

Palladium complexes containing ligands with hydrogen-bonding functionalities. Reactivity and catalytic studies with CO and olefins

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Abstract

The synthesis of the new bidentate N–N ligand 1-(2-(1-(pyridin-2-yl)ethylideneamino)ethyl)-3-ethylurea (**PyUr**) with a urea substituent attached to the imine nitrogen is reported. This ligand has been used to form palladium complexes and study the potential influence of the urea group (as a hydrogen bonding unit and a hemilabile ligand) in the insertion of CO and olefins into Pd–C bonds. The reaction of **PyUr** with [Pd(CH₃)(Cl)(COD)] to yield [Pd(CH₃Cl)(**PyUr**)] (**1**) is reported. A crystallographic study of this complex was carried out showing that the urea moieties are involved in a series of intermolecular hydrogen bonding interactions. Upon removal of the chloride from the coordination sphere of **1** (by addition of AgBF₄) the urea group of **PyUr** coordinates to the palladium centre stabilizing an otherwise coordinatively unsaturated complex. The reaction of these complexes with CO to yield [Pd{C(=O)CH₃}Cl(**PyUr**)] (**3**) and [Pd{C(=O)CH₃}(**PyUr**)](BF₄) (**4**) is also discussed. Following on from these reactions, the copolymerization of CO and styrene using **1** as a catalyst was studied and is herein reported. The copolymers synthesized using **1** as a catalyst were obtained in moderate yields and showed to have a narrow size distribution. The same reaction was performed using a palladium complex coordinated by an analogous pyridine ligand but without a hydrogen bonding substituent. The results of the copolymerization reactions showed that, although slightly better yields and larger molecular weights were obtained with the **PyUr**-containing catalyst, the hydrogen bonding groups in **PyUr** have little influence on the course of the reaction. To explore further the reactivity of the palladium complexes, the reaction between [Pd(CH₃Cl)(**PyUr**)](BF₄) (**2**) and CH₂=CHCH₂OH was carried out to yield the allyl complex [Pd(η³-CH₂CHCH₂)(**PyUr**)] (**6**). The crystal structure of this complex is also reported.

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1. Introduction

Several palladium(II) complexes with bidentate phosphorous or nitrogen ligands have shown to be efficient catalysts for CO/alkene copolymerization reactions

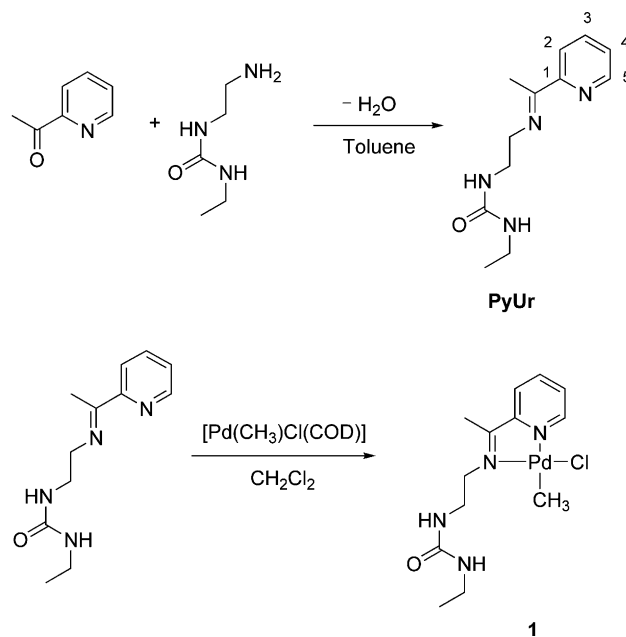
[1,2]. The properties and yields of the polymeric products obtained in these reactions are highly dependent on the nature of the chelating ligand and the conditions used to perform the polymerization (e.g., the reaction solvent, the presence of an oxidant or a co-catalyst, the temperature and the CO pressure). Due to the high-performance properties of these copolymers, over the past few years there has been an increasing interest in developing better catalytic systems for their preparation

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[3]. Several detailed studies on improving the catalyst performance and determining the catalytic mechanism have been carried out by Brookhart [4–7], Consiglio [8–14], Carfagna [15,16], Claver [3,17–21], Drent [22,23], Milani [24–27], Nozaki [28,29], Sen and van Leeuwen [30–34] among others. An important part of this investigations, has concentrated in designing new ligands that, when coordinated to the palladium centre, provide the appropriate electronic and steric environment to yield more active and selective catalysts. For example, it has been established that the nature of the ligand's coordinating atoms (usually phosphorous or nitrogen) has a great impact on the molecular weight of the final polymeric product [10]. The stereoregularity of the final polymers, on the other hand, can be modified by changing the steric and electronic properties of the ligand [17,20] or by using chiral species [13,14,35–37]. Besides the nature of the ligands, the reaction conditions also have an important impact on the catalytic performance of the system. Several systematic studies have appeared in the literature showing how the reaction temperature, CO pressure [26,29], nature of the complex's counterions [18,38,39] and the reaction solvent [40] can greatly modify the yields and molecular weights of the polymers produced.

As part of our ongoing interest in the supramolecular chemistry of metal complexes, we have engaged in studying catalytically active metals coordinated by ligands that contain hydrogen bonding motifs. The rationale behind this approach is to combine the catalytic performance of the metal with the molecular recognition properties of hydrogen-bonding groups to yield a more selective and efficient catalyst. In order to explore this approach, the palladium-catalyzed copolymerization of CO and olefins was chosen as a model reaction. This reaction proceeds by subsequent alternating migratory insertions of an alkyl group to CO and an acyl group to an olefin; these alternating insertions generate species such as $[\text{Pd}]\text{-C}(=\text{O})\text{R}$ and $[\text{Pd}]\text{-CHPh-CH}_2\text{-C}(=\text{O})\text{R}$ which are potential hydrogen bond acceptors (via the lone pairs of the carbonyl's oxygen). Since some of the structural properties of the resulting polymer depend on the geometrical constraints imposed by the catalyst on the migratory insertions, a hydrogen-bonding ligand (coordinated to the catalytic centre) could in principle influence the course of the reaction. Herein, we report the synthesis and structural characterization of the new palladium(II) metal complex $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{PyUr})]$ (**1**) which contains the urea-substituted pyridine ligand **PyUr** (see Scheme 1).

We also report that upon removal of the chloride ligand from this complex, the complex $[\text{Pd}(\text{CH}_3)(\text{PyUr})]\text{-}[\text{BF}_4]$ (**2**) is stabilized by interaction of the urea's carbonyl group with the metal centre. To investigate the potential role played by the hydrogen bonding moiety and the hemilabile nature of the ligand on the reactivity



Scheme 1.

of the complex, the reaction of **1** with CO and styrene under mild conditions was investigated and the results are herein presented. The reaction between **1** and 2-propen-1-ol ($\text{CH}_2=\text{CHCH}_2\text{OH}$) has also been carried out to investigate the potential interactions between the urea group of the ligand and the $-\text{OH}$ group of the olefin. Interestingly, in this reaction an organometallic transformation of the 2-propen-1-ol yields an allyl palladium(II) complex which has been structurally characterized.

2. Results and discussion

2.1. Synthesis and structural characterization of $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{PyUr})]$ (**1**)

The mono-substituted pyridine **PyUr** was prepared by heating to reflux a toluene solution of 2-acetylpyridine and $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHC}(=\text{O})\text{NHCH}_2\text{CH}_3$ and removal of the water via a dean-stark apparatus. The solid obtained from this reaction was characterized as **PyUr** on the basis of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopies, Cl^+ mass spectrometry (including an accurate mass determination which gave the correct molecular formula for the $[\text{M} + \text{H}]^+$ ion) and elemental analyses.

