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Fluxional chloro-pyrrole–Pd(II) complex to cationic η^2-pyrrole–Pd(II) complex: subtlety in structure-directed bonding mode†

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Fluxionality in η^1-aromatic carbocyclic-ligated Pd(II) complexes is retained if the η^1-carbon is replaced with an N atom through "hemilabile" palladium–carbon η^1-pyrrole ligation. Herein, we report and characterize a tetra-coordinated neutral chloro-pyrrole–Pd(II)-π-allyl complex, which shows dynamic behavior at room temperature. Upon chlorine abstraction by $AgSbF_6$, a cationic palladium complex is formed, where the coordination sphere of the metal is completed by the coordination of one C=C double bond of the pyrrole ring. This cationic η^2-pyrrole-ligated Pd(II)-π-allyl complex was characterized crystallographically. The coordination mode of the pyrrole in these isostructural complexes subtly changes with a change in carbon ligand (σ or π).

Two or more forms of one molecule can interchange reversibly among themselves due to molecular fluxionality, and this process occurs through the exchange of atoms with respect to symmetry-equivalent positions.[1] Fluxional molecules have taken a special place in chemistry due to the temperature-dependent dynamic nature of their stereoelectronic properties.[2] The fluxionality of molecules has been utilized in catalysis.[3–5] Specifically, the fluxionality of metal-containing molecules has an influence on catalytic activity.[5,6]

In some palladium complexes, there is an uncommon bonding interaction between the metal and the *ipso* carbon of a coordinated aromatic ring.[7–9] Ligands with a β-aryl ring or a biaryl motif form such palladium complexes, which are very rare in the literature. All these complexes are formed through η^1-aromatic carbocyclic ligation. Some of these complexes are shown in Fig. 1 (complex I–III). Sarkar *et al.* modified the ligand by replacing the *ipso* carbon with nitrogen and showed another type of fluxional "hemilabile" palladium–carbon bonding interactions through η^1-pyrrole ligation in complex **1** (Fig. 1).[10] Although such interactions are indeed rare, a few instances of such uncommon bonding between palladium and carbon have been described by different groups.[11–17] The existence of such "weak" bonds underscores the interplay of subtle orbital overlaps that are probably intimately linked with the stereochemical arrangement of atoms around the metal, *i.e.* dependent on the specific structure of the molecule. Once such a structure is distorted, the bonding may weaken and/or disappear altogether. In the context of our study with palladium complex **1** (Fig. 1), we sought to investigate the nature of the bonding interaction between pyrrole and palladium, where palladium is coordinated with a π-allyl ligand. In the fluxional Pd-complexes with η^1-ligation shown in Fig. 1, the coordination number of the metal ion is four. In this study, we synthesized a tetra-coordinated pyrrole–Pd(II)-allyl complex and explored its fluxionality. Furthermore, we extended the work to the synthesis of η^2-pyrrole-ligated Pd(II) complexes along with molecular orbital calculations to study the nature of bonding in these complexes.

Palladium(II) complex **2** bearing 1-(2-diphenylphosphino phenyl)-2,5-dimethyl-1*H*-pyrrole (**L1**) was prepared from the dimeric complex $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and is shown in Scheme 1. Treatment of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with the ligand **L1**[18] in dichloromethane resulted in a yellow solution which produced a yellow complex **2** (Scheme 1) in good yield after solvent evaporation. Complex **2** was characterized in the solution phase by NMR spectroscopy. The ^{1}H NMR spectrum of complex **2** is distinctly different from the spectrum of ligand **L1** and it can be recognized by the peaks of the allyl group. The single peak in the ^{31}P NMR spectra (δ 11.91 ppm) indicates that the reaction presented in Scheme 1 produces only complex **2**.

