



Review

Synthesis, stability and reactivity of palladium(0) olefin complexes bearing labile or hemi-labile ancillary ligands and electron-poor olefins

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ARTICLE INFO

Article history:

Received 23 March 2010

Accepted 11 April 2010

Available online 20 April 2010

Dedicated to Prof. Fred Basolo

Keywords:

Palladium(0) olefin complexes

Labile and hemi-labile ligands

Deactivated olefins

ABSTRACT

An overview of the general features of electron-poor olefin stabilized palladium(0) complexes bearing labile and hemi-labile ancillary ligands is presented. In particular, we have summarized the synthetic methodologies, the ligands commonly used, and the characterization of such complexes. The behavior of these species in solution is also described with particular attention to their fluxional rearrangements and reactivity. Thus, olefin exchange reactions are described and a comprehensive order of coordinative capability of the most widely used electron-poor alkenes is presented. The reactions of the title complexes dealing with olefin isomerization, oxidative addition, and formation of palladacyclopentadiene derivatives are eventually reported together with their main structural characteristics.

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1. Introduction

The importance of palladium and its complexes as catalysts is of the utmost interest and a general attempt at reviewing exhaustively such a topic might represent an almost impossible challenge [1]. Therefore, any investigation on particular aspects of the characteristics and of the reactions promoted by palladium complexes needs to be specifically addressed. Among all the palladium catalysts, the zero-valent derivatives bearing coordinated olefins are particularly important since they are often used or identified as the active catalytic species in a variety of cross-coupling reactions [2–16]. Moreover, the bonding attitude of olefins toward palladium(0) was extensively studied from theoretical and structural point of view [17] and were developed on the basis of the original work of Dewar [18] and Chatt and Duncanson [19]. At the best of our knowledge, however, the intrinsic characteristics of the olefin palladium(0) complexes bearing labile and hemi-labile ancillary ligands were never analyzed in detail. As a matter of fact, these complexes display interesting features since a coordinating site might be easily available upon partial or total displacement of the ancillary ligand.

We therefore, think that a thorough investigation on the synthesis and the reactivity of these complexes could be useful in rationalizing and planning their design and use. Thus, the synthetic approach, the stability, the peculiar fluxional rearrangements in solution and some stoichiometric reactions of Pd(0) alkene derivatives with ancillary bi- and ter-dentate ligands bearing only labile (N–N, N–S, N–S–N, S–N–S) or hemi-labile (P–N, P–S, P–N–N) coordinating atoms and electron-poor olefins will be discussed in this paper.

2. The olefins in the synthesis of palladium(0) complexes

Irrespective of the nature of the ancillary ligands, the stability and hence the synthesis of palladium(0) olefin derivatives strongly depends on the electronic characteristics of the olefins themselves. Olefins bearing electron withdrawing groups at unsaturated carbons (deactivated olefins) stabilize the low oxidation state of palladium since they favour the electron back donation from the electron rich metal centre to the π^* antibonding orbitals of the alkenes and therefore the separation under mild conditions of their derivatives becomes feasible in many cases. The resulting shape of the ensuing complexes does not longer fit the Dewar, Chatt–

Duncanson approach since it assumes the typical metallocyclopropane structure with a remarkable lengthening of the C=C bond and the consequent out-of-plane bending of the substituents at the unsaturated carbons [20] (X-ray diffraction studies of several Pd(0) olefin complexes will be presented later). The most commonly used olefins in the synthesis of palladium(0) derivatives together with their abbreviations are reported in Scheme 1 (other unsaturated species occasionally described will be defined when necessary).

The olefins tetramethyl-ethene-tetracarboxylate (tmetc) [21] and *cis*- and *trans*-1,2-bis[(4-methylphenyl)sulphonyl]ethene (*c*-sulf, *t*-sulf) [22] can be obtained according to published methods. All the other alkenes reported in the scheme are commercially available grade products.

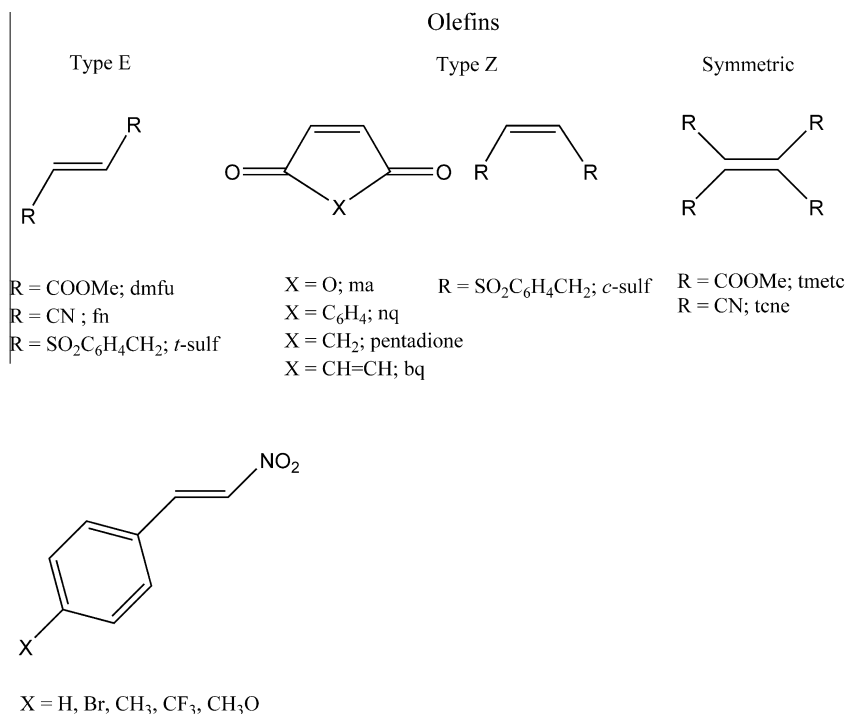
3. Synthesis of the palladium(0) olefin complexes

The synthesis of the palladium(0) olefin complexes of general formula $[\text{Pd}(\eta^2\text{-ol})(\text{L-L}'\text{-L}'')]$ where L–L'–L'' represents a generic labile or hemi-labile bi- or ter-dentate ligand (L = L' = L'', or L = L'' ≠ L') and ol the stabilizing olefin can be achieved by means of some different protocols.

Protocol (a): This protocol, consisting in reacting the complex $\text{Pd}_2(\text{DBA})_3\cdot\text{CHCl}_3$ [23] (DBA = dibenzyliden-acetone) with the appropriate ligand and olefin in anhydrous acetone under inert atmosphere, represents the first synthetic method [24,25] which is still widely employed [26]. It is noteworthy that the complex $\text{Pd}_3(\text{TBAAC})_3\cdot\text{CHCl}_3$ [27] (TBAAC = tribenzylidenacetone) can be used as an alternative starting substrate [24].

