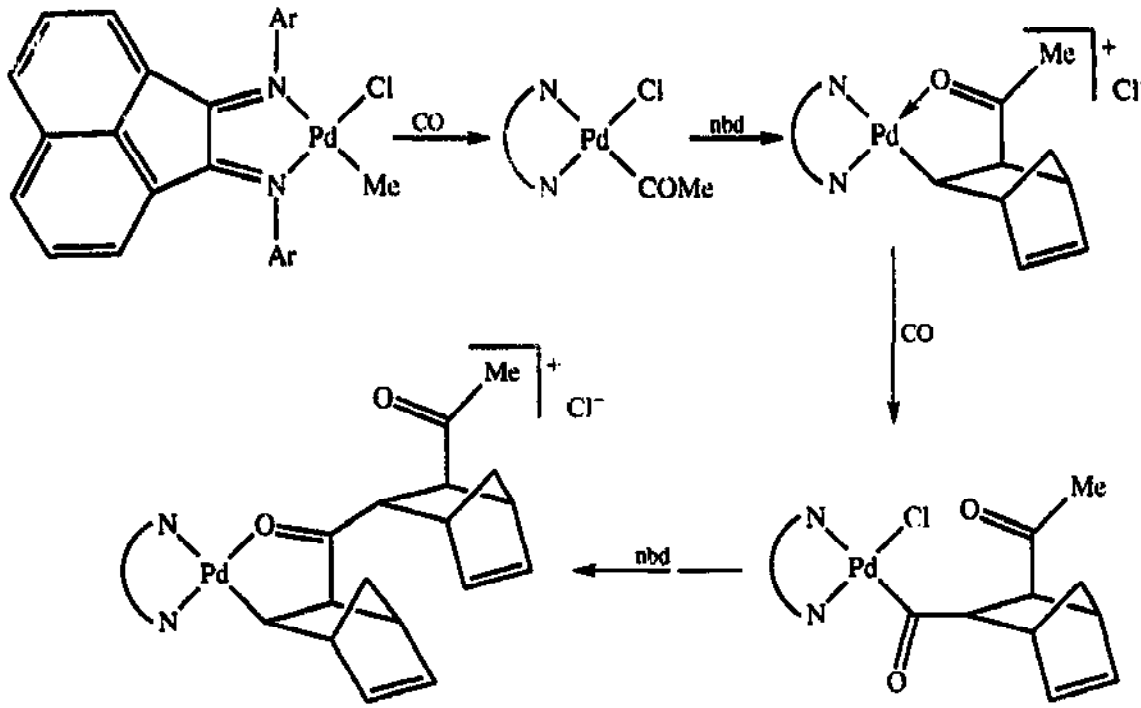
Scheme 12.



(24)

Neutral complexes containing Ar-bian may be activated for CO or alkene insertion by the dissociation of the Cl^- ligand, allowing coordination of the CO/alkene cis to the alkyl/acyl group prior to insertion from a four-coordinate intermediate [63,65]. However, an alternative insertion pathway via a five-coordinate intermediate is possible. It is thought that the rigidity of the Ar-bian ligand prevents competing processes, such as dissociation of one of the donor N atoms, from occurring. It is interesting to note that the rates of insertion are higher for complexes containing Ar-bian ligands than for complexes containing diphosphine ligands [65].

Furthermore, in contrast to complexes of Ar-bian, rates of insertion for diphosphine complexes decreased as the rigidity of the ligand increased (inhibition of the insertion reaction has also been noted for complexes containing rigid N-O-type ligands [71]). It is apparent that ligand flexibility is not an important prerequisite for insertion in palladium complexes of Ar-bian. Other factors must be more important, for example the lack of necessity for the Pd(An-bian) complex to isomerise to produce the



Scheme 13.

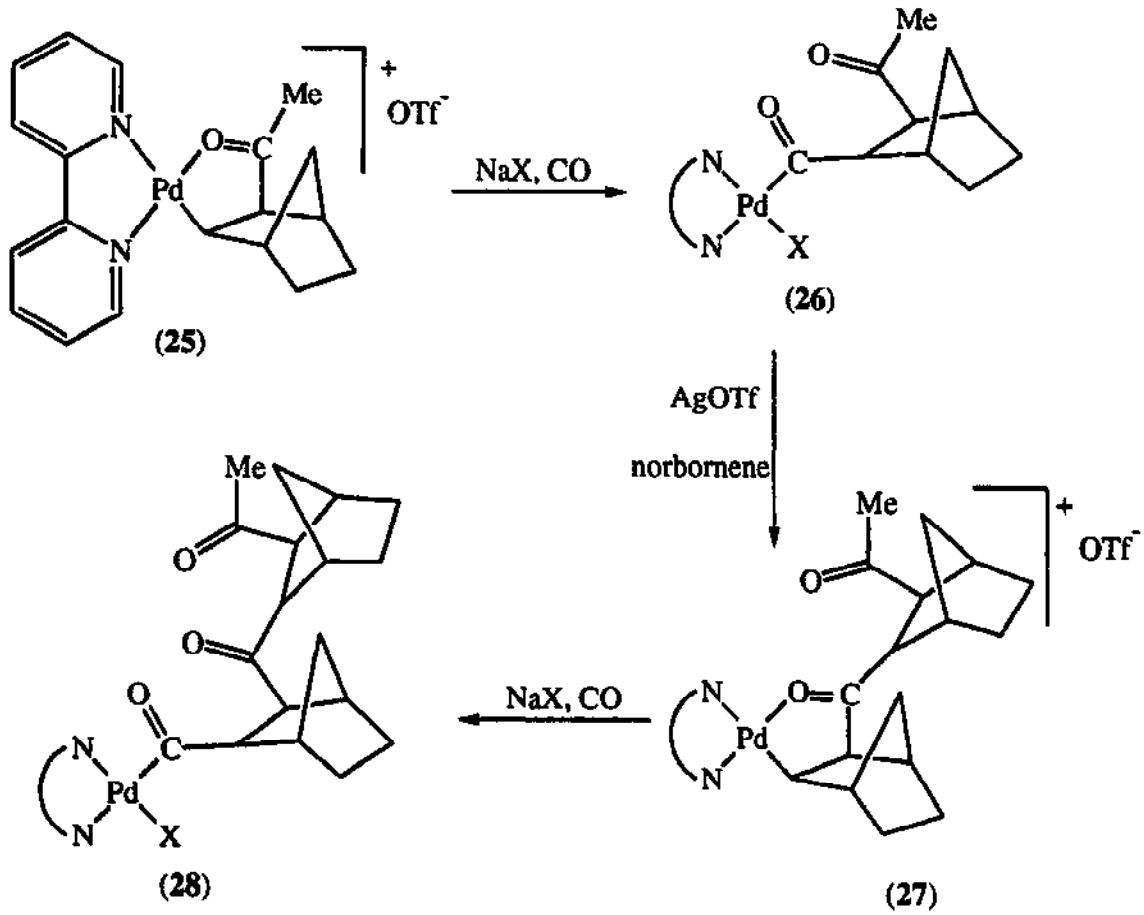
requisite pre-insertion intermediate (cis configuration of groups undergoing migratory insertion), the lower trans influence of the dinitrogen ligand compared with the diphosphine species (reducing the likelihood of low energy pathways for de-insertion and leading to increased electrophilicity of the CO) [65].