The fluxionality of the complex can be understood from its dynamic behavior, which was perceptible in its NMR spectra at variable temperature (Fig. 2). The synthesized complex **2** showed a fluxional behavior in the solution phase. The two methyl groups of the pyrrole ring of complex **2** seem to be non-equivalent, but, at room temperature, they are in equilibrium

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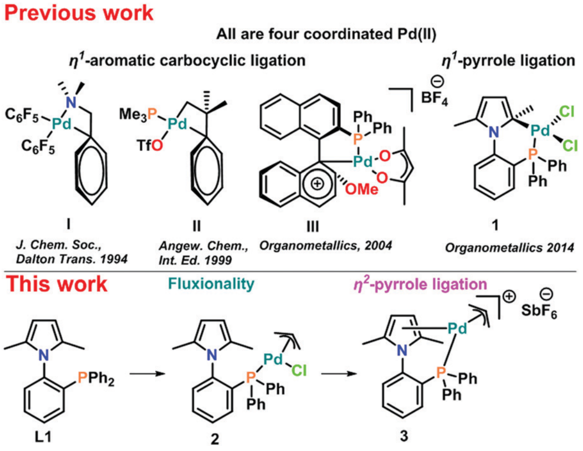
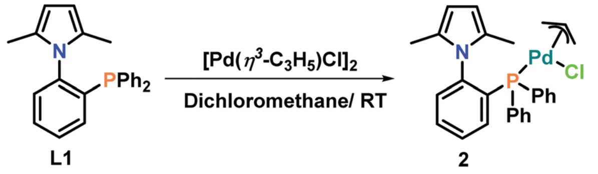


Fig. 1 Fluxional Pd-complexes and exploration of new complexes.



Scheme 1 Synthesis of complex **2**.

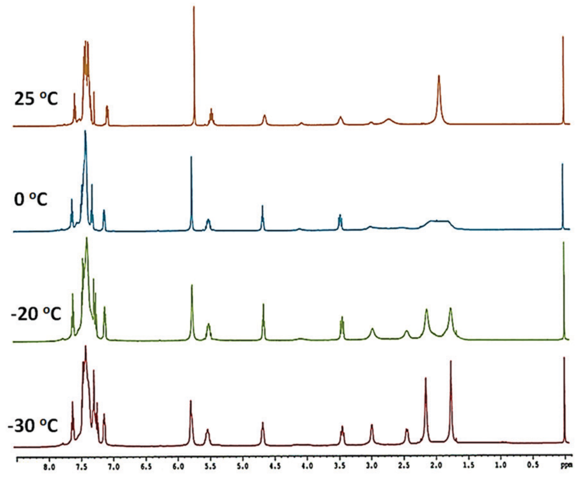


Fig. 2 ^{1}H NMR spectra of complex **2** at different temperatures.

and appear as equivalent. The six-proton broad singlet at 1.93 ppm is assigned to the two methyl groups on pyrrole. The protons 3H and 4H of pyrrole are indistinguishable; they appear as a sharp two-proton singlet at 5.72 ppm. The high-field three-proton singlet decoalesced into two signals (2.19 and 1.52 ppm) of equal intensity at −30 °C, but the singlet at 5.72 ppm revealed a small degree of line broadening (Fig. 2). Therefore, the rotation of the C–N bond is restricted at low temperature. At the coalescence temperature (0 °C) and below (−20 °C), the rate of exchange was calculated and the values are 444.06 and 160 rotations, respectively (see ESI†). The relatively broad signals of π-allyl protons at room temperature are better resolved as the temperature is lowered.