Protocol (b): The low-valent palladium complexes are obtained as side products in reactions of reductive elimination, by addition of an electron-poor olefin to the reaction mixture. This method was employed by Crociani and co-workers and sometime represents a useful alternative to protocol (a). The precursor is a palladium allyl derivative bearing a bidentate ligand which is reacted with BPh_4^- or amines. The elimination of the phenyl-allyl or amino-allyl moieties yields the palladium(0) species which is stabilized by *fn*, *dmfu* or *ma* [28,29].

Protocol (c): Irrespective of the nature of the ancillary ligand, different palladium olefin derivatives can be obtained by exchange between the coordinated and a different entering olefin. As will be discussed later, the coordinative capability of the electron-poor olefins can be very different. Therefore, different derivatives can be synthesized simply by adding an appropriate and better



Scheme 1. Structures and abbreviations of the most used olefins reported in the paper.

coordinating olefin to a solution of a complex containing a labile alkene [26,30,31].

Protocol (d): Analogously, different palladium(0) olefin complexes can be obtained by the exchange of the ligands [32–34]. Again the coordinating capability of the exchanged ligands is a strict prerequisite.

As a particular case, the method successfully used by Elsevier and co-workers in the synthesis of the olefin complexes of palladium bearing σ -donor monodentate nitrogen ligands must be mentioned [35]. This approach is based on the reaction between the complex [Pd(nbd)(ma)] (nbd = norbornadiene) and the monodentate ligands L (L = C₅H₅N, C₆H₅NH₂, (C₂H₅)₂NH, NH₃) and represents a powerful method for the preparation of complexes that would be hard to synthesize otherwise. The starting complex [Pd(nbd)(ma)] was prepared according to the method of Ishii and co-workers [36].

4. The labile and hemi-labile ligands

The most common labile and hemi-labile ligands used in the synthesis of palladium(0) olefin complexes are summarized in the following Scheme 2.

In the case of the ligand PNN, no palladium(0) olefin derivatives were isolated. Vrieze and co-workers however, were able to separate a complex containing the PNN ligand and palladium(0) without any stabilizing coordinated olefins (naked palladium) [45]. Similar species could be employed as starting materials for the subsequent synthesis of olefin derivatives whose stability might arise from the interplay between the olefin coordinating capability and the ligand chelating effect. At the best of our knowledge, no studies on this particular field were carried out so far.

5. Characterization of the complexes

The remarkable metal–alkene π -back donation becomes apparent when the chemical shifts of the alkene protons and carbons are

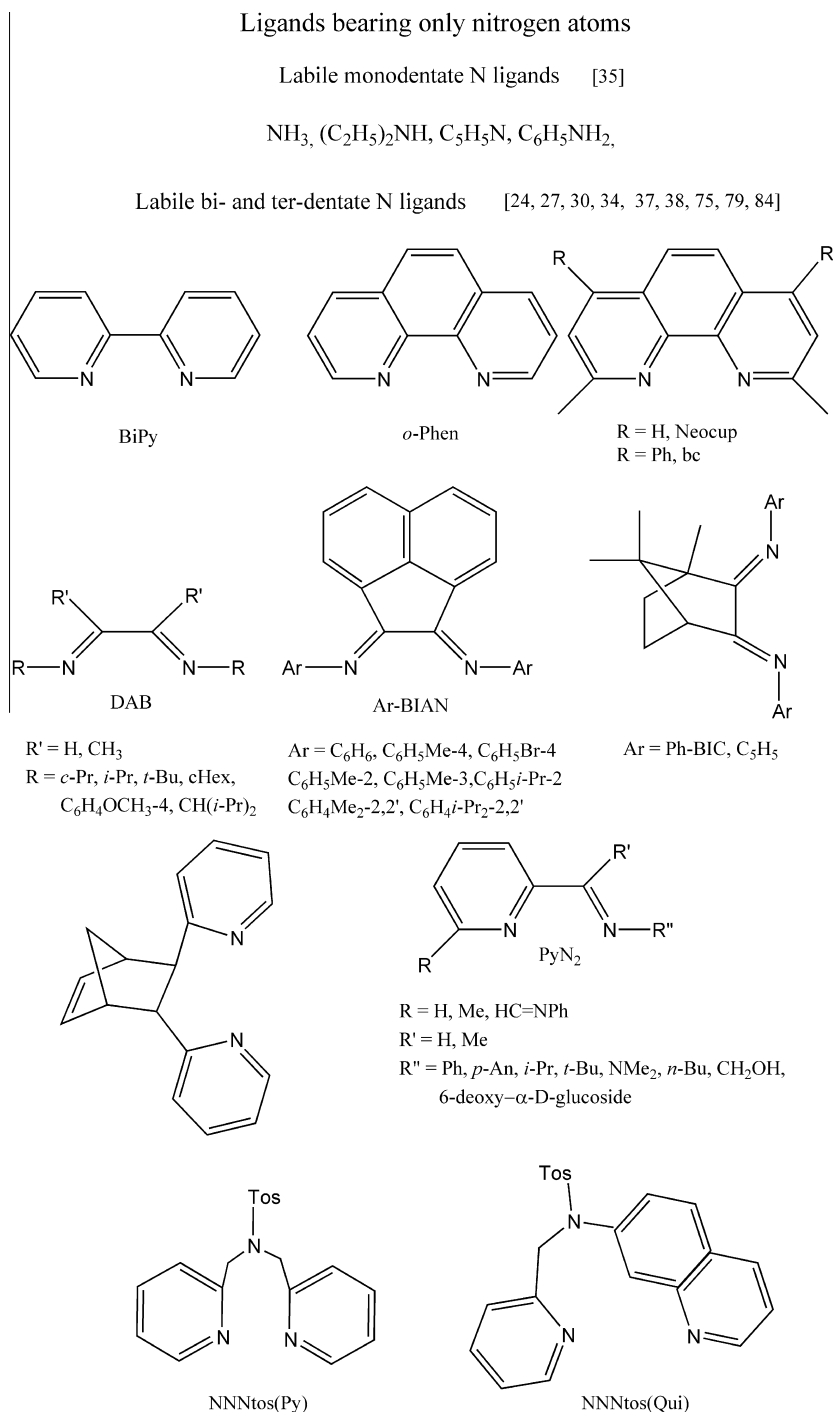
compared with those of the uncoordinated moieties. As a matter of fact, the chemical shifts of the protons and carbons ascribable to the coordinated olefins resonate at 2–3.5 and 80–120 ppm, respectively, upfield with respect to those of the free uncoordinated molecules. As expected, as a further confirmation a shift to lower frequency of the $\nu_{C=O}$ and $\nu_{C=N}$ stretching (when present) is also noticed in the IR spectra of the complexes. On the contrary, when N–N, N–S and N–P molecules are employed as ancillary ligands their ¹H NMR signals are all shifted downfield, indicating the predominant σ -nature of the ensuing bonds. The formation of different isomers as a function of the olefin structure and of the symmetry of the ancillary ligand can be observed (Scheme 3) [4,30,32,34,40–43]. Usually these species undergo extensive fluxionality and the RT ¹H NMR spectra of the complexes are characterized by rapid interconversion among isomers and only averaged spectra are detectable.

