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Chemical Communications

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View Article Online
DOI: 10.1039/D0CC04065G

COMMUNICATION

Synthetic Access to a Phosphorescent Non-Palindromic Pincer Complex of Palladium by a Double Oxidative Addition – Comproportionation Sequence†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A highly luminescent non-palindromic [(C^C^N)Pd] pincer complex forms upon reacting 3-pyridine-substituted 2,2'-diiodo-biphenyl with [Pd(PPh$_3$)$_4$]. This case study establishes for the first time that the title compound is formed via a double oxidative addition – comproportionation sequence. DFT and TDDFT calculations complement mechanistic and photophysical characterizations.

Pincer complexes[1] of platinum and gold gained increasing attention during the past 30 years due to their simple preparation[2] and appealing photophysical properties making them interesting for applications in photocatalysis[3] and electroluminescent devices,[4, 5] but in the field of catalysis[6] and biomedical applications[7] as well. Contrasting the plethora of investigations concerned with diphenylpyridine-based (C^N^C) pincer complexes, only one example of palladium (**1**) has been published in the literature until now (Figure 1).[8] Missing investigations on the (C^N^C) palladium complexes are, among other, mainly caused by the lack of feasible methods for their synthesis reported so far, and the fact that the only photophysically investigated complex [(C^N^C)Pd^{II}(py)] (py = pyridine) exhibits only poor luminescence properties in contrast to its platinum analogue.[9] Nevertheless, there are few reports on other emissive Pd complexes.[10] Che and co-workers developed tetradentate (C^C^N^O) ligands and applied them for the synthesis of Pd^{II} complexes highly phosphorescent in solution at room temperature.[11] A tetradentate ligand scaffold is certainly superior to tridentate pincers regarding the ability to suppress vibrational relaxation pathways of photoexcited states due to the even more rigid nature. However, tetradentate ligands occupy all coordination sites of a square-planar complex, which may not be desirable in view of potential catalytic applications.[12] For example, the (C^N^C) moiety was proven to show very promising chemical properties at ligated Au^{III} centres making them interesting for new chemical transformations.[13]

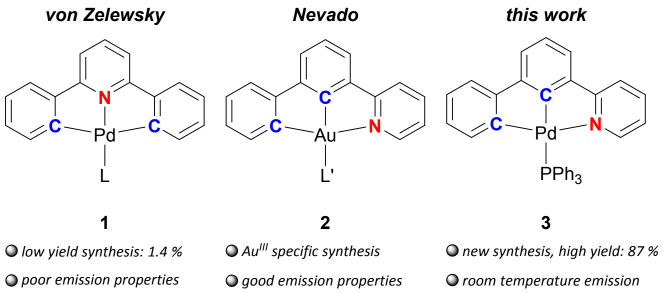

Figure 1. [(C^N^C)Pd^{II}] pincer complex **1** (L = SEt$_2$, pyridine) and [(C^C^N)Au^{III}] complexes **2** (L' = Cl, F, acetylide, aryl) reported in the literature; complex **3** described

In 2015, Nevado and co-workers described a non-palindromic[12, 14] biphenyl-based (C^C^N) ligand employed for cyclometalated Au^{III} complexes (**2** in Figure 1).[15] The non-palindromic (C^C^N) pincer ligand differs from the palindromic (C^N^C) motif regarding chemical properties due to the stronger *trans* influence of the carbon donor of the central phenyl ring.[15, 16] In addition, the [(C^C^N)Au^{III}] complexes outperform the majority of [(C^N^C)Au^{III}] analogues regarding emission quantum yields making them attractive for optoelectronic devices.[17] The higher emission efficiency was traced back to stronger ligand field splitting of the non-palindromic (C^C^N) scaffold compared to the (C^N^C) analogue (*cf.* Section S 5, ESI† for an in-depth discussion).[15, 18]

Here, we present a simple procedure for the preparation of a non-palindromic [(C^C^N)Pd^{II}] complex based on a double oxidative addition of 2,2'-diiodobiphenyl substituted in 3-position with pyridine. This simple high-yield synthesis of a palladium(II) pincer complex **3** employing two phenyl rings and one pyridine donor makes this structural motif accessible for investigations and applications, which are until now mainly covered by platinum, gold and other transition metals.[19] We use the analysis of photophysical properties as tool to shed light on the non-palindromic nature and impact of the (C^C^N) motif.