Boersma and coworkers found [64,66] that by the addition of a large excess of NaX (X=Cl, I) to $[Pd(C_7H_{10}COMe)(bpy)]SO_3CF_3$ (**25**) the stable neutral complex $[Pd(C_7H_{10}COMe)(bpy)X]$ could be generated into which a further molecule of CO can be inserted, yielding the isolable acyl complex $[Pd(COC_7H_{10}COMe)(bpy)X]$ (**26**). Removal of the halide ligand with $AgOSO_2CF_3$ generates the cationic complex $[Pd(COC_7H_{10}COMe)(bpy)]SO_3CF_3$ into which a further molecule of norbornene can be inserted giving the double insertion complex $[Pd(C_7H_{10}COC_7H_{10}COMe)(bpy)]SO_3CF_3$ (**27**). Continuing this process, the complex $[Pd(COC_7H_{10}COC_7H_{10}COMe)(bpy)I]$ (**28**) was prepared and a crystal structure obtained [64,66] (Scheme 14). A number of other strained olefins were also found to give stable multi-insertion products [66].

In discussing the insertion mechanism Boersma and coworkers [66] reiterate several important points alluded to by other authors. It not possible to categorically propose a single pathway for insertion; both associative and dissociative pathways are possible. For alkene insertion, a solvent-promoted partial Pd-X bond breaking is suggested, allowing alkene coordination cis to the acyl group prior to insertion. To maximise both alkene and CO [57] insertion rates a non-coordinating anion is required. A non-coordinating anion also allows coordination of the β carbonyl group, preventing β-elimination of the olefin. To isolate stable acyl complexes it is necessary to block decarbonylation routes, i.e. by occupying vacant sites cis to the acyl group.

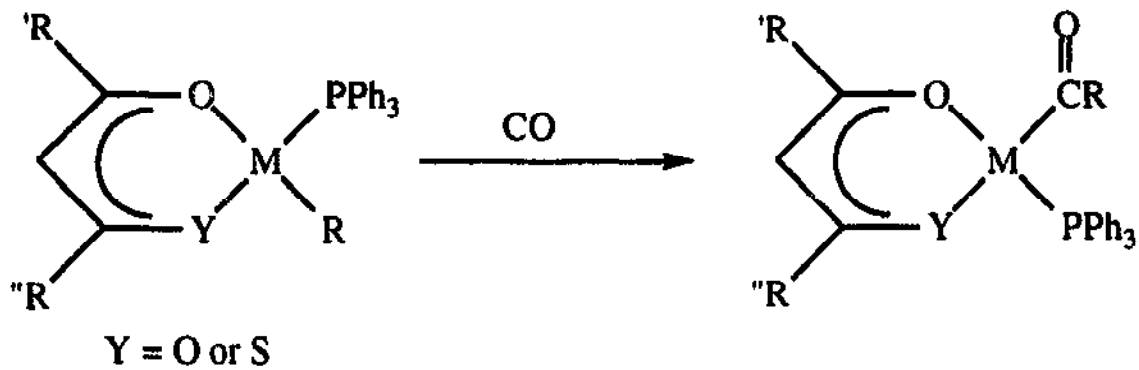
A number of reports relating to insertion from complexes containing neutral tridentate ligands have been published (N-N-N [26,27,68]; P-N-N [69]; P-O-N [67]). The insertion of CO [68,69] and, for the first time for a system with a tridentate ligand, the co-reaction of CO-ethylene [67] have been reported. The likelihood of associative insertion pathways is implicit in the carbonylation behaviour of complexes containing rigid tridentate N-N-N ligands [26] (see Section 3).

Hydrocarbyl complexes containing chelating anionic ligands of various types and with a variety of donor atoms have been investigated in recent years [70–75]. Cavell and coworkers focused on CO insertion for a range of neutral palladium and platinum hydrocarbyl complexes containing β-diketonate-type ligands $[MR(\beta\text{-dik})(PPh_3)]$ (M = Pd, Pt; β-dik = β-diketonate (acac), monothio-β-diketonate (sacac); R = Me, Ph) [70] (Scheme 15). The rate of CO insertion was found to depend on the nucleophilicity of the donor system. The insertion rate for palladium complexes with different β-dik ligands decreased according to bzsacac > tfacac > acac > sacac. On the basis that a weakly coordinated ligand facilitates carbonylation, a pathway involving insertion from a four-membered intermediate was favoured. A dissociative pathway is also favoured in a recent systematic series of studies on d^8 metal complexes containing anionic, bidentate ligands based on picolinic acid [71–74]. Cavell and coworkers investigated CO insertion in the hydrocarbyl complexes [MR(N-O)L]



Scheme 14.

(where M = Pt, Pd, Ni; R = Me, Et, aryl; N–O = pyridine carboxylate (pyca), 8-hydroxyquinoline; L = phosphine, py, 4Me-py, NMe_2Ph, $P(OMe)_3$) [71,72,74]. Platinum complexes (**29**) containing pyca showed unusual lability [71]. Weakly bound ligands, L, favoured rapid insertion and surprisingly facile de-insertion (Scheme 16). For the complex $[PtEt(pyca)PPh_3]$ facile β-elimination, forming plati-

