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Synthesis and characterization of palladacyclopentadiene complexes with N-heterocyclic carbene ligands

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ABSTRACT

New palladacyclopentadiene compounds containing different chelate NHC-thioether and NHC-pyridine ligands have been prepared by transfer of the functionalized carbenes from the respective silver complexes to the polymeric precursors $[PdC{-}COOR)_4]_n$ (R = Me, *t*-Bu). Their dynamic behaviour in solution was discussed and the solid-structure of **2c** was determined by X-ray crystallography.

The treatment of $[Pd(C{-}COOCH_3)_4]_n$ with two equivalents of the carbene silver complexes led to the $(NHC)_2Pd(C_4{-}COOCH_3)_4$ derivatives (**3c**–**i**), a new class of compounds with only Pd–C bonds. A serious limitation to this synthetic procedure is an excessive steric crowding around the metal centre.

The complexes **3** are present in solution as a mixture of two atropoisomers, due to restricted rotation around the Carbene–Pd bond. The kinetics of equilibration between the two configurational isomers was studied for complex **3c**, which was also structurally defined by X-ray crystallography (*anti* isomer).

Finally a synthetic protocol was set up for the synthesis of mixed NHC-Phosphine and NHC-Isocyanide palladacyclopentadiene complexes. In this procedure the order of addition of the reactants is of great importance.

1. Introduction

The palladacyclopentadiene fragment $Pd(C{-}COOR)_4$ is an interesting organometallic building unit that is obtained by oxidative homocoupling of acetylenic esters to Pd(0) substrates [1] and the mechanistic study of this process was the subject of some previous publications by our group [2]. Its synthetic importance arises from the fact that this organometallic functional group was involved in the Pd(0)-catalysed [2+2+2] alkyne cyclotrimerization and cocyclotrimerization of acetylenes with alkenes, dienes or allenes [1–3]. Furthermore its reactivity toward organic halides or molecular halogens resulted in the production of (σ-dienyl)palladium compounds formed by a sequence of oxidative addition/reductive elimination through a transient Pd(IV) intermediate (Scheme 1) [4]. Remarkably such process was stereospecific and usually only the *cis*-arrangement of the esteric functions at the double bonds was obtained. Since the addition of molecular halogens [4] or organotin [5] reagents allowed the displacement of the dienyl fragment from the metal, it was possible to take advantage of this synthetic strategy to produce dienes with a *Z*–*Z* configuration. In this respect only a limited number of methods are available for the stereospecific preparation of dienes from acetylenes [6].

In this context the features of spectator ligands are of great importance; it was proved that the ability to couple two alkynes decreases with the π-acceptor capability and steric bulkiness of the ancillary ligands of the starting Pd(0) compounds. In some cases the monoalkyne-Pd(0) complexes were isolated instead of the palladacyclopentadiene derivatives even with excess of alkynes (i.e. with L = $P(OPh)_3$ [1b], or L–L = 2,9-dimethylphenanthroline [7]). In any case several mononuclear complexes $[L_2Pd(C{-}COOR)_4]$ are reported in the literature with monodentate or bidentate supporting ligands [1,2a,3d,8]. Among them *N*-heterocyclic carbenes have been scantily utilized in spite of their ubiquitous utilization as spectator ligands in palladium organometallic chemistry [9] and to the best of our knowledge the two examples shown in Scheme 2 only have been described so far.

Complex **a** was observed by Elsevier and co-workers as a by-

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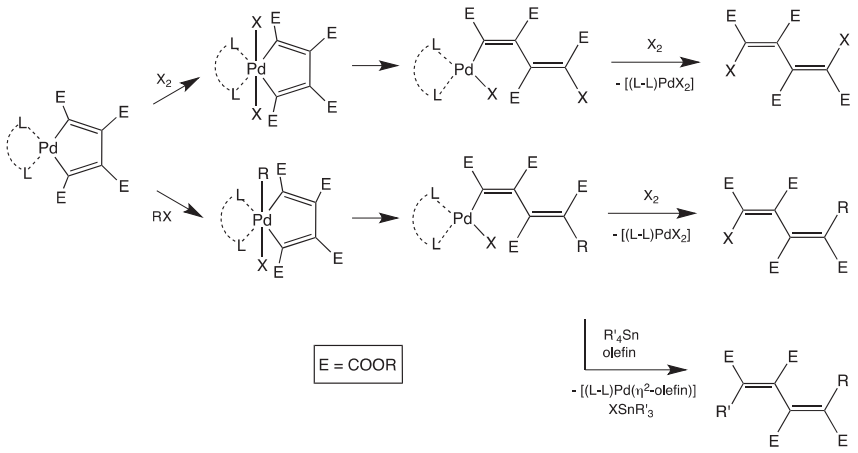
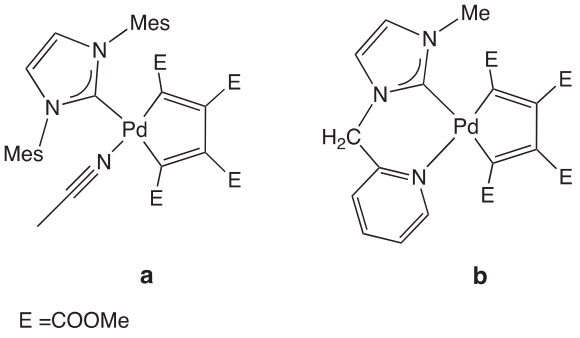


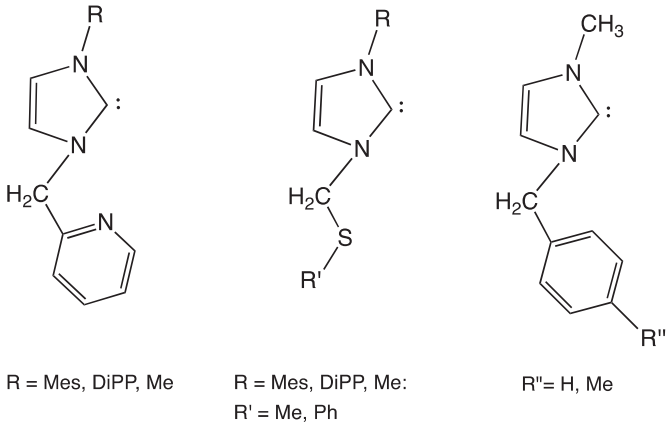
Scheme 1. Reactivity of the palladacyclopentadiene fragment.



Scheme 2. The two palladacyclopentadiene complexes bearing N-heterocyclic carbenes ligands described in the literature.

product in the Pd(NHC)-catalysed semihydrogenation of alkynes [10] whereas complex **b** was detected by our group when studying the reaction of [(Me–NHC–CH_2Py)Pd(η^2-MA)] (MA = maleic anhydride) with an excess of dimethylbutynedioate [11].

In the present paper we intend to partially fill this gap by describing the general procedures for the synthesis of some different classes of palladacyclopentadienes stabilized by NHC ligands. Furthermore the structural features and solution behaviour of these new complexes will be discussed in detail.



Scheme 3. N-heterocyclic carbene ligands used in this work.

The monodentate or heteroditopic N-heterocyclic carbene ligands employed are summarized in Scheme 3.

2. Results and discussion

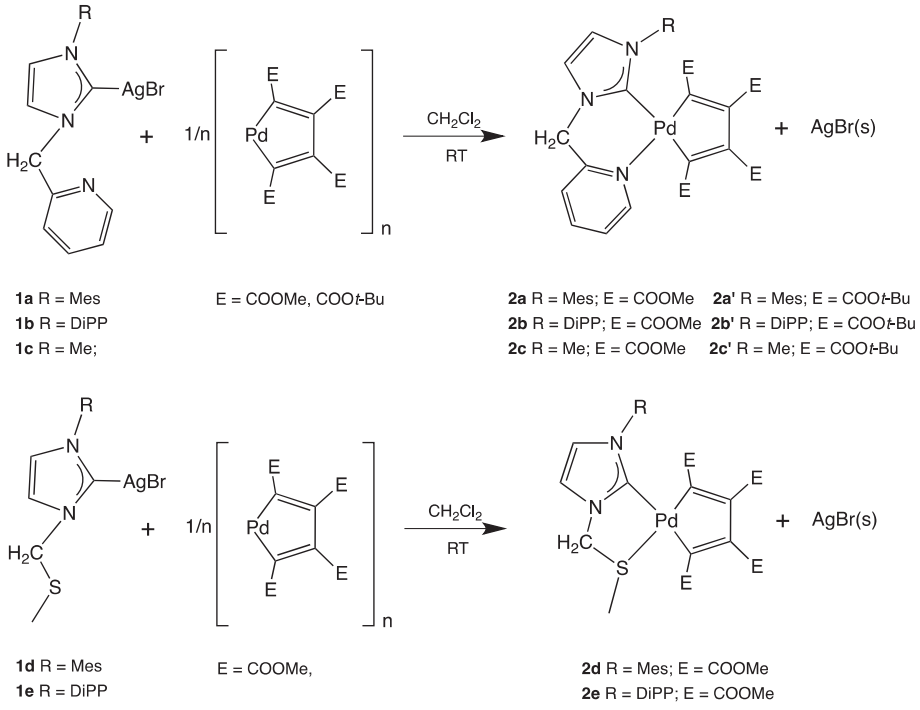
2.1. NHC-pyridine and NHC-thioether chelate palladacyclopentadiene complexes

The silver-mediated transfer of functionalized carbene ligands onto appropriate palladium precursors was the synthetic strategy employed to achieve the title complexes [12]. In more detail these compounds were prepared by stoichiometric treatment of the respective silver complexes **1** [13] with the polymeric precursors $[Pd(C\text{-}COOR)_4]_n$ [2a] (R = Me, *t*-Bu), in dichloromethane at room temperature. The precipitation of silver bromide was observed almost immediately and the final products could be easily isolated from the reaction mixtures after filtration.

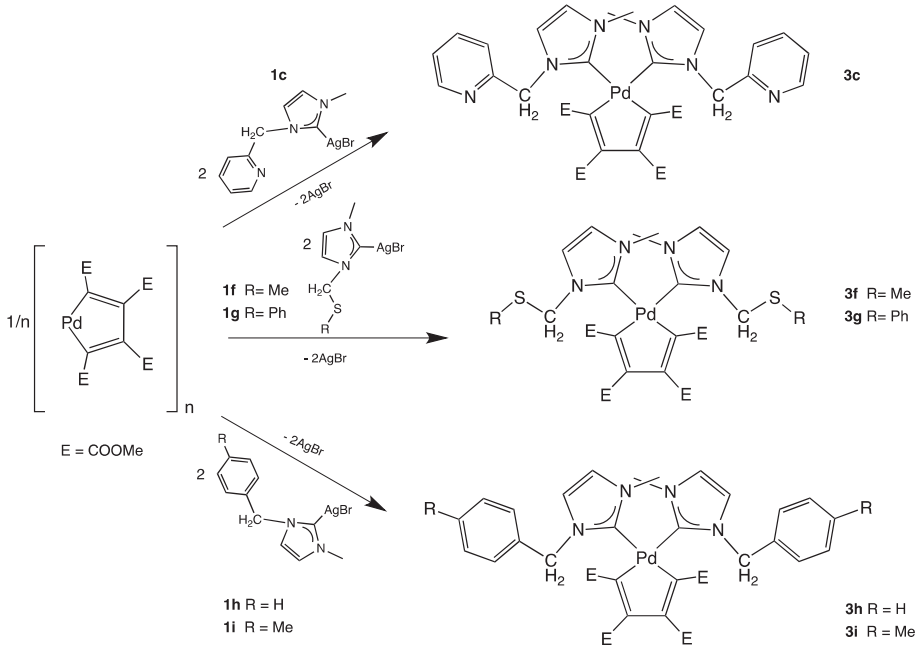
All the complexes reported in Scheme 4 were obtained in high yield and purity, independently of the nature of the second coordinating function (pyridyl or methylthioether group), the number of chelate ring members (five or six) and substituents (COOMe or COO*t*-Bu) on the cyclometallated system. The only exception is represented by the reaction of the scarcely bulky complex **1f**, which preferentially produces the bis-carbene complex (see Scheme 5), leaving half $[Pd(C\text{-}COOR)_4]$ polymer unreacted.