On decreasing the temperature, however, the “freezing” of the fluxional rearrangements reveals the existence of the isomers which usually are present in solution in different concentrations. Notably, in some case it is possible to distinguish between the relative structure of the diastereoisomers by means of low temperature NOE experiments [4,41].

6. Fluxional rearrangements

In complexes of general formula [Pd(η^2 -olefin)(L–L')] fluxionality can entail metal-olefin and/or metal-ancillary ligand rearrangements which are usually described by the following reported processes and depicted in Scheme 4:

- (1) propeller-like olefin rotation. This is the earliest and most frequently proposed mechanism [30,42,43,46–48];
- (2) olefin–metal dissociation followed by recombination [30];
- (3) intermolecular associative process with free alkene, via the intermediacy of a [M(η^2 -olefin)₂(L–L')] complex [30,48];



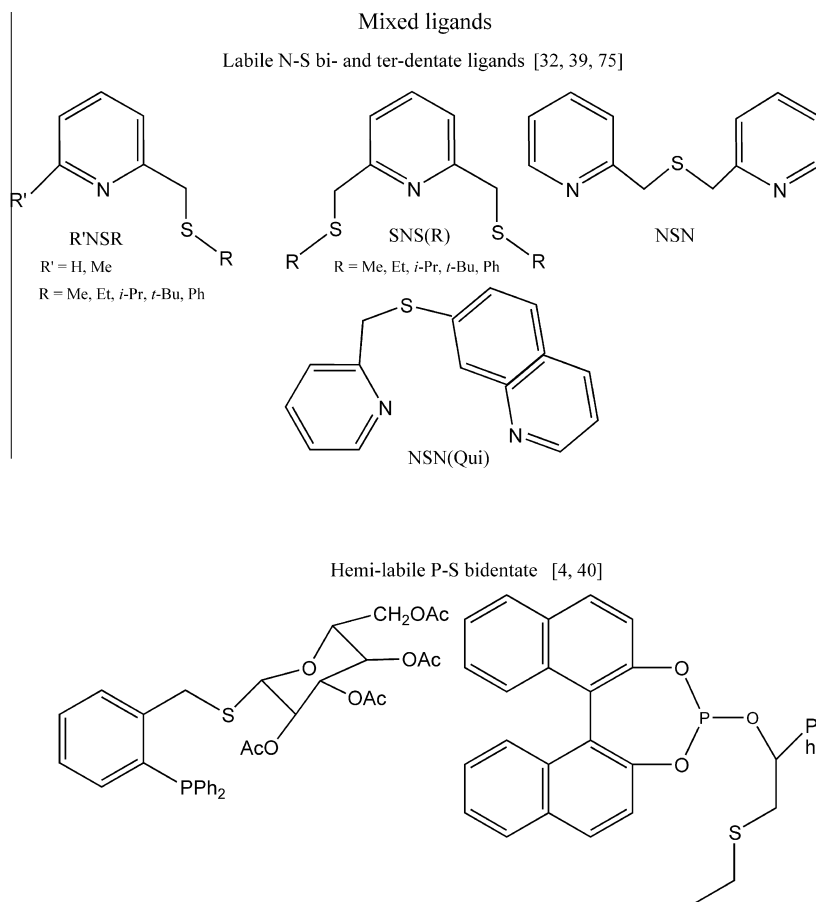
Scheme 2. Structures, abbreviations (when adopted) and references of the most cited ligands.

- (4) metal-L or metal-L' bond dissociation followed by rotation of the ancillary ligand and recombination (olefin *pseudo*-rotation) [42,43];
- (5) intermolecular exchange with the free ancillary ligand L-L'. In this case, a mechanism has been proposed which involves an olefin-metal dissociation step [30].

In the case of complexes bearing non-planar asymmetric ligands and Z-type olefins, any of the processes reported above might be taken into account in order to describe the isomeric rearrangement. On the contrary, in the case of complexes bearing asymmetric planar and non-planar ligands with E-type olefins, ole-

fin rotation (1) or *pseudo*-rotation (4) cannot be taken into account since in these cases the olefin enantio-face coordinated to palladium remains unchanged as a result of the propeller-like fluxional rearrangement and any process described in entries (2), (3) and (5) may explain the observed rearrangements.

The inversion between rotamers can be also originated by the absolute inversion of the configuration of a coordinating atom if present in the ancillary ligand as a hybrid sp^3 . In particular, ancillary bidentate ligands with one trivalent sulfur atom [49,50] coordinating a low-valent palladium bearing Z-type olefins may display apparent olefin rotation when the residual metallophilic lone pair on sulfur attacks the metal centre [4,26,32,39]. Notably, it has been



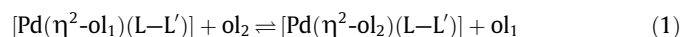
Scheme 2 (continued)

noticed that the apparent olefin rotation can also originate from the collapse of a dimeric species produced by action of the lone pair on sulfur which attacks another palladium centre *via* a bimolecular mechanism [51,52]. In these cases it has been demonstrated that the authentic olefin propeller-like rotation occurs at a negligible rate with respect to that observed when the associative mechanism is operative. Therefore, this further process must be also taken into account when the fluxional rearrangement of low-valent palladium olefin derivatives is considered (Scheme 5).

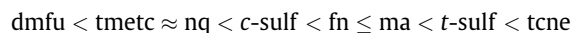
Finally, the rearrangement due to the attack of a coordinating atom lying on a dangling uncoordinated wing of a potentially ter-dentate ligand on the palladium centre can be also taken into consideration as a peculiar case of fluxionality [39]. The attack induces a fast (on the NMR time scale) windscreen-wiper like movement with the companion simplification of the 1H NMR spectrum. This phenomenon is observable also in the case of palladium olefin complexes with dendrimers bearing potentially ter-dentate pyridylthioethers as ancillary ligands (Scheme 6) [53,54].