To get more clear evidence of dynamic behavior, we used single crystal X-ray crystallography to characterize complex **2** (Fig. 3), which was crystallized from acetone-hexane. The crystal structure of complex **2** reveals a near planar ligand arrangement at the palladium center where the metal is attached to one phosphine group, one chloride and one π-allyl group. It is clear that the pyrrole ring is oriented orthogonal to the phenyl ring and there is no bonding interaction with palladium (C2–Pd: 3.49 Å and N–Pd: 3.57 Å). A hindered rotation around the Ar–N axis at low temperature would explain the decoalescence phenomenon involving the two methyl groups. In this crystal structure, the pyrrole ring forms a 22.10° angle with the C–N axis, which facilitates the aforesaid rotation of pyrrole along the C–N axis. However, it is possible, at low temperature, that the angle decreases and the rotation becomes restricted due to the steric interaction between methyl groups and the allyl unit. The low temperature separation of π-allyl protons provides evidence of such interactions (Fig. 2).

Since complex **2** is already a 16e species with P, Cl and π-allyl donors, coordination by pyrrole is no longer necessary. Had the coordination by pyrrole been a strong one, in complex **2** the π-allyl group would have slipped into a η^1-allyl bonding mode to maintain the 16e configuration. We do not observe any such π to σ slippage of the allyl group.

By removing the chloride ion from Pd(II) in complex **2**, the newly synthesized complex **3** would be short of two electrons, becoming cationic. We then wished to examine whether coordination by pyrrole to Pd(II) is necessary in the new complex **3**, as seen in complex **1**.

Treatment of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with the ligand **L1** in dichloromethane resulted in a yellow solution that turned orange with the addition of $AgSbF_6$. After evaporation of the solvent under reduced pressure, the orange solid obtained was purified by recrystallization from acetone-hexane (Scheme 2).

The ^{1}H NMR spectrum of the pure complex **3** reveals two singlets at 1.89 and 1.34 ppm corresponding to methyl groups at the 2- and 5-position of pyrrole. Pyrrole 3H and 4H also appear as two distinct singlets at 6.16 and 6.64 ppm. The signals due to protons on the π-allyl group appear at the expected regions as

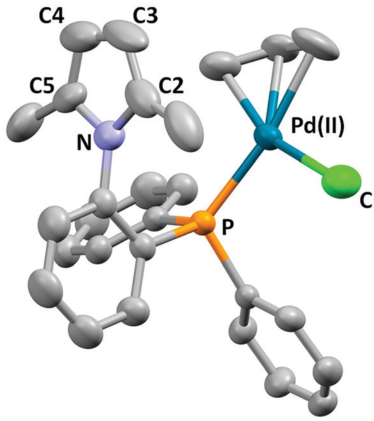
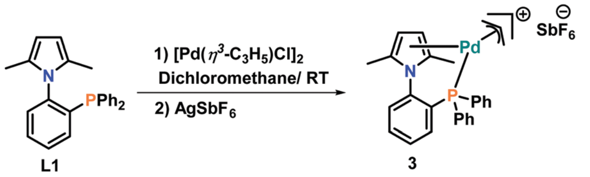


Fig. 3 Crystal structure of complex **2** at 30% probability level (CCDC number 2043271).†



Scheme 2 Synthesis of complex **3**.

well-separated multiplets. The signals due to other aromatic protons are clustered between 7.07 and 7.72 ppm (for more details, see Experimental section and ESI†). Well-separated signals for the methyl protons as well as 3H and 4H of pyrrole in complex **3** suggested an unsymmetrical and unwavering disposition of the pyrrole group.

The ORTEP diagram of a crystal of complex **3** (Fig. 4) disclosed that the bond between the pyrrole ring and palladium is not a formal σ-bond as was observed for complex **1** reported earlier.[10] The molecule has a distorted square planar arrangement around palladium where the metal is attached to phosphine, pyrrole and π-allyl groups. Pyrrole is bonded with palladium purely *via* an η^2-type of interaction; the C2–Pd and C3–Pd bond distances in complex **3** are nearly equal (2.386 and 2.371 Å, respectively). The C4–Pd and C5–Pd distances are 3.099 and 3.465 Å, respectively, which are larger than the C–Pd bond distance in η^4-coordinated Pd complexes.[19] This discarded the possibility of an η^4 coordination of pyrrole to Pd(II), leading to an 18-electron complex. Though η^2-pyrrole coordination to other metals, *e.g.* Os(II), Re(I) and W(0), has already been characterized crystallographically,[20–22] this η^2-pyrrole–Pd(II) interaction in complex **3** is reported and crystallographically characterized for the first time.

