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Cyclopalladated acetate dimers: Crystal structures and VT-NMR

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Abstract

The X-ray structure of two cyclopalladated acetate bridged dimers has been solved, and they are shown to exhibit an open-book type core, analogous to those that have been previously reported. Variable temperature NMR studies on these molecules demonstrates that this core persists in chloroform solution, resulting in restrictions to the movement of ancillary parts of the molecule. The barrier to rotation of a pendant phenyl ring against this core has been measured: $\Delta H^{\ddagger} = 56\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^{\ddagger} = 0$.

Keywords: Cyclometallation; Cyclopalladation; Palladium; VT-NMR; X-ray structure

1. Introduction

The study of the cyclometallation reaction is of considerable interest, both from a mechanistic point of view [1] and because of its role in the functionalisation of C–H bonds [2–6]. We have recently published a couple of papers dealing with the mono- and di-cycloplatination of diphenylpyridines [7,8], and another one that dealt with the unusual situation that can lead to the formation of a carbene species [9]. Here, we discuss some aspects of the cyclopalladation of diphenylpyridines, and the structure of the resulting complexes. The cyclopalladation reaction is of particular interest due to the role of palladium catalysts in C–C bond forming reactions [10], with a recent computational study identifying likely agostic intermediates in the reaction pathway [11].

2. Synthesis

Two new organopalladium compounds have been synthesized, via the direct reaction of a substituted pyridine with palladium acetate which proceeds cleanly at 60 °C in acetic acid to yield a cyclopalladated species in high yield (Scheme 1). A cursory inspection of the NMR spectra reveals nothing more unusual than overlapping peaks and further purification is not found to be necessary: crystals of a suitable standard for single-crystal X-ray diffraction could be isolated easily. A crystal of pure diphenyl pyridine was also the subject of an X-ray diffraction study; nothing unusual was revealed, but details are recorded here for completeness (Fig. 1).

3. Solid-state structures

The crystal structures of both (**1**) and (**2**) were solved. Whilst crystals of (**1**) were twinned and the structure could not be refined to publication standard, it is clear that it has the same principal features exhibited by the structure of (**2**) (Fig. 2), which we will discuss in more detail: selected bond lengths and angles are recorded in Table 1. Both (**1**) and (**2**) exhibit dimeric structures with the two halves related by a C_2 rotation. At the heart of the molecules are the two palladiums bridged by the two acetates; these bridges fold the two halves of the molecule back on each other, rather like an open book. In the two structures reported here we have a close Pd–Pd

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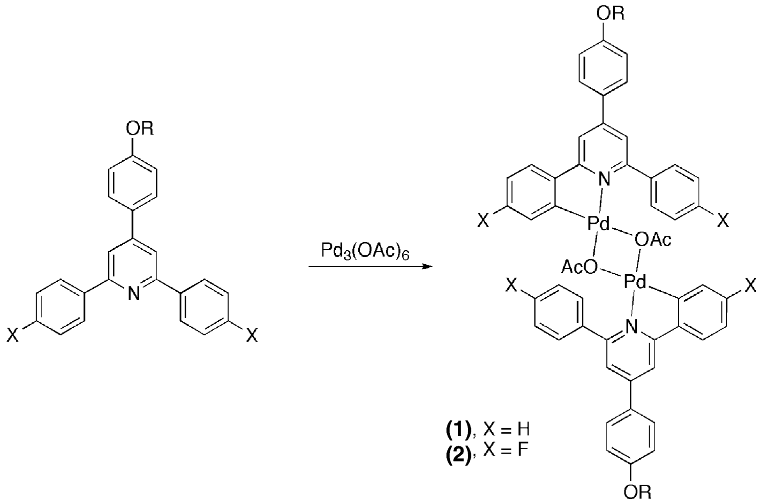

Scheme 1.