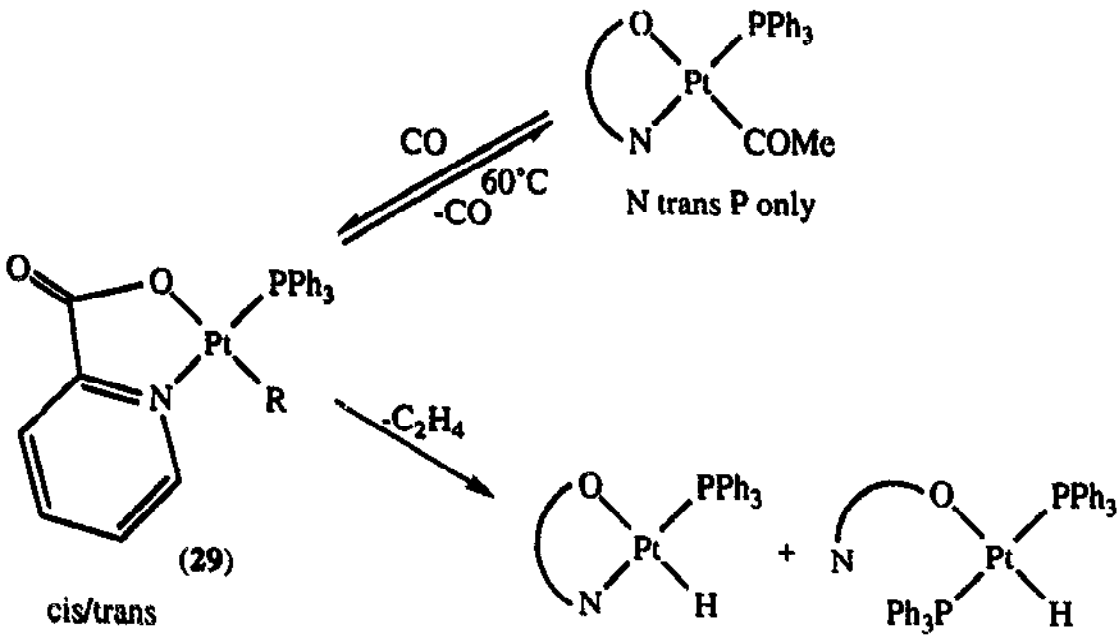


Scheme 15.

num-hydride species occurred (Scheme 16). Hemilability of the N-O ligand was also implied; when the rigid 8-hydroxyquinoline was used as the chelate no insertion, de-insertion or elimination was observed.

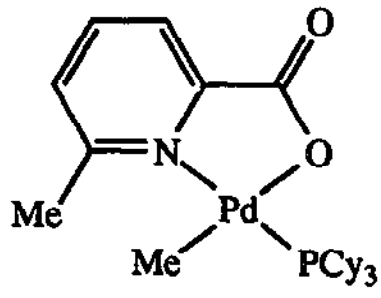
The rate of carbonylation in palladium pyca complexes was highly dependent on the basicity of the phosphine, with maximum activity obtained with the weakly bound PPh_3 and no activity found for the highly basic PCy_3 [72]. Activity decreased in the order PPh_3 (rel. activity = 3.6) > $PMePh_2$ (0.96) > $P(CH_2Ph)_3$ (0.17) > PMe_2Ph (0.01) ≫ PCy_3 (0). The very low activity of the complex containing PMe_2Ph and the inactivity of the complex with PCy_3 provide specific evidence that the associative insertion route is not favoured for these complexes. The implication is that unless CO can find a suitable coordination site insertion does not proceed. It is apparent that CO is unable to displace the py moiety of the chelate [72]. However, when bonding between the py N and Pd is substantially weakened by substituents on the py ring carbonylation does occur, even with PCy_3 as the phosphine [73]. The methylpalladium complexes [PdMe(chelate)(PCy_3)] containing the chelates 6-Me-pyridine carboxylate (**30**) and 4-nitro-pyridine carboxylate (**31**) readily insert CO to give the acyl compounds. The 6-methyl group exerts a predominantly steric influence and the 4-nitro group acts as an electron-withdrawing moiety and reduces electron density on the py N [73]. The results strongly favour a dissociative insertion pathway for these complexes.

Arylnickel complexes of pyca, [Ni(aryl)(pyca)PR_3)], were found to be single component catalysts for the oligomerisation and polymerisation of ethylene and the copolymerisation of CO and ethylene [74]. Based on catalytic behaviour in the presence of excess phosphine (a relatively small decrease in activity with a large change in product distribution was observed) it was suggested that insertion into



Scheme 16.

the growing chain occurred from a five-coordinate intermediate, i.e. an associative route was proposed for the nickel complexes.



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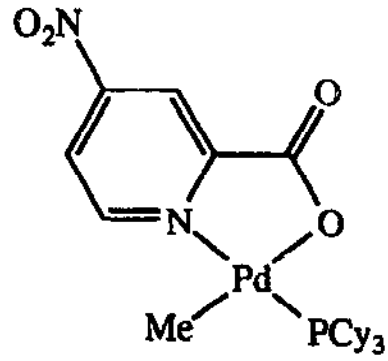


(31)

6.3. *Alkene insertion*

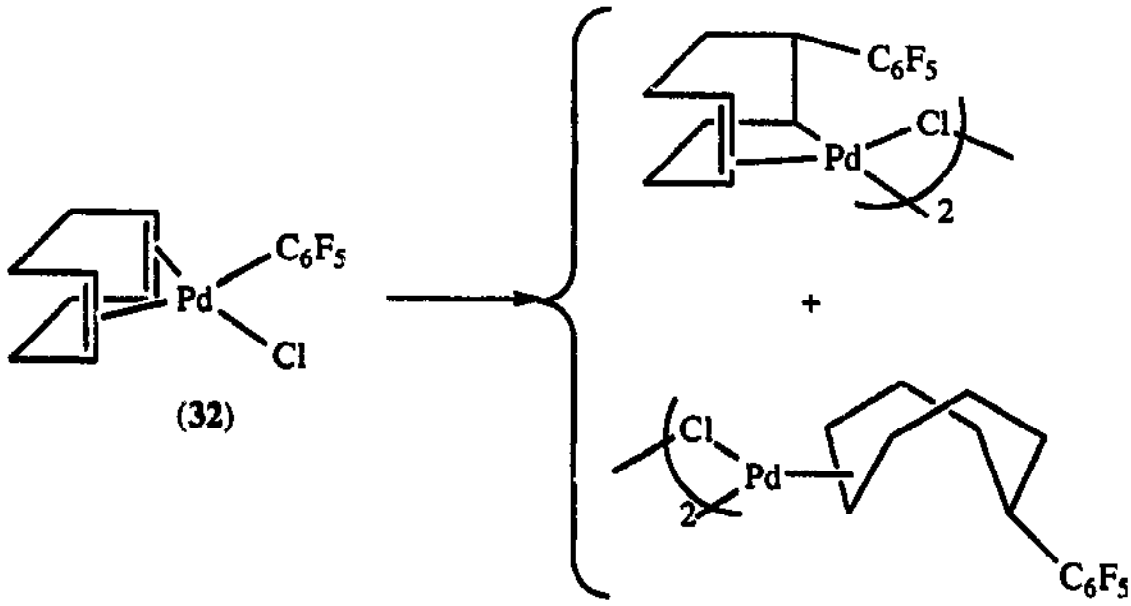
In recent years there have been a large number of investigations in which insertion of an olefin or an alkyne forms part of the reaction scheme. These have included for example such reactions as the coupling of aryl halides to alkenes to give arylated alkenes (so called Heck chemistry and related reactions) [78–85], reactions of dienes [86] and reactions of alkenes with nucleophiles [87]. However, in most of these studies the specific insertion step has not been discussed and consequently they will not be reviewed here.

