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Review

Pyridylthioethers: a promising class of polydentate ligands in palladium and platinum coordination

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Contents

Abstract

The role of bi- and ter-dentate pyridylthioether ligands in palladium and platinum coordination and organometallic chemistry is discussed. The binding ability of these ligands concerning the proton, copper and palladium is revisited. Moreover, the reactivity imparted by these ligands to several types of metal complexes in low and high oxidation states is examined. The complexes and the reactions explored are (i) allyl derivatives with respect to allyl amination (ii) olefin complexes and olefin exchange equilibrium reactions (iii) methyl derivatives and reactions of allene insertion. The synthesis of pyridylthioether-based dendrimers is also taken into account together with their solution behaviour when used as ancillary ligands in allyl metallo-dendrimer derivatives when the allylamination reactions are considered.

Keywords: Palladium; Pyridylthioether ligands; Amination; Olefin exchange; Insertion reactions

1. Introduction

The role of ligands in coordination and organometallic chemistry does not need emphatic presentation since their fundamental importance in determining the morphology and the chemical–physical properties of the molecules is well documented by an impressive wealth of literature data. Conversely, the description of a specific class of ligands could represent a useful target, especially if the latter display interesting features which can be transferred to the metal substrates on coordination. For this reason, we decided to condense into this paper the principal results we obtained in the last decade of research on pyridylthioether ligand derivatives with the aim of presenting to the scientific community an interesting and versatile tool which proves to be in some respect innovative, mainly when the metal-carbon insertion reactions are considered. Since our scientific interest is principally confined to the synthesis, characterisation and stoichiometric reactivity of platinum group metals, we hope to kindle the curiosity of other research groups who, on the basis of their specific competence and interest, may foster the advancement of knowledge particularly in

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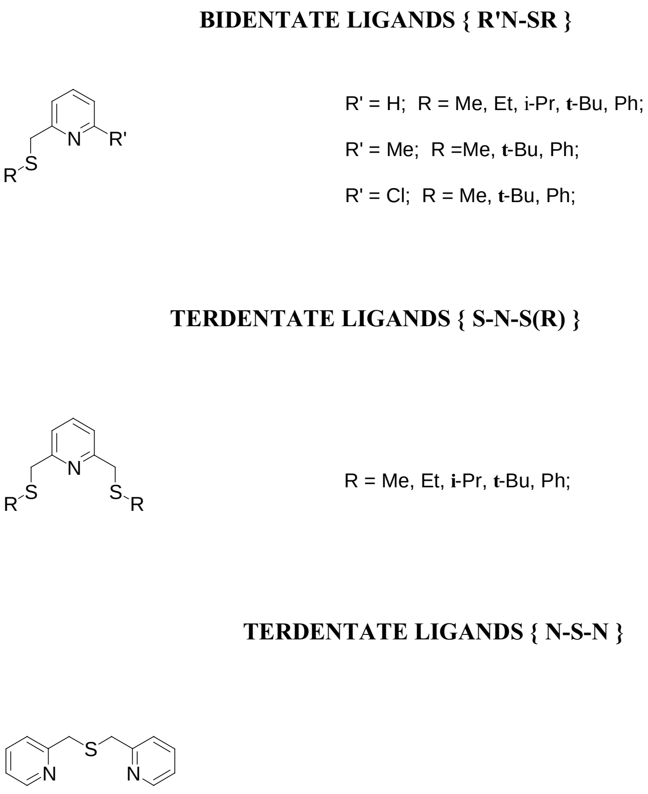
the field of applied catalysis and of the reactivity of other metal groups. We firstly planned in the 90s the synthesis of pyridylthioether ligands with the goal of selective separation of heavy metals distributed in aqueous industrial wastes. The basic idea lay in the association of a sulphur atom, whose affinity for platinum group metals is well recognised, with a pyridine nitrogen. The resulting ligand would display a remarkable ability in stabilising metals in high and low oxidation states. The chelating capability and the selectivity in coordinating palladium and copper were immediately apparent [1] and this fact prompted us to develop the large selection of both potentially terdentate and bidentate pyridylthioether ligands which were employed in subsequent systematic studies (see below). These are reported in Scheme 1.

Moreover, the versatility of this atom combination was further demonstrated by the production of dendritic ligands which were used in the synthesis of the related metal complexes whose reactivity was also assessed. The synthesis of the dendritic fragments and of the related metal derivatives together with their reactivity will be discussed in a separate section.

Meanwhile several new N-S-based ligands where synthesised and some reports appeared, principally devoted to enantioselective allyl substitution [2–12]. However, none of those ligands has the structure of our molecules which, as will be shown further on, impart a peculiar reactivity to the palladium complexes.



Scheme 1.

2. Synthesis of bidentate and terdentate ligands

The synthesis of pyridylthioether ligands is based on the nucleophilic attack of the thiolate RS^- species on 2,6-bis(chloromethyl)pyridine derivative (terdentate ligands) or 6-R′,2(chloromethyl)pyridine ($R' = H$, Me, Cl) (bidentate ligands) [1,13–18]. In the case of the bidentate 6-chloro derivatives, the precursor 6-chloro, 2(chloromethyl)pyridine was synthesised according to the method of Lee and Chi [19]. Almost all the ligands were separated by chromatography over silica gel as a yellowish oil (S-N-S(*t*-Bu) and S-N-S(Ph) derivatives are deliquescent solids) and were identified by elemental analysis and NMR spectrometry. The hydrogen or the methyl substituent in position 6 of the pyridine ring is particularly, easily identified by ^{1}H NMR and its signal undergoes a marked downfield shift upon metal coordination.