It is well known that Pd(II) forms stable 16e complexes with a large variety of ligands, where the metal ion is placed at the center of a square-planar (or distorted square-planar) coordination environment.[23] In complex **3**, in addition to 2e donation from the phosphine and 4e donation from the π-allyl group around the central Pd(II) ion with 8 electrons, the 16e configuration comprises 2e η^2-coordination by the pyrrole. Only a limited number of examples exist of η^2-coordination by arenes or heteroarenes to transition metals in organometallic complexes. Harman has extensively reported the chemistry of η^2-arene complexes of Os(II).[24,25] Entropy controlled, intramolecular η^2-arene coordination has been reported for palladium in mononuclear[7,26–29] and dinuclear[30,31] complexes or clusters.[17,32,33] Organometallic complexes featuring η^2-heteroarenes are relatively rare. Harman[34] described η^2-pyrrole complexes of Os(II) and Winter[35–40] studied η^2-pyrazolate complexes of a variety of metal ions.[41] The complex **3** is the first η^2-pyrrole–Pd(II) complex that has been isolated and structurally characterized. Only Pregosin reported[7] analogous complexes where η^2-arene coordination is facilitated by a neighboring phosphine donor.

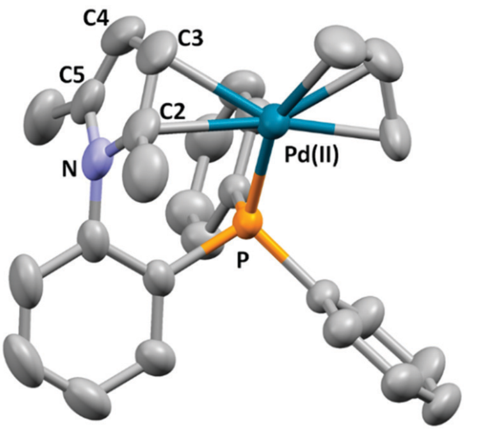


Fig. 4 The crystal structure of the molecular complex **3** at 30% probability level. SbF$_6$ is omitted for clarity (CCDC number 2043272).†

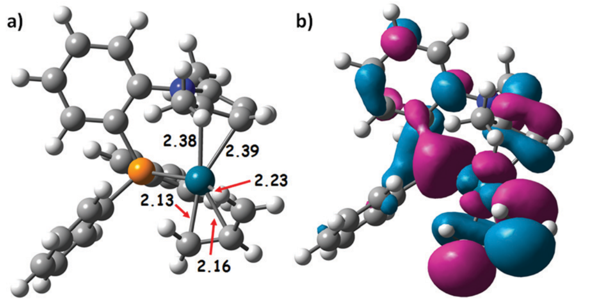


Fig. 5 (a) Optimized structures of **3**; (b) highest occupied molecular orbital of **3**. Bond distances are shown in Å. Hydrogen atoms are omitted for clarity in the molecular orbital picture.

Molecular orbital calculations using DFT were carried out for complex **3**, which reveal η^2-pyrrole–Pd(II) bonding in the energy-minimized structure (Fig. 5a). It is reasonable to assume that orbital orientation for the best overlap with a σ-donor will not be the same as required by a π-donor ligand (Fig. 5b). The bonding in complexes **1** and **3** differ in this respect. There was a possibility of the formation of η^1-ligation of pyrrole to Pd(II) in complex **3** just like in complex **1**. To obviate this possibility, we conceived model **4** (Fig. 6a) and optimized its structure using DFT calculations. The optimized results showed that model **4** is