The resulting complexes **2** were mainly characterized by NMR spectroscopy. The definitive proof of the chelating coordination mode of the heteroditopic ligands is the splitting of the methylene linker signals into an AB system (or two doublets) in the ^{1}H NMR spectra recorded at 253 K. However, due to flipping [14] of chelate ring (or rapid in-place inversion of stereogenic sulphur [15] atom for the complexes **2d** and **2e**), which renders the coordination plane as the symmetry plane of the molecule, these signals are broadened at room temperature. Notably for the most sterically hindered complexes **2a**′, **2b**′ and **2c**′, this movement becomes operative only at higher temperatures. Furthermore the ^{1}H NMR spectra at 253 K of the complexes bearing the bulky substituents on the heterocyclic nitrogen atoms (Mes or DiPP), exhibit two different signals for the *ortho* methyl or *ortho* *i*-propyl groups and for the *meta*-hydrogens stemming from the hindered rotation around the C–N bond. For the less sterically crowded cyclopalladate systems **2a**–**2d**, this rotation restriction is overcome at 298 K and complete coalescence of the signals can be observed.

In the ^{13}C NMR spectra the signals of the coordinated carbenic



Scheme 4. Synthesis of the chelate complexes **2**.



Scheme 5. Synthesis of the bis(NHC) palladacyclopentadiene complexes **3**.

carbon are typically found between 181 and 186 ppm, which compare well with the reported literature data for divalent palladium species bearing similar ligands [16]. Finally the presence of the palladacyclopentadiene fragment is clearly testified by the four distinguishable systems of signals relative to the four different COOR groups observed in both ^{1}H and ^{13}C NMR spectra of all complexes **2**.

Our expectations were confirmed by X-ray analysis of complex **2c**, crystals of which were grown by slow diffusion of diethyl ether in a dichloromethane solution (an ORTEP [17] view is shown in Fig. 1 and a selection of bond distances and angles is summarized in Table 1).

The geometry around the palladium centre is distorted square planar tending toward a tetrahedral arrangement. The four positions around the central Pd are occupied by the 1,4 carbons of the 1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-diene-1,4-diyl anionic ligand, the pyridine nitrogen and the carbene carbon of the ligand. The deviations from the basal plane are: 0.053(2) for N3,

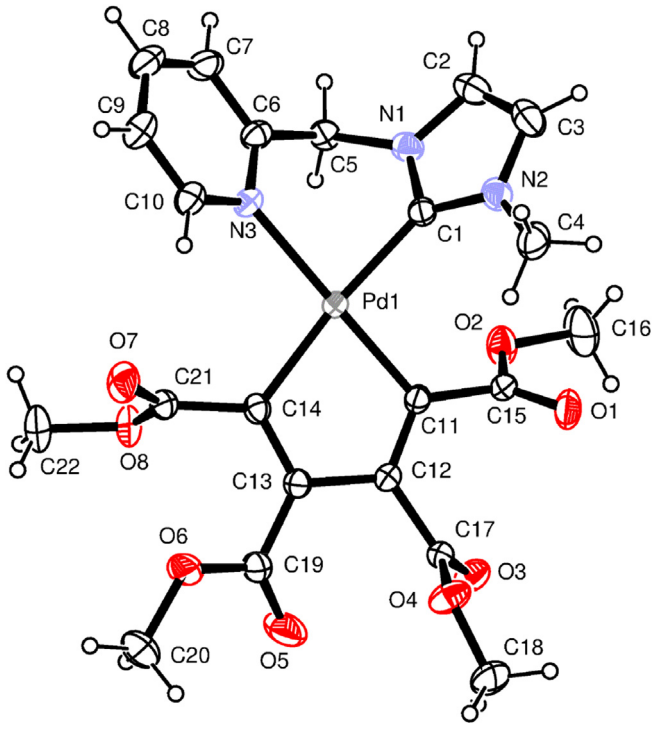


Fig. 1. ORTEP view of complex **2c** showing the thermal ellipsoids at 30% probability level.

Table 1
Selected bond distances and angles (Å and degrees) for **2c** and **3i**.

Distances	2c	3i
Pd1–C1	2.027(2)	2.084(3)
Pd1–N3	2.140(2)	
Pd1–C11	2.013(2)	2.040(3)
Pd1–C14	2.072(2)	
C11–C12	1.338(3)	1.347(4)
C12–C13	1.475(3)	
C12–C12′		1.490(6)
C13–C14	1.349(3)	
Angles		
C1–Pd1–N3	83.94(8)	
C1–Pd1–C1′		94.25(17)
C1–Pd1–C11	95.01(9)	171.96(13)
C1–Pd1–C11′		93.36(11)
C1–Pd1–C14	173.91(9)	
N3–Pd1–C11	175.40(8)	
N3–Pd1–C14	101.88(8)	
C11–Pd1–C14	79.32(9)	
C11–Pd1–C11′		79.16(17)

−0.0592(2) for C1, 0.062(2) for C11 and −0.0157(2) Å for C14. The palladacyclopentadiene ring is approximately planar with a maximum deviation from the mean plane for C14 of 0.052(1) Å. The Pd1–C14 and Pd1–C1(NHC) bonds (2.072(2) and 2.027(2) Å) are somewhat lengthened due to the mutual *trans*-influence, as compared to the Pd–C11 distance of 2.013(2) Å and to the Pd–C average bond length of 2.00 Å observed in Pd complexes with the same anionic ligand where the carbon atoms are in *trans* position to nitrogens [2a,4,18].

2.2. Bis(NHC) palladacyclopentadiene complexes

When the [Pd(C–COOR)$_4$] precursor was treated with two equivalents of the silver complexes **1c**, **1f**–**i**, it gave smoothly and exclusively the bis-carbene derivatives **3** (Scheme 5):

It is worth noting that these complexes were obtained only by reducing the steric crowding of the reactants. In particular one of the N-substituents of the imidazolium scaffold was in any case the small methyl fragment and the electron-withdrawing substituents of the cyclometalladed system were the less encumbered COOMe groups. On the contrary the reaction between [Pd(C–COOR)$_4$]$_n$ and the bulky silver complexes **1a** and **1b** or **1d** and **1e** produced unfailingly the corresponding chelate derivatives even in the presence of a large excess of silver substrate. An analogous result was observed using the sterically demanding [Pd(C–COO*t*-Bu)$_4$]$_n$ with any of the silver complexes **1**.

At variance, as we have already reported, in the case of the less hindered silver complex **1f** the bis-chelate derivative **3f** was produced exclusively, even when employing a defect of silver reactant.

The criticality of steric features in these systems is apparent when observing the X-ray crystal structure of complex **3c** (see later).

The ^{1}H and ^{13}C NMR spectra of complexes **3** show two sets of signals suggesting the presence in solution of a mixture of two configurational isomers. We surmise that this differentiation arises from the two possible orientations of the wingtip imidazole substituents with respect to the coordination plane (Scheme 6).

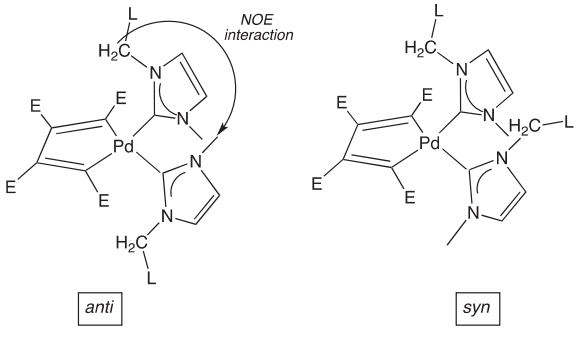
The assignment of the signals of each isomer is based on an NOESY experiment, which shows for the *anti* isomer an intense cross peak between one of the bridged CH_2 protons of the first ligand and the N–CH_3 group of the other.

The NMR spectra of each isomer of species **3** are simplified in comparison with those of the corresponding chelate derivatives **2**. The higher symmetry of the compounds reduces to half the number of different OCH_3 signals in ^{1}H NMR spectra of OCH_3, CO and cyclometallated C=C in the ^{13}C NMR spectra.

Moreover, provided that the imidazole rings are substantially perpendicular to the Pd-coordination plane (see later the X-Ray structure of complex **3c**), the two methylene links in each isomer will be diasterotopic. This will generate a splitting of the ^{1}H NMR signals into mutually coupled doublets (or into an AB system).

All the $^{13}C_{NHC}$–Pd resonances fall in the narrow range of 180–182 ppm, differing significantly from the shifts of other neutral *cis*-(NHC)$_2$Pd(II) species reported in the literature (e.g. for *cis*-(NHC)$_2$PdMe$_2$ δ ≈ 200 ppm [19] and for *cis*-(NHC)$_2$PdX$_2$ δ ≈ 170–175 ppm [20]).

The rate of interconversion between the *syn* and *anti* derivatives depends on the rotation barrier around the Pd–C(carbene) bond whereas the relative final abundance is determined by the relative stabilities of the two atropoisomers. In our systems these parameters are such that, starting from the initial composition obtained immediately after the transmetalation process [21], the final



Scheme 6. Antropoisomers of the complexes **3**: NOE interaction in the *anti* isomer.

isomeric mixture was generally achieved in some weeks (in CD_2Cl_2 solution at room temperature) with a predominance of the *syn* isomers ([*syn*]/[*anti*] ≈ 2 for the NHC-thioether complexes 3**f** and 3**g** and ≈3 for the NHC-aryl complexes **3h** and **3i**). A partial exception is represented by the NHC-pyridine complex **3c**, for which the equilibration is faster, requiring about three days. This circumstance allows a detailed kinetic study. In particular a set of concentration *vs* time data for the isomers *anti* and *syn* could be obtained with high precision from the relevant ^{1}H NMR signals of a solution of the isolated complex **3c** [21] (Fig. 2).