Investigations of alkene insertions into metal-carbon bonds are often impeded by difficulties in observing the pre-insertion *cis*-(alkyl-alkene) intermediate and the final inserted product. The reasons are that once the pre-insertion intermediate is formed insertion is very facile and, likewise, the final inserted product generally has a low energy pathway for decomposition, namely β-elimination. Another problem is to provide a suitable cis coordination site for the alkene prior to insertion. However, a number of alkyl-alkene species have been identified (Section 4) and, recently, various approaches have been developed to overcome difficulties in observing these intermediates. Espinet and coworkers [88] have structurally characterised a *cis*-alky/alkene palladium complex [PdCl(C_6F_5)(COD)] (**32**) and identified two isomeric insertion products both resulting from endo attack of the C_6F_5 group on the cyclooctadiene double bond (i.e. the C_6F_5 group and the Pd atom both attach to the same face of the cyclooctadienyl ring) (Scheme 17).

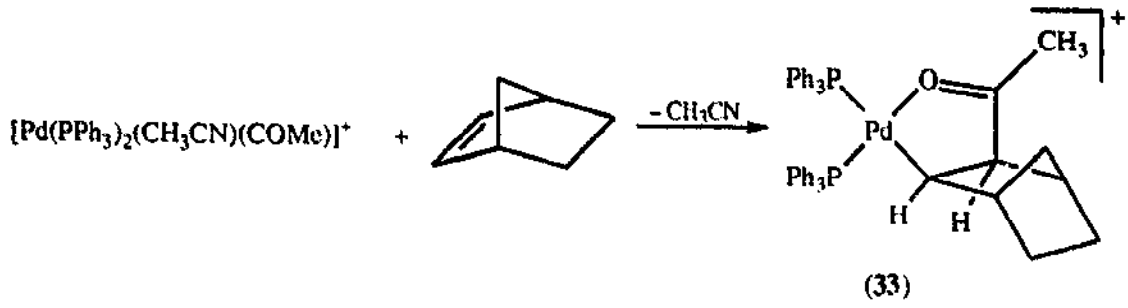
Insertion of strained alkenes or alkenes without β-hydrogens into metal-acyl bonds has also allowed isolation or identification of inserted products. In important studies on migratory insertion Sen and coworkers have investigated the insertion of olefins such as norbornene, norbornadiene and dicyclopentadiene into the platinum-acyl [89] and palladium-acyl [90] bonds of the neutral and cationic complexes [$Pd(PPh_3)_2(Cl)(COR)$] and [{$M(PPh_3)_2(CH_3CN)(COR)$}BF_4]. The product (**32**)

from the reaction of $[\{Pd(PPh_3)_2(CH_3CN)(COMe)\}BF_4]$ with norbornene (Scheme 18) was isolated and a crystal structure obtained.

Both the palladium and the acetyl group lie on the exo face of the norbornyl group, indicating that the product was formed via syn-insertion of the norbornene into the palladium-acyl bond [90]. No intermediates from the insertion process were observed and the authors could not unambiguously establish a mechanism for olefin insertion into the metal-acyl bond. However, it was proposed that the pathway involved insertion from a four-coordinate intermediate formed by olefin displacement of the a etonitrile ligand in the case of the cationic species, or by displacement of the PPh_3 in the neutral complex. In a related study, Boersma et al. [91] investigated the insertion of strained olefins (norbornene and dicyclopentadiene) into the palladium-acyl bond of cationic complexes containing chelating N-N ligands, obtained by treating [PdI(COMe)(N-N)] (N–N = tetramethylenediamine (tmeda), 2,2'-bipyridine (bpy)) with $AgOSO_2CF_3$. Stable insertion products resulted. An X-ray structure was obtained for the product $[Pd(Cl_{10}H_{12}COMe)(bpy)]SO_3CF_3$ (**25**), and in



Scheme 17.



Scheme 18.

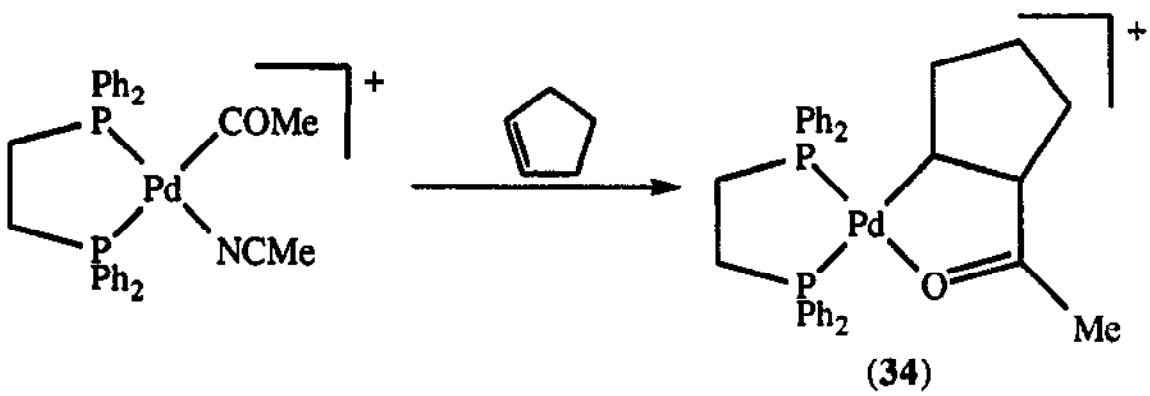
agreement with previous observations [77,90] the complex was stabilised by coordination of carbonyl oxygen to the metal centre. The insertion product is consistent with an exo mode of insertion, and the authors propose that reaction probably proceeds via a four-coordinate intermediate.

Yamamoto and coworkers [92] have looked at similar insertion reactions involving a cationic complex, *cis*-[Pd(COMe)(MeCN)(dppe)]BF_4 (**34**), containing the chelating phosphine dppe, with the alkenes cyclopentene, cycloheptene and methylacrylate. Insertion of cyclopentene gives a crystalline complex stabilised by intramolecular chelation through the carbonyl group (Scheme 19).