3. Synthesis of dendritic ligands

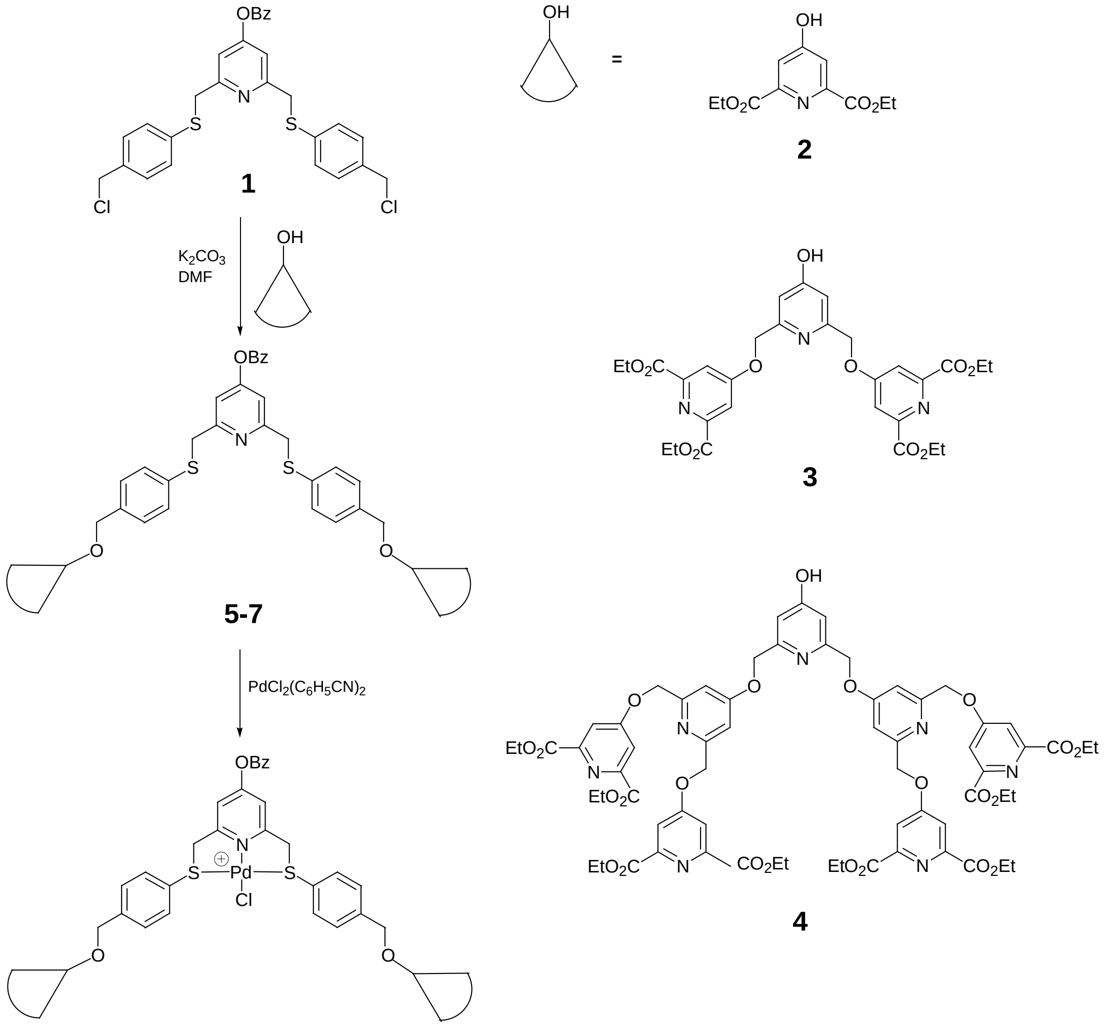
Our interest in preparing dendritic systems incorporating pyridylthioether units stems from our investigations on the Pd(II) 2,6-bis(methylthiomethyl)pyridine complex [1]. Due to its high stability constant and its interesting chemical properties this complex proved instrumental in the synthesis of palladium-containing metallodendrimers.

The synthetic methodology we have developed relies upon the initial synthesis of pyridine-based structures bearing one or more metal anchoring sites which are subsequently reacted with transition metal complexes to give the desired metallodendrimers.