In this case we observed that the changes in the concentrations of the *anti* and *syn* isomers followed a reversible first-order rate law according to the differential equation:

$$\text{rate} = k_1[anti] - k_{-1}[syn] \quad (1)$$

Data analysis yielded the rate constants $k_1 = (6.41 \pm 0.02) \times 10^{-6}\ s^{-1}$ and $k_{-1} = (1.85 \pm 0.01) \times 10^{-6}\ s^{-1}$. The equilibrium constant calculated as the ratio of rate constants ($K_E = 3.47 \pm 0.03$) agrees well with the estimated value obtained from integration of the ^{1}H NMR spectra of the final equilibrium mixture ($K_E = 3.6$). Moreover a DFT calculation indicated that the *anti* isomer is more stable than the *syn* isomer, with a $\Delta G^\circ = -0.6$ kcal/mol, corresponding to a value of $K_E = 2.75$, in reasonable accord with the experimental data. Apparently the *anti* configuration guarantees a lower steric strain in the structure of the complex.

In other respects the first order dependence of the rate strongly supports the hypothesis of an intramolecular rearrangement (rotation around the Pd–C(carbene) bond) and rules out the possibility of a bimolecular process such as the exchange between two carbene ligands bonded to different metal centres. The latter mechanistic option was previously proposed in the case of unsaturated Pd(0) complexes [22] or of less encumbered Pd(η^3-allyl) compounds [13], but it does not seem feasible in these sterically congested systems.

Finally the higher rate of isomerization recorded for complex **3c** with respect to the iso-structural species **3h** suggests some sort of assistance by the pyridine nitrogen in the rotational process.

Crystals of the *anti* isomer of complex **3c** suitable for X-ray diffraction structure determination were obtained by crystallization from diethyl ether-dichloromethane. An ORTEP [17] view of this complex is shown in Fig. 3 and a selection of bond distances and angles is given in Table 1.

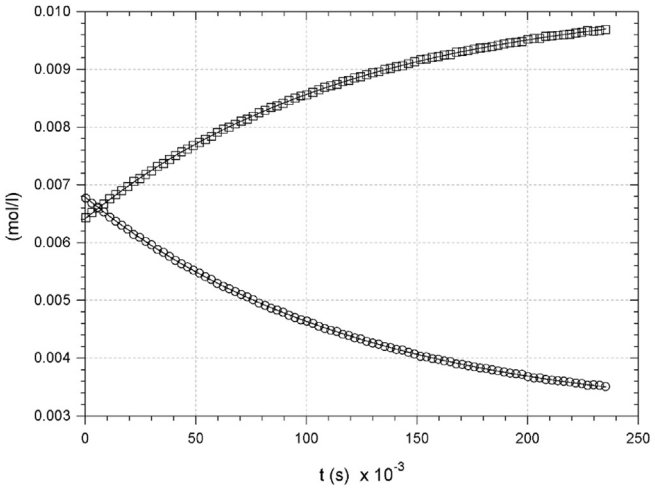


Fig. 2. Fit of concentrations of isomers *anti* and *syn* of the species **3c** to time according to eq. (1) in CD_2Cl_2 at 25 °C ($[3c]_{tot} = 1.3 \times 10^{-2}$ mol dm^{-3}).

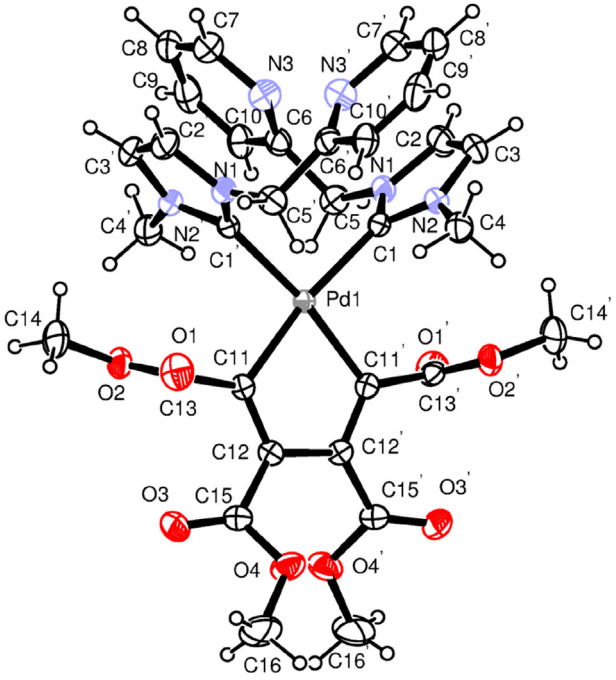


Fig. 3. ORTEP view of complex **3i** (*anti* isomer) showing the thermal ellipsoids at 30% probability level.

The structure displays a C_2 symmetry with the crystallographic twofold axis passing through the palladium atom and the midpoint of the C12–C12′ bond.

The geometry around the palladium centre is distorted square planar toward a tetrahedral arrangement. The four positions around the central Pd are occupied by the 1,4 carbons of the cyclometallated system and two C(carbene) atoms of two NHC ligands. The deviations of the four carbons from the basal plane are: 0.046(3) for C1, −0.046(3) for C1′, 0.054(3) for C11 and −0.054(3) Å for C11′. The palladacyclopentadiene ring is approximately planar with maximum deviations from the mean plane for C12 and C12′ of 0.027(3) and −0.27(3) Å, respectively. The Pd1–C1 and Pd1–C11 bond distances of 2.079(3) and 2.046(2) Å indicate mutual *trans* influence if compared with Pd–C(carbene) bonds (having distances in the range of 1.96–2.00 Å), as observed in Pd complexes where the Pd–C(carbene) bonds are in *trans* positions to nitrogen atoms [23]. The carbene(NHC) *trans*-influence can be highlighted also in Pd *trans* biscarbene complexes where the Pd–C(carbene) bonds in mutual *trans* position display a significant Pd–C lengthening with distances in the range 2.017–2.137 Å [24].

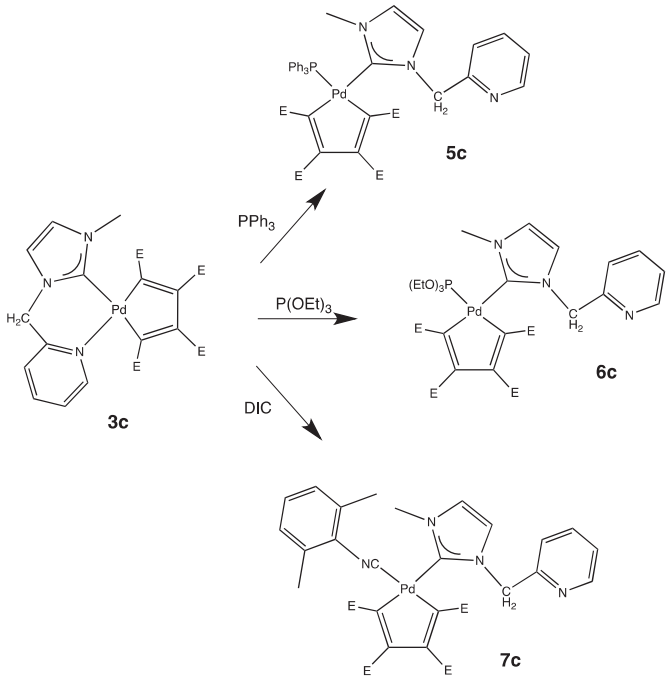
2.3. Mixed NHC-Phoshine and NHC-Isocyanide palladacyclopentadiene complexes

The most direct synthetic way to achieve the title compounds was to open the chelate ring of complexes **2**, thereby setting a coordinative site free for an entering ligand.

In the case of NHC-pyridine complex **2c**, this procedure was smooth and the simple addition of an equivalent of PPh_3, $P(OEt)_3$ or 2,6-dimethylisocyanide (DIC) allowed the formation of mixed complexes **5c**–**7c** by selective release of the most labile pyridyl wing (Scheme 7).

All the three complexes could be isolated and fully characterized.

The coordination of the P-donor ligands is clearly demonstrated by the significant down-field shift of its signal recorded in the ^{31}P



Scheme 7. Synthesis of the mixed NHC-Phoshine and NHC-Isocyanide Palladacyclopentadiene complexes **5c**, **6c** and **7c**.

{^{1}H} NMR spectra of the complexes **5c** ($\Delta\delta$ = 33 ppm) and **6c** ($\Delta\delta$ = 13 ppm). Moreover, the presence of DIC in the coordinative sphere of complex **7c** is testified (in addition to the appearance of all expected signals of this ligand in the ^{1}H and ^{13}C{^{1}H} NMR spectra) by the strong peak at 2174 cm^{-1} observed in its IR spectrum and ascribable to the CN stretching of the coordinated isocyanide. Finally in all three complexes the removal of the pyridyl group from the metal center is confirmed by the shift to higher field of the diagnostic H^6 and C^6 ($\Delta\delta \approx -0.5$ ppm and $\Delta\delta \approx -3$ ppm respectively) with respect to their resonance position in the starting chelate complex **3c**.

Encouraged by these results we considered the more general possibility of using monodentate NHC ligands. From the thermodynamic point of view the simultaneous introduction of one equivalent of monodentate carbene and of a monodentate phosphine or isocyanide ligand into the polymeric precursors [Pd(C–COOMe)$_4$]$_n$ may produce selectively the mixed complexes only if these compounds are significantly more stable than the two corresponding homoleptic derivatives. Thus we preliminarily performed a DFT theoretical study to verify such occurrence. The results are summarised in Scheme 8 [25].

It is apparent that in both cases examined the mixed compounds are thermodynamically favoured. This is probably the consequence of a synergic "push–pull" stabilization of the two couples of ligands NHC-triarylphoshine and NHC-isocyanide as some other previous papers seem to indicate [26]. In any way this necessary prerequisite does not ensure the success of the synthesis and the problem has to be considered also from the kinetic point of view. As a matter of fact, for a fast and clean preparation of the mixed complex **5i** or from the [Pd(C–COOMe)$_4$] precursor, one equivalent of triphenylphosphine must be added before or simultaneously to one equivalent of the silver carbene derivatives **1i** whereas the preliminary introduction of the latter produces a mixture of complexes [(PPh$_3$)$_2$Pd(C–COOMe)$_4$] and [(NHC)$_2$Pd(C–COOMe)$_4$] (**3i**). The subsequent conversion of these two derivatives into the mixed complex **5i** was very slow and associated to an extensive decomposition to metallic palladium. This experimental piece of evidence seems to indicate that reactions (*a*) and (*b*) are significantly faster than (*c*) and (*d*) (Scheme 9).

On the other hand, when L is 2,6-dimethylisocyanide (DIC), the rate of reaction (*b*) becomes comparable to the rate of reaction (*c*), so that prior or simultaneous addition of this ligand with respect to the silver carbene derivative **1i** does not guarantee the immediate and selective formation of the mixed complex **7i.** Consequently a significant amounts of complexes [(DIC)$_2$Pd(C–COOMe)$_4$] and [(NHC)$_2$Pd(C–COOMe)$_4$] (**3i**) are also initially present in the reaction mixture. These compounds gradually convert into the mixed species (in this case without decomposition) through reaction (*d*) which remains very slow. Summing up the selective synthesis of the mixed complex **7i** requires a reaction time of about 48 h and not just the few minutes required for complex **5i** containing triphenylphosphine.