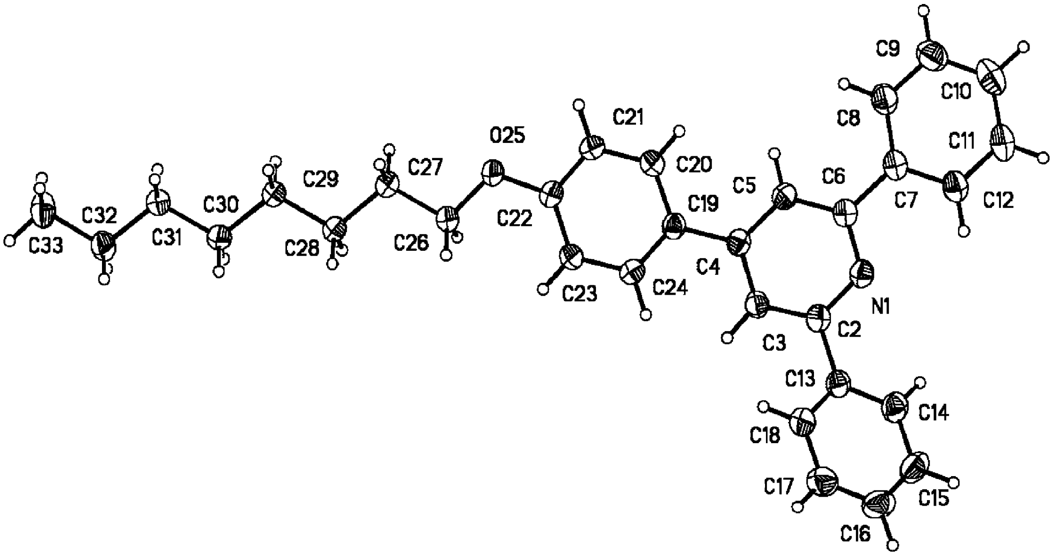

Fig. 1. The X-ray structure of the diphenyl pyridine ligand.

contact of 2.9029(12) Å in (**1**) and 2.9067(9) Å in (**2**); the planes of the cyclometallated rings end up being close to parallel (inclined at 11.6(6) and11.8(3)° to each other in (**1**) and (**2**), respectively), and the unmetallated phenyl rings are inclined at angles of 59.4(3) and 43.9(3)° to the pyridine ring. In the structure of (2) the Pd–N distance is 2.074(5) Å, the Pd–C distance is 1.969(6) Å. This Pd–C distance is significantly shorter that the average Pd–C single bond, in line with the expectation that the five membered metallocycle has significant aromatic character [12]; other authors [13] have related short Pd–C bond distances with the π back bonding of the metallic centre to the aromatic system. The Pd–O distances are 2.159(5) (O *trans* to C) and 2.058(5) (O *trans* to N), with this difference being readily attributed to the greater *trans* influence shown by carbon, compared with nitrogen.

A survey of the Cambridge Crystallographic Database [14] reveals 78 similar structures of dimeric cyclopalladated compounds with a carboxyl bridged core. The mean Pd–Pd distance in these structures is 2.952 Å, with max and min values at 2.823 and 3.281 Å (one outlier with a Pd–Pd distance of 3.413 Å is reported for the hugely sterically crowded cyclopalladated di(orthotolyl)(*t*-butyl)phosphine compound [15]). The question of when a Pd–Pd interaction constitutes a bond seems clear: the covalent radius of a square planar palladium is reported as being 1.31 Å [16], thus only with complexes having Pd–Pd distances of 2.62 Å or less does the question arise. All of the 78 structures mentioned above have Pd–Pd distances greater than 2.62 Å and thus none should be considered as having a Pd–Pd bond. Interestingly, of these 78 structures, 14 (mean Pd–Pd distance = 2.872, min = 2.831, max = 2.939 Å) are shown as having a bond, whereas 64 (mean Pd–Pd distance = 2.969, min = 2.823, max = 3.281 Å) are shown as not having a bond. Our Pd–Pd distance is thus well within the normal range.