The new palladium complex $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{PyUr})]$ (**1**) (see Scheme 1) was then prepared from the reaction of **PyUr** and $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{COD})]$ in CH_2Cl_2 . This compound was fully characterized by ^1H NMR and IR spectroscopies, FAB^+ mass spectrometry and elemental analyses. To confirm the above formulation crystals of

1 suitable for an X-ray crystallographic analysis were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the compound. The X-ray analysis showed the structure (see Fig. 1) to be disordered, containing both *cis* and *trans* isomers in a ca. 65:35 ratio (vide infra). The **PyUr** ligand coordinates to the metal via the adjacent pyridyl and imino nitrogen centres. The geometry at palladium is distorted square planar with *cis* angles in the range $78.9(3)$ – $101.0(3)^\circ$, the acute angle being associated with the bite of the **PyUr** ligand. The Pd–N(1) [2.066(8) Å] and Pd–N(7) [2.114(7) Å] distances do not differ significantly from those in, for example, the complex $(\mu_2$ -1,1'-bis((pyrid-2-yl)methyleneamino)ferrocene)-dichloro-dimethyl-dipalladium [41]. The *N,N'* chelate ring is planar to within 0.019 Å and the C(7)=N(7) bond [1.269(10) Å] retains its double bond character. The geometry about C(9)–C(10) is *gauche* and the torsional twist about N(7)–C(9) is ca. 99° .

Glide-related molecules are linked by a pair of N–H···O hydrogen bonds between the urea N–H groups of one molecule and the carbonyl oxygen atom of another, to form chains that extend in the crystallographic *c*-direction. Adjacent centrosymmetrically related chains are linked by π – π stacking interactions (see Fig. 2).

As indicated by the X-ray crystallographic determination, both the *cis* and *trans* isomers of **1** (based on the relative position of the methyl group and the pyridine ring) are present in the bulk of the crystalline sample. Inspection of the ^1H NMR spectrum of a solution of **1** shows that all the signals are repeated indicating the existence of the two isomers in solution as well (in an

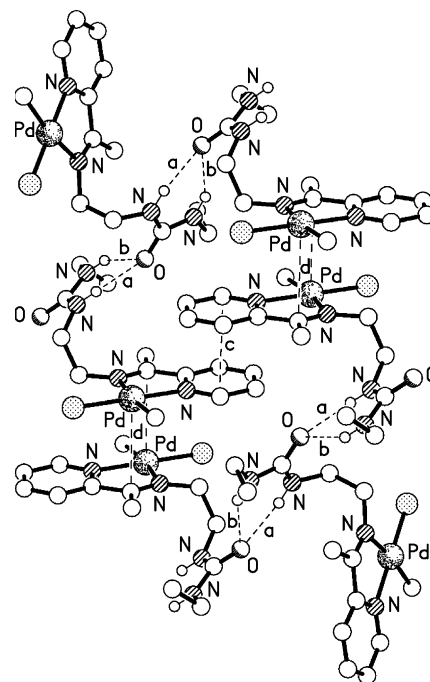


Fig. 2. Hydrogen bonding and stacking interactions between molecules in the structure of **1**. The N–H···O hydrogen bonds have N···O, H···O (Å), N–H···O ($^\circ$); (a) 2.89, 2.06, 154; (b) 3.07, 2.26, 149. The centroid···centroid and mean interplanar separations (c) are 3.74, 3.33 Å, respectively, and the Pd···C(7) distance (d) is 3.48 Å.

approximately one-to-one ratio). The most sensitive signal for the assignment of the two different isomers is the proton on the 5 position of the pyridine (H^5 in Scheme 1). In *trans*-**1** (where the methyl group is *trans* to the pyridine – see Scheme 2) the chloride has a strong deshielding effect on H^5 . As a consequence this proton appears at a considerable higher chemical shift in *trans*-**1** ($\delta = 8.98$ ppm) than the corresponding proton in *cis*-**1** ($\delta = 8.59$ ppm). On the other hand, the urea protons for one of the two isomers are shown as two broad resonances at 5.01 and 5.73 ppm (no clear coupling can be observed), while the urea protons of the other isomer

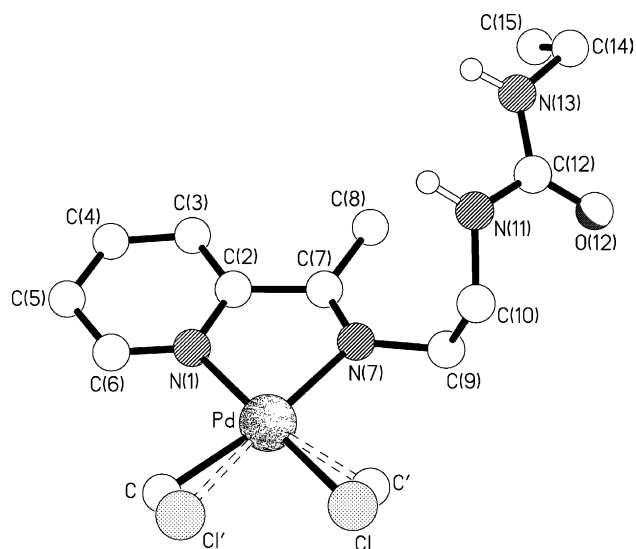
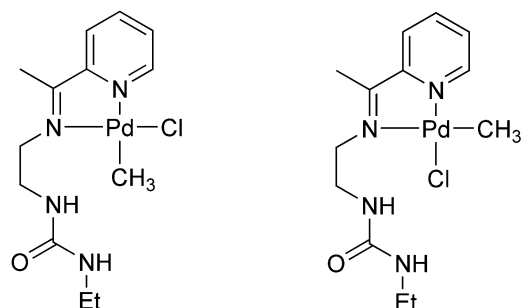


Fig. 1. The molecular structure of **1**. Selected bond lengths (Å) and angles ($^\circ$) for the major occupancy conformer; Pd–Cl 2.196(4), Pd–C 2.11(3), Pd–N(1) 2.066(8), Pd–N(7) 2.114(7), Cl–Pd–C 88.1(8), Cl–Pd–N(1) 179.8(3), Cl–Pd–N(7) 101.0(3), C–Pd–N(1) 92.0(9), C–Pd–N(7) 170.8(8), N(1)–Pd–N(7) 78.9(3).



trans-**1**

cis-**1**

Scheme 2.

appear as two well defined triplets (due to the coupling of the N–H with the methylene protons) at 5.25 and 5.82 ppm, respectively. The isomer associated with the latter pair of N–H resonances (at lower field) is likely to be the one displaying the stronger hydrogen bonding interactions. If an intramolecular hydrogen-bonding interaction between the urea of the ligand and the chloride on the palladium is invoked (assuming that the supramolecular interactions observed in the solid state structure are not retained in solution), it is then likely that the latter values of the N–H chemical shifts correspond to *cis*-**1** (see Scheme 2).

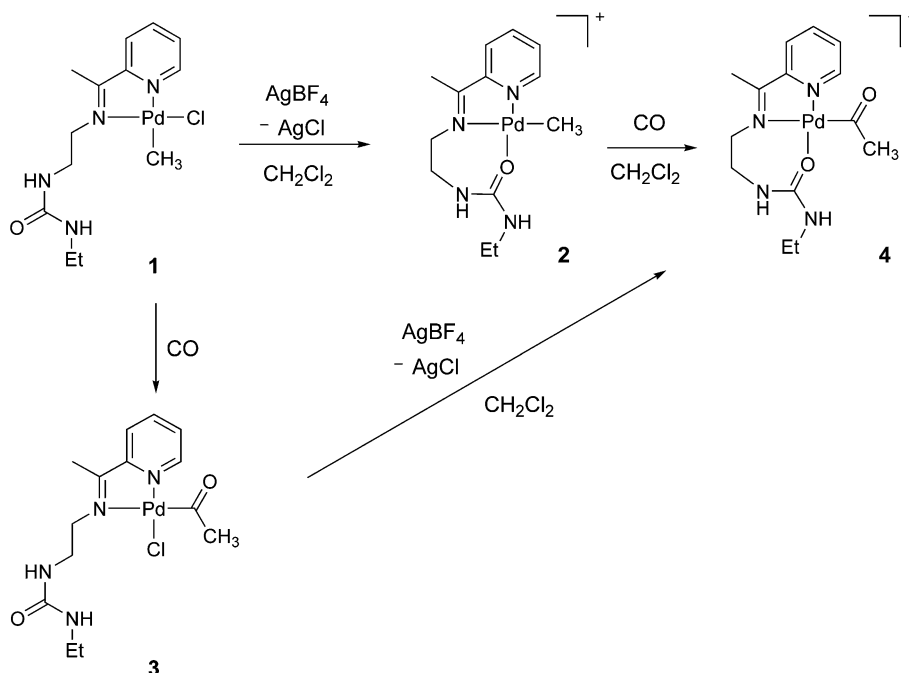
2.2. Reaction of **1** and its de-halogenated derivative $[\text{Pd}(\text{CH}_3)(\text{PyUr})][\text{BF}_4]$ (**2**) with CO

Besides acting as a hydrogen bonding moiety, the urea of the **PyUr** ligand can also coordinate to the metal centre in an intramolecular fashion via the oxygen atom of the C=O group (and hence the ligand could be considered a hemilabile one). These two features of the ligand could influence the catalytic activity of complex **1** for the copolymerization of CO and an olefin.