3. Conclusions

In this contribution we have proposed the synthesis and full characterization of a scarcely explored class of palladium(II) complexes containing the organometallic building unit Pd(C-COOR)$_4$ and N-heterocyclic carbene ligands with various substituents in the wingtip position. The presence of a second coordinating function on the ligands has allowed us to obtain κ^2-*C,N* or κ^2-*C,S* chelate structures with one pyridyl-carbene or one thioethereal-carbene moiety per metal upon coordination at the palladium center. We have shown that the fluxional behaviour of these new compounds is strictly correlated with the nature of the second coordinating function and the steric strain of the whole system.

On the other hand, the introduction of two equivalents of the less encumbered ligands per unity of Pd(C–COOMe)$_4$ has led to the selective synthesis of bis-NHC complexes which represent a rare class of organopalladium complexes with only Pd–C bonds. These derivatives are present in solution as a mixture of two configurational isomers differing for the two possible orientations of the wingtip imidazole substituents with respect to the coordination plane. In one case we were able to study the kinetics of equilibration between the two atropoisomers.

Finally we have defined a synthetic strategy for the selective preparation of mixed NHC-phoshine and NHC-isocyanide palladacyclopentadiene complexes.

4. Experimental section

4.1. Materials

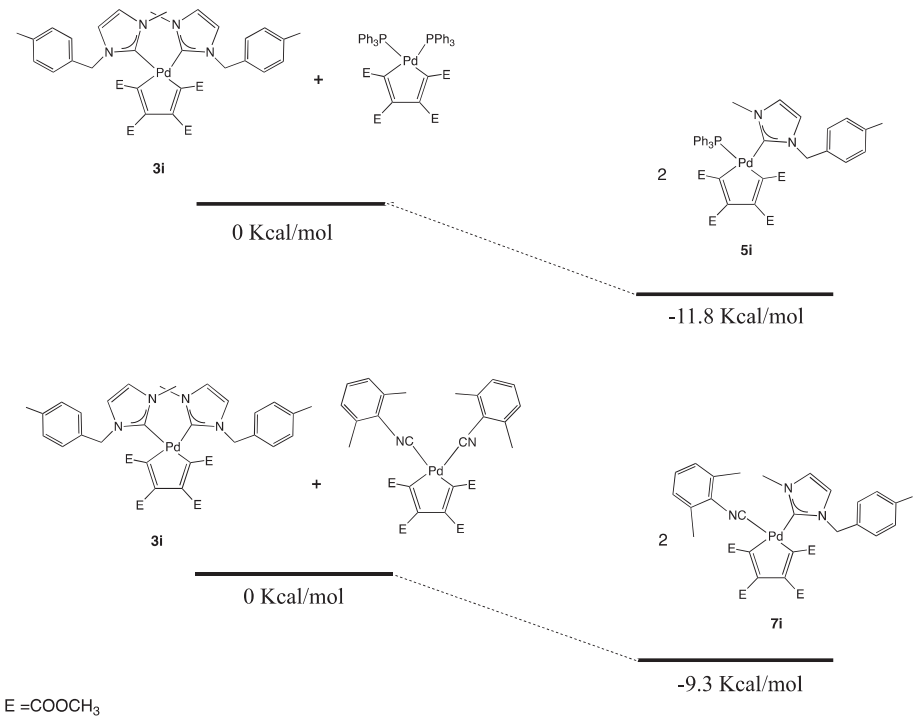
Unless otherwise stated, all operations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were purified by standard procedures and distilled under argon immediately prior to use. 1D and 2D-NMR spectra were recorded on a Bruker 300 Avance spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR).

Peaks are labelled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). The proton and carbon assignment was performed by ^{1}H-2D COSY, ^{1}H-2D NOESY, ^{1}H–^{13}C HMQC and HMBC experiments.

IR spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer.

UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier Temperature Programmer) apparatus.

The polymeric precursors [Pd(C-COOR)$_4$]$_n$ (R = Me; *t*-Bu) [2a], {[1-(2-pyridyl)methylene-3-(2,4,6-trimethyl]imidazolyl-2-ene}



Scheme 8. ΔG (Kcal mol^{-1}) related to complexes **3i**, **7i** and **5i.**

silver bromide (**1a**) [14a],{[1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}silver bromide (**1b**) [14a],{[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1c**) [11] ,{[1-(metylthio)methylene-3-(2,4,6-trimethyl)] imidazolyl-2-ene}silver bromide (**1d**) [13],{[1-(metylthio)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}silver bromide (**1e**) [13],{[1-(methylthio)methylene-3-methyl]imidazolyl-2-ene} silver bromide (**1f**) [13],{[1-(phenylthio)methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1g**) [11],{[1-benzyl-3-methyl]imidazolyl-2-ene}silver bromide (**1h**) [13],{[1-(4-methylphenyl) methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1i**) [13], were prepared according to published procedures.

4.1.1. Synthesis of {[1-(2-pyridyl)methylene-3-(2,4,6-trimethyl] imidazolyl-2-ene}Pd(C—COOMe)$_4$ ***(2a)***

To a solution of $[Pd(C—COOMe)_4]_n$ (0.086 g, 0.219 mmol) in 30 mL of anhydrous dichloromethane was slowly added 0.102 g (0.219 mmol) of {[1-(2-pyridyl)methylene-3-(2,4,6-trimethyl]imidazolyl-2-ene}silver bromide (**1a**) dissolved in 20 mL of anhydrous dichloromethane. The mixture was stirred for 30 min with the progressive precipitation of silver bromide, and then it was passed through a Millipore filter. The clear solution was concentrated under reduced pressure and the addition of diethylether induced the precipitation of the title product as a light yellow solid. It was filtered off and washed with diethyl ether and *n*-pentane.

Yield 0.124 g (85%). ^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.21 (bs, 6H, *o*-mesityl-CH_3), 2.37 (s, 3H, *p*-mesityl-CH_3), 3.24 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 5.17 (bs, 1H, NCH_2), 5.99 (bs, 1H, NCH_2), 6.86 (d, J = 1.9 Hz, 1H, CH═CH Im), 7.03 (s, 2H, *m*-mesityl-H), 7.25 (d, J = 1.9 Hz, 1H, CH═CH Im), 7.42 (ddd, J = 7.7, 4.6, 1.3 Hz, 1H, 5-Pyr); 7.60 (d, J = 7.7 Hz, 1H, 3-Pyr); 7.89 (td, J = 7.6, 1.7 Hz, 1H, 4-Pyr), 8.64 (d, J = 4.6 Hz, 1H, 6- Pyr). ^{13}C {^{1}H } NMR (CD_2Cl_2, 75 MHz, ppm) δ: 19.3 (CH_3, *o*-mesityl), 20.6 (CH_3, *p*-mesityl), 50.0 (CH_3, $COOCH_3$), 50.8 (CH_3, $COOCH_3$), 50.9 (CH_3, $COOCH_3$), 51.0 (CH_3, $COOCH_3$), 56.3 (CH_2, CH_2-Pyr), 120.5 (CH, CH═CH Im), 123.6 (CH, CH═CH Im), 123.9 (CH, 3-Pyr), 124.4 (CH, 5-Pyr), 129.5 (CH, *m*-mesityl), 134.0 (C, *o*-mesityl), 134.8 (C, *i*-mesityl), 138.3 (C, C═C), 138.8 (CH, 4-Pyr), 140.2 (C, *p*-mesityl), 149.0 (C, C═C), 152.8 (CH, 6-Pyr), 153.9 (C, C═C), 154.4 (C, 2-Pyr), 163.4 (C, CO), 166.0 (C, CO), 173.4 (C, CO), 174.8 (C, CO), 178.3 (C, C═C), 183.0 (C, NHC). IR (KBr): 1700 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{30}H_{31}N_3O_8Pd$: C, 53.94; H, 4.68; N, 6.29. Found C, 53.84; H, 4.64; N, 6.36%.

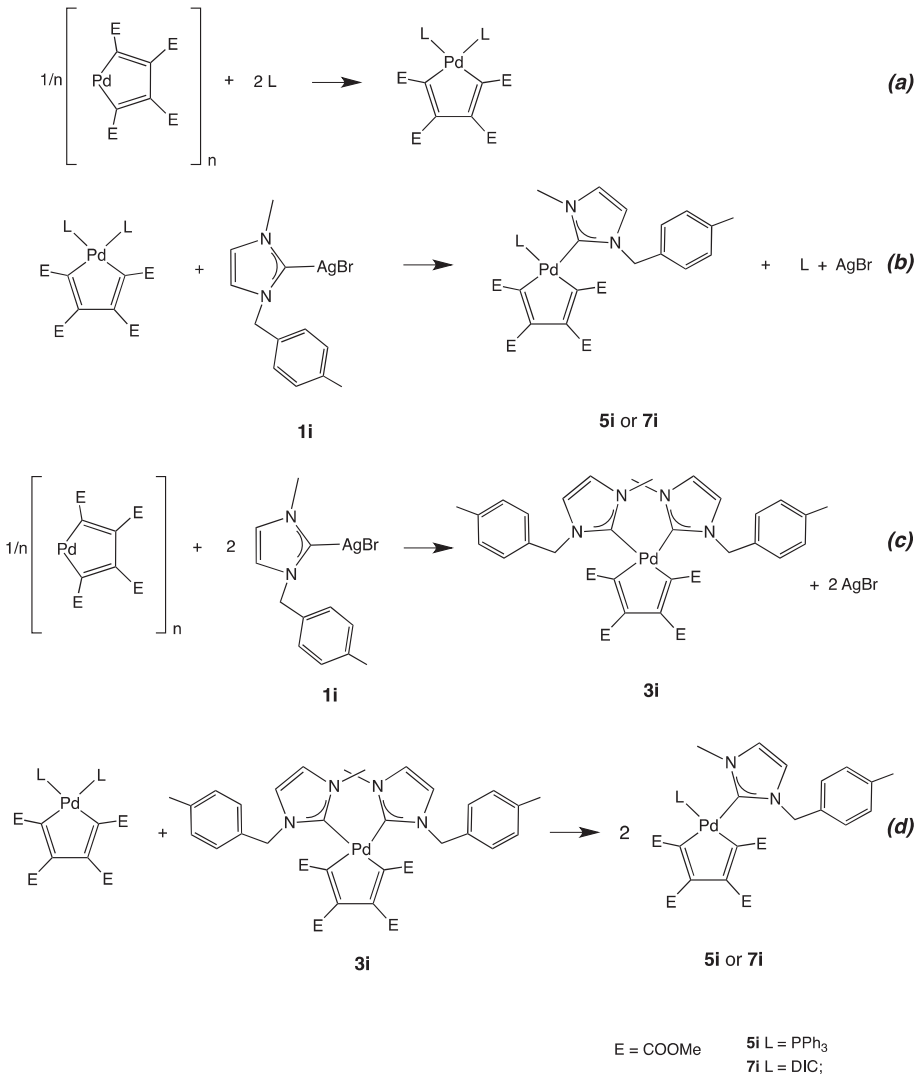
4.1.2. Synthesis of {[1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl]imidazolyl-2-ene}Pd(C—COOMe)$_4$ ***(2b)***

This complex was prepared in an analogous manner as that described for **2a**, using 0.079 g (0.203 mmol) of $[Pd(C—COOMe)_4]_n$ and 0.103 g (0.203 mmol) of {[1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}silver bromide (**1b**) to yield a white powder.