In a recent study, we have described the synthesis of pyridine-substituted 2,2'-diiodobiphenyl **5** as suitable pre-ligand for the preparation of [(C^C^N)Au^{III}] complexes.[20] Our initial intention was to use this diiodobiphenyl for the preparation of a Pd^{IV}

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† Electronic Supplementary Information (ESI) available: [Experimental details, NMR data, X-ray crystal structure data, quantum chemical calculations]. See DOI: 10.1039/x0xx00000x

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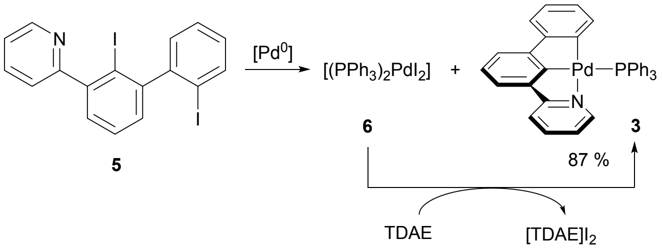
complex by double oxidative addition of Pd^0 into both iodophenyl groups of **5**. Bautista and co-workers reported on the oxidative addition of aryl iodides to Pd^{II} to readily happen if the aryl iodide exhibits a functional group, which is able to coordinate to the Pd^{II} centre.[21] Thus, we reacted **5** with [Pd(PPh$_3$)$_4$] in toluene (Scheme 1).



Scheme 1 Synthesis of [(C^C^N)Pd^{II}] complex **3**. [Pd^0] = [Pd(PPh$_3$)$_4$]. Conditions: toluene, 100 °C, 4 h.

Upon heating, the formerly yellow solution turned dark red (Figure S1, ESI†). After workup, two species could be isolated in equal amounts by manually picking crystals: [(PPh$_3$)$_2$PdI$_2$] (**6**) and the palladium(II) pincer complex **3.**

Full conversion of pre-ligand **5** was achieved by addition of one equivalent of tetrakis(dimethylamino)ethylene (TDAE) to reduce **6** *in situ*.[22] Following this procedure, the pincer complex **3** was obtained in 87 % overall yield in form of a yellow microcrystalline solid, which is luminescent under UV irradiation. Instead of [Pd(PPh$_3$)$_4$], the dichloride [(PPh$_3$)$_2$PdCl$_2$] may also be used when employing two equivalents TDAE.

The structure of **3** in the solid-state (Figure 2) shows the palladium centre being coordinated in a distorted square-planar fashion. The long Pd–P bond length of 236.8 pm is indicative for the strong *trans* influence of the carbon donor of the central phenyl ring and is comparable to the Pd–P bond length of typical Pd^0 phosphine complexes.[23] The calculated (RI-TPSS-D3(BJ)/def2-TZVP) Pd–P bond length of the hypothetical palindromic analogue [(C^N^C)Pd^{II}PPh$_3$] was found to be 224 pm, i.e., 12 pm shorter than experimentally found for **3** (calculated: 236 pm).

The simultaneous formation of pincer complex **3** in oxidation state +II and the diiodide **6** *a priori* suggested the intermediary formation of a Pd^{IV} species and their comproportionation with not yet reacted Pd^0 precursors. In principle, a bimetallic process involving the oxidative addition of two different metal centres into the two iodophenyl groups of **5** and subsequent intramolecular transmetalation could also be plausible. Such a bimetallic process should lead to a mixture of non-, mono- and diactivated **5** and derived products. However, the reaction compiled in Scheme 1 always yielded equal amounts of **3** and diiodide **6** with approximately 50 % conversion of pre-ligand **5**, which disagrees with a bimetallic mechanism.

To shed further light on this reaction, we performed a control experiment and reacted 2,2'-diiodobiphenyl (**S1**) with [Pd(PPh$_3$)$_4$] (Scheme S2, ESI†) upon which the diiodide **6** formed as well. However, the other product(s) of this reaction, a yellow solid, we were not able to identify. ^{31}P NMR spectroscopic investigations showed more than ten different NMR signals. Thus, the lateral pyridine donor of **5** is crucial for the formation of **3**.