7. Olefin exchange

The stability of the Pd(0) olefin complexes is of remarkable importance in modulating the reactivity of these species especially when they are employed in catalysis. It is also apparent that their stability is governed by the steric and electronic characteristics of the olefins themselves. Therefore, in order to assess the coordinative capability of different olefins toward Pd(0) complexes, reaction (1) has been studied in detail:



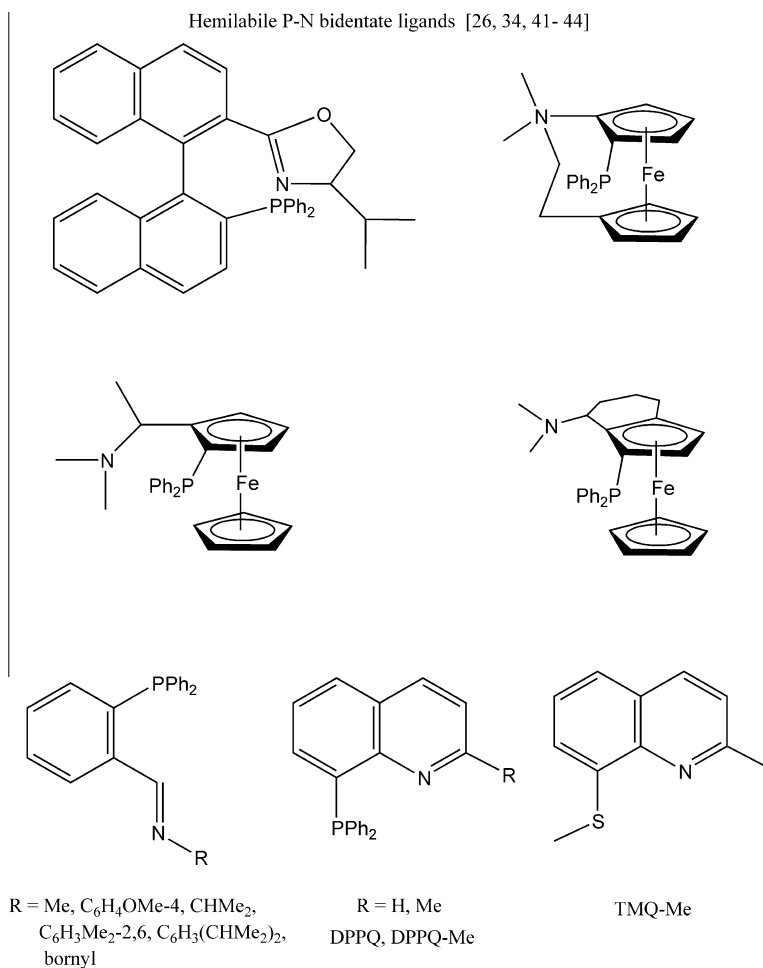
As a matter of fact, in contrast with Pt(0) complexes [55] palladium derivatives give rise to equilibrium reactions which can be studied by means of spectrophotometric and spectrometric techniques. A comparative study quite recently appeared [26] which, while confirming the stabilization capability of the olefins hitherto studied [30–32], also analyzes the influence of the nature of the ancillary ligands in determining the stability constants. The olefin stability order can be summarized as follows, while the comparison that takes into account the nature of some ancillary ligands is reported in Table 1 [26].



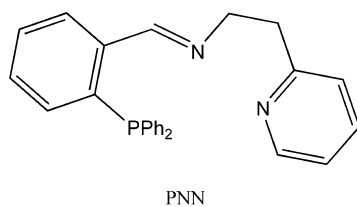
It is noteworthy that the introduction of the complex $[Pd(\eta^2-nq)(Neocup)]$ as the reference compound allowed the determination of the exchange equilibrium constants among nq and several alkynes. Interestingly, the alkyne dma ($MeOCC \equiv CCOOMe$) is more efficient in stabilizing the palladium(0) derivatives than the alkene dmfu which bears the same carboxymethyl substituents (Table 2).

Bulky ligands stabilize the Pd(0) alkyne complexes [56] which otherwise might add a further alkyne molecule to give palladium(II) cyclopentadienyl derivatives [57–60] according to a mechanism that was recently proposed and will be discussed later [44,61,62].

Taking advantage from the peculiar steric characteristics of the tetramethyl-ethene-tetracarboxylate (tmetc) the olefin exchange equilibria were also studied from the kinetic point of view [26,31,32,34,39,43,63–65]. It has been shown that the rates of exchange are strongly dependent on the steric requirement of the ancillary ligand and the mechanism is associative in nature.



Hemilabile terdentate ligand [45]



Scheme 2 (continued)

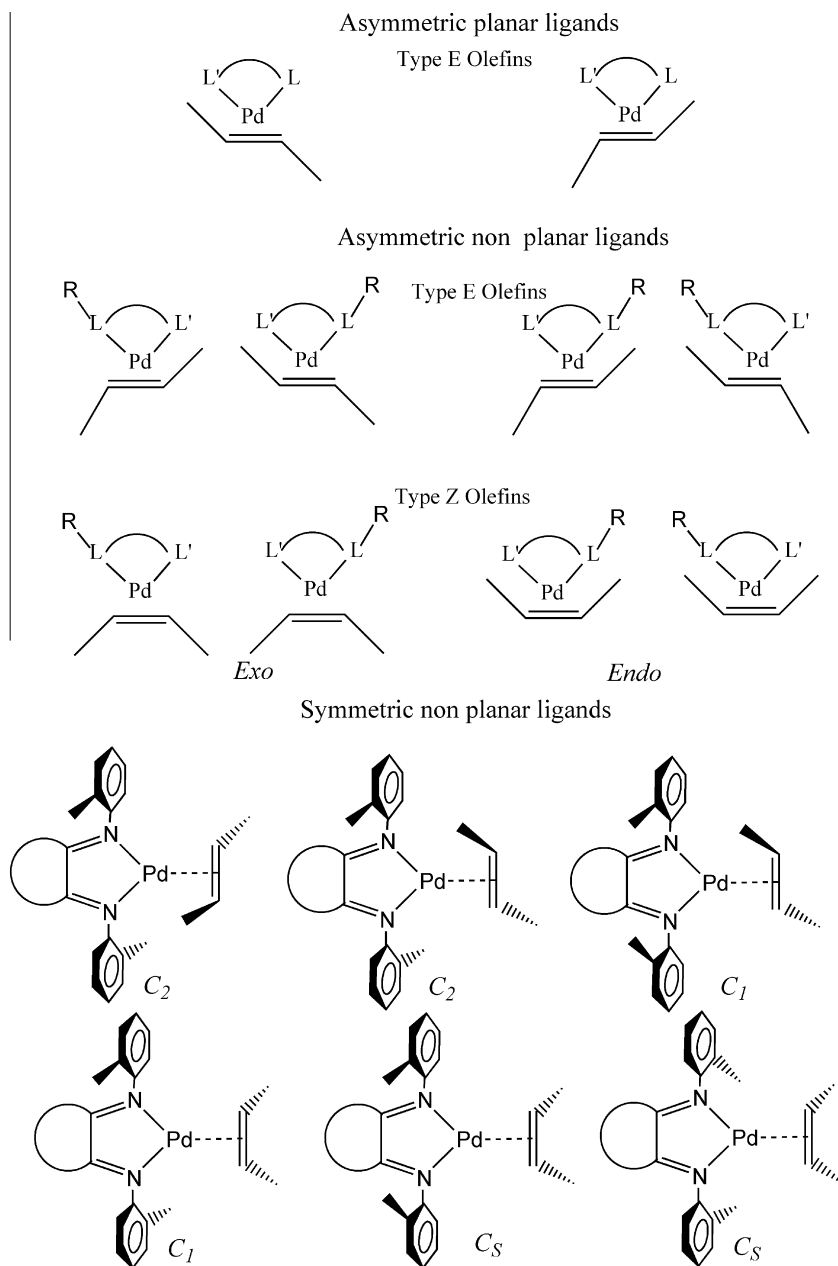
As a matter of fact, the activation enthalpies associated with the exchange reaction are small ($\Delta H^\ddagger \leq 13.2 \text{ kcal mol}^{-1}$), while the entropy values are significantly negative ($-36 < \Delta S^\ddagger < -20 \text{ cal mol}^{-1} \text{ K}^{-1}$).