Yield: 0.114 g (79%). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 0.59 (bs, 3H, *i*Pr-CH_3), 1.19 (bs, 3H, *i*Pr-CH_3) 1.59 (bs, 6H, *i*Pr-CH_3) 2.78 (bs, 2H, *i*Pr-CH), 3.09 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 5.21 (bs, 1H, CH_2Py), 6.00 (bs, 1H, CH_2Py), 6.88 (d, J = 1.8 Hz, 1H CH═CH Im), 7.21 (d, J = 1.8 Hz, 1H CH═CH Im), 7.29 (d, J = 7.7 Hz, 2H, *m*-Ph), 7.38–7.45 (m, 2H, *p*-Ph 5-Py), 7.60 (d, J = 7.7 Hz, 1H, 3-Py), 7.88 (td, J = 7.7, 1.6 Hz, 1H, 4-Py), 8.57 (d, J = 4.5 Hz, 1H, 6-Py). ^{13}C {^{1}H} NMR (CD_2Cl_2, ppm) δ: 23.7 (CH_3, *i*Pr-CH_3), 26.8 (CH_3, *i*Pr-CH_3), 28.6 (CH, *i*Pr-CH), 50.0 (CH_3, OCH_3), 50.8 (CH_3, two signals overlapped, OCH_3), 51.6 (CH_3, OCH_3), 56.4 (CH_2, CH_2-Pyr), 120.3 (CH, CH═CH Im), 123.9 (CH, CH═CH Im), 124.2 (CH, 3-Pyr), 124.2 (CH, *m*-Ph), 125.2 (CH, 5-Pyr), 129.3 (CH, *p*-Ph), 134.6 (CH, *i*-Ph), 138.9 (CH, 4-Pyr), 140.4 (C, C═C), 145.0 (C, *o*-Ph), 148.1 (C, C═C), 152.2 (CH, 6-Pyr), 154.6 (CH, 2-Pyr), 155.3 (C, C═C), 163.6 (C, CO), 165.8 (C, CO), 173.5 (C, CO), 174.6 (C, CO), 177.0 (C, C═C), 183.8 (C, NHC). IR (KBr): 1697 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{33}H_{37}N_3O_8Pd$: C, 55.82; H, 5.25; N, 5.92. Found C, 55.94; H, 5.20; N, 5.87%.

4.1.3. Synthesis of {[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}Pd(C—COOMe)$_4$ ***(2c)***

This complex was prepared in an analogous manner as that described for **2a**, using 0.114 g (0.291 mmol) of $[Pd(C—COOMe)_4]_n$



Scheme 9. Reactions involved in the synthesis of palladacyclopentadiene complexes **5i** and **7i.**

and 0.1015 g (0.291 mmol) of {[1-(2-pyridyl)methylene-3-methyl] imidazolyl-2-ene}silver bromide (**1c**) to give light yellow microcrystals.

Yield: 0.145 g (90%). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 3.40 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.72 (s, 3H, NCH_3), 3.73 (s, 3H, OCH_3), 5.07 (bd, H, NCH_2), 5.83 (bd, H, NCH_2), 6.78 (d, J = 1.5 Hz, 1H, CH═CH Im), 7.08 (d, J = 1.5 Hz, 1H, CH═CH Im), 7.33 (ddd, J = 7.7, 5.4, 1.0 Hz, 1H, 5-Pyr), 7.56 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.84 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 8.66 (d, J = 5.4 Hz, 1H, 6-Pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 37.4 (CH_3, NCH_3), 50.3 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 51.2 (CH_3, OCH_3), 51.2 (CH_3, OCH_3), 56.5 (CH_2, NCH_2), 121.3 (CH, CH═CH Im), 121.4 (CH, CH═CH Im), 124.1 (CH, 5-Pyr), 124.7 (CH, 3-Pyr), 138.5 (CH, 4-Pyr), 141.1 (C, C═C), 148.4 (C, C═C), 152.7 (C, 6-Pyr), 154.1 (CH, 2-Pyr), 155.7 (C, C═C). 164.3 (C, C═O), 166.1 (C, C═O), 175.1 (C, C═O), 175.7 (C, C═O), 177.5 (C, C═C), 180.5 (C, NCN). IR (KBr): 1689 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{22}H_{23}N_3O_8Pd$: C, 46.86; H, 4.11; N, 7.45. Found C, 46.78; H, 4.12; N, 7.36%.

4.1.4. Synthesis of {[1-(2-pyridyl)methylene-3-(2,4,6-trimethyl] imidazolyl-2-ene}Pd- ***(2a')***

The synthesis of the title complex is analogous to that of **2a**, starting from 0.064 g (0.114 mmol) of [Pd(C-COOt-Bu)$_4$] and 0.053 g (0.114 mmol) of {[1-(2-pyridyl)methylene-3-(2,4,6-trimethyl]imidazolyl-2-ene}silver bromide (**1a**) to give a light yellow solid.

Yield 0.076 g (79%). ^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.21 (bs, 6H, *o*-mesityl-CH_3), 2.37 (s, 3H, *p*-mesityl-CH_3), 3.24 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 5.17 (bs, 1H, NCH_2), 5.99 (bs, 1H, NCH_2), 6.86 (d, J = 1.9 Hz, 1H, CH═CH Im), 7.03 (s, 2H, *m*-mesityl-H), 7.25 (d, J = 1.9 Hz, 1H, CH═CH Im), 7.42 (ddd, J = 7.7, 4.6, 1.3 Hz, 1H, 5-Pyr); 7.60 (d, J = 7.7 Hz, 1H, 3-Pyr); 7.89 (td, J = 7.6, 1.7 Hz, 1H, 4-Pyr), 8.64 (d, J = 4.6 Hz, 1H, 6- Pyr). ^{13}C {^{1}H } NMR (CD_2Cl_2, 75 MHz, ppm) δ: 19.3 (CH_3, *o*-mesityl), 20.6 (CH_3, *p*-mesityl), 50.0 (CH_3, $COOCH_3$), 50.8 (CH_3, $COOCH_3$), 50.9 (CH_3, $COOCH_3$), 51.0 (CH_3, $COOCH_3$), 56.3 (CH_2, CH_2-Pyr), 120.5 (CH, CH═CH Im), 123.6 (CH, CH═CH Im), 123.9 (CH, 3-Pyr), 124.4 (CH, 5-Pyr), 129.5 (CH, *m*-mesityl), 134.0 (C, *o*-mesityl), 134.8 (C, *i*-mesityl), 138.3 (C, C═C), 138.8 (CH, 4-Pyr), 140.2 (C, *p*-mesityl), 149.0 (C, C═C), 152.8 (CH, 6-Pyr), 153.9 (C, C═C), 154.4 (C, 2-Pyr), 163.4 (C, CO), 166.0 (C, CO), 173.4 (C, CO), 174.8 (C, CO), 178.3 (C, C═C), 183.0 (C, NHC). IR (KBr): 1707 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{42}H_{55}N_3O_8Pd$: C, 60.32; H, 6.63; N, 5.02. Found C, 60.39; H, 6.74; N, 5.12%.

4.1.5. Synthesis of {[1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl]imidazolyl-2-ene}Pd(C-COOt-Bu)$_4$ ***(2b')***

This complex was prepared in an analogous manner as that

described for **2a**, using 0.064 g (0.114 mmol) of $[Pd(C{-}COOt\text{-}Bu)_4]_n$ and 0.058 g (0.114 mmol) of {[1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}silver bromide (**1b**) to yield a white powder.

Yield 0.078 g (77%) ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 0.59 (bs, 3H, *i*Pr-CH_3), 1.19 (bs, 3H, *i*Pr-CH_3) 1.59 (bs, 6H, *i*Pr-CH_3) 2.78 (bs, 2H, *i*Pr-CH), 3.09 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 5.21 (bs, 1H, CH_2Py), 6.00 (bs, 1H, CH_2Py), 6.88 (d, J = 1.8 Hz, 1H CH=CH Im), 7.21 (d, J = 1.8 Hz, 1H CH=CH Im), 7.29 (d, J = 7.7 Hz, 2H, *m*-Ph), 7.38–7.45 (m, 2H, *p*-Ph 5-Py), 7.60 (d, J = 7.7 Hz, 1H, 3-Py), 7.88 (td, J = 7.7, 1.6 Hz, 1H, 4-Py), 8.57 (d, J = 4.5 Hz, 1H, 6-Py).

^{13}C {^{1}H} NMR (CD_2Cl_2, ppm) δ: 23.7 (CH_3, *i*Pr-CH_3), 26.8 (CH_3, *i*Pr-CH_3), 28.6 (CH, *i*Pr-CH), 50.0 (CH_3, OCH_3), 50.8 (CH_3, two signals overlapped, OCH_3), 51.6 (CH_3, OCH_3), 56.4 (CH_2, CH_2-Pyr), 120.3 (CH, CH=CH Im), 123.9 (CH, CH=CH Im), 124.2 (CH, 3-Pyr), 124.2 (CH, *m*-Ph), 125.2 (CH, 5-Pyr), 129.3 (CH, *p*-Ph), 134.6 (CH, *i*-Ph), 138.9 (CH, 4-Pyr), 140.4 (C, C=C), 145.0 (C, *o*-Ph), 148.1 (C, C=C), 152.2 (CH, 6-Pyr), 154.6 (CH, 2-Pyr), 155.3 (C, C=C), 163.6 (C, CO), 165.8 (C, CO), 173.5 (C, CO), 174.6 (C, CO), 177.0 (C, C=C), 183.8 (C, NHC). IR (KBr): 1699 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{45}H_{61}N_3O_8Pd$: C, 61.53; H, 7.00; N, 4.78. Found C, 61.60; H, 6.94; N, 4.88%.

4.1.6. Synthesis of {[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}Pd(C-COOt-Bu)$_4$ (2c')

This complex was prepared in an analogous manner as that described for **2a**, using 0.064 g (0.114 mmol) of $[Pd(C\text{-}COOt\text{-}Bu)_4]_n$ and 0.035 g (0.114 mmol) of {[1-(2-pyridyl)methylene-3-methyl] imidazolyl-2-ene}silver bromide (**1c**) to give a light yellow powder.

Yield 0.0665 g (81%). ^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 1.19 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 1.49 (s, 9H, $C(CH_3)_3$), 1.50 (s, 9H, $C(CH_3)_3$), 3.85 (s, 3H, NCH_3), 4.93 (d, 1H, J = 14.6 Hz, NCH_2), 5.83 (d, 1H, J = 14.6 Hz, NCH_2), 6.78 (d, J = 1.8 Hz, 1H, CH=CH Im), 7.08 (d, J = 1.8 Hz, 1H, CH=CH Im), 7.33 (ddd, J = 7.7, 5.3, 0.7 Hz, 1H, 5-Pyr), 7.46 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.81 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 8.73 (ddd, J = 5.3, 1.7, 0.7 Hz, 1H, 6-Pyr). ^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) δ: 27.9 (CH_3, $C(CH_3)_3$), 28.3 (CH_3, $C(CH_3)_3$), 28.4 (CH_3, $C(CH_3)_3$), 28.6 (CH_3, $C(CH_3)_3$), 38.1 (CH_3, NCH_3), 55.7 (CH_2, NCH_2), 77.9 (C, $C(CH_3)_3$), 79.0 (C, $C(CH_3)_3$), 79.3 (C, $C(CH_3)_3$), 79.4 (C, $C(CH_3)_3$), 120.7 (CH, CH=CH Im), 121.8 (CH, CH=CH Im), 123.9 (CH, 5-Pyr), 124.5 (CH, 3-Pyr), 138.3 (CH, 4-Pyr), 144.1 (C, C=C), 147.1 (C, C=C), 153.9 (C, 2-Pyr), 154.1 (CH, 6-Pyr), 158.6 (C, C=C), 164.1 (C, C=O), 164.5 (C, C=O), 170.4 (C, C=O), 174.8 (C, C=O), 174.8 (C, C=C), 182.1 (C, NCN). IR (KBr): 1698 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{34}H_{47}N_3O_8Pd$: C, 55.77; H, 6.47; N, 5.74. Found C, 55.82; H, 5.39; N, 5.82%.