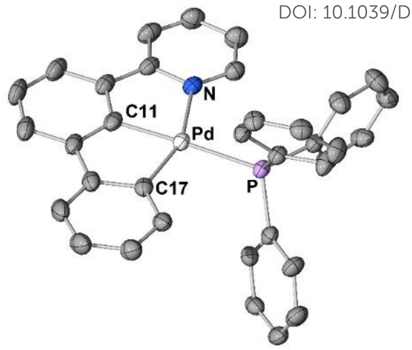


Figure 2 Molecular structure of **3**. Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Only one molecule of the asymmetric unit is shown. Selected bond lengths (pm) and angles (°): Pd–P 236.8(9), Pd–N 218.8(3), Pd–C11 197.3(4), Pd–C17 204.0(4), N–Pd–C11 78.3(2), C11–Pd–C17 79.7(2).

We further investigated the mechanistic pathway in more detail by DFT calculations (Scheme 2). Additional pathways are discussed in the Supporting Information (Section S6, ESI†).

[Pd(PPh$_3$)$_4$] is known to lose one or two ligands upon solvation making the Pd^0 atom reactive for oxidative addition.[24] We assume that, in a first step, [Pd^0(PPh$_3$)$_3$] oxidatively adds into the C–I bond of the central (**B**$_{cis}$) or lateral (**BB**$_{cis}$) iodophenyl group of **5** with loss of one PPh$_3$ ligand (L). A coordination of Pd^0 to the pyridine donor (**[5-PdL$_3$]**) does probably not precede a central addition since the hard donor pyridine will most likely not replace the softer PPh$_3$. Interestingly, the formation of **B**$_{cis}$ is slightly favoured over **BB**$_{cis}$ although the former is more sterically hindered. However, we identified dispersion interactions responsible for the opposite finding since optimization of structures without dispersion-corrected DFT[25] predicts the lateral addition to be favoured by −10.9 kJ mol^{-1}. Dispersion interaction was shown to often be responsible for chemical properties standing in contrast to considerations only based on a molecule's bulk, e.g. the dimerization of the (bulky) *tert*-butyl substituted Gomberg radical.[26]

After a first oxidative addition[‡] and *cis-trans* isomerization (**B**$_{trans}$/**BB**$_{trans}$) one PPh$_3$ is displaced leading to the Pd^{II} species **C**$_{trans}$ and **CC**$_{trans}$, respectively. The former is highly stabilized due to (C^N) chelation. Thus, **CC**$_{trans}$ is calculated to be 54.4 kJ mol^{-1} higher in energy than **C**$_{trans}$. We note that (C^N) cyclometalation of **B**$_{cis}$ may precede *cis-trans* isomerization (cf. Scheme S5, ESI†). Species **C**$_{trans}$ and **CC**$_{trans}$ undergo a second oxidative addition to form the same Pd^{IV} intermediate **D**$_{trans}$, stabilized by the (C^C^N) pincer. A species **G** with a second coordinated PPh$_3$ instead of pyridine is disfavoured by an energy of 79.4 kJ mol^{-1}. Thus, the pyridine donor not only lowers the energy of intermediates of the pathway involving central oxidative addition (blue), but also stabilizes Pd^{IV} intermediates as well. Finally, **D**$_{trans}$ readily comproportionates with [Pd(PPh$_3$)$_3$] to form the final products **6** and **3**.

Pincer complex **3** shows a blue shifted absorption in the less polar solvent CH$_2$Cl$_2$ compared to tetrahydrofurane (THF) indicating a charge-transfer character of the first absorption bands (Figure 3). Slight vibronic structures with line spacings of