With this in mind we first investigated the ability of **PyUr** to use the urea C=O group to coordinate to palladium by removing the chloride from compound **1**. Upon addition of one equivalent of AgBF_4 to **1**, the immediate precipitation of AgCl and the formation of a yellow solution were observed. A yellow solid was isolated from the reaction mixture and formulated as $[\text{Pd}(\text{CH}_3)(\text{PyUr})][\text{BF}_4]$ (**2**) on the basis of spectroscopic and analytical data. This complex proved to be very sta-

ble, not only as a solid, but also in solution with non-coordinating solvents. This strongly suggests that the C=O group of the urea is interacting intramolecularly with the palladium center (see Scheme 3). The FAB(+) mass spectrum of this species indicated the presence of $[\text{Pd}(\text{CH}_3)(\text{PyUr})]^+$ at 355 a.m.u. (molecular peak) while the ^1H NMR spectrum showed the presence of only one set of urea N–H signals (in contrast to **1** where two isomers are observed) at 6.05 and 6.58 ppm. The IR spectrum of the compound indicated a shift in the C=O stretching frequency (1637 cm^{-1}) relative to the corresponding stretching frequency in **1** (1625 cm^{-1}).

Once it was established that the urea group can coordinate to the palladium center in an intramolecular fashion and stabilize complex **2**, we shifted our attention to investigating the reactivity of both **1** and **2** towards CO. This insertion reaction is one of the essential steps in the copolymerization of CO and olefins, hence studying it could provide some insight into the potential ability of the urea substituent of **PyUr** to influence the catalytic performance of the palladium(II) complex. Carbon monoxide was bubbled through a solution of **1** for 5 min resulting in a bright yellow solution from which a yellow solid was isolated. Full characterization of this product revealed it to be the palladium–acyl complex $[\text{Pd}\{\text{C}(\text{=O})\text{CH}_3\}\text{Cl}(\text{PyUr})]$ (**3**). A band at 1682 cm^{-1} in the IR spectrum of this sample indicated the presence of the $-\text{C}(\text{=O})\text{CH}_3$ fragment. The ^1H NMR spectrum of this species showed it to be a 1:1 mixture of the *cis* and *trans* isomers. Two singlets (in a 1:1 ratio) between 2.50 and 2.55 ppm were observed and assigned to the methyl protons of $-\text{C}(\text{=O})\text{CH}_3$ for each one of the two isomers.



Scheme 3.

As in the ^1H NMR spectrum of complex **1**, that one of **3** showed the presence of two different urea groups (for each one of the two isomers); four broad signals (two of which were resolved as triplets) of equal intensity were observed between 4.95 and 5.85 ppm and assigned to the two different sets of urea N–H resonances for the *cis* and *trans* isomers. The formulation of the product was further confirmed by FAB(+) mass spectrometry (which showed the molecular peak at 421 a.m.u.) and by elemental analyses.

Since the palladium-catalyzed copolymerization of CO and olefins requires a vacant coordination site on the metal centre, it was of interest to study the behavior of **3** upon removal of the chloride from the coordination sphere. This was carried out by addition of one equivalent of AgBF_4 to a solution of **3** in CH_2Cl_2 which produced the immediate precipitation of AgCl (see Scheme 3). The reaction mixture was filtered and from the filtrate a yellow solid was isolated and characterized as $[\text{Pd}\{\text{C}(=\text{O})\text{CH}_3\}(\text{PyUr})][\text{BF}_4]$ (**4**) on the basis of spectroscopic and structural data. Recrystallization of **4** from a mixture of CH_2Cl_2 and hexane resulted in the formation of yellow plate-like crystals which were analyzed by X-ray crystallography. The single crystal X-ray structure shows the tridentate coordination of the PyUr ligand (via the imine and pyridine nitrogen atoms and by the intramolecular coordination of the urea C=O), the remaining site on the metal being occupied by the C-bonded acetyl group (see Fig. 3). The geometry at palladium is distorted square planar with *cis* angles in the range $77.9(4)$ – $102.1(3)^\circ$, the acute angle

being associated with the *N,N'* chelate. The Pd–N(1) [2.038(10) Å], Pd–N(7) [2.170(8) Å] and Pd–C(16) [1.975(12) Å] distances do not differ significantly from those observed in, for example, the complex acetylchloro-(2-(*N*-isopropyl)-carbaldiminopyridine)-palladium(II) [32], and the Pd–O(12) bond length [2.062(9) Å] is typical of carbonyl *trans* to pyridyl [42]. The *N,N'* chelate ring is planar to within only 0.03 Å, having a slight envelope distortion with N(1) lying 0.076 Å out of the plane of the other four atoms, which are coplanar to within 0.004 Å. The C(7)=N(7) bond [1.272(14) Å] retains its double bond character.

Despite the change from the bidentate coordination of the PyUr ligand in **1** to the tridentate coordination seen here in **4** there is a retention of a *gauche* geometry about the C(9)–C(10) bond. The only hydrogen bonding interactions are between the urea N–H groups and the BF_4 anion, which is disordered (see Fig. 3). Although the C(7)=N(7) bond of one molecule is positioned over the symmetry related pyridyl ring of another, the separation of 3.8 Å is too long to represent any significant intermolecular stacking interaction.

The solid state structure of this complex is consistent with its spectroscopic characterization in solution. The ^1H NMR spectrum of **4** shows the expected signals for the methyl groups of the acyl fragment coordinated to the palladium (singlet at 2.56 ppm), the methyl of the ligand's imine group (singlet at 2.40 ppm) and the methyl group of the ethyl side chain of the ligand (a triplet at 1.19 ppm). The protons of the N–H groups appear as broad signals at 6.11 and 6.70 ppm and, as expected due to geometrical constraints, only one isomer is possible. As is shown in Scheme 3, complex **4** was also prepared successfully by bubbling CO gas through a solution of the de-halogenated complex **2**.

2.3. CO/styrene copolymerization

Once it was shown the facile insertion of CO into the Pd–C bond of **1** and the ability of the urea carbonyl group to stabilize complex **4**, the catalytic properties of **2** (generated in situ by removing the chloride of **1** with silver salts) for the copolymerization of CO and styrene were investigated. As indicated before, the features of the system that could lead to distinct catalytic properties are the hemilability of PyUr and the presence of the urea groups as hydrogen bonding units.

The CO/styrene copolymerization reactions were carried out by first dissolving **1** in 2,2,2-trifluoroethanol in the presence of AgX ($\text{X} = \text{BF}_4$ or PF_6) to remove the chloride from the coordination sphere. The precipitated AgCl was removed by filtration and an excess of styrene was added to the filtrate. The reaction mixture was placed in an autoclave, pressurized to 10 atm with CO and stirred for 24 h. The polymers formed were separated and purified following established procedures,

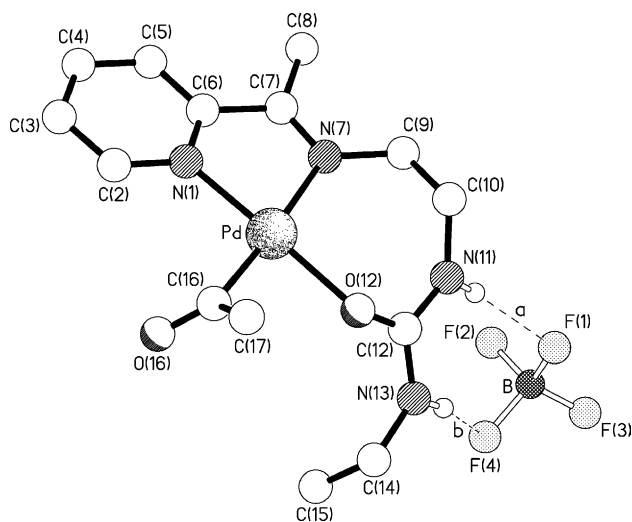
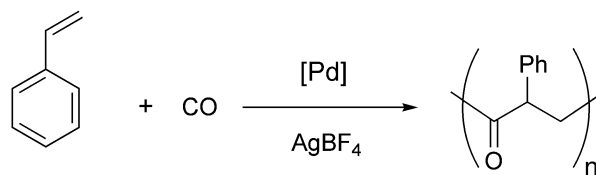