Incidentally, the values of ΔH^0 and ΔS^0 related to the equilibrium reaction were also determined and the ensuing values span a narrow interval ($-3.5 < \Delta H^0 < -0.7 \text{ kcal mol}^{-1}$; $-11 < \Delta S^0 < 0.7 \text{ cal mol}^{-1} \text{ K}^{-1}$) [31,38]. In the paper of Landis and co-workers [38], the intimate mechanism of olefin exchange in complexes bearing the bulky bc ancillary ligand, is described in terms of inverse-electron-demand ligand substitution in which, at variance with the accepted mechanism describing the orbital interaction as an attack of the HOMO of the olefin on the LUMO of the coord-

inatively unsaturated palladium, an interaction between the HOMO of palladium and the LUMO of the alkene has been suggested. Such a mechanism may be better described as a redox neutral process which is strongly in accord with the experimental evidence which indicates that the ensuing Pd(0) complexes are more stabilized by the olefins carrying the more electron withdrawing groups.

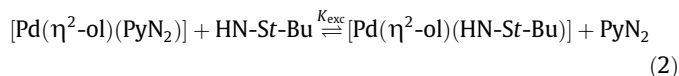
8. Ancillary ligand exchange

At the best of our knowledge the exchange reactions among ancillary ligands in the case of olefin derivatives of palladium(0) were quantitatively studied only in the case of the exchange be-



Scheme 3. Isomers derived from the combination among olefins and ligands.

tween the ligands 2-pyridylmethanimine (PyN₂) and 2-methylthio-*t*-butyl pyridine HN-*St*-Bu [32].

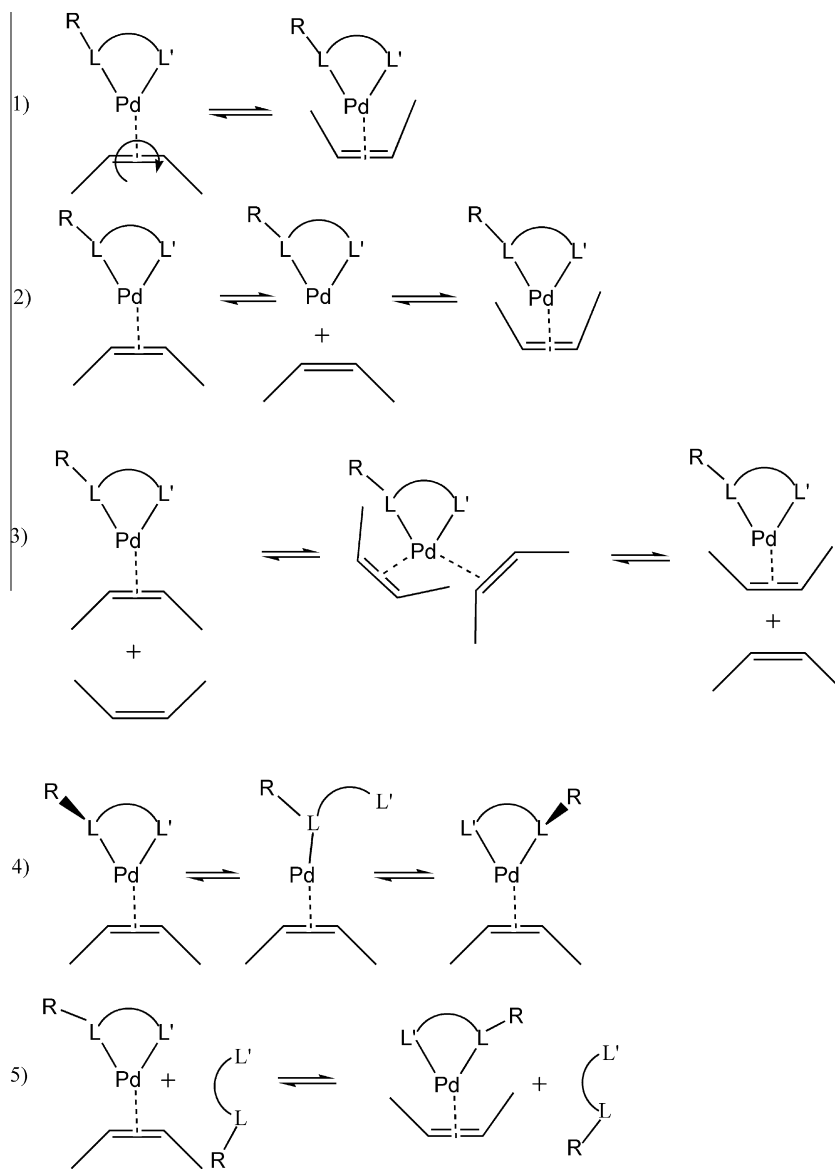


The complexes [Pd(η²-ol)(PyN₂)] (ol = fn, tmetc, nq, ma) were spectrophotometrically titrated with a CHCl₃ solution of the ligand HN-*St*-Bu. The ensuing K_{exc} span a very narrow interval (2.5 ≤ K_{exc} ≤ 7.1) and these determinations demonstrate (i) the scarce influence of the olefin on the coordinating capability of different ligands and (ii) the very similar coordinating ability between the labile ligands N–N or N–S (the latter observation is in accord with former determinations of the ligands exchange equilibria in the case of Pd(II) allyl complexes [66,67]).