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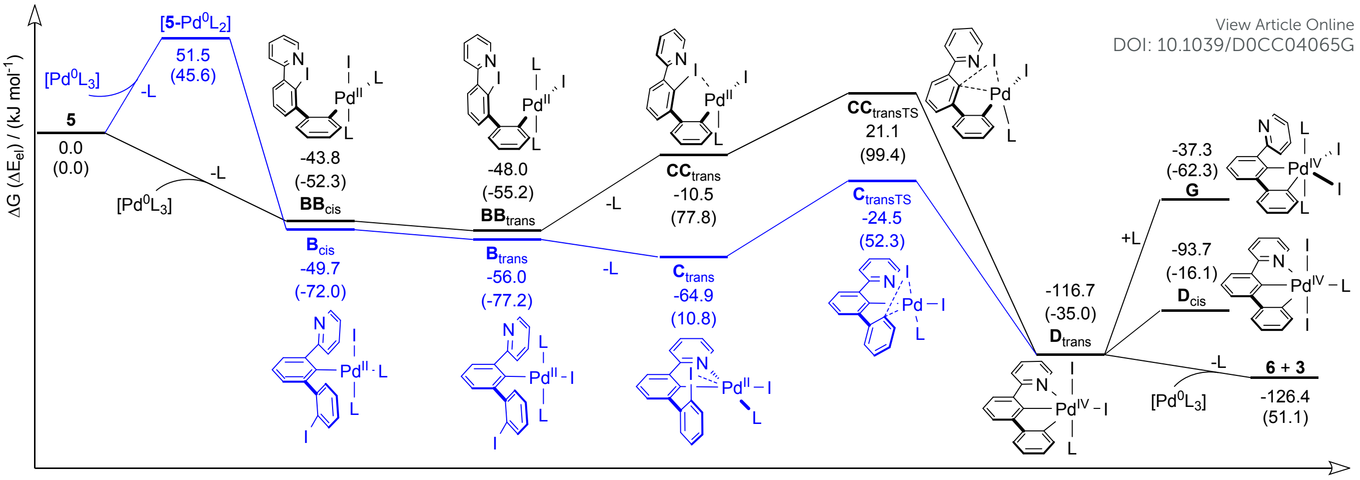

Scheme 2 Mechanism of formation of **3** by comproportionation of intermediate Pd^{IV} species $\mathbf{D}_{trans}$ and Pd^0. The pathway starting by oxidative addition of the central aryl iodide is coloured in blue. All calculations were done on the RI-TPSS-D3(BJ)/def2-TZVP (SMD: toluene) level of theory at 298.15 K and 0.1 MPa. L = PPh_3. ΔG: Gibbs free energy. Electronic energies E_{el} are given in brackets. Additional pathways of higher energy intermediates and computational details are given in the Supporting Information.

ca. 1300 cm^{-1}, i.e. the frequency of pincer breathing modes,[5, 27] indicate $\pi \rightarrow \pi^*$ IL/MLCT transitions. This assignment is supported by TD-DFT calculations (Section S4, ESI†).

Complex **3** exhibits intense yellow phosphorescence in the solid-state at room temperature with a quantum yield of 10 %. This finding underlines the extraordinary electronic impact of the non-palindromic pincer since palladium complexes luminescent at room temperature are rare.[10] An emission lifetime of 0.4 μs is indicative for a phosphorescence process. **3** shows no luminescence in liquid solution, probably due to structural distortions in the excited state.[28] However, in frozen THF solution at 77 K we observe similar emission with a notably longer lifetime of 0.37 ms, thus, standing in line with a decreased vibronic relaxation. The vibronic structured emission of **3** (Figure 3, red and purple) is comparable to the signature of other (C^C) and (C^N^C) cyclometalated complexes and indicates a metal-perturbed, pincer-centred $\pi^* \rightarrow \pi$ transition.[5, 27] Again, this is supported by TD-DFT calculations (Figure 4) showing the donor orbital of the $S_0 \leftarrow T_1$ transition being a π^* orbital of the pincer with major contribution of the pyridine ring.