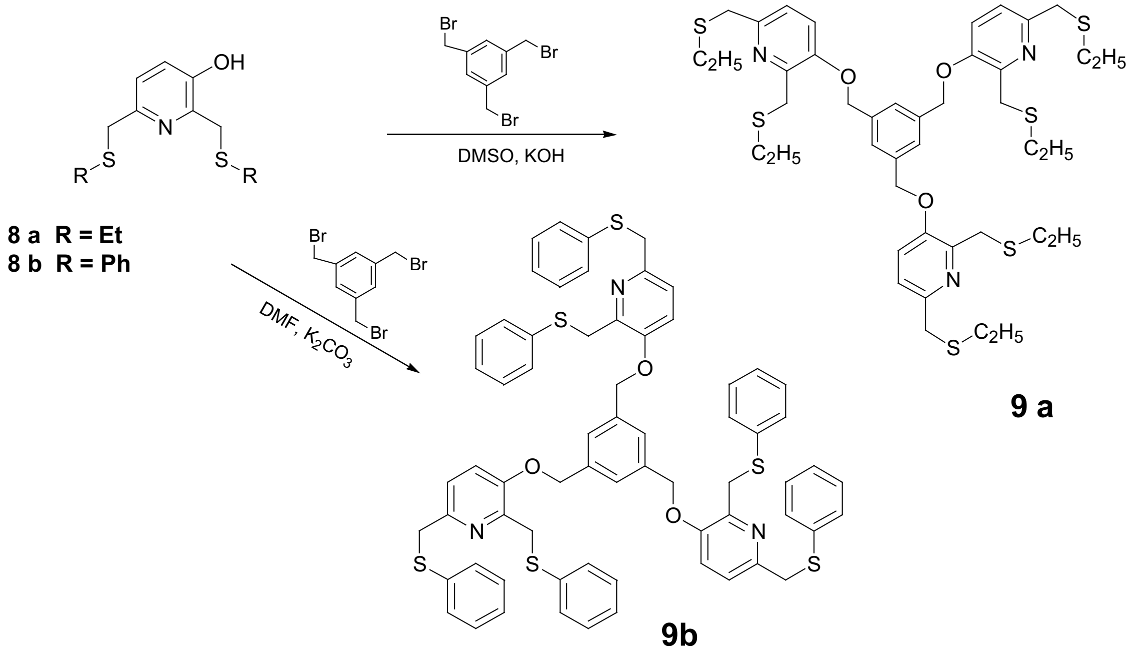
Our initial approach to the construction of pyridylthioether-containing dendrimers focused on the convergent assembly of pyridine-based dendritic frameworks in which only one pyridylthioether unit is present. In these syntheses the key building block was 4-benzyloxy-2,6-bis(4-chloromethylphenylthiomethyl)pyridine **1**, which was coupled under Williamson etherification conditions (K_2CO_3/DMF) with the pyridine-based dendritic fragments **2-4** [20] to give the dendritic wedges **5-7** [21], shown in Scheme 2. These precursors then react with $Pd(PhCN)_2Cl_2$ to yield the corresponding metallodendrimers (Scheme 2), which were characterised unambiguously by NMR spectroscopy and MALDI–TOF mass spectrometry.

In view of these successful results, first and second generation dendritic macromolecules incorporating three and nine pyridylthioether moieties were assembled.

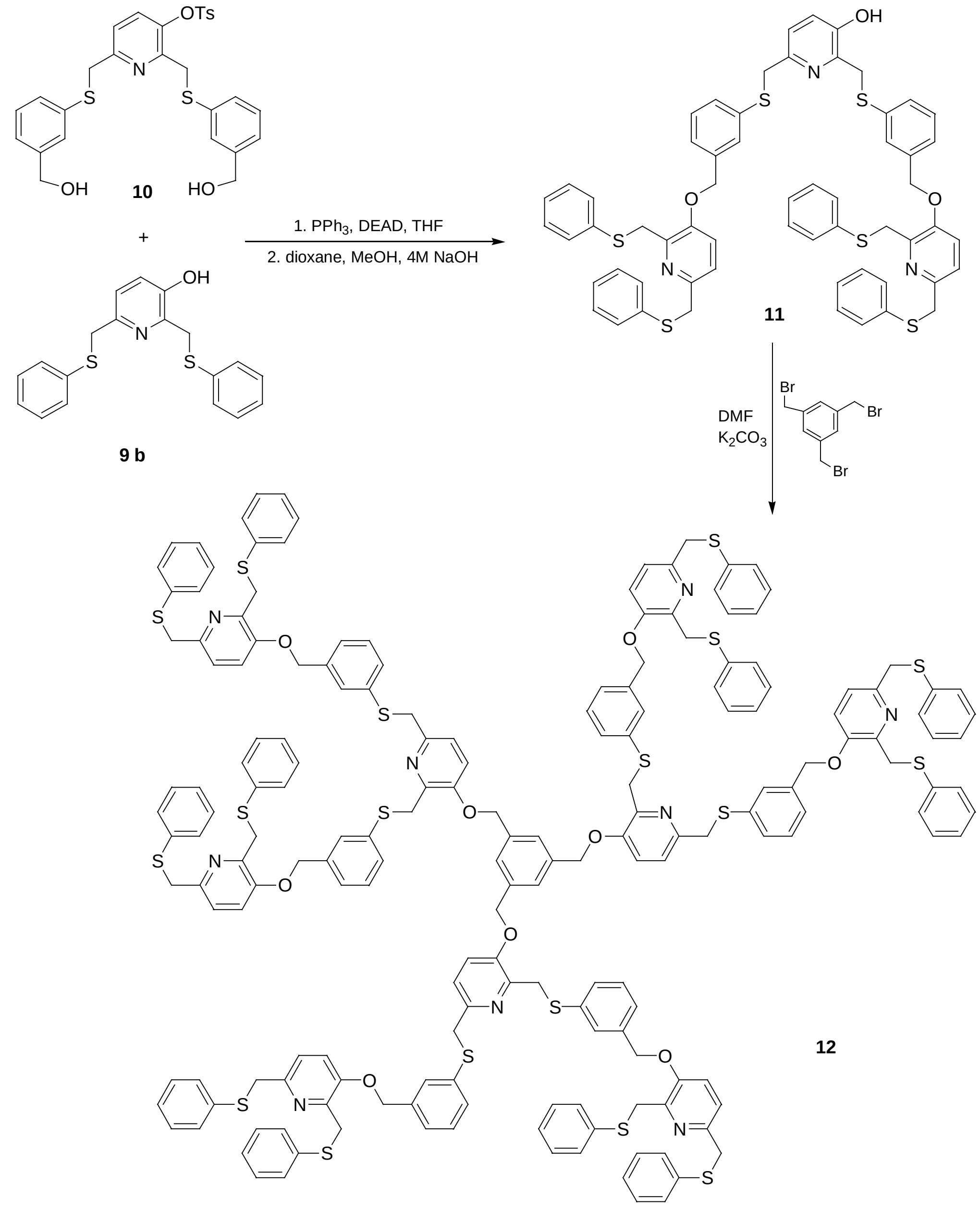
The synthetic route to the dendritic scaffolds **9** and **12** involved the reaction of the trifunctional core α, α', α''-tribromomesitylene with the pyridylthioether **8** (**8a** [22] and **8b** [23], Scheme 3) and the dendritic fragment **11** [23], derived from the de-protection under basic conditions (dioxane/methanol, NaOH 4M) of the parent compound obtained by coupling via a Mitsunobu ether synthesis of 2,6-bis[((3-hydroxymethylphenyl)thio)