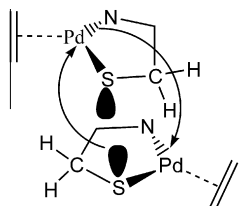
9. Reactivity of the palladium(0) olefin complexes

9.1. Alkene isomerization

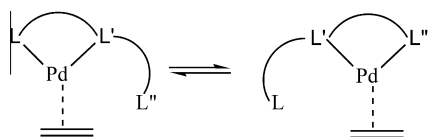
In some cases the palladium(0) olefin complexes induce steric rearrangement of the coordinated olefin. It was experimentally and theoretically demonstrated that dimethyl maleate and (*Z*)-1,2-bis[(4-methylphenyl)sulfonyl]ethene) undergo isomerization into their *trans* counterparts catalyzed by the complexes [Pd(η²-dmfu)(DPPQ)] and [Pd(η²-dmfu)(DPPQ-Me)]. In order to rationalize such behavior, it was surmised that such rearrangement is due to the cooperative influence of the two coordinating groups of the ancillary ligand on the Pd-olefin bond and to the presence of electron withdrawing conjugated systems on the reacting olefin. In this respect, the high *trans* stabilizing effect of the phosphine group activates the complex obtained upon substitution of dmfu by dimethyl



Scheme 4. Topological representation of possible isomerization mechanisms.



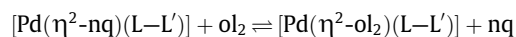
Scheme 5. Associative mechanism of isomerisation.



Scheme 6. The windscreen-wiper mechanism.

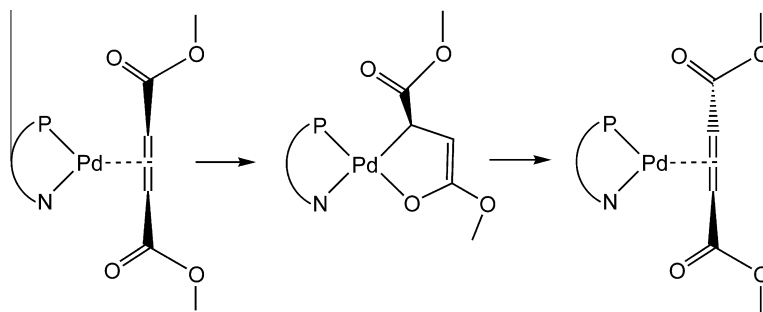
Table 1

Comparative olefin exchange equilibrium constants for the reaction:



ol_2 $\text{L-L}'$	dmfu	fn	ma	$K_{\text{Ema}}/K_{\text{Efn}}$
HN-SMe		17	18	1.05
HN-Set		12	16	1.33
HN-Si-Pr		6.7	9	1.35
HN-St-Bu		5.5	6.9	1.25
HN-SPh		8.4	7.2	0.86
MeN-SPh		16	49	3.06
BiPy	1.8×10^{-4}	2.5	4.8	1.92
Phen		3.9	10.7	2.74
DPPQ	3.0×10^{-4}	1.4	4.5	3.2
DPPQ-Me	3.8×10^{-4}	12.1	38	3.14
PyN ₂	1×10^{-3}	4.55	8.17	1.80
Neocup	3.2×10^{-4}	311	630	2.02

* Not determined for solubility problems [26].



Scheme 7. The mechanism of isomerization of the coordinated olefin.

maleate (or (*Z*)-1,2-bis[(4-methylphenyl)sulfonyl]ethene) with the consequent formation of the intermediate **I** which eventually collapses into the final complex [68] (Scheme 7).

9.2. Oxidative addition

The oxidative addition reactions have been widely investigated but despite the impressive number of papers appeared so far quite a few quantitative kinetic determinations dealing with palladium(0) olefin substrates have appeared in the literature. As a matter of fact, Amatore and Jutand together or independently have published a great number of investigations on the oxidative addition of Pd(0) substrates in the presence of phosphine or phosphorus derivatives but, at the best of our knowledge, studies dealing with palladium(0) derivatives bearing olefins and ancillary ligands taken into consideration in this paper are very rare [69]. In one case the starting palladium(0) derivatives treated with phosphine were

polyolefin macrocyclic substrates [70] which were recently reviewed [71].

In the case of the complexes $[\text{Pd}(\eta^2\text{-dmfu})(\text{P-NR})]$ (P-NR = iminophosphane; R = C₆H₄OMe-4) an exhaustive investigation on the oxidative attack of IC₆H₄CF₃-4 (ArI) was carried out in different solvents and at different temperature [13].

The proposed stepwise mechanism consists of (a) a solvolytic path with a zero order rate with respect to ArI involving the reactive species $[\text{Pd}(\text{P-NR})(\text{Sol})]$ formed in the olefin dissociation and (b) a parallel path with a first order rate with respect to ArI involving the species $[\text{Pd}(\eta^2\text{-dmfu})(\text{Sol})(\kappa^1\text{P-NR})]$ formed in the pre-equilibrium dissociation of the Pd–N bond. On the basis of the results reported in Table 3 the mechanism reported in Scheme 8 was proposed.

It is apparent that the most effective solvent is CH₃CN thanks to its large k_1 due to its coordinative characteristic while the most efficient concentration dependent path (highest k_2) reasonably takes place in the non-polar toluene.

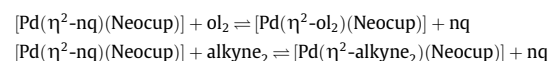
As a particular case of oxidative addition, the oxidative allyl transfer represents an important step in the palladium catalyzed nucleophilic substitution of allylic compounds. The study of the mechanism of the oxidative allyl transfer from an allyl cation to palladium(0) was therefore undertaken [72]. By means of a great wealth of kinetic determinations carried out with different concentration conditions of the reactants and at different temperatures it has been shown that the allyl oxidative transfer involves two consecutive equilibrium reactions. In the first equilibrium the allyl cation removes the stabilizing olefin from the palladium(0) complex, thereafter the successive step represents the reverse stage of the allylamine that was studied elsewhere [73,74] (Scheme 9).