Alkene insertion into acylpalladium bonds for complexes containing chelating phosphines has also been investigated by Vrieze and coworkers [93]. The influence of ligands and anions on insertion into palladium-acyl and -carbomethoxy bonds for both neutral [PdCl(COMe)(dppp)] and cationic [PdR(P-P)(L)]$^+SO_3CF_3^-$ complexes was studied. The cationic acyl complexes reacted with a range of strained, activated and simple alkenes to give insertion products and intramolecular coordination of the ketone oxygen was again observed. As previously noted for the insertion of CO, the rate of alkene insertion was higher for phosphines with larger bite angles, i.e. dppp>dppe. Insertion of norbornadiene into the palladium-acyl bond of the neutral complex [PdCl(COMe)(dppp)] led to the formation of two products, the exo insertion product (**35**) and a nortricyclenyl insertion product (**36**) formed from attack on the endo face of norbornadiene. Nortricyclenyl insertion products formed from nucleophilic attack on the endo face of norbornadiene have been noted before for palladium-phosphine systems [94].

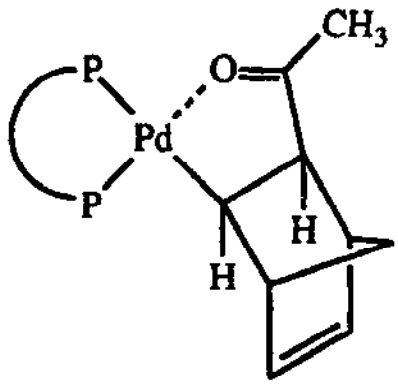
In considering insertion of styrene into the palladium acyl bond of cationic complexes [Pd(P-P)(COMe)(CH_3CN)]$^+SO_3CF_3^-$ Vrieze and coworkers found that the acetyl group attacked the β-carbon of styrene. The regioselectivity in this insertion step was attributed to steric influences of the acetyl group controlling the direction of styrene coordination prior to insertion [93].

De Felice and coworkers have investigated a series of neutral and cationic hydrocarbylplatinum complexes containing chelating diazabutadiene-type ligands (Scheme 20) [95]. On reaction of cationic aryl complexes with alkenes they observed



(**34**)

Scheme 19.



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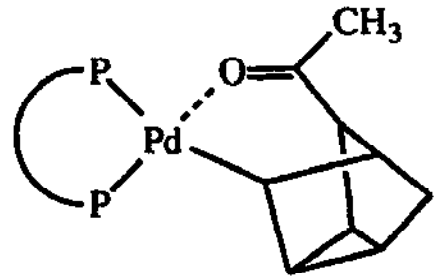
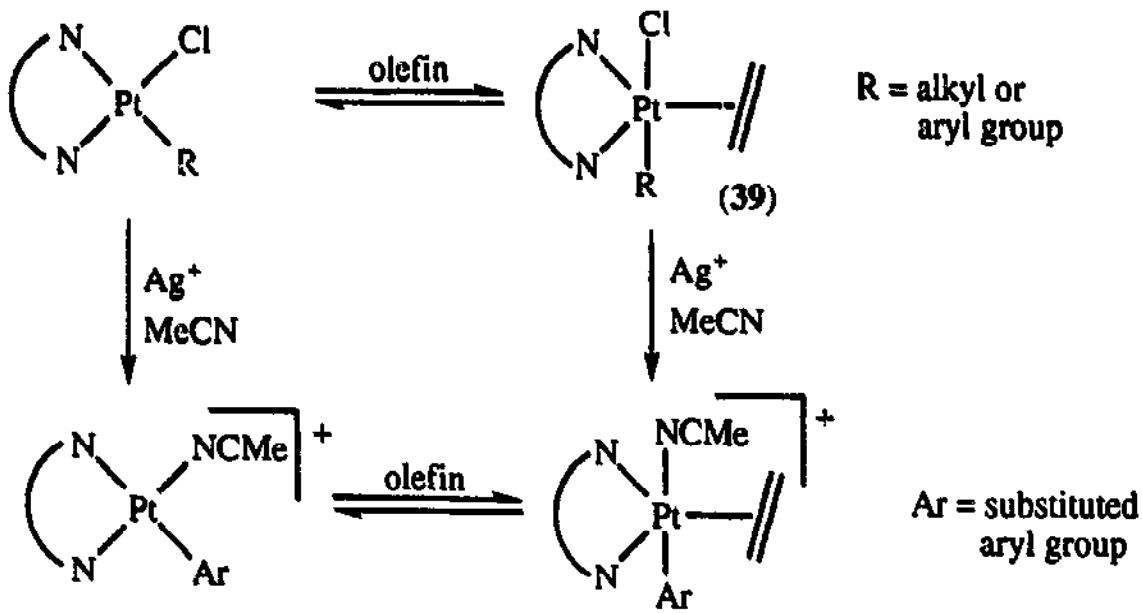


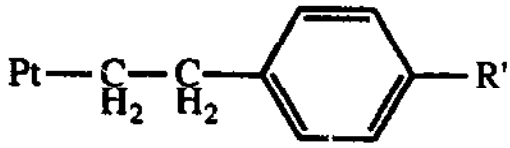
(36)

complex behaviour involving olefin insertion and a 1,2-shift of the platinum on the benzene ring. Complexes of type (**37**) and (**38**) were observed. Depending on the steric requirements of the N-N ligands, five-coordinate intermediates (**39**) containing an alkene in the equatorial plane have been identified, and, where a particularly sterically demanding ligand (2,9-dimethyl-1,10-phenanthroline) is employed, stable five-coordinate species have been isolated.

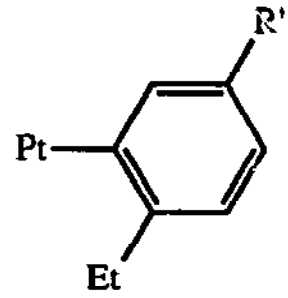
To explain the complex reaction behaviour the authors propose a concerted mechanism. One pathway involving a normal migratory insertion pathway to give product (**37**) and the second pathway passing through an unknown intermediate to give (**38**) (Scheme 21). Possible pathways involving a previously characterised [79] alkyl-η^2 aryl metallocycle intermediate or a benzyneplatinum species were not favoured because of their failure to satisfactorily explain the observed reaction



Scheme 20.