Scheme 2.



Scheme 3.



Scheme 4.

methyl]-3-hydroxypyridine *p*-toluene sulfonate **10** with the building block **8b** (Scheme 4).

The structures of the dendrimers obtained were confirmed by the usual techniques including NMR and IR spectroscopies, MALDI–TOF mass spectrometry as well as elemental analysis.

4. Binding ability of the S-N-S(Me) ligand

We determined the binding ability of 2,6-bis(methylthiomethyl)pyridine (S-N-S(Me)) with proton, palladium(II) and copper(II) [1]. To the best of our knowledge no further determinations with other substrates have been made so far. The affinity of S-N-S(Me) toward Pd(II) was high as expected, being several orders of magnitude larger than those determined for Cu(II) and H$^+$ (Table 1). The difference in the coordinating capability allowed the selective separation of Pd(II) from an acid (pH ≈ 3) solution containing both Pd(II) and Cu(II) salts [1]. Moreover, different macro-

Table 1
Formation constants for the reaction:
$\text{S-N-S(Me)} + \text{M} \overset{K_f}{\Longleftrightarrow} \text{S-N-S(Me)M}$

M	$\log K_f$
H$^+$	4.04
Cu^{++}	4.6
Pd^{++}	28.92

porous polystyrenes were functionalised as chloromethyl derivatives and reacted with 2,6-bis(methylthiometyl)-3-hydroxypyridine yielding a chelating resin which displays selective sorption for Pd(II) in the presence of other metals (Fe(III), Co(II), Ni(II), and Cu(II), 150-fold excess) [13]. Incidentally, the macroscopic and microscopic acid dissociation constants in water for the conjugated diprotic acid of 2,6-bis(methylthiomethyl)-3-hydroxypyridine were determined [24].

5. Nucleophilic substitution reactions on Pt(II) and Pd(II) derivatives of S-N-S(Me)

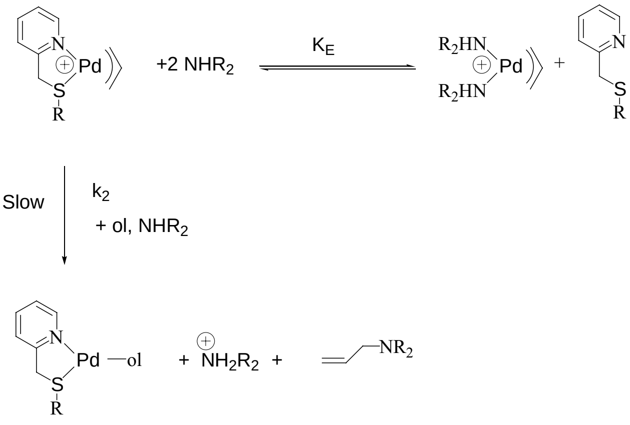
The complex $[Pt(S\text{-}N\text{-}S(Me))Cl]^+$ was used as the standard substrate in order to build up a reactivity scale toward nucleophilic substitution on mono-cationic platinum(II) complexes [25]. This problem was debated for many years since the n^0_{Pt} scale was first proposed by Pearson and co-workers in the 60s [26,27]. The inadequacy of this reactivity scale when charged platinum complexes are involved was soon apparent and this fact prompted several research groups to search for new suitable standard substrates [28–31]. The species $[Pt(S\text{-}N\text{-}S(Me))Cl]^+$ was reacted in aqueous solution with many entering groups and an extensive nucleophilicity scale was then proposed thanks to the remarkable stability of the substrate in solution and to its suitable reactivity, which were both traced back to the polarizability of sulphur and to the not negligible π-acceptor capability of the coplanar (with respect to the main coordination plane) pyridine group. The π-back bonding properties of the S-N-S(Me) ligand were also invoked in a subsequent paper [32] dealing with the displacement of pyridine from the complex $[Pd(S\text{-}N\text{-}S(Me))(Py)]^{++}$ by water and chloride ion. Comparison of the pK_a of the aquo-derivative $[Pd(S\text{-}N\text{-}S(Me))(H_2O)]^{++}$ (4.7) with the pK_as of analogous species $[Pd(dien)(H_2O)]^{++}$ and $[Pd(Me_5dien)(H_2O)]^{++}$ (≈7) and of the reactivity of the related pyridine species toward pyridine displacement leads to the conclusion that back donation on coplanar pyridine tunes the electrophilicity and consequently the reactivity of the system. Quite curiously, at that time no great importance was attached to the nature of chelating sulphur atoms since the authors did not trust too much the so-called *cis* effect which was interpreted as a kinetic assistance of the species *cis* to the leaving group in nucleophilic substitution reactions in d^8 systems. However, the presence of the two diastereoisomers (meso and DL) was recognised and the rate of their mutual conversion (which does not influence the overall substitution rate) was determined.