4.1.7. Synthesis of {[1-(metylthio)methylene-3-(2,4,6-trimethyl)] imidazolyl-2-ene}Pd(C–COOMe)$_4$ (2d)

The synthesis of the title complex is analogous to that of **2a**, starting from 0.0900 g (0.231 mmol) of $[Pd(C{-}COOMe)_4]$ and 0.100 g (0.231 mmol) of {[1-(metylthio)methylene-3-(2,4,6-trimethyl)]imidazolyl-2-ene}silver bromide (**1d**) to give a yellow solid.

Yield 0.124 g (84%). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.28 (bs, 6H, *o*-aryl-CH_3), 2.34 (s, 3H, *p*-aryl-CH_3), 2.37 (s, 3H, S–CH_3), 3.13 (s, 3H, O–CH_3), 3.56 (s, 3H, O–CH_3), 3.59 (s, 3H, O–CH_3), 3.70 (s, 3H, O–CH_3), 5.05 (bs, 2H, CH_2S), 6.89 (d, J = 1.9 Hz, 1H, CH=CH Im) 7.02 (bs, 2H, *m*-aryl-H), 7.36 (d, J = 1.9 Hz, 1H, CH=CH Im).

^{13}C {^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 18.2 (CH_3, *p*-mesityl-CH_3), 19.4 (CH_3, *o*-mesityl-CH_3), 20.9 (CH_3, S–CH_3), 50.9 (CH_3, O–CH_3), 51.1 (CH_3, O–CH_3), 51.2 (CH_3, O–CH_3), 51.3 (CH_3, O–CH_3), 55.3 (CH_2, SCH_2), 120.0 (CH, CH=CH Im), 129.7 (CH, *m*-mesityl-CH); 134.1(C, *i*-mesityl-C); 135.2 (C, *o*-mesityl-C); 143.8 (C, C=C), 151.8 (C, C=C), 154.4 (C, C=C), 163.6 (C, CO), 166.6 (C, CO), 172.1 (C, CO), 175.8 (C, C=C), 176.1 (C, CO), 186.0 (C, NCN). IR (KBr): 1695 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{26}H_{30}N_2O_8PdS$: C, 49.02; H, 4.75; N, 4.40. Found C, 49.12; H, 4.82; N, 4.36%.

4.1.8. Synthesis of {[1-(metylthio)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}Pd(C–COOMe)$_4$ (2e)

The synthesis of the title complex is analogous to that of **2a**, starting from 0.0826 g (0.211 mmol) of $[Pd(C{-}COOMe)_4]$ and 0.1005 g (0.211 mmol) of {[1-(metylthio)methylene-3-(2,6-diisopropylphenyl)]imidazolyl-2-ene}silver bromide (**1e**) to give a yellow solid.

Yield 0.119 (83%). ^{1}H NMR (CDC3, T = 233 K, ppm) δ: 0.80 (d, J = 6.9 Hz, 3H, *i*Pr-CH_3), 1.20 (d, J = 6.9 Hz, 3H, *i*Pr-CH_3), 1.43 (d, J = 6.9 Hz, 6H, *i*Pr-CH_3), 1.44 (d, J = 6.9 Hz, 6H, *i*Pr-CH_3), 2.26 (s, 3H, S–CH_3), 2.59 (sept, 1H, J = 6.9 Hz, ^{i}Pr-CH), 2.96 (s, 3H, O–CH_3), 3.52 (s, 3H, O–CH_3), 3.54 (sept partially obscured, 1H, J = 6.8 Hz, *i*Pr-CH), 3.52 (s, 3H, O–CH_3), 3.56 (s, 3H, O–CH_3), 3.68 (s, 3H, O–CH_3), 4.83 (d, 1H, J = 13.2 Hz, CH_2S), 5.28 (d, 1H, J = 13.2 Hz, CH_2S), 6.96 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.29 (d, J = 7.9 Hz, 1H, *m*-aryl-H), 7.39 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.45 (t, J = 7.9 Hz, 1H, *p*-aryl-H). ^{13}C {^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 17.9 (CH_3, S–CH_3), 22.2 (bs, CH_3, *i*Pr-CH_3), 25.9 (bs, CH_3, *i*Pr-CH_3), 28.8 (bs, CH_3, *i*Pr-CH_3), (CH, *i*Pr-CH not detectable), 50.9 (CH_3, O–CH_3), 51.1 (CH_3, O–CH_3), 51.3 (CH_3, O–CH_3), 51.7 (CH_3, O–CH_3), 55.1 (CH_2, SCH_2), 119.9 (CH, CH=CH Im), 124.4 (CH, *m*-aryl-CH); 125.6 (CH, CH=CH Im), 129.4 (CH, *p*-aryl-CH); 135.3 (C, *i*-aryl-C); 143.1 (C, C=C), 144.6 (C, *o*-aryl-C); 151.9 (C, C=C), 153.9 (C, C=C), 163.4 (C, CO), 166.9 (C, CO), 172.0 (C, CO), 176.1 (C, CO), 176.7 (C, C=C), 186.4 (C, NCN). IR (KBr): 1697 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{29}H_{36}N_2O_8PdS$: C, 51.29; H, 5.34; N, 4.13. Found C, 51.36; H, 5.39; N, 4.21%.

4.1.9. {κ^1-C-[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}$_2$Pd(C–COOMe)$_4$ (3c)

0.1180 g (0.328 mmol) of {[1-(2-pyridyl)methylene-3-methyl] imidazolyl-2-ene}silver bromide (**1c**) dissolved in 5 mL of anhydrous dichloromethane was added to 15 mL of a solution of $[Pd(C{-}COOMe)_4]_n$ (0.064 g, 0.164 mmol) in the same solvent. The mixture was stirred for 30 min at RT, whereupon the greyish silver salt precipitated and then filtered through a Millipore filter. The clear solution was concentrated under reduced pressure and addition of diethylether induced precipitation of the final product as a whitish solid, which was filtered off and washed with diethylether and *n*-pentane.

Yield 0.106 g (90%). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm): *syn*-isomer δ: 3.18 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.88 (s, 3H, NCH_3), 5.27, 5.32 (AB system, J = 16.1 Hz, 2H, NCH_2), 6.86 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.90 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.12 (ddd, J = 7.7, 4.9, 1.0 Hz, 1H, 5-Pyr), 7.24 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.56 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 8.42 (d, J = 4.9 Hz, 1H, 6-Pyr); *anti*-isomer δ: 3.25 (s, 3H, OCH_3), 3.58 (s, 3H, NCH_3), 3.63 (s, 3H, OCH_3), 5.32, (d J = 16.1 Hz, 1H, NCH_2), 5.71, (d J = 16.1 Hz, 1H, NCH_2), 6.65 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.78 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.07 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.18 (ddd, J = 7.7, 4.9, 1.0 Hz, 1H, 5-Pyr), 7.54 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 8.47 (d, J = 4.9 Hz, 1H, 6-Pyr).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 38.0 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 55.6 (CH_2, NCH_2), 121.0 (CH, CH=CH Im), 121.9 (CH, CH=CH Im), 122.6 (CH, 5-Pyr), 123.5 (CH, 3-Pyr), 136.8 (CH, 4-Pyr), 144.2 (C, C=C), 149.2 (C, 6-Pyr), 155.0 (CH, 2-Pyr), 165.2 (C, C=O), 169.2 (C, C=C), 176.9 (C, C=O), 181.3 (C, NCN); *anti*-isomer δ: 37.4 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 55.6 (CH_2, NCH_2), 120.6 (CH, CH=CH Im), 122.0 (CH, 3-Pyr), 122.3 (CH, CH=CH Im), 122.7 (CH, 5-Pyr), 136.8 (CH, 4-Pyr), 143.9 (C, C=C), 149.2 (C, 6-Pyr), 155.7 (CH, 2-Pyr), 165.3 (C, C=O), 169.2 (C, C=C), 176.9 (C, C=O), 182.0 (C, NCN).). IR (KBr): 1692 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{32}H_{34}N_6O_8Pd$: C, 52.14; H, 4.65; N, 11.40. Found C,

52.20; H, 4.56; N, 11.33%.

4.1.10. Synthesis of {κ¹-C-[metylthio)methylene-3-methyl] imidazolyl-2-ene}$_2$Pd(C–COOMe)$_4$ (3f)

This complex was prepared in an analogous manner as that described for 3c, using.

0.112 g (0.338 mmol) of {[1-(metylthio)methylene-3-methyl] imidazolyl-2-ene} silver bromide (**1f**) and 0.066 g (0.169 mmol) of [Pd(C–COOMe)$_4$]$_n$.

Yield 0.097 g (87%; off-white solid) ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: *syn*-isomer δ: 2.10 (s, 3H, SCH_3), 3.31 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.83 (s, 3H, NCH_3), 4.94 (d, J = 13.8 Hz, 1H, SCH_2), 5.09 (d, J = 13.9 Hz, 1H, SCH_2), 6.92 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.26 (d, J = 1.9 Hz, 1H, CH=CH Im); *anti*-isomer δ: 1.87 (s, 3H, SCH_3), 3.30 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 4.00 (s, 3H, NCH_3), 4.94 (d, J = 13.9 Hz, 1H, SCH_2), 5.26 (d, J = 13.9 Hz, 1H, SCH_2), 6.96 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.19 (d, J = 1.9 Hz, 1H, CH=CH Im).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 15.2 (CH_3, SCH_3), 38.1 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 53.3 (CH_2, SCH_2), 119.9 (CH, CH=CH Im), 122.4 (CH, CH=CH Im), 144.3 (C, C=C), 165.1 (C, C=O), 168.5 (C, C=C), 176.7 (C, C=O), 181.3 (C, NCN). *anti*-isomer δ: 13.9 (CH_3, SCH_3), 38.3 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 54.0 (CH_2, SCH_2), 119.7 (CH, CH=CH Im), 122.7 (CH, CH=CH Im), 144.3 (C, C=C), 165.1 (C, C=O), 168.4 (C, C=C), 176.7 (C, C=O), 181.5 (C, NCN). IR (KBr): 1692 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{24}H_{32}N_4O_8PdS_2$: C, 42.70; H, 4.78; N, 8.30. Found C, 42.88; H, 4.88; N, 8.39%.