(37)



(38)

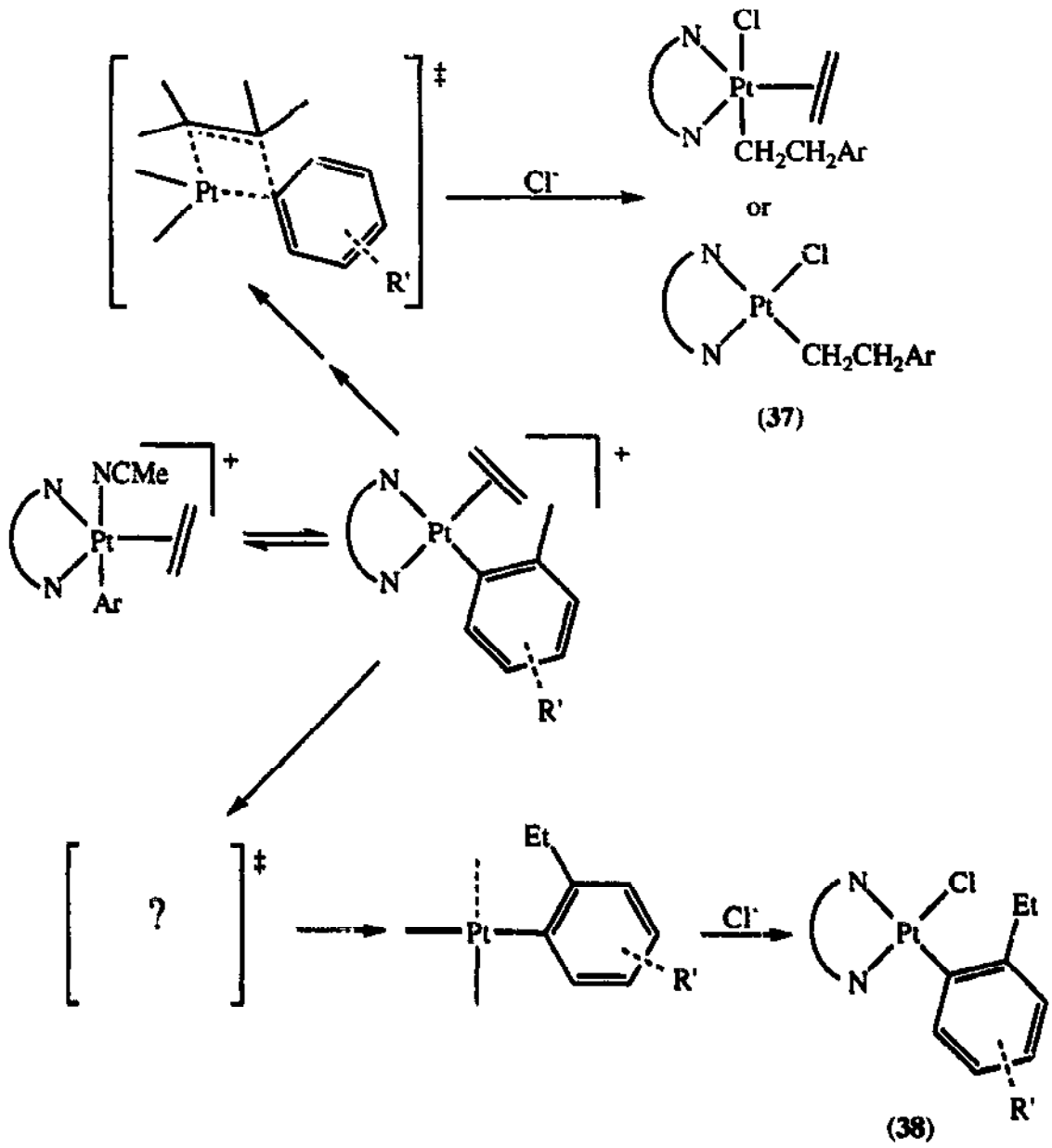
behaviour. The nature of the pre-insertion intermediate (whether five-coordinate of four-coordinate) could not be identified.

The migratory insertion of norbornene into the palladium-carbon bond of a cationic phenylpalladium complex containing the tridentate ligand *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (**40**) has been investigated by Boersma and coworkers [96]. The insertion process is followed by intramolecular activation of a phenyl C-H bond to give an unexpected ortho-substituted arylpalladium complex. A proposed mechanism for the complete process was presented (Scheme 22). Migratory insertion is thought to occur from a four-coordinate intermediate, a vacant site for norbornene coordination resulting from dissociation of one of the ligand NMe_2 groups [96].

In a study of the insertion of norbornene into the palladium-carbon bond of electron-rich, neutral palladium aryl complexes [Pd(dippp)(Ph)Cl](*dippp = di-isopropylphosphinopropane*) containing chelating phosphine ligands, Milstein and coworkers [84] compared the insertion mechanism with complexes containing monodentate phosphine ligands. Based on the effects of added free phosphine and free Cl^- on insertion rates, two different insertion pathways were proposed for the two different complex types. The chelated complexes were believed to react through halide dissociation followed by alkene coordination, giving a cationic intermediate. Migration of the aryl group to the alkene is followed by fast re-association of the halide to give the observed product. Reaction of the monodentate complexes is thought to proceed via displacement of a phosphine ligand by the alkene to give a neutral intermediate. Migratory insertion leads to a tricoordinate product which rapidly decomposes.

Surprisingly, Milstein and coworkers found that insertion rates for chelated complexes increased as the bite angle of the chelate decreased [84]. This is the reverse of that previously noted for CO insertion and for insertions in hydrido olefin complexes of Pt and Pd [97]. This was explained in terms of electronic and steric stabilisation of the alkene coordination prior to migration.