6. Bidentate pyridylthioether Pd(II) allyl complexes

Because of its synthetic applications, the nucleophilic attack at a coordinated allyl group has been widely investigated [33–36]. An impressive number of palladium allyl complexes bearing different ancillary ligands were studied. In the field of mixed donor chelating ligands, different pairs of potentially coordinating atoms were especially considered [34,37–43]. We examined the behaviour of palladium allyl derivatives bearing both bidentate and potentially terdentate pyridyl-thioether ancillary chelates when reacting with aliphatic amines. In these systems the steric and electronic properties of the substrates were finely tuned by modification of the sulphur substituents R or by inserting a substituent in the pyridine ring. (Scheme 1) On the basis of allyl symmetry the allyl complexes derived from the bidentate ligands can be grouped into two different classes of compounds. Thus, the unsubstituted allyl moiety generates two diastereoisomers (each diastereoisomer consisting of two enantiomers) owing to the different mutual orientation between the substituent at the C_2 central allyl carbon and the R substituent at sulphur. Usually at room temperature fast inversion of the absolute sulphur configuration and apparent allyl rotation lead to a mediated situation in which a singlet attributable to CH_2-S protons and two broad signals ascribable to the *syn* and *anti* allyl protons are clearly detectable by means of NMR technique. The structure distribution becomes apparent at low temperature when the “freezing” of the two diastereoisomers allows the observation of several signals. Among these, two AB systems, due to two CH_2-S protons contiguous to the diastereotopic sulphur and eight doublets, ascribable to *anti* and *syn* allyl protons, are particularly diagnostic [14,15]. The unsymmetric allyl moiety gives rise at low temperature to the coexistence of four diastereoisomers (again, each diastereoisomer consisting of two enantiomers) but only in the case of $[Pd(\eta^3\text{-}C_3H_3Me_2)(N\text{-}S\text{-}t\text{-}Bu)]^+$ were four signals detectable at low temperature which could be ascribed to the *t*-butyl group, thereby confirming the isomer distribution [15].

The mechanism governing the reactivity of the pyridylthioether allyl complex toward secondary amines may be summarised by the following Scheme 5:

$$k_{obs} = \frac{k_2[NHR_2]}{1 + K_E[NHR_2]^2/[N\text{-}SR]_0} \qquad (1)$$

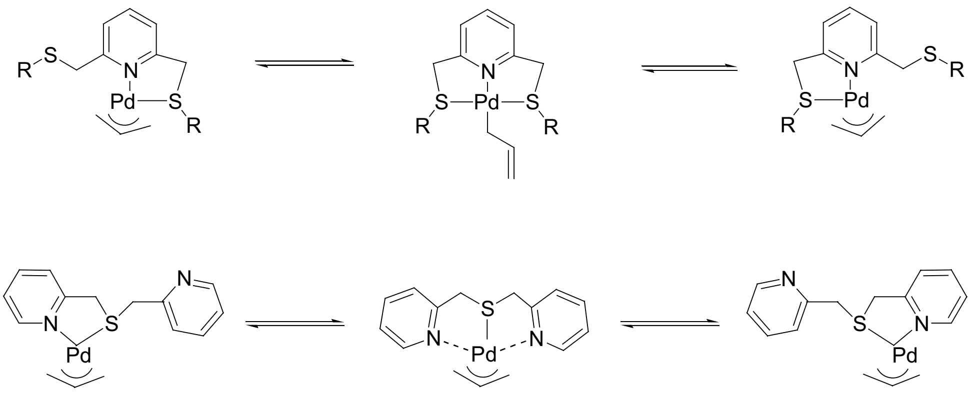


Scheme 5.