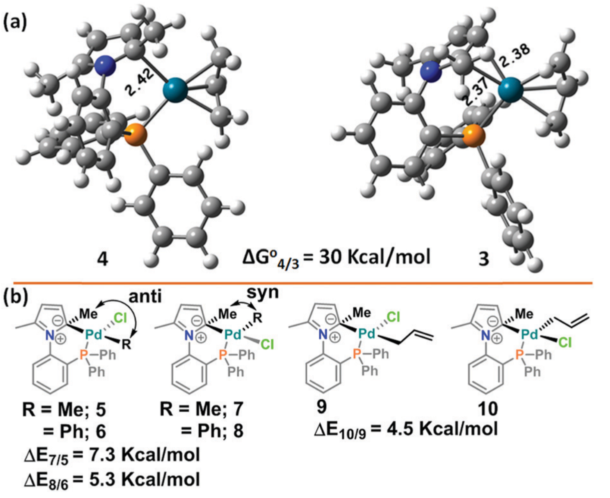


Fig. 6 DFT calculations of isostructural complexes showing that the coordination mode between the pyrrole moiety and Pd(II) depends on the σ or π donor carbon ligands of the complex.

30 kcal mol^{-1} less stable than complex **3** and the η^1-bond in model **4** is larger than both η^2-bonds of complex **3** (Fig. 6a).

We therefore investigated whether η^1 bonding by pyrrole through C2 is allowed for isostructural complexes if one chlorine atom is replaced by an alkyl or an aryl group (both σ-donors), using DFT calculations. According to theoretical calculations, η^1 coordination of pyrrole was found to be the preferred mode of bonding in the optimized structures of *anti*-isomers (**5** and **6**) (Fig. 6b). Since *anti*-isomers were found to be clearly more stable than *syn*-isomers (**7** and **8**) ($\Delta E_{8/6}$ = 5.3 or $\Delta E_{7/5}$ = 7.3 kcal mol^{-1}), the *syn*-isomers were not observed. In any case, theory predicts that an alkyl or aryl group at the *anti*-position would favor an unusual bond-η^1-coordination of pyrrole to the metal center. Encouraged by these results, molecular calculations were also performed on structures **9** and **10** (Fig. 6b) to optimize their geometries (starting structural parameters were taken from crystallographic data of complex **1** and Cl was replaced by a σ-allyl group). Structure **9** was 4.5 kcal mol^{-1} more stable than structure **10** according to the calculation. Both structures, however, are less stable (**9** by 6 kcal mol^{-1} and **10** by 10.5 kcal mol^{-1}) than the optimized structure of complex **3** (Fig. 5a). On one hand, this would explain why we do not observe any trace of **9** or **10** in the ^{1}H NMR spectrum. On the other, theory lends support to the preference of η^2-coordination by pyrrole in π-allyl complex **3**.

It is interesting to note that the order of the *trans* effect of the ligand is Ph > Me > allyl, but the order of energy difference in *syn*/*anti*-complexes (Fig. 6b) is Me > Ph > allyl. This change in order can be explained with the help of the size of the substituents. The phenyl ring attached to Pd interacts with the Ph rings of PPh_2 in complex **6**. This effect destabilizes the complexes somewhat, which is responsible for the decrease of energy. Such steric interaction is absent in the case of **5** (R = Me).

Conclusions

To summarize, we explored bonding preferences between pyrrole and a palladium ion in the framework of a structurally constrained, chelating ligand environment. We have synthesized and characterized a tetra-coordinated pyrrole–Pd(II)-π-allyl complex which shows dynamic behavior at room temperature. An η^2-pyrrole coordination has been crystallographically characterized for the first time in a Pd-π-allyl complex. Theoretical calculations reveal that the mode of coordination of a pyrrole moiety in isostructural complexes is often subtly dependent on the nature of carbon ligands (σ or π) present in the complex.

Conflicts of interest

There are no conflicts to declare.

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