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N^N^C platinum(II) and palladium(II) cyclometallates of 6,6′-diphenyl-2,2′-bipyridine, L: Crystal and molecular structure of [Pd(L–H)Cl]

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ABSTRACT

Reaction of $K_2[PtCl_4]$ or $Na_2[PdCl_4]$ with 6,6′-diphenyl-2,2′-bipyridine, L, gives the cyclometallated species [Pt(L–H)Cl], **1**, and [Pd(L–H)Cl], **2**, respectively, where L–H is a terdentate N^N^C anionic ligand originated by direct activation of a $C(sp^2)$–H bond. The crystal structure of **2** has been solved by X-ray diffraction and compared to that of the analogous complex [Pd(L′–H)Cl] L′ = 6-phenyl-2,2′-bipyridine. The second phenyl ring in **2** entails a considerable distortion of the coordination around the metal. A similar distortion is also to be expected in the analogous compound **1,** due to the almost equal covalent radii of palladium(II) and platinum(II).

From the complexes **1** and **2** the chloride can be displaced with $AgBF_4$ and substituted by CO or PPh_3 to give the corresponding cationic species. By reaction of **1** with $Na[BH_4]$ substitution of H^- for Cl^- can be achieved: the rare hydrido complex [Pt(L–H)H], stabilized only by nitrogen ligands, was isolated in the solid state and fully characterized in solution. It is noteworthy that in the case of the 6-phenyl-2,2′-bipyridine the analogous terminal hydride [Pd(L′–H)H] is unstable. In platinum chemistry the reaction of 6-substituted 2,2′-bipyridines is known to give either N^N^C or N′^C(3) rollover cyclometallation, depending on the nature of the metal precursor. In the case of 6,6′-Ph_2-2,2′-bipy cyclometallation was also shown to undergo multiple C–H activation giving the C^N^C pincer complex [Pt(L-2H)(DMSO)]. The latter species can be related to complex **1**: indeed its reaction with HCl produces complex **1** and [Pt(L–H)(DMSO)Cl], a rollover species with a pendant phenyl substituent.

1. Introduction

Cyclometallated derivatives of late transition metals with heterocyclic nitrogen ligands [1] have attracted, and still attract, great attention due to the considerable range of their potential applications in many fields such as organic synthesis [2], homogeneous catalysis [3], novel materials [4] and medicinal chemistry [5].

In recent years interest in C^N cyclometallates has mostly been addressed to platinum(II) derivatives due to their potential applications as chemosensors [6], switches [7], metallomesogens [8] and luminescent devices [9e,15]. Besides the classical bidentate C^N ligands, as time went up more complex molecules have been used, potentially able to act as terdentate ligands, and many cyclometallates with different sequence of donor atoms, e.g., N^N^C [10], N^C^N [11], and C^N^C [12], have been synthesized. A particular interest was devoted to species with planar aromatic terdentate ligands, typically, e.g., those arising from 6-aryl-2,2′-bipyridines. This planar motif implies a delocalized π system which can give rise to peculiar photophysical and photochemical properties, involving, *inter alia*, weak non-covalent interactions such as d^8–d^8, π–π, or C–H···π interactions [13]. In this framework much studied ligands have been 6-phenyl-2,2′-bipyridine, (L′), able to act as an N^N^C donor [14], compounds **A** (Chart 1), 1,3-dipyridyl-benzene, an N^C^N pincer ligand [9], compounds **B**, and 2,6-diphenyl-pyridine [13a,16], which can give rise to C^N^C compounds **C.** On the whole compounds **A-C** remind those of the neutral ligand terpy, compounds **D**.

Recently it has been shown that ligands such as 6-phenyl-2,2′-bipyridine and 6,6′-diphenyl-2,2′-bipyridine have a rich organometallic chemistry depending on the nature of the platinum precursor. In the case of 6-Ph-2,2′-bipy two divergent behaviour have been reported: with an inorganic precursor, typically an alkaline salt of $[PtCl_4]^{2-}$, activation of an ortho C–H bond of the pendant phenyl substituent is achieved with loss of HCl: an N^N^C cyclometallate is obtained in good yields [14a] (compound **A**). At variance, by reaction with an organo precursor, e.g., the electron-rich

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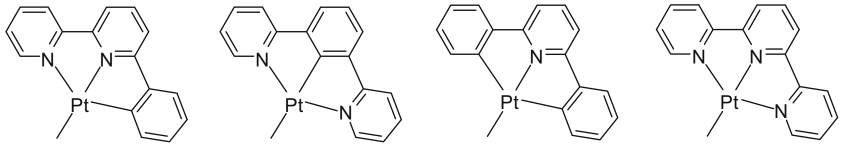
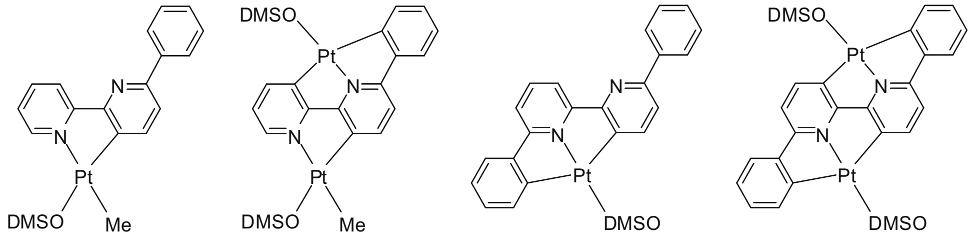


A **B** **C** **D**

Chart 1.