Fig. 3. The molecular structure of **4**. Selected bond lengths (Å) and angles ($^\circ$): Pd–N(1) 2.038(10), Pd–N(7) 2.170(8), Pd–O(12) 2.062(9), Pd–C(16) 1.975(12), N(1)–Pd–N(7) 77.9(4), N(1)–Pd–O(12) 177.7(3), N(1)–Pd–C(16) 98.1(5), N(7)–Pd–O(12) 102.1(3), N(7)–Pd–C(16) 176.0(5), O(12)–Pd–C(16) 81.9(5). The N–H \cdots F hydrogen bonds to the major occupancy (67%) BF_4 anion have N \cdots F, H \cdots F (Å), N–H \cdots F ($^\circ$): (a) 2.90, 2.04, 158; (b) 2.97, 2.09, 166.

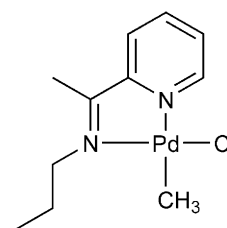
and were characterized by NMR and IR spectroscopies, melting point and by MALDI-TOF mass spectrometry to determine their molecular weights (see Table 1 for details). In both cases the co-polymer was obtained in moderate yields (49 and 63 g of copolymer/g Pd for the reaction with AgPF₆ and AgBF₄, respectively). The molecular weight of the copolymers (determined by MALDI-TOF spectrometry) was 4202 and 5650 a.m.u., respectively, which is comparable to the molecular weights previously reported for other palladium–(N–N) catalysts under similarly mild experimental conditions (relatively low CO pressure and at room temperature). The polydispersity of these products is remarkably low with values of 1.03 (in the presence of PF₆[−]) and 1.06 (in the presence of BF₄[−]). The ¹³C{¹H} NMR spectra of the two copolymers is consistent with a stereoregular material [16] since strong signals for CO, C_{ipso}, CH and CH₂ were observed at 210.8, 135.5, 54.4 and 43.0 ppm, respectively (values given for the copolymer obtained using AgBF₄ – very similar values were observed for the one obtained in the presence of AgPF₆). These chemical shifts are very close to those previously reported for alternating head-to-tail syndiotactic CO/styrene copolymers [15]. In all cases, besides the main peak corresponding to the C_{ipso} of the syndiotactic polymer at 135.5 ppm, two very small resonances at slightly higher chemical shifts (around 136 and 137 ppm) were also observed indicating that the polymers are nearly but not 100% stereochemically pure (Scheme 4).

In order to evaluate if the urea groups of **PyUr** indeed had an influence on the copolymerization reaction, the palladium(II) compound [Pd(CH₃)Cl(**PyPr**)] (**5**) was also prepared (see Scheme 5). This complex is analogous to **1** but the ligand **PyPr** does not contain urea groups that could influence the catalysis (instead it contains a simple propyl chain).

In spite of our initial hypothesis that the urea groups would have an important effect on the copolymerization reaction, the results obtained using **5** as a catalysts are similar to those obtained with **1** (see Table 1 and experimental details). The most important difference observed when doing these experiments, was the presence of larger amounts of black palladium



Scheme 4.

**5**

Scheme 5.

(which made the copolymers grey and more difficult to purify) when using **5** in comparison to the reactions with **1**. It should also be noted that the reaction using **1** and AgBF₄ gave the best yield and higher molecular weight copolymer. The above two facts suggests that, although the urea groups might not influence the manner in which the migratory insertions take place, **1** is probably a more robust catalyst than **5**. This might be due the hemilabile nature of **PyUr** which has been shown to stabilize, by coordination, species such as **2** and **4**. Further studies will be required to investigate if this enhanced stability can be exploited at higher temperatures to obtain better yields and higher molecular weight polymers.

2.4. Reactivity of **4** with 2-propen-1-ol

There is growing interest in developing catalysts for the polymerization of functionalized olefins – especially those with polar substituents such as –OH, –NH₂ or –COOH [43,44]. One of the key problems

Table 1

Selected data for the CO/styrene copolymers obtained using either **1** or **5** as catalysts in the presence of silver salts to remove the chloride ion from the coordination sphere

Catalyst	AgX	Mass of polymer (g)	g polymer/g Pd	Melting point (°C) (pure)	M _w (g/mol)	M _w /M _n
1	AgPF ₆	0.636	49	246–250	4202	1.03
1	AgBF ₄	0.823	63	252–254	5650	1.06
5	AgPF ₆	0.646	49	248–254	4612	1.04
5	AgBF ₄	0.745	57	246–252	4250	1.03

All reactions were carried out at room temperature, using 2,2,2-trifluoroethanol as a solvent and under 10 atm of CO pressure. In all cases 0.127 mmol of the corresponding palladium catalyst was used.

to overcome in this type of reaction is the reactivity of the substituents towards the catalytic metal center. Late transition metals are an ideal starting point for such polymerization studies since they are better suited to tolerate functional groups. Considering that the complexes studied throughout the present work contain a ligand with a hydrogen bonding motif, we rationalized that this ligand could, in principle, establish supramolecular interactions with the substituent group of an incoming functionalized olefin. This in turn could reduce the potential unwanted reactions between the functional group and the palladium centre of the corresponding complex and favor the insertion of the olefin into the Pd–C bond (which could subsequently be the basis for a polymerization or copolymerization process). Consequently, the reaction between **2** (generated by reacting **1** with one equivalent of AgBF_4) and a large excess of 2-propen-1-ol ($\text{CH}_2=\text{CHCH}_2\text{OH}$) was investigated. After stirring the reaction mixture for 12 h, it was filtered (to remove some black palladium formed) and from the filtrate a white solid was isolated and characterized as the unexpected palladium-allyl product $[\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PyUr})]\text{-}[\text{BF}_4]$ (**6**). The ^1H NMR spectrum of this product showed the characteristic resonances for the ligand and also two doublets at 3.40 and 4.06 ppm (integrating to two protons each) and a triplet of triplets at 5.89 ppm (integrating to one proton) that can be assigned to the two non-equivalent CH_2 groups of the allyl ligand and to the central CH group of this moiety. The proposed formulation was also consistent with the observed FAB(+) mass spectrum which showed a peak at 381 a.m.u. with very high intensity which can be assigned to $[\text{Pd}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PyUr})]^+$. Crystals suitable for an X-ray crystal structure determination were obtained from slow diffusion of diethyl ether onto a CH_2Cl_2 solution of the complex. The X-ray structure of **6** is shown in Fig. 4. Here, the PyUr ligand adopts the same bidentate N,N' coordination geometry observed in **1**, the allyl group occupying the remaining coordination sites on the metal centre. The allyl carbon atoms C(16), C(17) and C(18) lie 0.17, -0.49 and 0.08 Å, respectively, from the $\{\text{PdN}_2\}$ coordination plane. The Pd–N and Pd–C distances (see Fig. 4) are very similar to those observed in other η^3 -allyl-pyridyl- and η^3 -allyl-pyridyl-imino-palladium(II) complexes [45–47]. The N,N' chelate ring has an envelope conformation with the palladium atom lying 0.14 Å out of the plane of the remaining atoms, which are coplanar to within 0.003 Å. The PyUr ligand retains the C(9)–C(10) *gauche* geometry observed in the other two complexes. Glide-related molecules are linked by an $\text{N-H}\cdots\text{O}$ hydrogen bond between N(11)–H in one molecule and the urea carbonyl oxygen atom O(12) of another; the $\text{N}\cdots\text{O}$ and $\text{H}\cdots\text{O}$ distances are 2.95 , 2.10 Å, and