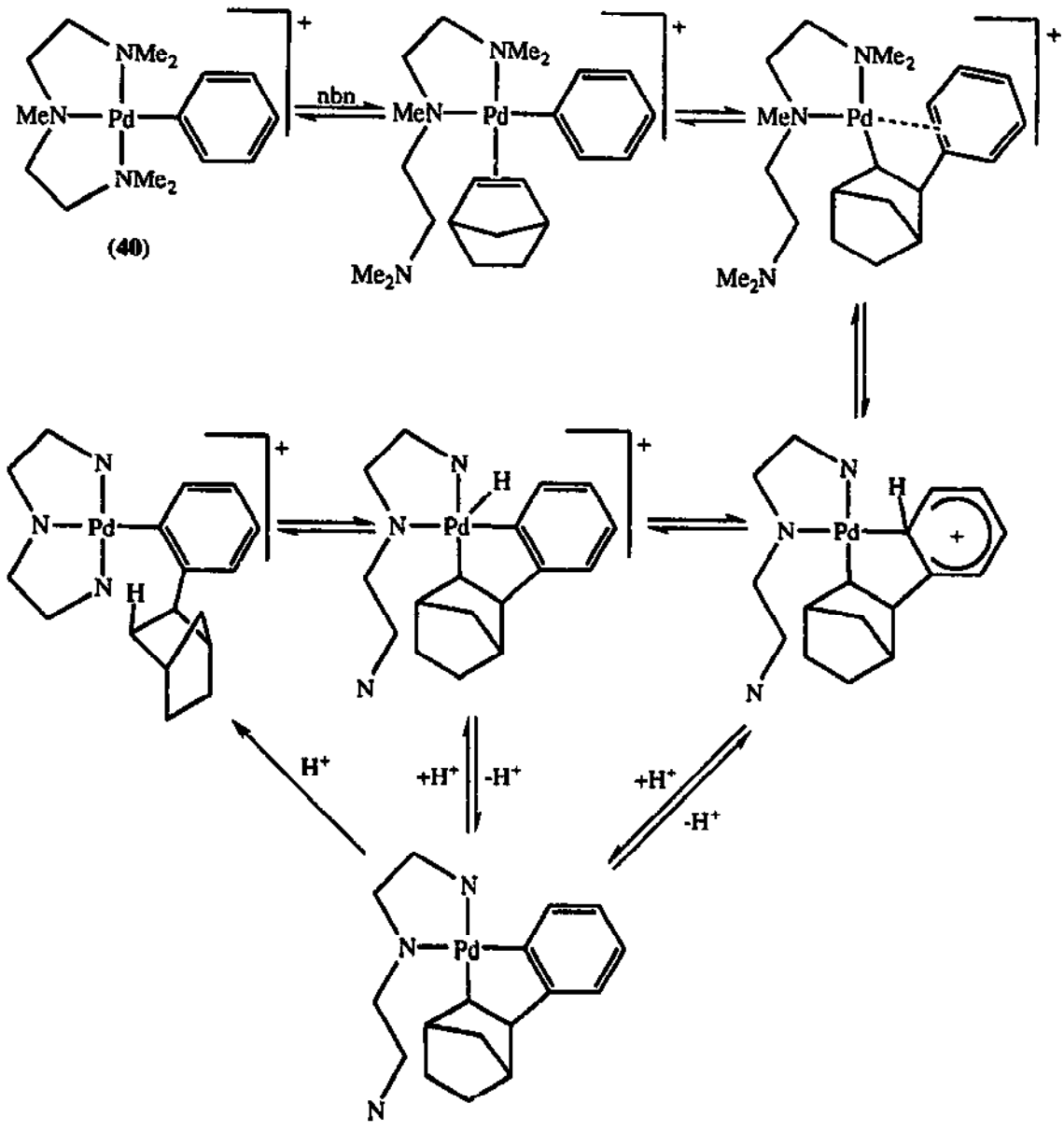
Intramolecular insertion of an alkene into the palladium-carbon bond of several methylpalladium complexes [PdMe(chelate)(SP)] (chelate = acetylacetonate, 3-mercapto-1-phenylbut-2-en-1-onate, pyca; SP = styryldiphenylphosphine) (**41**) containing anionic chelating ligands with mixed donor groups has been investigated by Cavell and Jin [24]. Migration occurred more rapidly with complexes containing the O-O and O-S chelates albeit with some decomposition. The reaction was cleanest with the N-O chelate: no decomposition was evident, a crystalline product was



Scheme 21.

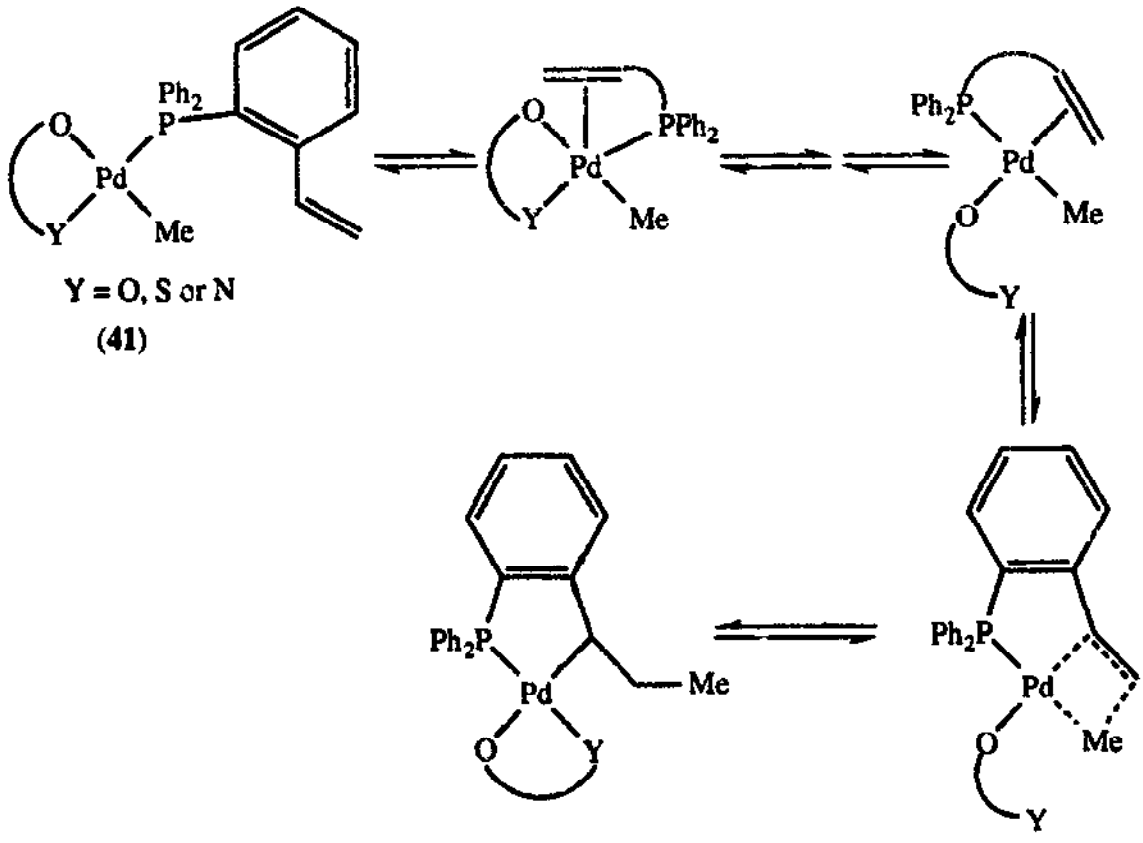
isolated in high yield and microanalytical data obtained. A mechanism was proposed involving pre-coordination of the vinyl double bond promoting partial dissociation of the chelate ligand to give a four-coordinate *cis*-alkene/alkyl intermediate from which migratory insertion occurred. Kinetic data provided evidence in support of the proposed mechanism. The reaction pathway is given in Scheme 23.