E **F** **G** **H**

Chart 2.

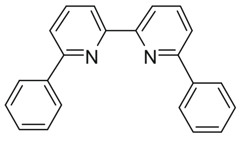
[Pt(Me)$_2$(DMSO)$_2$], activation of the C(3)–H(3) bond of the substituted pyridine ring occurs with loss of CH$_4$, and a C(3)–(N′) "roll-over" cyclometallate is formed [17] (Chart 2, compound **E**). With the same organo precursor an analogous behaviour has also been observed for the disubstituted 6,6′-Ph$_2$-2,2′-bipy, with activation both of a C(aryl)–H and a C(pyridyl)–H bond, to give compound **G** [18]. More complex dinuclear species, which imply multiple C–H activations have also been synthesized for both the ligands, compounds **F** and **H**, respectively. (Chart 2) [17,18]

Herein we describe the behaviour of the 6,6′-diphenyl-2,2′-bipyridine, **L**, in the reaction with the inorganic precursors [PtCl$_4$]$^{2-}$ and [PdCl$_4$]$^{2-}$, and compare it with that of the 6-phenyl-2,2′-bipyridine. The effect of the additional phenyl substituent on the stability and reactivity of some new cyclometallates is discussed. The X-ray structure of [Pd(L–H)Cl] is also reported.

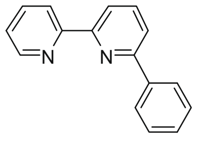
2. Results and discussion

2.1. Synthesis of Pt(L–H)Cl (*1*) and Pd(L–H)Cl (*2*)

The ligand 6,6′-diphenyl-2,2′-bipyridine was synthesized from 2,2′-bipyridine and phenyl lithium, as previously described [18]. Throughout this paper **L** and **L**′ indicate 6,6′-diphenyl-2,2′-bipyridine and 6-phenyl-2,2′-bipyridine, respectively.

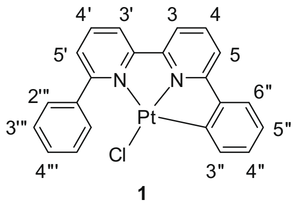


6,6'-diphenyl-2,2'-bipyridine, L



6-phenyl-2,2'-bipyridine, L'

The cyclometallated compound [Pt(L′–H)Cl], a well-known N^N^C derivate of type **A** which has attracted great attention for its outstanding properties especially in photochemistry, can be obtained by reaction of K$_2$[PtCl$_4$] under classical conditions (water, HCl, reflux temperature, see Section 2). In order to compare the behaviour of the ligands **L** and **L**′, the reaction of **L** with K$_2$[PtCl$_4$] was carried out under the same experimental conditions. The outcome of the reaction, according to analytical data, is a cyclometallate [Pt(L–H)Cl], **1**. The ^{1}H NMR spectrum indicates a not symmetric ligand due to the absence of an aromatic proton with respect to the ligand. Compared with [Pt(L′–H)Cl], the spectrum shows four spin systems of 4, 3, 3 and 5 aromatic protons, corresponding to a disubstituted phenyl, two disubstituted pyridines and a mono-substituted phenyl ring, respectively. The part of the spectrum relative to protons away from the second phenyl ring (e.g., H4", H5", H6", and H5) is almost superimposable to that of [Pt(L′–H)Cl]. A ^{1}H 2D COSY spectrum allowed us to fully assign the proton resonances.



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The appearance of the spectrum is dependent on the concentration of **1**, however we were unable to gain clear indication of intermolecular interactions.

The cyclopalladation reaction was performed under the same conditions, from Na$_2$[PdCl$_4$], to give compound **2**, [Pd(L–H)Cl]. Also in this case analytical and spectroscopic data are consistent with cyclometallation and a terdentate behaviour of the L–H ligand.

X-ray quality crystals of compound **1** were not obtained: at variance, suitable crystals of the palladium complex **2**, were collected by slow diffusion of di-isopropyl ether into a chloroform solution at room temperature.

2.2. X-ray crystal structure of compound *2*

The structure of **2** consists of the packing of [Pd(L–H)Cl] molecules (L = 6,6′-diphenyl-2,2′-bipyridine) in the triclinic space group $P\bar{1}$. The L–H anion behaves as a terdentate ligand, with the deprotonated phenyl ring bonded to the palladium atom, whereas the other phenyl ring remains pending (see Fig. 1).

The structure of **2** is unusual because there are four crystallographically independent molecules in the asymmetric unit. In order to favour the comparison between the four molecules, we have used the same labels and numbering for corresponding atoms of the molecules, adding three different markers to three of them. So, the four metal atoms are labeled Pd, Pd′, Pd*, and Pd#, and the molecules to which they belong carry the same markers, and will