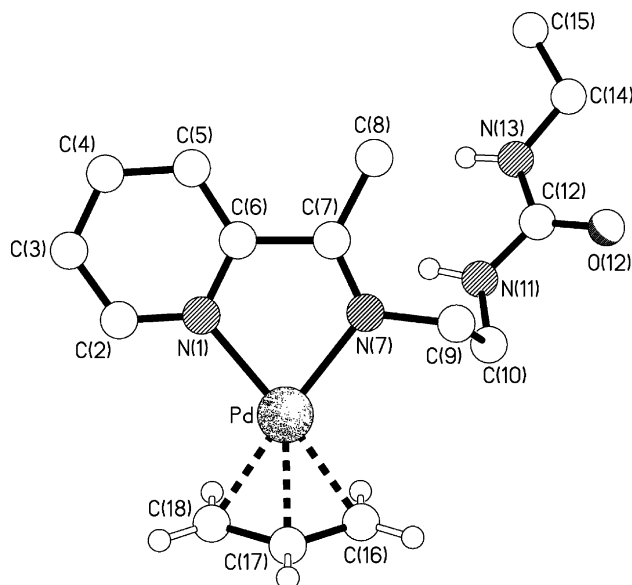
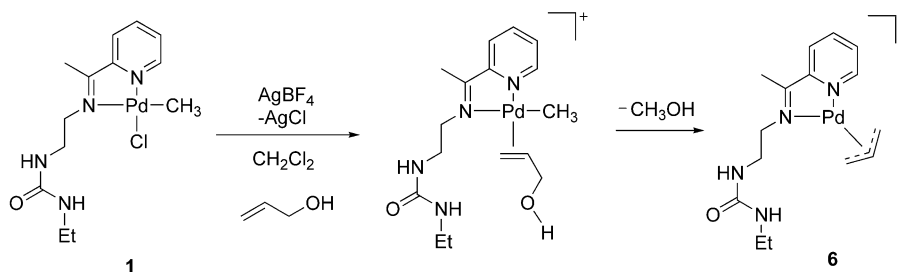


Fig. 4. The molecular structure of **6**. Selected bond lengths (Å) and angles ($^\circ$): Pd–N(1) 2.088(6), Pd–N(7) 2.091(6), Pd–C(16) 2.132(7), Pd–C(17) 2.111(9), Pd–C(18) 2.135(8), C(7)–N(7) 1.284(9); N(1)–Pd–N(7) $78.2(2)$.

the $\text{N-H}\cdots\text{O}$ angle is 157° . There is a weak π – π stacking interaction between the pyridyl rings of centrosymmetrically related pairs of molecules; the centroid \cdots centroid and mean-interplanar separations are 4.17 and 3.51 Å, respectively. There are no interactions involving the BF_4 anion.

The formation of complex **6** from **2** and $\text{CH}_2=\text{CHCH}_2\text{OH}$ was not expected (since an insertion of the olefin into the Pd–C bond was being sought) but it is nevertheless not surprising. It is well established in the literature that species with formula $\text{CH}_2=\text{CHCH}_2\text{X}$ (where X = halides, $-\text{OAc}$, $-\text{OR}$, $-\text{OH}$) yield palladium-allyl complexes – many of which are intermediate species for various palladium-mediated organic transformations [48–51]. As is shown in Scheme 6, upon removal of the chloride from the coordination sphere of **1**, it is likely that in the presence of a large excess of olefin, an intermediate species with the olefin coordinated to the metal centre in a π fashion is formed. Although this species could in principle proceed to the wanted migratory insertion, a re-arrangement of the olefin takes place with elimination of CH_3OH and formation of the stable palladium-allyl complex **6**.

Due to this reaction being so favorable, it was not possible to evaluate if the hydrogen-bonding groups of the ligand in **2** would have an influence on the insertion of the functionalized olefin into the Pd– CH_3 bond. Investigations with other substituted olefins are currently underway to determine the potential importance of the hydrogen bonding moieties in this organometallic transformation.



Scheme 6.

3. Conclusions

The urea-substituted N–N pyridine ligand **PyUr** has been successfully prepared and coordinated to palladium yielding the new metal complex $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{PyUr})]$. Upon removal of the chloride from the coordination sphere of **1**, the urea group of the ligand interacts with the vacant coordination site of the palladium centre forming the stable complex $[\text{Pd}(\text{CH}_3)(\text{PyUr})][\text{BF}_4]$. This complex has been shown to be a good catalyst for the copolymerization of CO and styrene at room temperature, without the need of adding any co-catalysts and at relatively low CO pressures. The hemilability of the ligand seems to provide the appropriate coordination environment to render a stable complex that catalyzes the reaction with very little apparent decomposition (and hence little contamination of the polymeric product by metallic palladium). Further studies will be required to explore the full catalytic capabilities of this complex. For example, due to its stability, it is likely that the complex will be compatible with catalytic processes performed at higher temperatures. Regarding the influence of the hydrogen bonding units in the nature of the final polymeric product, the results obtained so far do not suggest that they play an important role in the catalytic process. However, it would be interesting to explore if an alkyl linker of a different length (for example increasing by one CH_2 group the length of the chain) would have an influence on the way the ligand's urea interacts with the rest of the complex.

4. Experimental

4.1. General procedures

All manipulations were carried out in an atmosphere of purified and dry nitrogen using standard Schlenk line techniques unless otherwise stated. Solvents were dried from the appropriate drying agent, degassed and stored under nitrogen. All commercially available solid starting materials were not further purified. All liquid starting materials were dried over molecular sieves and thoroughly degassed by freeze–pump–thaw prior to use.

^1H and ^{13}C NMR spectra were recorded on a JEOL-EX270 spectrometer (270.17, 67.94 MHz, respectively) with TMS as internal reference. IR spectra were recorded on a Research Series FT-IR using KBr disks in the range $4000\text{--}500\text{ cm}^{-1}$. The compounds $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{COD})]$ [52], 1-(2-aminoethyl)-3-ethylurea [53] and *N*-(*n*-propyl)-2-pyridylmethanimine (**PyPr**) [54] were synthesised according to previously reported procedures.

4.2. Synthesis of 1-(2-(1-(pyridin-2-yl)ethylideneamino)ethyl)-3-ethylurea (**PyUr**)

2-acetylpyridine (2.02 ml, 18.02 mmol) was placed in a flask containing $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHC}(\text{=O})\text{NHCH}_2\text{CH}_3$ (2.51 g, 18.9 mmol) in dry toluene (20 ml). The mixture was refluxed for 4 h using a Dean–Stark apparatus to remove the water formed in the reaction. Upon cooling a solid product precipitated. The volume of the toluene was then reduced under reduced pressure and ether was added to precipitate more solid. The solid was then recrystallized by using a CH_2Cl_2 /hexane mixture giving a pale cream product. Yield = 3.61 g, 15.43 mmol, 86%. Anal. Found: C 61.48; H 7.78; N 24.00. $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}$ requires C: 61.52; H: 7.74; N: 23.91%. ^1H NMR in CDCl_3 : δ 1.08 (t, 3H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 7.0$ Hz), 2.35 (s, 3H, $-\text{N}=\text{C}-\text{CH}_3$), 3.18 (dt, 2H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 7.0$ Hz, 6.5 Hz), 3.57 (broad, 4H, $-\text{CH}_2\text{CH}_2-$), 4.91 (broad, 2H, NH), 7.28 (dd, 1H, pyridine- H^4 , $^3J_{\text{HH}} = 6.2$ Hz), 7.70 (dd, 1H, pyridine- H^3 , $^3J_{\text{HH}} = 7.9$ Hz), 7.99 (d, 1H, pyridine- H^2 , $^3J_{\text{HH}} = 7.9$ Hz), 8.59 (d, 1H, pyridine- H^5 , $^3J_{\text{HH}} = 4.7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ in CDCl_3 : δ 14.7 (CH_3CH_2-), 15.5 ($-\text{N}=\text{C}-\text{CH}_3$), 35.2 (CH_3CH_2-), 41.5, 52.9 (CH_2CH_2), 120.9 (pyridine-C2), 124.3 (pyridine-C4), 136.3 (pyridine-C3), 148.4 (pyridine-C5), 157.4 (C=O), 159.2 (pyridine-C1), 168.3 (C=N). MS-Cl(+) *m/z* (rel. intensity): 235 (100) $[\text{M} + \text{H}]^+$, 132 (38) $[\text{H}_2\text{NCH}_2\text{CH}_2\text{NC}(\text{O})\text{NH}\text{Et}]^+$. Accurate mass Cl 235.1548 $[\text{M} + \text{H}]^+$ $\text{C}_{12}\text{H}_{19}\text{N}_4\text{O}$.