4.1.11. Synthesis of {κ¹-C-[metylthio)methylene-3-phenyl] imidazolyl-2-ene}$_2$Pd(C–COOMe)$_4$ (3g)

This complex was prepared in an analogous manner as that described for 3c, using.

0.129 g (0.328 mmol) of {[1-(metylthio)methylene-3-phenyl] imidazolyl-2-ene} silver bromide (**1g**) and 0.064 g (0.164 mmol) of [Pd(C–COOMe)$_4$]$_n$.

Yield 0.113 g (86%; light brown solid). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 3.28 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.82 (s, 3H, NCH_3), 5.45 (d, J = 14.3 Hz, 1H, SCH_2), 5.92 (d, J = 143 Hz, 1H, SCH_2), 6.79–6.84 (m, 2H, CH=CH Im), 7.24–7.27 (m, 5H, SPh); *anti*-isomer δ: 3.26 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.84 (s, 3H, NCH_3), 5.26 (d, J = 14.2 Hz, 1H, SCH_2), 5.90 (d, J = 14.2 Hz, 1H, SCH_2), 6.96 (d, J = 1.8 Hz, 1H, CH=CH Im), 6.79–6.84 (m, 1H, CH=CH Im, overlapped to the corresponding signals of the endo isomer), 7.24–7.27 (m, 5H, SPh).

^{13}C{^{1}H } NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 38.1 (CH_3, NCH_3), 50.6 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 54.9 (CH_2, SCH_2), 120.2 (CH, CH=CH Im), 122.2 (CH, CH=CH Im), 127.7 (CH, Ph *p*-C), 129.3 (CH, Ph *o*-C), 131.0 (CH, Ph *m*-C), 133.6 (C, Ph *i*-C), 144.1 (C, C=C), 165.1 (C, C=O), 168.4 (C, C=C), 176.7 (C, C=O), 181.5 (C, NCN); *anti*-isomer δ: 38.1 (CH_3, NCH_3), 50.6 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 54.9 (CH_2, SCH_2), 120.0 (CH, CH=CH Im), 122.6 (CH, CH=CH Im), 128.1 (CH, Ph *p*-C), 129.4 (CH, Ph *o*-C), 131.5 (CH, Ph *m*-C), 133.3 (C, Ph *i*-C), 143.9 (C, C=C), 165.0 (C, C=O), 168.4 (C, C=C), 176.8 (C, C=O), 181.4 (C, NCN). IR (KBr): 1689 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{34}H_{36}N_4O_8PdS_2$: C, 51.10; H, 4.54; N, 7.01. Found C, 51.18; H, 4.60; N, 7.12%.

4.1.12. Synthesis of {κ¹-C-{[1-benzyl-3-methyl]imidazolyl-2-ene}$_2$Pd(C–COOMe)$_4$ (3h)

This complex was prepared in an analogous manner as that described for **3c**, using 0.118 g (0.328 mmol) of {[1-benzyl-3-methyl]imidazolyl-2-ene}silver bromide (**1h**) and 0.064 g (0.164 mmol) of [Pd(C–COOMe)$_4$]$_n$.

Yield 0.114 g (94%; white solid). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 3.31 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.95 (s, 3H, NCH_3), 5.28 (d, J = 15.1 Hz, 1H, NCH_2), 5.74 (d, J = 15.1 Hz, 1H, NCH_2), 6.55 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.87 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.88–6.90 (m, 2H, Ph), 7.20–7.30 (m, 3H, Ph); *anti*-isomer δ: 3.29 (s, 3H, OCH_3), 3.55 (s, 3H, NCH_3), 3.64 (s, 3H, OCH_3), 5.19 (d, J = 15.8 Hz, 1H, NCH_2), 5.74 (d, J = 15.8 Hz, 1H, NCH_2), 6.71 (s, 2H, CH=CH Im), 6.88–6.90 (m, 2H, Ph), 7.20–7.30 (m, 3H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 38.1 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 54.0 (CH_2, NCH_2), 120.3 (CH, CH=CH Im), 121.9 (CH, CH=CH Im), 128.0 (CH, Ph *p*-C), 128.1 (CH, Ph *o*-C), 128.7 (CH, Ph *m*-C), 135.2 (C, Ph *i*-C), 143.9 (C, C=C), 165.2 (C, C=O), 169.0 (C, C=C), 176.9 (C, C=O), 181.8 (C, NCN); *anti*-isomer δ: 37.2 (CH_3, NCH_3), 50.5 (CH_3, OCH_3), 50.9 (CH_3, OCH_3), 54.0 (CH_2, NCH_2), 120.4 (CH, CH=CH Im), 122.5 (CH, CH=CH Im), 126.7 (CH, Ph *o*-C),127.9 (CH, Ph *p*-C), 128.7 (CH, Ph *m*-C), 135.9 (C, Ph *i*-C), 143.7 (C, C=C), 165.1 (C, C=O), 169.0 (C, C=C), 176.9 (C, C=O), 182.0 (C, NCN). IR (KBr): 1692 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{34}H_{36}N_4O_8Pd$: C, 55.55; H, 4.94; N, 7.62. Found C, 55.64; H, 4.92; N, 7.56%.

4.1.13. Synthesis of {κ¹-C-{[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}$_2$ Pd(C–COOMe)$_4$ (3i)

This complex was prepared in an analogous manner as that described for **3c**, using 0.123 g (0.328 mmol) of {[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1h**) and 0.064 g (0.164 mmol) of [Pd(C–COOMe)$_4$]$_n$.

Yield 0.109 g (87%; light brown solid). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 2.31 (s, 3H, tolyl-CH_3), 3.30 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.93 (s, 3H, NCH_3), 5.09 (d, J = 15.0 Hz, 1H, NCH_2), 5.21 (d, J = 15.0 Hz, 1H, NCH_2), 6.55 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.85 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.79 (d, J = 8.2 Hz, 2H, toyl *o*-H), 7. 04 (d, J = 8.2 Hz, 2H, toyl *m*-H); *anti*-isomer δ: 2.33 (s, 3H, tolyl-CH_3), 3.29 (s, 3H, OCH_3), 3.60 (s, 3H, NCH_3), 3.64 (s, 3H, OCH_3), 5.14 (d, J = 15.6 Hz, 1H, NCH_2), 5.66 (d, J = 15.6 Hz, 1H, NCH_2), 6.69 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.73 (d, J = 1.9 Hz, 1H, CH=CH Im), 6.78 (d, J = 8.2 Hz, 2H, tolyl *o*-H), 7. 06 (d, J = 8.2 Hz, 2H, tolyl *m*-H). ^{13}C {^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) *syn*-isomer δ: 27.7 (CH_3, tolyl-CH_3), 36.1 (CH_3, NCH_3), 48.6 (CH_3, OCH_3), 48.9 (CH_3, OCH_3), 51.8 (CH_2, NCH_2), 118.3 (CH, CH=CH Im), 119.8 (CH, CH=CH Im), 126.2 (CH, tolyl *o*-C), 127.4 (CH, tolyl *m*-C), 130.2 (C, tolyl *p*-C), 135.8 (C, tolyl *i*-C), 142.3 (C, C=C), 163.2 (C, C=O), 167.2 (C, C=C), 175.0 (C, C=O), 179.7 (C, NCN); *anti*-isomer δ: 19.1 (CH_3, toyl-CH_3), 35.5 (CH_3, NCH_3), 48.6 (CH_3, OCH_3), 48.9 (CH_3, OCH_3), 51.9 (CH_2, NCH_2), 118.3 (CH, CH=CH Im), 120.5 (CH, CH=CH Im), 125.0 (CH, tolyl *o*-C), 127.5 (CH, tolyl *m*-C), 130.9 (C, tolyl *p*-C), 135.8 (C, tolyl *i*-C), 141.8 (C, C=C), 163.2 (C, C=O), 167.2 (C, C=C), 175.0 (C, C=O), 179.9 (C, NCN). IR (KBr): 1692 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{36}H_{40}N_4O_8Pd$: C, 56.66; H, 5.28; N, 7.34. Found C, 56.78; H, 5.36; N, 7.39%.

4.1.14. {κ¹-C-[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}(PPh$_3$)Pd(C–COOMe)$_4$ (5c)

0.064 g (0.120 mmol) of {[1-(2-pyridyl)methylene-3-methyl] imidazolyl-2-ene}Pd(C–COOMe)$_4$ were dissolved in 15 mL of anhydrous dicloromehane. To this solution was slowly added 0.0336 g (0.128 mmol) of triphenylphosphine and the mixture was stirred for 15 min. Evaporation under vacuum to a small volume and addition of diethylether induced the precipitation of the final product as a light yellow solid. It was filtered off and washed with diethylether and *n*-pentane.

Yield 0.081 g (83%). ^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.55 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3), 3.23 (s, 3H, NCH_3), 3.63 (s, 3H, OCH3), 3.64 (s, 3H, OCH_3), 5.08 (d, J = 14.6 Hz, 1H, NCH_2), 5.32 (d, J = 14.8 Hz, 1H, NCH_2), 6.50 (d, J = 1.8 Hz, 1H, CH=CH Im), 6.95 (d, J = 1.8 Hz, 1H, CH=CH Im), 7.14 (m, 1H, 5-Pyr), 7.22–7.39 (m, 16H, 3-Pyr, PPh), 7.52 (td, J = 7.5, 1.6 Hz, 1H, 4-Pyr), 8.28 (d, J = 4.7 Hz, 1H, 6-Pyr). ^{13}C {^{1}H} NMR (CDCl3, T = 298 K, ppm) δ: 36.8 (CH_3, NCH_3), 49.8 (CH_3, OCH_3), 50.6 (CH_3, OCH_3), 51.0 (CH_3, OCH_3), 51.1 (CH_3,

OCH_3), 55.4 (CH_2, NCH_2), 121.5 (CH, CH=CH Im), 122.0 (CH, CH=CH Im), 122.8 (CH, 5-Pyr), 124.2 (CH, 3-Pyr), 136.8 (CH, 4-Pyr), 145.2 (C, C=C), 148.1 (C, C=C), 149.0 (C, 6-Pyr), 154.1 (CH, 2-Pyr), 164.3 (C, C=O), 165.1 (C, C=C), 166.5 (C, C=O), 174.9 (C, C=C), 175.0 (C, C=O), 175.7 (C, C=O), 179.2 (C, NCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 27.4 (s, PPh_3). IR (KBr): 1697 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{40}H_{38}N_3O_8PPd$: C, 58.15; H, 4.64; N, 5.09. Found C, 58.20; H, 4.70; N, 5.18%.

4.1.15. {κ¹-C-[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}{P(OEt)₃}Pd(C−COOMe)₄ (6c)

This complex was prepared in an analogous manner as that described for **5c**, starting from 0.051 g (0.092 mmol) of {[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}Pd(C−COOMe)$_4$ and 0.0172 mL (0.099 mmol) of triethyl phoshite.