The exhaustive studies carried out led to several conclusive remarks that can be rationalised on the basis of the steric and electronic characteristics of both entering amines (NHR_2) and ancillary bidentate pyridylthioether ligands (N-SR). Thus, the overall reaction rate as dictated by the kinetic expression (1) is not only influenced by the concentration, the basicity and the bulkiness of the entering amine but also by the chelating properties of the pyridylthioether ligands and therefore by the constant concentration of free ancillary ligand ($[\text{N-SR}]_0$) that is added to the reaction solution. The latter exerts on the substrate a fundamental influence since it can modulate the electronic density on the metal centre thereby affecting the electrophilic properties of the coordinated allyl group. The less chelating ligand resulted in the more activated species with respect to amine attack. Thus, other things being equal, the aryl substituent at the coordinating sulphur imparts the highest reactivity to the substrates together with the presence of a methyl group in position 6 of the coordinating pyridine ring. This effect can be easily traced back to the electron-withdrawing properties of the aryl fragment but it appears in contrast with the increased basicity of the 6-methyl-substituted pyridine. Apparently the methyl substituent of the pyridine ring induces a distortion on the main coordination plane of the complex, causing a generalised instability of the substrates which become more reactive. As a matter of fact the increased reactivity toward amine attack parallels the values of the K_E equilibrium constant which is a measure of the ease of N-SR ligand displacement. The interplay between k_2 and K_E turns into an unfavourable situation in the case of attack on the allyl substrates as can be deduced from Eq. (1), since the fraction of reactive species decreases with increasing K_E (although addition of a large amount of free N-SR ligand could in principle reduce the effect). Incidentally, the pyridylthioether ligands display a coordination capability similar to that of α-diimine species, as can be deduced from the values of displacement equilibrium constants K_E independently determined in both systems [15,44].

7. Terdentate pyridylthioether Pd(II) allyl complexes

As a part of our research on palladium promoted nucleophilic substitution on allyl substrates we extended our studies to palladium allyl complexes containing potentially terdentate ligands [16,45] with the aim of investigating a promising issue in the field of synthetic applications [46] and to shed light on the reactivity of η^1-coordinated allyl complexes, this peculiar coordination mode being promoted by ter-coordination of the ancillary ligand [46b]. The ensuing kinetic data, while providing new pieces of information on the reactivity of allyl derivatives, did not allow any qualified conclusion on the behaviour of the η^1-coordinated allyl fragment since the potentially terdentate S-N-S (or N-S-N) ligands only induce a generalised fluxionality in the systems without modifying their reactivity toward amination. In other words, the kinetic results could be traced back to those obtained with analogous bidentate ancillary ligands. Thus, the S-N-S derivatives behave analogously to the complexes containing 6-substituted pyridylthioether bidentate species, while those derived from N-S-N ligands behave similarly to the complexes bearing the unsubstituted N-S(Ph) fragment. Apparently, the potentially terdentate pyridylthioether ligand does not influence the overall reactivity of the complexes since the ensuing tercoordinate η^1-allyl species should be thought of as a short-lived, less reactive intermediate [16]. However, a significant difference in the fluxional behaviour of the complexes bearing S-N-S or N-S-N ligands emerges from the comparison of their variable temperature ^{1}H NMR spectra. The S-N-S ligands in their wind screen wiper-like movement (which is operative also at very low temperature) promote the formation of intermediates in which the allyl moiety is η^1-coordinated. Conversely the N-S-N derivatives, although undergoing an analogous movement, are not able to force the allyl fragment into the η^1-coordination mode and the resulting fluxionality is better described as a fast exchange between the pyridine nitrogen atoms [16]. A schematic representation of the phenomenon is reported in the following Scheme 6 where the charges are omitted for clarity:



Scheme 6.

8. Pd(II) allyl complexes bearing pyridyldithioether-based dendrimers as ancillary ligands

Another class of peculiar Pd(II) allyl complexes were synthesised using pyridyldithioether-based dendrimers as ancillary ligands. The reactivity of the ensuing substrates was studied with respect to allyl amination using piperidine as reacting amine and the influence on the reactivity of the dendritic wedges was carefully assessed [21b]. The allyl amination reaction takes place by the same stepwise mechanism previously described (Scheme 5); in this respect no substantial differences could be detected in the reaction behaviour between the simple terdentate and the dendritic terdentate species. However, the kinetic analysis of the stepwise mechanism provides kinetic and thermodynamic information on the system so that the influence of increasing bulkiness of the dendritic wedges can be analysed in terms of accessibility to the allyl fragment (k_2) and coordinating capability of the ligand itself (K_E). Therefore some structural information could be obtained from the evaluation of easily obtained kinetic data. As a matter of fact, a decrease of k_2 and an increase of K_E values are observed on going from the second to the third dendrimer generation. This result indicates that some sort of severe distortion with concomitant destabilisation of the whole structure is involved when the electronic and steric interaction between the third generation dendritic wedges is operative.

9. Pyridylthioether Pd(0) or Pt(0) olefin complexes

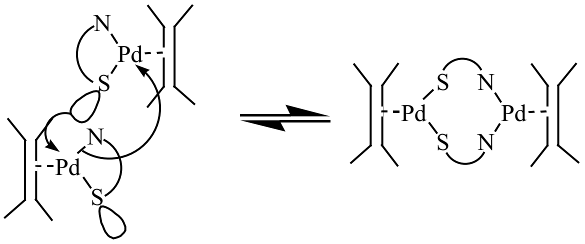
As can be seen in Scheme 5 the products of allyl amination are the allyl-amine and the Pd(0) olefin stabilised derivative. Such a substrate can also be synthesised directly by reacting a stoichiometric amount of $Pd_2(DBA)_3{\cdot}CHCl_3$ (or $Pt_2(DBA)_3$) with the bidentate or terdentate pyridylthioether ligand and the appropriate deactivated olefin [17,18,47]. Moreover, a number of dendritic-based Pd(0) olefin substrates were synthesised and characterised [22,23], in addition to the monomeric species. The stability of the Pd(0) complexes is dictated by the electronic and steric characteristics of the olefin (the deactivated olefins used in our work are: tetramethylethylene tetracarboxylate (TMETC), naphthoquinone (NQ), fumaronitrile (FN), maleic anhydride (MA), tetracyanoethylene (TCNE) and by the nature of the ancillary pyridylthioether ligand. As a matter of fact the stability of the complexes (which is of paramount importance in catalysis) increases with increasing electron affinity of the olefins. In this respect an exhaustive study based on the following reaction scheme was carried out and the stability order among olefins and as a function of the ancillary ligand was assessed:

$$[(\mathrm{RN\text{-}SR'})\mathrm{Pd}(\mathrm{ol}_1)] + \mathrm{ol}_2 \Longleftrightarrow [(\mathrm{RN\text{-}S\text{-}R'})\mathrm{Pd}(\mathrm{ol}_2)] + \mathrm{ol}_1 \qquad (2)$$

The stability trend which was shown to have a general validity is the following: TMETC $\approx$ NQ $<$ FN $\approx$ MA $\ll$ TCNE. Moreover, in the case of the exchange between NQ and TMETC, owing to the steric requirement of the bulky TMETC and to the favourable absorption spectrum in the UV–vis region, the kinetics of olefin exchange could be followed by UV–vis spectrophotometric technique and the activation parameters were determined from measurements at different temperatures. The olefin exchange reaction turned out to be associative in nature and characterised by a low activation enthalpy and a remarkably negative activation entropy. At variance with the observed behaviour in the case of olefin exchange in complexes with bidentate ligands, the substrates bearing a terdentate pyridylthioether moiety undergo (in addition to the main associative attack) a fairly observable reaction which is independent of the concentration of the entering olefin. This fact was ascribed to the parallel dissociative path induced by the dangling arm of the ligand which coordinates to the metal centre and promotes the displacement of the coordinated olefin [18].

As far as the kinetic investigations are concerned our most exhaustive study concerned the pyridylthioether olefin complexes of Pt(0). It is well known that the reactivity with respect to substitution reactions in platinum(II) substrates is, in general, three orders of magnitude lower than that occurring in analogous palladium(II) species. Since this reactivity order is maintained also in the case of Pt(0) and Pd(0) complexes, we were able to assess the reactivity trend of the deactivated olefins when they act as entering moiety in the olefin exchange reactions [47]. The ensuing reactivity order is: MA $>$ FN $\approx$ NQ $\gg$ TMETC. This behaviour was traced back essentially to the steric requirements of both entering and leaving olefins. As a matter of fact, TMETC displays a reactivity which is at least six orders of magnitude less than that of MA whose concomitant and favourable electronic and steric (*Z* structure) features render this olefin the most reactive. This trend does not parallel the scale of thermodynamic stability which is less dependent on the steric demand of the stabilising olefins. Moreover, the increased reactivity with respect to substitution was also confirmed by a comparative X-ray analysis among the structures of three pyridyl-methanimine derivatives of Pt(0) containing FN, MA and DMF as coordinating olefins, respectively. The structures clearly support the hypothesis that the most labile olefin is DMF (at least among the studied ones) whose bond lengths (longer Pt-N, shorter C=C) can be easily ascribed to the lower coordinating capability of DMF itself.

All the pyridylthioether olefin complexes undergo several temperature dependent rearrangements in solution and these processes can be conveniently analysed by means of NMR spectrometry. The fluxional rearrangements are usually interpreted in terms of different mechanisms which can be grouped in the following list: (1) inversion of sulphur absolute configuration (2) propeller-like olefin rotation (3) Pd-olefin bond cleavage and recombination; (4) Pd–N or Pd–S bond cleavage and ligand rotation and recombination



Scheme 7.

(olefin pseudo-rotation) (5) intermolecular olefin exchange (6) intermolecular ancillary ligand exchange. Points (5) and (6) need free olefin and/or free ancillary ligand in solution (partial decomposition). A combination of at least two of these mechanisms could explain all the rearrangements observed in the pyridylthioether olefin complexes. Although the inversion of sulphur configuration represents in these systems the less energetic rearrangement occurring at lower temperature, it is not always easy to reveal the process occurring at higher temperature. In the case of the complex [Pd(η^2-TMETC)(HN-S(Me))] we were able to propose a mechanism triggered by the lone pair at sulphur belonging to one complex that attacks the palladium atom of another substrate, originating a bimolecular intermediate (see Scheme 7). This collapse gives rise to the observed fluxionality (olefin pseudo-rotation) [48].

10. Pd(II) methyl complexes

Addition of the appropriate pyridylthioether ligand to a solution of [PdCl(Me)(COD)] [49] in toluene leads to the methyl palladium complexes of the type [PdCl(Me)(N-S)] (N-S = bidentate or terdentate species). These substrates proved to be reactive with respect to insertion of unsaturated molecules across the Pd–C bond. This reaction and generally the insertion reaction into the metal–carbon bond is of widespread importance in several synthetic paths toward C–C bond formation [50]. In particular, these substrates become very reactive when ligands bearing a substituent in position 6 of the pyridine ring are used [51]. From the comparison between the crystal structures of the complexes [PdCl(Me)(HN-S*t*-Bu)] and [PdCl(Me)(MeN-S*t*-Bu)] it appears that the latter displays a marked distortion of the main coordination plane. The enhanced reaction rate was ascribed to this particular atom disposition which can be looked at as a transition state-like structure (Fig. 1).