4.3. Synthesis of $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{PyUr})]$ (**1**)

PyUr (0.89 g, 3.85 mmol) was dissolved in CH_2Cl_2 (50 ml) giving a pale yellow solution. $[\text{Pd}(\text{CH}_3)\text{Cl}(\text{COD})]$ (1.00 g, 3.85 mmol) was added in one portion

to the solution which became a bright yellow suspension. The reaction mixture was allowed to stir for a further 20 min. The volume of CH_2Cl_2 was reduced to about 15 ml and the reaction mixture was filtered. The solid was washed with ether (20 ml) and dried under reduced pressure. The product contained a mixture of the *cis* and *trans* isomers. Yield = 1.32 g, 3.38 mmol, 88%. Anal. Found: C: 39.76; H: 5.54; N: 14.30. $\text{C}_{13}\text{H}_{21}\text{N}_4\text{OPdCl}$ requires C: 39.91; H: 5.41; N: 14.32%. ^1H NMR in CDCl_3 for *trans* isomer: δ 0.70 (s, 3H, PdCH_3), 1.08 (t, overlapping with *cis* isomer, 3H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.0$ Hz), 2.54 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 3.17–3.45 (m, 4H, $-\text{CH}_2\text{CH}_2-$, overlapping with *cis* isomer), 3.99 (t, 2H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.0$ Hz), 5.01 (br, 1H, NH), 5.73 (br, 1H, NH), 7.57 (m, 1H, pyridine- H^4 overlapping), 7.82 (m, 1H, pyridine- H^2 , overlapping), 7.98 (ddd, pyridine- H^3 , $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, $^3J_{\text{HH}} = 3.5$ Hz), 8.98 (dd, pyridine- H^5 , $^3J_{\text{HH}} = 6.0$ Hz, $^3J_{\text{HH}} = 3.5$ Hz). ^1H NMR in CDCl_3 for *cis* isomer: δ 0.90 (s, 3H, PdCH_3), 1.08 (t, overlapping with *trans* isomer, 3H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.0$ Hz), 2.46 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 3.17–3.45 (m, 2H, $-\text{CH}_2\text{CH}_2-$, overlapping with *trans* isomer), 4.13 (t, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.5$ Hz), 5.25 (t, NH, $^3J_{\text{HH}} = 6.0$ Hz), 5.82 (t, NH, $^3J_{\text{HH}} = 6.0$ Hz), 7.57 (m, 1H, pyridine- H^4 , overlapping), 7.82 (m, 1H, pyridine- H^2 , overlapping), 8.04 (ddd, pyridine- H^3 , $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HH}} = \text{unresolved}$, $^3J_{\text{HH}} = 2.0$ Hz), 8.59 (dd, pyridine- H^5 , $^3J_{\text{HH}} = 4.5$ Hz, $^3J_{\text{HH}} = \text{unresolved}$). IR ($\nu_{\text{max}}/\text{cm}^{-1}$) (KBr): 3351, 3346 (N–H), 2964, 2932, 2889 (C–H), 1625 (C=O), 1598, 1567 (pyridine C=C and C=N). FAB(+)-MS m/z (relative intensity): 393 (4) [LPdMeCl] $^+$, 377 (50) [LPdCl] $^+$, 355 (100) [LPdMe] $^+$, 340 (51) [LPd] $^+$.

4.4. Synthesis of [$\text{Pd}(\text{CH}_3)(\text{PyUr})$][BF_4] (2)

Complex **1** (0.15 g, 0.38 mmol) was dissolved in CH_2Cl_2 (20 ml). AgBF_4 (0.08 g, 0.40 mmol) was added in one portion to the mixture, resulting in the precipitation of AgCl from the reaction. This mixture was stirred for 15 min and then filtered through a glass-fibre filter. The resulting yellow solution was evaporated to dryness and washed with diethyl ether (15 ml). Yield = 0.12 g, 0.27 mmol, 71%. Anal. Found: C: 36.88; H: 4.44; N: 12.32. $\text{C}_{13}\text{H}_{20}\text{N}_4\text{OPdBF}_4 \cdot 0.25\text{C}_4\text{H}_8\text{O}$ requires C: 36.57; H: 4.82; N: 12.19%. ^1H NMR in CDCl_3 : δ 1.13 (t, 3H, CH_2CH_3 , $^3J_{\text{HH}} = 7.5$ Hz), 1.17 (s, 3H, PdCH_3), 2.38 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 3.19 (m, 2H, $-\text{CH}_2\text{CH}_3$), 3.62 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 6.05 (br, 1H, NH), 6.58 (br, 1H, NH), 7.58 (ddd, 1H, pyridine- H^4 , $^3J_{\text{HH}} = 7.0$ Hz, $^3J_{\text{HH}} = 5.5$ Hz, $^4J_{\text{HH}} = 1.0$ Hz), 7.83 (dd, 1H, pyridine- H^2 , $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = \text{unresolved}$), 8.09 (ddd, 1H, pyridine- H^3 , $^3J_{\text{HH}} = 9.5$ Hz, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.5$ Hz), 8.55 (dd, 1H, pyridine- H^5 , $^3J_{\text{HH}} = 4.5$ Hz, $^4J_{\text{HH}} = \text{unresolved}$). IR ($\nu_{\text{max}}/\text{cm}^{-1}$) (KBr): 3339 (N–H), 1637 (C=O), 1560 (C=N), 1063 (BF_4). FAB(+)-

MS m/z (rel. intensity): 355 (18) [$\text{Pd}(\text{CH}_3)(\text{PyUr})$] $^+$, 340 (9) [LPd] $^+$, 295 (3) [$\text{LPd}-\text{NHCH}_2\text{CH}_3$] $^+$.

4.5. Preparation of [$\text{Pd}\{\text{C}(\text{=O})\text{CH}_3\}\text{Cl}(\text{PyUr})$] (3)

Complex **1** (0.15 g, 0.38 mmol) was partially dissolved in CH_2Cl_2 (25 ml). Carbon monoxide was bubbled at atmospheric pressure through the solution and a clear yellow solution formed immediately. The carbon monoxide was bubbled through the mixture for a further 5 min. Hexane (25 ml) was added to the mixture and the reaction solvent was slowly removed under reduced pressure, resulting in the precipitation of a bright yellow solid. Yield = 0.11 g, 0.26 mmol, 69%. A mixture of *cis* and *trans* in an approximately 1:1 ratio was obtained. Anal. Found: C: 39.78; H: 5.21; N: 13.37. $\text{C}_{14}\text{H}_{21}\text{N}_4\text{O}_2\text{PdCl}$ requires C: 40.14, H: 5.02, N: 13.38%. ^1H NMR in CDCl_3 for *trans* isomer: δ 1.07 (t, 3H, $-\text{CH}_2\text{CH}_3$, overlapping with *cis* isomer), 2.48 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 2.54–2.60 (s, 3H, $\text{Pd}-\text{C}(\text{=O})\text{CH}_3$ overlapping with *cis* isomer), 3.16 (m, 2H, $-\text{CH}_2\text{CH}_2-$, overlapping with *cis* isomer), 3.44 (m, 2H, $-\text{CH}_2\text{CH}_2-$, overlapping with *cis* isomer), 4.02 (t, 2H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.5$ Hz), 5.74 (br, s, 1H, NH), 5.85 (br, t, 1H, NH), 7.56 (ddd, 1H, pyridine- H^4 overlapping), 7.83 (m, 1H, pyridine- H^2 overlapping), 8.02 (m, 1H, pyridine- H^3 overlapping), 8.84 (d, 1H, pyridine- H^5 , $^3J_{\text{HH}} = 4.5$ Hz). ^1H NMR in CDCl_3 for *cis* isomer: δ 1.07 (t, 3H, $-\text{CH}_2\text{CH}_3$, overlapping with *trans* isomer), 2.45 (s, 3H, $\text{CH}_3\text{C}=\text{N}$), 2.54–2.60 (s, 3H, $\text{Pd}-\text{C}(\text{=O})\text{CH}_3$ overlapping with *trans* isomer), 3.16 (m, 2H, $-\text{CH}_2\text{CH}_2-$, overlapping with *trans* isomer), 3.44 (m, 2H, $-\text{CH}_2\text{CH}_2-$, overlapping with *trans* isomer), 3.86 (t, 2H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{HH}} = 6.5$ Hz), 4.95 (br, s, 1H, NH), 5.14 (br, t, 1H, NH), 7.56 (ddd, 1H, pyridine- H^4 overlapping), 7.83 (m, 1H, pyridine- H^2 overlapping), 8.02 (m, 1H, pyridine- H^3 overlapping), 8.37 (d, 1H, pyridine- H^5 , $^3J_{\text{HH}} = 5.0$ Hz). IR ($\nu_{\text{max}}/\text{cm}^{-1}$) (KBr): 3366, 3314 (N–H), 1682, 1663 (C=O), 1632 (C=N), 1574 (pyridine). FAB(+)-MS m/z (rel. intensity): 421 (5) [$\text{M} + \text{H}$] $^+$, 383 (12) [$\text{M}-\text{Cl}$] $^+$, 377 (22) [$\text{M}-\text{C}(\text{O})\text{Me}$] $^+$, 355 (82) [PyUrPdMe] $^+$, 340 (100) [PyUrPd] $^+$.