9.3. Formation of palladacyclopentadiene complexes

The mechanism of attack of substituted alkynes on palladium(0) olefin derivatives bearing bi- and ter-dentate ligands giving palladacyclopentadiene complexes was studied in detail for the first time [44,75]. The reactivity of the complexes was found to be strongly dependent on the bulkiness of the entering alkyne

Table 2

Alkene or alkyne exchange equilibrium constants directly determined or calculated as a combination of the directly measured K_E values (Table 1), for the reactions:



ol ₂ /alkyne	K_E
pna	0.000082 ± 0.000001
dmfu	0.00032 ± 0.00002
dbua	0.018 ± 0.003
nq	1
deta	2.73 ± 0.7
dma	3.78 ± 0.6
cis-sulf	62 ± 16
fn	310 ± 50
ma	630 ± 180
trans-sulf	4650 ± 1700

pna = (4-Nitro-phenyl)-propynoic acid methyl ester (*p*-NO₂C₆H₄-C≡C-COOMe).

dbua = But-2-yneedioic acid di-*t*-butyl ester (*t*-BuOOC-C≡C-COOC*t*-Bu).

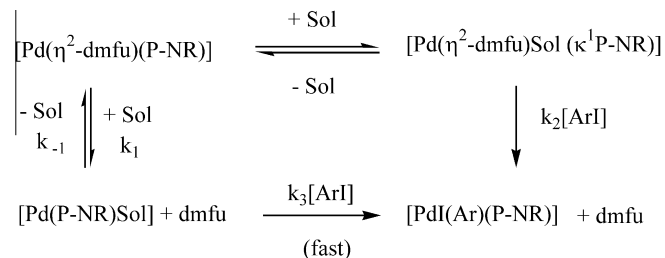
deta = But-2-yneedioic acid diethyl ester (EtOOC-C≡C-COEt).

dma = But-2-yneedioic acid dimethyl ester (MeOOC-C≡C-COOMe).

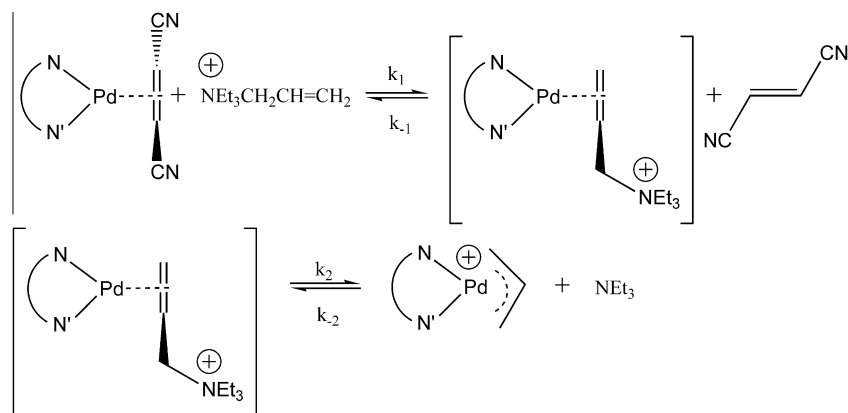
Table 3

Kinetic constants for the oxidative addition of ArI to $[\text{Pd}(\eta^2\text{-dmfu})(\text{P-NR})]$ in different solvents at 25 °C in the presence of dmfu (30-fold in excess).

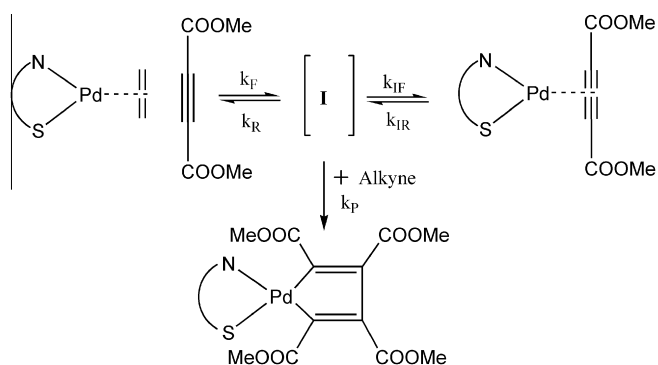
Solvent	k_1 (s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)
DMF	2.6 × 10 ⁻⁵	2.9 × 10 ⁻⁴
THF	4.8 × 10 ⁻⁵	2.1 × 10 ⁻³
CHCl ₃	7.1 × 10 ⁻⁵	1.1 × 10 ⁻³
Toluene	8.7 × 10 ⁻⁵	6.7 × 10 ⁻³
CH ₃ CN	8.3 × 10 ⁻⁴	3.8 × 10 ⁻³



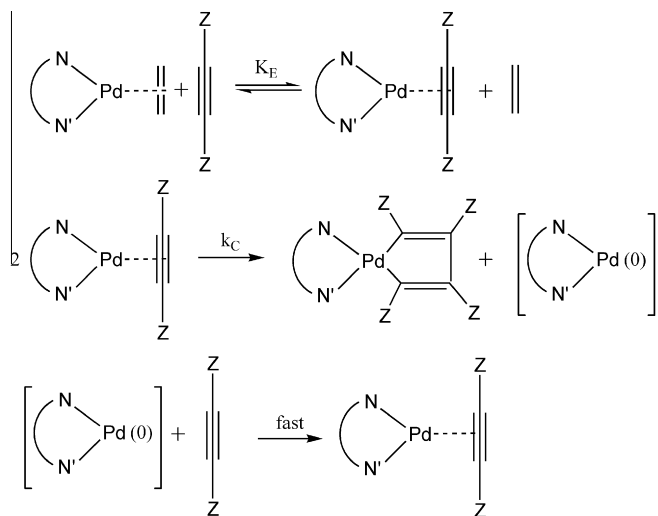
Scheme 8. The mechanism of oxidative addition of IC₆H₄CF₃-4 to $[\text{Pd}(\eta^2\text{-dmfu})(\text{P-NR})]$.



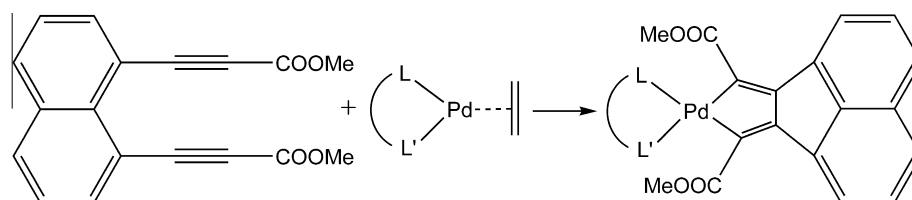
Scheme 9. The mechanism of oxidative allyl transfer.



Scheme 10. Mechanism of formation of a metallacyclopentadiene by addition of an alkyne to palladium olefin derivatives.



Scheme 11. Mechanism of formation of a metallacyclopentadiene by addition of an alkyne to palladium olefin derivatives involving naked palladium as intermediate.