From the systematic studies carried out on these substrates the following observations were made.

(1) Steric hindrance at the allene moiety depresses the rate of insertion by one to two orders of magnitude.
(2) Steric hindrance at the sulphur substituent R depresses the rate by less than one order of magnitude.
(3) The presence of a substituent in position 6 of the pyridine ring (Me, Cl) causes a marked increase of the reaction rate (from three to almost six orders of magnitude).
(4) The highest rate constants of allene insertion are achieved when R and R′ are electron-withdrawing fragments (R = Ph; R′ = Cl).

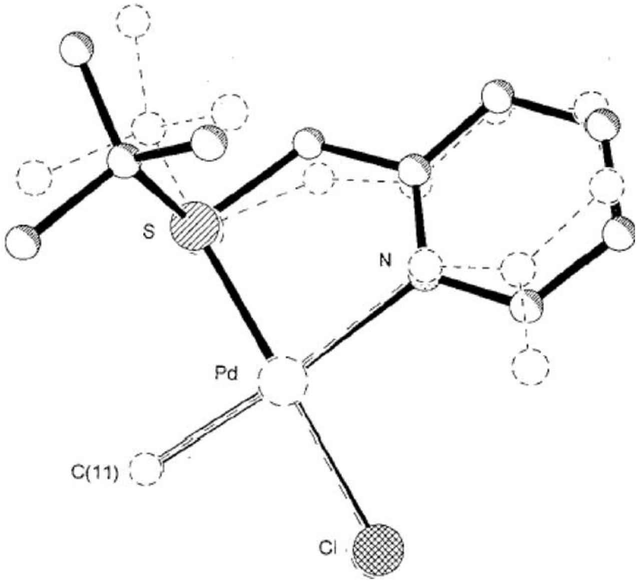


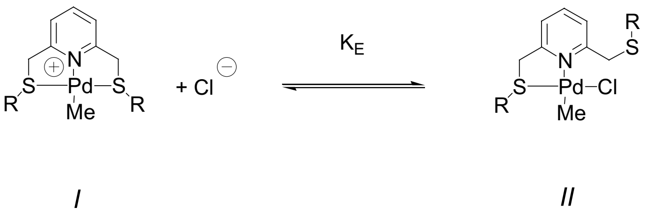
Fig. 1. Superimposition of the molecular structures of complexes [PdCl(Me)(HN-S*t*-Bu)] and [PdCl(Me)(MeN-S*t*-Bu)].

As a matter of fact, to the best of our knowledge this very peculiar combination produces the highest insertion rate observed so far. Very probably, the corresponding solvento species (which can be obtained by silver triflate-promoted halide abstraction from the substrates) would display a higher reactivity if compared with that of their parent halide derivatives. However, they would also display a higher instability.

Highly efficient metal-based systems for the activation of the C–Cl bond in the Heck olefin arylation with unactivated aryl chloride have been described previously [52].

It appears that the classical asynchronous mechanism governing the nucleophilic attack to a square planar substrate is also operative in this case. The destabilisation of the ground state by distortion renders the complex more prone to nucleophilic attack of allene which represents the most energetically disfavoured rate determining step. Thus, the subsequent fast migration of the methyl group does not affect the overall observed rate constant. Moreover, the flexible structure of the ligand due to the presence of an sp^3 sulphur atom is of primary importance since it couples distortion (i.e. propensity to nucleophilic attack) with sufficient stability within the same molecule.

If a potentially terdentate pyridylthioether ligand is used as an ancillary moiety in methyl palladium complexes it is possible to modulate the insertion rate by addition of a suitable amount of chloride ion [53]. As a matter of fact, the following equilibrium is operative in solution (Scheme 8).



Scheme 8.

Species I is present as the triflate OTf salt whereas the chloride is added as triethylbutylammonium chloride (TEBACl).

Since the equilibrium mixture is well shifted to the left and species II is by far more reactive than species I (species II can be compared with analogous bidentate 6-pyridine substituted distorted species) the addition of TEBACl to the solution induces the formation of the reactive substrate and thereby favours the subsequent insertion reaction. In this respect the less reactive but more stable complex 1 (as OTf salt) could be stored without particular precautions for a long time and used as reactive substrate by the mere addition of chloride. As can be deduced from the peculiar coordinating capability of the N-S-N ligand (vide supra), addition of TEBACl to a solution containing the complex [Pd(N-S-N)Cl(Me)] will not affect the reactivity of the substrate. In this case the equilibrium above is completely shifted to the right and therefore addition of chloride cannot alter the equilibrium position. The reactivity of such a species thereby proves quite comparable with that of the bidentate undistorted N-S species with analogous electronic and steric characteristics. In both cases chloride abstraction leads to the formation of truly terdentate unreactive species and in this respect no advantages could be obtained from this strategy, which is often used to increase the overall reaction rate.

The insertion reaction can be extended to other unsaturated molecules (i.e. activated alkynes) and these studies are still under way in our laboratories. However, it is yet possible to anticipate that again the pyridylthioether palladium methyl derivatives will display a remarkable reactivity also with these organic substrates.

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