4.6. Synthesis of [$\text{Pd}\{\text{C}(\text{=O})\text{CH}_3\}(\text{PyUr})$][BF_4] (4)

Method A – A solution of complex **2** was prepared by addition of AgBF_4 (0.05 g, 0.25 mmol) to a solution of complex **1** (0.10 g, 0.25 mmol) in CH_2Cl_2 (15 ml). The precipitated AgCl was removed by filtration from the solution and then $\text{CO}_{(\text{g})}$ was bubbled through the filtrate for 2 min. An immediate change of colour to a brighter and more intense yellow solution was observed. A small amount of a black solid precipitated which was filtered and the solvent from the resulting filtrate was removed under reduced pressure. Diethyl ether was added to the residue and rapidly stirred to yield a fine yellow

solid. Yield = 0.10 g, 0.21 mmol, 85% (the products obtained via method A and B have practically the same spectroscopic characterisation; only one of them is show below).

Method B – AgBF₄ (0.025 g, 0.13 mmol) was added in one portion to a solution of complex **3** (0.05 g, 0.12 mmol) in CH₂Cl₂ (15 ml) resulting in the precipitation of AgCl. The reaction mixture was left stirring for 10 min and then filtered. A yellow solid was formed by addition of hexane (10 ml) to the filtrate. The solid was washed with diethyl ether (10 ml) and dried under reduced pressure. Yield = 0.04 g, 0.085 mmol, 71%. Anal. Found: C: 35.75; H: 4.68; N: 11.61. C₁₄H₂₁N₄O₂PdBF₄ requires: C: 35.72; H: 4.50; N: 11.90%. ¹H NMR in CDCl₃: δ 1.19 (t, 3H, –CH₂CH₃, ³J_{HH} = 7.0 Hz), 2.40 (s, 3H, CH₃C=N), 2.56 (s, 3H, Pd–C(=O)CH₃), 3.11 (m, 2H, –CH₂CH₃), 3.50 (m, 2H, –CH₂CH₂–), 3.64 (m, 2H, –CH₂CH₂–), 6.11 (br, 1H, NH), 6.70 (br, 1H, NH), 7.64 (ddd, 1H, pyridine-H⁴, ³J_{HH} = 7.5 Hz, ³J_{HH} = 5.5 Hz, ⁴J_{HH} = 1.0 Hz), 7.93 (d, pyridine-H^{2,3}, ³J_{HH} = 7.5 Hz), 8.11 (dd, 1H, pyridine-H⁵, ³J_{HH} = 9.5 Hz, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.5 Hz), 8.51 (dd, 1H, pyridine-H⁵, ³J_{HH} = 4.5 Hz, ⁴J_{HH} = unresolved). IR (ν_{max}/cm⁻¹) (KBr): 3404 (N–H), 1701 (C=O), 1643 (C=O), 1599 (C=N pyridine), 1084 (BF₄). FAB(+)-MS *m/z* (rel. intensity): 386 (14) [M–BF₄]⁺, 355 (100) [PyUrPdMe]⁺, 340 (47) [PyUrPd]⁺.

4.7. Synthesis of [Pd(CH₃)Cl(PyPr)] (**5**)

Ligand **PyPr** (0.22 g, 1.38 mmol) was dissolved in dichloromethane (30 ml) to give a pale yellow solution. To this was added [Pd(CH₃)Cl(COD)] as a solid (0.365 g, 1.38 mmol) giving a yellow suspension. The mixture was then stirred for 20 min, after which time the volume was reduced to ca. 15 ml under reduced pressure and the solid collected by filtration. The yellow solid was washed with diethyl ether (20 ml) and dried under reduced pressure to give a solid containing both the *cis* and *trans* isomers of **5**. Yield 0.36 g, 1.13 mmol, 82%. Anal. Found: C, 41.40; H, 5.26; N, 8.62. C₁₁H₁₇N₂PdCl requires: C, 41.40; H, 5.37; N, 8.78%. ¹H NMR in CDCl₃ for *trans* isomer: δ 0.98 (s, 3H, Pd–CH₃), 1.00 (t, 3H, –CH₂CH₂CH₃, ³J_{HH} = 7.4 Hz, overlapping with *cis* isomer), 1.72 (m, 2H, –CH₂CH₂CH₃, overlapping with *cis* isomer) 2.36 (s, 3H, CH₃–C=N), 3.96 (t, 2H, –CH₂CH₂CH₃, ³J_{HH} = 7.4 Hz), 7.56 (dd, 1H, pyridine-H⁴, ³J_{HH} and ⁴J_{HH} = unresolved, overlapping), 7.77–7.96 (m, 2H, pyridine-H^{2,3} overlapping), 9.16 (d, 1H, pyridine-H⁵, ³J_{HH} = 4.9 Hz). ¹H NMR in CDCl₃ for *cis* isomer: δ_H = 0.88 (s, 3H, Pd–CH₃), 1.05 (t, 3H, –CH₂CH₃, ³J_{HH} = 7.4 Hz, overlapping with *trans* isomer), 1.76 (m, 2H, –CH₂CH₂CH₃, overlapping with *trans* isomer), 2.44 (s, 3H, CH₃–C=N), 3.75 (t, 2H, –CH₂CH₃,

³J_{HH} = 7.8 Hz), 7.60 (dd, 1H, pyridine-H⁴, ³J_{HH} and ⁴J_{HH} = unresolved, overlapping with *trans* isomer), 7.77–7.96 (m, 2H, pyridine-H^{2,3} overlapping with *trans* isomer), 8.65 (d, 1H, pyridine-H⁵, ³J_{HH} = 5.4 Hz). IR (ν_{max}/cm⁻¹, KBr): 2966 (C–H), 2935 (C–H), 2875 (C–H), 1587 (C=N imine), 1566 (C=N pyridine).

4.8. General procedure for the CO/Styrene co-polymerization

The corresponding palladium pre-catalyst (either **1** or **5**) was dissolved in the minimum amount of 2,2,2-trifluoroethanol (~20 ml) and one equivalent of the silver salt added as a solid. The resulting yellow solution was stirred for 15 min and then filtered to remove the AgCl formed. To this was added styrene and the solution put into an autoclave anaerobically. The vessel was pressurized to 10 atm with CO(g) and stirred at room temperature for 24 h, after which time the vessel was opened and the polymer suspension removed. The suspension was reduced to dryness on the rotary evaporator to give the crude pale grey polymer which was then washed with dichloromethane, diethyl ether and methanol and dried under reduced pressure. Purification of the polymers was achieved by dissolving them in hexafluoroisopropanol followed by filtration through cotton wool and celite in a pipette to remove black palladium. The solvent was then allowed to evaporate and the white polymer collected and dried under reduced pressure. Yields were calculated using the mass of polymer produced and assuming a perfectly alternating polymer.