Yield 0.058 g (87% white solid). ^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 1.16 (t, J = 7.0 Hz, 9H, $POCH_2CH_3$), 3.19 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 4.03 (s, 3H, NCH_3), 3.91 (m, 6H, $POCH_2CH_3$), 5.43, 5.40 (AB system, J = 15.0 Hz, 2H, NCH_2), 6.91 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.04 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.27 (ddd, J = 7.7,4.9,1.0 Hz, 1H, 5-Pyr), 7.53 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.72 (td, J = 7.7, 1.8 Hz, 1H, 4-Pyr), 8.60 (d, J = 4.8 Hz, 1H, 6-Pyr).$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 16.1(d, J_{CP} = 7.2 Hz, CH_3, $POCH_2CH_3$) 37.4 (CH_3, NCH_3), 50.6 (CH_3, OCH_3), 50.8 (CH_3, OCH_3), 51.1 (2 CH_3, OCH_3), 56.0 (CH_2, NCH_2), 61.0 (CH_2, $POCH_2CH_3$) 121.3 (CH, CH=CH Im), 122.1 (CH, CH=CH Im), 123.1 (CH, 5-Pyr), 123.8 (CH, 3-Pyr), 137.0 (CH, 4-Pyr), 146.5 (C, C=C), 146.7 (C, C=C), 149.3 (C, 6-Pyr), 154.9 (CH, 2-Pyr), 164.4 (C, C=O), 166.6 (C, C=O), 169.9 (C, C=C), 175.5 (C, C=O), 176.4 (C, C=C), 176.5 (C, C=O), 178.2 (C, NCN).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 127.2 (s, $P(OEt)_3$). IR (KBr): 1696 cm^{-1} (ν_{CO}). Anal. Calcd for $C_{28}H_{38}N_3O_{11}PPd$: C, 46.07; H, 5.25; N, 5.76. Found C, 46.14; H, 5.32; N, 5.82%.

4.1.16. {κ¹-C-[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}(DIC)Pd(C−COOMe)₄ (7c)

This complex was prepared in an analogous manner as that described for **5c**, starting from 0.065 g (0.118 mmol) of {[1-(2-pyridyl)methylene-3-methyl]imidazolyl-2-ene}Pd(C−COOMe)$_4$ and 0.0162 g (0.123 mmol) of DIC (2,6 dimethyl isocyanide).

Yield 0.0714 g (89%; light yellow solid). ^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.10 (s, 6H, aryl-CH_3), 3.29 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.86 (s, 3H, NCH_3), 5.22 (d, J = 14.8 Hz, 1H, NCH_2), 5.65 (d, J = 14.8 Hz, 1H, NCH_2), 6.97 (d, J = 1.8 Hz, 1H, CH=CH Im), 7.01 (m, 1H, 5-Pyr), 7.04 (d, J = 7.8 Hz, 2H, aryl m-H), 7.20 (d, J = 7.8 Hz, 1H aryl p-H), 7.21 (d, J = 1.8 Hz, 1H, CH=CH Im), 7.60−7.63 (m, 2H, 3-Pyr, 4-Pyr), 8.28 (d, J = 4.8 Hz, 1H, 6-Pyr).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 18.1 (CH_3, Ar-CH3), 37.8 (CH_3, NCH_3), 50.7 (CH_3, OCH_3), 50.8 (CH_3, OCH_3), 51.1 (CH_3, OCH_3), 51.2 (CH_3, OCH_3), 55.9 (CH_2, NCH_2), 122.0 (CH, CH=CH Im), 122.5 (CH, 5-Pyr), 122.8 (CH, CH=CH Im), 123.9 (CH, 3-Pyr), 126.7 (C, aryl i-C), 127.8 (CH, aryl m-C), 129.5 (CH, aryl p-C), 135.1 (C, aryl o-C), 136.9 (CH, 4-Pyr), 145.3 (C, C=C), 146.3 (C, C=C), 149.3 (C, 6-Pyr), 155.1 (CH, 2-Pyr), 164.4 (C, C=O), 165.1 (C, C=O), 166.2 (C, C=C), 166.3 (C, C=C), 175.2 (C, C=O), 176.1 (C, C=O), 177.8 (C, NCN). IR (KBr): 1697 cm^{-1} (ν_{CO}); 2174 cm^{-1} (ν_{CN}). Anal. Calcd for $C_{31}H_{32}N_4O_8Pd$: C, 53.57; H, 4.64; N, 8.06. Found C, 53.64; H, 4.56; N, 8.12%.

4.1.17. Synthesis of {κ¹-C-{[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}(PPh₃)Pd(C−COOMe)₄ (5i)

0.050 g (0.128 mmol) of the polymer $[Pd(C{-}COOMe)_4]_n$ was dissolved in 15 mL of anhydrous dicloromehane and to this solution were successively added 0.034 g (0.128 mmol) of triphenylphosphine and 0.0480 g of {[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1i**). The mixture was stirred for 30 min at RT upon which the greyish silver salt precipitated; after filtration through a Millipore filter the resulting solution was concentrated under reduced pressure and the addition of diethylether induced the precipitation of the final product as a whitish solid. It was filtered off and washed with diethylether and *n*-pentane.

Yield 0.090 g (80%). ^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.33 (s, 3H, tolyl-CH_3), 2.56 (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3), 3.33 (s, 3H, NCH_3), 3.62 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 4.56 (d, J = 13.8 Hz, 1H, N−CH_2), 5.22 (d, J = 13.8 Hz, 1H, N−CH_2), 6.29 (d, J = 1.8 Hz, 1H, CH=CH Im), 6.51 (d, J = 1.8 Hz, 1H, CH=CH Im), 6.86 (d, J = 7.9 Hz, 2H, tolyl *m*-H), 7.06 (d, J = 7.9 Hz, 2H, tolyl *o*-H), 7,29−7.44 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.1 (CH_3, tolyl-CH_3), 37.0 (CH_3, NCH_3), 49.8 (CH_3, OCH_3), 50.7 (CH_3, OCH_3), 51.0 (CH_3, OCH_3), 51.1 (CH_3, OCH_3), 53.8 (CH_2, NCH_2), 120.0 (CH, CH=CH Im), 121.5 (CH, CH=CH Im), 129.4 (CH, tolyl *o*-C), 129.9 (CH, tolyl *m*-C), 130.6 (C, tolyl *i*-C), 138.3 (C, tolyl *p*-C), 145.5 (C, d, J_{CP} = 5.7 Hz, C=C), 148.2 (C, d, J_{CP} = 7.5 Hz, C=C), 165.1 (C, d, J_{CP} = 9.7 Hz, CO), 166.6 (C,CO), 170.0 (C, C=C), 171.5 (C, C=C), 174.9 (C, d, J_{CP} = 4.6 Hz, CO), 175.7 (C, d, J_{CP} = 5.1 Hz, CO), 178.9 (C, d, J_{CP} = 16.5 Hz, NCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 27.5. IR (KBr): $\nu_{C=O}$ = 1695, 1794 cm^{-11} (ν_{CO}). Anal. Calcd for $C_{42}H_{41}N_2O_8PPd$: C, 60.11; H, 4.92; N, 3.34. Found C, 60.27; H, 4.84; N, 3.39%.

4.1.18. Synthesis of {κ¹-C-{[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}(DIC)Pd(C−COOMe)₄ (7i)

To a solution of $[Pd(C{-}COOMe)_4]_n$ (0.064 g, 0.164 mmol) in 10 mL of anhydrous dichloromethane were successively added 0.0215 g (0.164 mmol) of DIC (2,6 dimethyl isocyanide) and 0.061 g (0.164 mmol) of {[1-(4-methylphenyl)methylene-3-methyl]imidazolyl-2-ene}silver bromide (**1i**). The mixture was stirred for two days in the dark and then passed through a Millipore filter to remove the silver bromide. The clear solution was evaporated to dryness and the resulting residue was treated with diethylether to give a whitish solid. After filtration the product was washed with small portions of diethylether and *n*-pentane.

Yield 0.082 g (71%). ^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.13 (s, 6H, aryl-CH_3), 2.15 (s, 3H, tol-CH_3), 3.31 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.87 (s, 3H, NCH_3), 5.09 (d, J = 15.0 Hz, 1H, N−CH_2), 5.58 (d, J = 15.0 Hz, 1H, N−CH_2), 6.94−6.97 (m, 4H, CH=CH Im, tol *m*-H), 7.06 (d, J = 7.6 Hz, 2H, aryl *m*-H), 7.14 (d, J = 8.0 Hz, 2H, tol *o*-H), 7.21 (t, J = 7.6 Hz, aryl *p*-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 18.6 (CH_3, aryl-CH_3), 21.3 (CH_3, tol-CH_3), 38.2 (CH_3, NCH_3), 51.2 (CH_3, OCH_3), 51.3 (CH_3, OCH_3), 51.5 (CH_3, OCH_3), 51.6 (CH_3, OCH_3), 54.8 (CH_2, NCH_2), 121.9 (CH, CH=CH Im), 122.8 (CH, CH=CH Im), 126.5 (C, aryl *i*-C), 128.3 (CH, aryl *m*-C), 128.4 (CH, tol *o*-C), 129.7 (CH, tol *m*-C), 129.9 (CH, aryl *p*-C), 133.3 (C, tol *i*-C), 135.5 (C, aryl *o*-C), 138.3 (C, tol *p*-C), 145.9 (C, C=C), 146.7 (C, C=C), 150.5 (C,CN), 164.8 (C, CO), 165.6 (C,CO), 166.6 (C, C=C), 166.9 (C, C=C), 175.7 (C, CO), 176.5 (C, CO), 178.4 (C, NCN). IR (KBr): ν_{CO} = 1697; ν_{CN} = 2174 cm^{-1}. Anal. Calcd for $C_{33}H_{35}N_3O_8Pd$: C, 55.98; H, 4.98; N, 5.93. Found C, 55.88; H, 4.88; N, 5.98%.

4.2. Kinetics measurements

The isomerization process of complex **3c** was studied by monitoring the concentration of the two isomeric species by integration of suitable ^1H NMR signals; the concentrations of the involved species were independently determined and their internal consistency was assured by the relevant mass balance equations. The NMR tube for the determination was prepared by dissolving 8 mg of the product in 0.8 mL of $CDCl_3$. Non-linear analysis of the data related to kinetics measurements was performed by a locally

adapted routine written in the ORIGIN® 7.5 environment.

4.3. Crystal structure determinations

The crystal data of compounds **2c** and **3i** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package [27] and corrected for Lorentz, polarization and absorption effects (SORTAV) [28]. The structure was solved by direct methods using the SIR97 [29] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-97 [30] and PARST [31] implemented in the WINGX [32] system of programs. The crystal data are given in Table 1S.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1059980 and 1059981 These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge, CB2 1EZ, UK [fax: (+44)1223–336033, e-mail: deposit@ccdc.cam.ac.uk]

4.4. Computational details

The geometrical optimization of the complexes was carried out without symmetry constraint, using the hyper-GGA functional MO6 [33,34] in combination with polarized triple-ζ-quality basis sets (LAN2TZ(f)) [35,36] and relativistic pseudopotential for the Pd atoms and a polarized double-ζ-quality basis sets (6–31 G(d,p)) for the other elements.

Solvent effects (dichloromethane, $\varepsilon = 8.93$) were included using CPCM [37,38].

The "restricted" formalism was applied in all the calculations. The zero-point vibrational energies and thermodynamic parameters were obtained [39] by means of the stationary points characterized by IR simulation.

The software used was Gaussian '09 [40] and all the computational work was carried out on Intel based x86-64 workstations.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.07.014.

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