While falling outside the specific guidlines of this review, an interesting study exploring the role of ligands in controlling insertion processes is that of Drent et al. [7]. The authors have investigated the formation of methylmethacrylate (MMA) from CO-propyne in acidic methanol as solvent using a catalyst species that is



Scheme 22.

generated in situ. The activity is high and the selectivity is exceptional. Whilst little experimental evidence is provided, an overall mechanism is provided for the formation of MMA (Scheme 24). It is proposed that the P-N ligand (**42**) has two primary functions which lead to the observed activity and selectivity. During the course of the reaction the py moiety of the ligand is protonated and acts as a proton carrier to facilitate the elimination of product (step 5 in the catalytic cycle). In addition, the bulky *o*-methyl group on the py ring controls the manner in which the propyne coordinates, and hence the regioselectivity of the migratory insertion step. To obtain MMA the pre-insertion intermediate must have the configuration shown in (**43**). The alternative propyne configuration (with the methyl group of propyne pointing

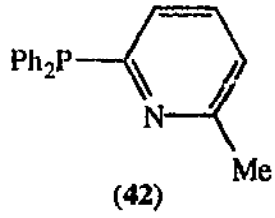


Scheme 23.

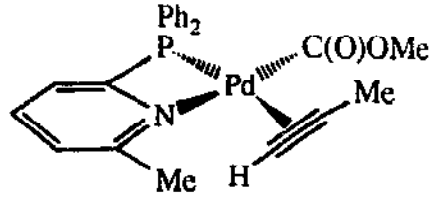
towards the py-methyl) leads to methyl crotonate, which is a minor by-product (0.05%) from the reaction.

7. Conclusions

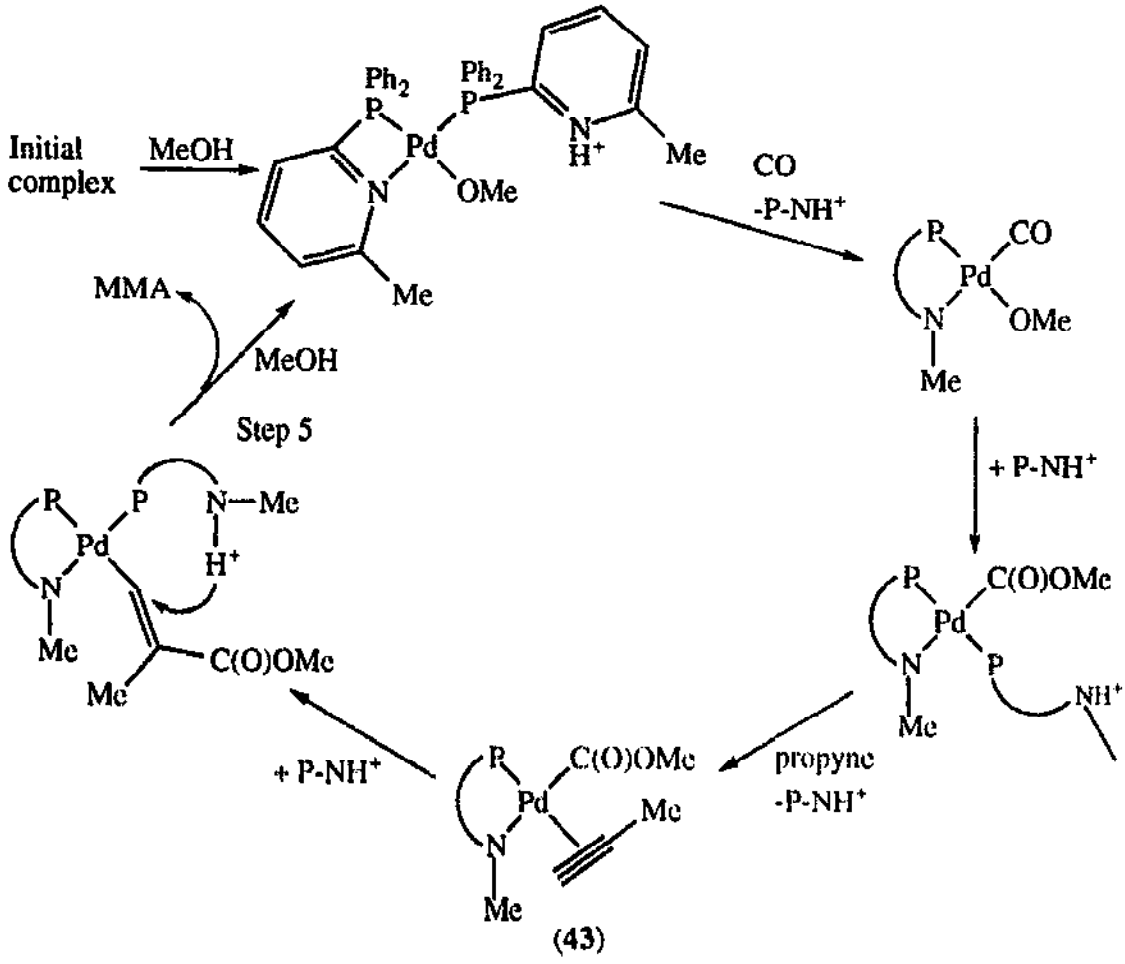
It is evident that considerable uncertainty regarding the details of the insertion pathway still exists. A consideration of the literature relating to the nature of the pre-insertion intermediate, whether four-coordinate or five-coordinate, attests to the likelihood that different pathways can be followed depending on ligands surrounding the metal centre, and it is possible that a complex may change pathways depending on reaction conditions [22]. Not only the nature of the ligand donor atoms (P or N, etc.) influence the insertion reaction; the type of donating group (amine N or imine N), the anion, the substrate and the solvent can also be important [66]. Exciting developments in the identification and isolation of reaction intermediates (including intermediates from model systems and from real catalyst systems) have taken place in recent years [33,34], allowing detailed assessments of the migratory insertion reaction to be applied with more confidence when designing catalyst systems. Surprising ligand influences have been identified, particularly among chelating ligands. Depending on the process of interest, symmetrical P-P or N-N ligands may



(42)



(43)



Scheme 24.

be preferred, giving higher insertion rates [20,58]. However, in terms of controlling selectivity, specially designed ligands with specific features may be desirable [7]. There have been relatively few studies using chelating ligands (investigations have concentrated primarily on P-P and N-N ligands), and very few where tridentate ligands have been employed. Hence, considerable scope exists for future ligand design programs. Further advances in theoretical modelling, in particular the level at which calculations are undertaken, may also provide important information on subtle electronic and steric influences of ligands and substrates.

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