4.8.1. Characterization of polymer formed using **1** and AgPF₆

Yield 0.64 g, 30%. *M*_w = 4202.80, *M*_n = 4086.25, *M*_w/*M*_n = 1.03. IR (ν_{max}/cm⁻¹, KBr): 1696 (C=O). ¹H NMR in a mixture of HFIP and CDCl₃: δ 7.53–6.61 (m, 5H, Ph), 4.12 (broad triplet, 1H, CHCH₂), 2.98 and 2.92 (each signal a broad doublet, 2H, CHCH₂). ¹³C{¹H} NMR in a mixture of HFIP and CDCl₃: δ 210.8 (C=O), 135.4 (Ph–C_i), 129.7, 128.5 (Ph–C_{o,m}), 54.4 (CH–CH₂), 43.0 (CH–CH₂), m.p. 246–250 °C.

4.8.2. Characterization of polymer formed using **1** and AgBF₄

Yield 0.82 g, 39%. *M*_w = 5650.60, *M*_n = 5339.44, *M*_w/*M*_n = 1.06. IR (ν_{max}/cm⁻¹, KBr): 1707 (C=O). ¹H NMR in a mixture of HFIP and CDCl₃: δ 7.23–6.60 (m, 5H, Ph), 4.10 (broad triplet, 1H, CHCH₂), 3.00 and 2.88 (each signal a broad doublet, 2H, CHCH₂). ¹³C{¹H} NMR in a mixture of HFIP and CDCl₃: δ 210.8 (C=O), 135.5 (Ph–C_i), 129.9, 128.5 (Ph–C_{o,m}), 54.4 (CH–CH₂), 43.0 (CH–CH₂), m.p. 252–254 °C.

4.8.3. Characterization of polymer formed using **5** and AgPF₆

Yield 0.65 g, 31%. $M_w = 4612.13$, $M_n = 4442.28$, $M_w/M_n = 1.03$. IR ($\nu_{\max}/\text{cm}^{-1}$, KBr): 1696 (C=O). ¹H NMR in a mixture of HFIP and CDCl₃: δ 7.26–6.57 (m, 5H, Ph), 4.12 (broad triplet, 1H, CHCH₂), 2.97 and 2.86 (each signal a broad doublet, 2H, CHCH₂). ¹³C{¹H} NMR in a mixture of HFIP and CDCl₃: δ 210.8 (C=O), 135.4 (Ph-C_i), 129.6, 128.4 (Ph-C_{o,m}), 54.3 (CH-CH₂), 43.0 (CH-CH₂), m.p. 248–254 °C.

4.8.4. Characterization of polymer formed using **5** and AgBF₄

Yield 0.74 g, 35%. $M_w = 4250.63$, $M_n = 4121.28$, $M_w/M_n = 1.03$. IR ($\nu_{\max}/\text{cm}^{-1}$, KBr): 1696 (C=O). ¹H NMR in a mixture of HFIP and CDCl₃: δ 7.26–6.57 (m, 5H, Ph), 4.07 (broad triplet, 1H, CHCH₂), 2.94 and 2.85 (each signal a broad doublet, 2H, CHCH₂). ¹³C{¹H} NMR in a mixture of HFIP and CDCl₃: δ 210.6 (C=O), 135.4 (Ph-C_i), 129.5, 128.4 (Ph-C_{o,m}), 54.2 (CH-CH₂), 42.9 (CH-CH₂), m.p. 246–252 °C.

4.9. Synthesis of [Pd(η^3 -CH₂CHCH₂)(PyUr)][BF₄]**(6)**

To a solution of **1** (0.10 g, 0.26 mmol) in CH₂Cl₂ (20 ml) solid AgBF₄ (0.05 g, 0.26 mmol) was added. The resulting mixture was left to stir for 15 min. The mixture was then filtered under nitrogen and degassed 2-propen-1-ol (10 ml) was added to the filtrate. The reaction mixture was left to stir overnight. After this time a small amount of a black solid was removed by filtration, followed by removal of all volatiles under reduced pressure. The resulting residue was then washed with diethyl ether (2 × 25 ml) to remove the excess olefin. Yield = 0.05 g, 0.11 mmol, 41%. Anal. Found C: 38.22; H: 5.41; 9.86 C₁₅H₂₃N₄OBF₄Pd requires: 38.45; H: 4.95; 11.96. ¹H NMR in CDCl₃: δ 1.03 (t, 3H, -CH₂CH₃, ³J_{HH} = 7.0 Hz), 2.54 (s, 3H, CH₃C=N), 3.13 (dq, 2H, -CH₂CH₃, ³J_{HH} = 7.0 Hz, ³J_{HH} = 5.5 Hz), 3.40 (d, 2H, CH₂CHCH₂, ³J_{HH} = 12.5 Hz), 3.62 (m, 2H, -CH₂CH₂-), 4.06 (d, 2H, CH₂CHCH₂, ³J_{HH} = 7.0 Hz), 4.13 (t, 2H, -CH₂CH₂-, ³J_{HH} = 5.0 Hz), 5.21 (br, 1H, NH), 5.71 (t, 1H, NH, ³J_{HH} = 5.5 Hz), 5.89 (tt, 1H, CH₂CHCH₂, ³J_{HH} = 12.5 Hz, ³J_{HH} = 7.0 Hz), 7.61 (ddd, 1H, pyridine-H⁴, ³J_{HH} = unresolved), 8.00 (br d, 1H, pyridine-H², ³J_{HH} = 8.0 Hz), 8.14 (ddd, 1H, pyridine-H³, ³J_{HH} = 9.5 Hz, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.5 Hz), 8.66 (dd, 1H, pyridine-H⁵, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = unresolved). IR ($\nu_{\max}/\text{cm}^{-1}$) (KBr): 3394 (N-H), 1647 (C=O), 1596 (C=N), 1563 (C=C), 1084, 1039 (BF₄). MS-FAB(+) *m/z* (rel. intensity): 381 (100) [M-BF₄]⁺, 340 (22) [PyUrPd]⁺.

4.10. Crystallography

Crystal data for **1**: C₁₃H₂₁N₄OClPd, $M = 391.19$, monoclinic, $P2_1/c$ (no. 14), $a = 9.2838(4)$, $b = 19.7967(14)$, $c = 9.0313(5)$ Å, $\beta = 103.274(4)^\circ$, $V = 1615.5(2)$ Å³, $Z = 4$, $D_c = 1.608$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 10.800$ mm⁻¹, $T = 293$ K, yellow prismatic needles; 2371 independent measured reflections, F^2 refinement, $R_1 = 0.058$, $wR_2 = 0.134$, 1826 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\max} = 120^\circ$], 207 parameters. CCDC 261365.

Crystal data for **4**: [C₁₄H₂₁N₄O₂Pd][BF₄], $M = 470.56$, monoclinic, $P2_1/c$ (no. 14), $a = 8.5822(12)$, $b = 17.359(2)$, $c = 12.8659(12)$ Å, $\beta = 98.960(9)^\circ$, $V = 1893.4(4)$ Å³, $Z = 4$, $D_c = 1.651$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 8.410$ mm⁻¹, $T = 293$ K, yellow plates; 2803 independent measured reflections, F^2 refinement, $R_1 = 0.061$, $wR_2 = 0.127$, 1737 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\max} = 120^\circ$], 256 parameters. CCDC 261366.

Crystal data for **6**: [C₁₅H₂₃N₄OPd][BF₄] · CH₂Cl₂, $M = 553.51$, monoclinic, $P2_1/c$ (no. 14), $a = 13.387(3)$, $b = 18.808(4)$, $c = 9.5682(14)$ Å, $\beta = 108.826(13)^\circ$, $V = 2280.2(8)$ Å³, $Z = 4$, $D_c = 1.612$ g cm⁻³, $\mu(\text{Cu K}\alpha) = 9.151$ mm⁻¹, $T = 183$ K, pale yellow platy needles; 3357 independent measured reflections, F^2 refinement, $R_1 = 0.055$, $wR_2 = 0.135$, 2631 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\max} = 120^\circ$], 310 parameters. CCDC 261367.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.03.037.

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