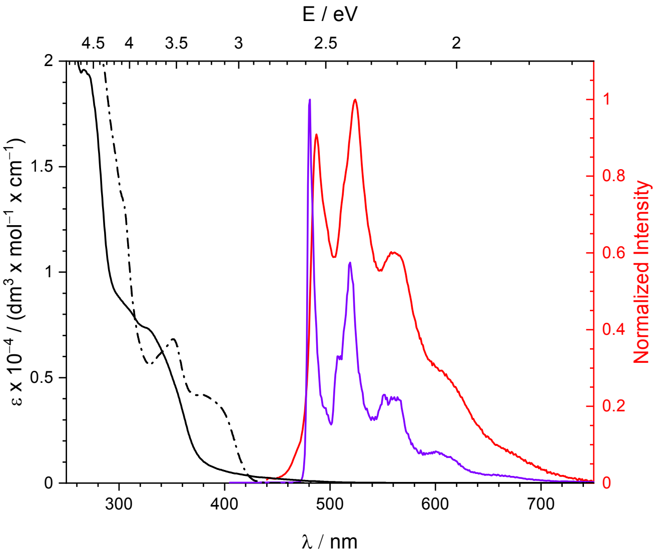

Figure 3 Absorption spectra of [(C^C^N)Pd(PPh_3)] (**3**) in CH_2Cl_2 (straight line) and THF (dotted line) and photoemission spectrum in the solid state at 293 K (red) and in frozen THF solution at 77 K (violet). Spectra were recorded under oxygen-free conditions.

In summary, a non-palindromic (C^C^N) complex of palladium with outstanding luminescence properties can be prepared by means of a double oxidative addition – comproportionation sequence of 3-pyridin-substituted 2,2′-diiodobiphenyl **5** and [Pd(PPh_3)$_4$]. The presented approach complements already known procedures for the synthesis of pincer complexes and extends the field of pincers invoking two phenyl donors to palladium. We could illustrate the strong *trans* influence of the carbon donor of the central phenyl ring of the pincer ligand, which may point to unique catalytic[16] and biological[29] properties currently under investigation in our group.

In the future, the presented synthetic principle may prove its viability in the development of pincer complexes invoking other metals than palladium as well; first promising results for nickel are shown in the Supplementary Information (Section S3, ESI†).

W. F. thanks the Carl-Zeiss Stiftung for a PhD scholarship and the Studienstiftung des Deutschen Volkes for general support. We thank Dr. Lilli Neumeier for determination of emission quantum yields and Dr. Sergei Lebedkin for the recording of emission spectra at low temperature.

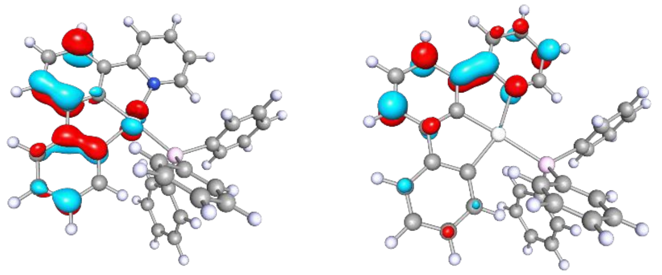

Figure 4. Spin orbitals (isovalue: 0.06 a.u.) of the phosphorescence transition $S_0 \leftarrow T_1$ of [(C^C^N)Pd(PPh_3)] (**3**) calculated by Spin-Flip-TDDFT (RI-PWLDA/def2-TZVP). Orbital contribution (square of orbital coefficients): 99.6 %. Calculated $S_0 \leftarrow T_1$ transition energy: −2.42 eV (T_1 optimized structure). Left: 152_β (acceptor orbital), right: 153_α (donor orbital).

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ We have not determined the transition state of the first oxidative addition, since the oxidative addition of aryl iodides to Pd^0 is known to readily happen.[30]

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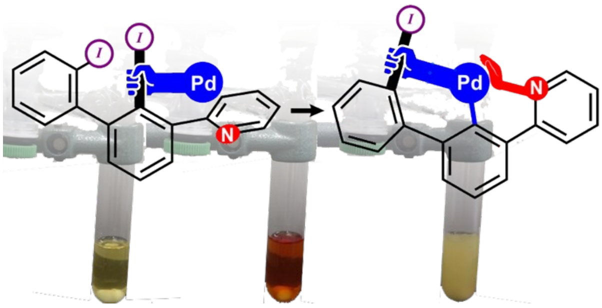

TOC:

A highly phosphorescent non-palindromic (C^C^N) palladium complex may be prepared by means of a double oxidative addition – comproportionation sequence, which is a new approach for the synthesis of non-palindromic pincer complexes.