Scheme 12. Formation of a fluoranthene-like cycle by addition of rigid bis-alkynes to palladium(0) olefin derivatives.

and on the electronic and steric characteristics of the ligands. The associative nature of the reaction was therefore established and the formation of an intermediate bearing both the olefin and the alkyne was suggested. Moreover, in keeping with the original observation of Ishii [76] it was noticed from the kinetic course that in the case of the bulky complex $[\text{Pd}(\eta^2\text{-ma})(\text{MeN-St-Bu})]$ reacting with dmbd (dmbd = dimethyl-2-butynedioate) the metastable $[\text{Pd}(\eta^2\text{-dmbd})(\text{MeN-St-Bu})]$ was formed. Such compound, however, does not represent a reactive intermediate but rather a reaction product (Scheme 10).

Moreover in the case of the complex bearing the hindered neocuproin (Neocup) as ancillary ligand the mono-alkyne derivative represents the only reaction product. This observation allowed a study dealing with the exchange equilibria among olefins and alkynes mentioned elsewhere [31]. Generally, when the pyridyl- and quinoline-thioether olefin complexes are taken into consideration the reactivity was markedly influenced only when chloride was in position 2 of the pyridine ring (CIN-SR). This phenomenon was ascribed to the lability of the chelate ligand induced by the unfavourable steric hindrance coupled with the lower basicity of the nitrogen of the deactivated pyridine. The easier entry of the first alkyne in the coordination sphere of the metal yielding the palladium intermediate bearing both the olefin and the alkyne explains the increased reactivity. It was also noticed that under mild NMR experimental conditions beside the main palladacyclopentadiene derivative the highly symmetric examethyl mellitate was formed. It was apparent that the examethyl mellitate was not produced by addition of a further dmbd molecule to the cyclopalladate species. Rather, the latter reacts with the mono-alkyne palladium(0) complex giving the hexamethyl mellitate and the highly reactive naked palladium species ($[\text{Pd}(\text{L-L}')]$) [61].

The intermediacy of the naked palladium was also invoked in a subsequent work dealing with the reactivity of the complex $[\text{Pd}(\eta^2\text{-dmfu})(\text{BiPy})]$ with dmbd and pna (methyl(4-nitrophenyl)propionate) [62]. A complex mechanism involving an efficient bimolecular self reaction of the complex $[\text{Pd}(\eta^2\text{-dmbd})(\text{BiPy})]$ to give the palladacyclopentadienyl species and the naked palladium was proposed and the mechanistic network completely resolved (Scheme 11).

A peculiar application of the addition of alkynes to palladium(0) derivatives is represented by the kinetic study of the reaction of rigid bis-alkynes moiety with palladium(0) complexes [77]. The cyclopalladate formed might represent a valuable precursor for the synthesis of fluoranthene-like cycles under mild conditions (Scheme 12).

10. X-ray diffractometric studies

10.1. Complexes bearing mono- bi- and ter-dentate nitrogen ligands

A significant number of palladium(0) olefin compounds bearing the title ligands was synthesized by several authors [30,31,35,37,75,78–86]. All the structures display the typical trigonal arrangement around the palladium centre with the Pd–N bond lengths being scarcely influenced by the olefin nature, spanning within 2.10 and 2.18 Å. The C=C bond length of the variety of used olefins is also scarcely affected, being confined in a narrow interval of 1.40 Å. Since the C=C bond in the free olefin displays a length of about 1.25 Å it has been proposed that the change in the hybridization of the olefin carbon is almost always operative with the consequent formation of a metallacyclopropane structure. In this case, the out-of-plane bending of the carbon substituents confirms the hypothesis although, in at least the case of the complex [Pd(η^2 -fn)(*t*-BuDAB)], the typical olefin sp^2 hybridisation is maintained [78]. Interestingly, when potentially ter-dentate nitrogen ligands are employed the usual trigonal arrangement around palladium is observed since one coordinating atom of the ligand itself remains uncoordinated. In the case of the complexes [Pd(η^2 -tmetc)(NNNtos(Py))], [Pd(η^2 -tmetc)(NNNtos(Qui))] and [Pd(η^2 -nq)(NNNtos(Qui))] reported in Ref. [75] coordination occurs *via* the aromatic pyridine (or quinoline) nitrogen with the consequent formation of an eight-membered ring, the central amino group of the ancillary ligand being uncoordinated in keeping with the general observation that electron delocalization from the electron rich metal centre to an electron accepting moiety (pyridine or quinoline) would better stabilize the ensuing molecule.

For the sake of completeness it may be interesting to cite the works of Gade, Spek, and Privalov in which ligands or olefins not described in Schemes 1 and 2 were used. However, no particular structural news arose from those studies [87–89].

10.2. Complexes bearing mixed bi- and ter-dentate N–S, P–S and P–N ligands

The palladium(0) olefin complexes with ancillary ligands bearing phosphorus and sulfur or nitrogen and sulfur as coordinating atoms are quite rare [4,36,40,75]. Owing to the different atomic radii the Pd–S bond length is somewhat longer than that of the Pd–N_{py} bond (~2.3 versus ~2.1 Å) irrespectively of the coordinating olefin. Notably, the Pd–N_{py} bond is always shorter than the bond between palladium and aliphatic nitrogen supporting the general observation of the partial π -acidic nature of the Pd–N_{py} bond.

When the potentially ter-dentate N–S–N ligand is employed, the usual trigonal arrangement around the metallic centre is achieved upon coordination of the sulfur which is the central coordinating atom in the ligand scaffold. In this case the pyridine ring constitutes the uncoordinated wing linked to the customary five-membered metallated ring [75].

In contrast with the compounds just described, hemi-labile auxiliary ligands containing phosphorus and nitrogen were more extensively studied [26,42,43,90–94]. Again, irrespectively of the stabilizing olefin the bond lengths are very similar among the fourteen complexes examined with the Pd–N bond length usually spanning within 2.11 and 2.25 Å. In two cases, however, when

the ancillary ligands are ferrocenyl derivatives the Pd–N bond length reaches ~2.5 Å [42,92]. The large majority of the Pd–P lengths lies in the proximity of 2.28 Å (2.27–2.29 Å). Again, in two cases the values of 2.34 and 2.23 Å can be found in the literature [93,94]. Owing to the π -back donation, the average Pd–P length is shorter than the Pd–S bond despite the larger atomic dimensions of the phosphorus atom. Finally, the bond lengths between the palladium and the olefin carbon *trans* to the phosphorus (Pd–C_{transP}) in any complex are longer than those in *cis* (Pd–C_{cisP}) (Pd–C_{transP} 2.10–2.15 Å; Pd–C_{cisP} 2.02–2.10 Å).

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