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Cyclometallated phenyl-pyridine palladium species. Monomeric complex formation with potentially bridging ligands

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ABSTRACT

The cyclometallated dinuclear (2-phenyl-pyridine)palladium acetate and chloride [{PdCl(phpy)}$_2$] and [{PdOAc(phpy)}$_2$] were reacted with potentially bridging *N*- and *S*-donor ligands. The *N*,*N*-ligands bind with only one nitrogen and form monomeric products. The *S*,*S*-ligand binds in a chelate mode, also forming a monomeric complex. 3,3-Dimethyl glutarate, on the other hand, binds in a bridging mode. An X-ray structure of the complex with naphthyridine is presented.

1. Introduction

Dinuclear palladium species with two strongly interacting Pd(III) atoms have been proposed to be catalytically relevant in various ligand-directed C–H activation reactions [1–6]. This Pd(III)–Pd(III) dimer is proposed to be formed via oxidation of Pd(II) and the stability of the lower oxidation state Pd–Pd structure relies on bridging ligands, that hold the two metal centres in proximity, and acetates and succinimides are the most common such ligands. However, despite binding two palladium atoms at a perfect interatomic distance, these ligands form relatively weak bonds to palladium and dimeric species are present in an equilibrium with monomers [2,4]. Having stronger binding ligands could potentially make the oxidation to a Pd(III)–Pd(III) dimer kinetically more favourable.

Úbeda and co-workers have described the syntheses and properties of dinuclear complexes bearing N–N, N–S, S–O and O–O bridging ligands together with strongly binding C–P bridging ligands (Fig. 1), but these compounds did not contain any standard cyclometallated substrate, such as phenyl-pyridine (phpy), and it is expected that the strongly binding C–P motif substantially increases the stability of the dinuclear structure [7–10].

Thus, no compounds with a more strongly binding "spectator" ligand have been synthesized and utilized in cyclometallation/C–H activation reactions. Hence, we were interested in expanding the scope of dinuclear palladium species bearing both a relevant metallacyclic ligand and a stronger, bridging spectator ligand. The ligand of choice should have a 1,3-disposition of the donor atoms, since a longer chain between the atoms would favour the chelate-type binding mode of the ligand, rather than the bridging mode. If, as in the case of acetate complexes, two bridging ligands are to be bound, they should be of X,L-type to maintain the overall complex neutrality. However, if the ligand binding is strong enough, one bridging ligand may be sufficient and then the binding type can vary. Potential donor atoms with a stronger interaction to palladium than O-atoms include mainly N, P or S. However, since the conditions of the ligand-directed C–H activation are normally oxidative, phosphorus ligands are expected to be inferior, since they may undergo irreversible oxidation to the corresponding phosphine oxides. Furthermore, soft phosphine ligands are less compatible with the higher oxidation states of palladium often associated with C–H activation reactions. The sulfur in X-binding mode is also expected to be prone to oxidation, but this oxidation can be reversible and may have positive or negative effects on the catalysis. In this contribution, we report the interaction of a palladium-phenyl pyridine moiety with *N*,*N*- and *S*,*S*-ligands with potential bridging properties.

2. Experimental

2.1. General

All manipulations were conducted under ambient conditions, unless noted. Solvents and chemicals were purchased from commercial suppliers and used as received. Compounds **1** [11], **4**

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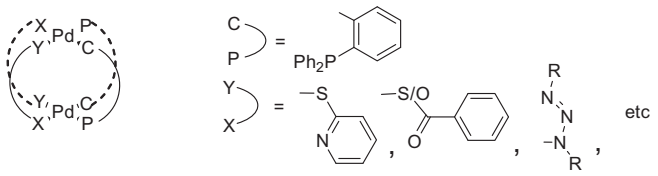

Fig. 1. General structures of complexes published by Úbeda [7–10].

[11], **5** [12,13] and 1,8-naphthyridine [14] were synthesized according to the literature. NMR spectra were acquired on a Bruker Avance 400 FT-NMR spectrometer (^{1}H: 400.1 MHz) or a Varian Unity INOVA 500 spectrometer (^{1}H: 499.76 MHz). Residual solvent peaks were used as an internal reference. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

2.2. Synthesis of [PdCl(naphthyridine)(phpy)] (**2**)

Compound **1** [{PdCl[(phpy)}$_2$] (20 mg, 0.034 mmol, 1 equiv) was added to a solution of 1,8-naphthyridine (1,8-diazanaphthalene) (8.8 mg, 0.068 mmol, 2 equiv) in CH_2Cl_2 (2 mL). The resulting solution was stirred overnight at room temperature, evaporated to dryness and the solid was recrystallized from CH_2Cl_2–Et_2O. Complex **3** was obtained as a colourless solid (25 mg, 86% yield). X-ray quality crystals were obtained by recrystallization from CD_2Cl_2/MeCN/pentane solution.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 9.48 (d, J = 5.3 Hz, 1H), 9.40 (m, 2H), 8.44 (d, J = 8.0 Hz, 2H), 7.88 (m, 1H), 7.72 (d, J = 9.1 Hz, 1H), 7.70 (dd, J = 8.0, 4.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.23 (m, 1H), 7.02 (m, 1H), 6.68 (m, 1H), 5.72 (d, J = 7.7 Hz, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2): δ 225.0, 166.3, 154.6, 154.5, 152.4, 146.3, 139.3, 139.1, 133.4, 129.6, 125.3, 124.9, 123.9, 123.8, 122.8, 118.9.

Elemental *Anal.* Calc. for [2($C_{19}H_{14}ClN_3Pd$), $1H_2O$]: C, 52.43; H, 3.47; N, 9.66. Found: C, 52.63; H, 3.68; N, 9.53%.

2.3. Synthesis of [Pd(azaindole)(Cl)(phpy)] (**3**)

Compound **1** (10 mg, 0.017 mmol, 1 equiv) was added to a solution of 7-azaindole (4 mg, 0.034 mmol, 2 equiv) in CH_2Cl_2 (2 mL). The resulting solution was stirred for 10 min at room temperature, filtered through Celite and evaporated to dryness. The product was recrystallized from CH_2Cl_2 or CH_2Cl_2–Et_2O mixtures to result in an off-white solid (10 mg, 71% yield).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.88 (br s, 1H), 9.42 (d, J = 5.8 Hz, 1H), 8.57 (dd, J = 4.5, 2.6 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.85 (td, J = 7.8, 3.9 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.48 (dt, J = 7.8, 1.8 Hz, 1H), 7.38 (dt, J = 4.4, 2.3 Hz, 1H), 7.25 (ddd, J = 7.7, 5.6, 1.9 Hz, 1H), 7.17 (ddd, J = 7.5, 5.8, 1.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.79 (td, J = 7.5, 1.8 Hz, 1H), 6.63 (dt, J = 4.0, 2.0 Hz, 1H), 5.91 (d, J = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 166.2, 154.4, 152.2, 147.8, 146.5, 146.0, 139.6, 133.6, 131.4, 130.0, 126.8, 125.4, 123.9, 123.3, 122.8, 119.0, 117.6, 102.7.

Elemental *Anal.* Calc. for $C_{18}H_{14}ClN_3Pd$: C, 52.20; H, 3.41; N, 10.14. Found: C, 52.13; H, 3.58; N, 10.06%.

2.4. Synthesis of [{Pd(phpy)}$_2$(OCOCH$_2$)$_2$C(CH$_3$)$_2$] (**6**)

Compound **4** [{PdOAc(phpy)}$_2$] (10 mg, 0.017 mmol, 1 equiv) was added to a solution of 3,3-dimethylpentanedioic acid (3.0 mg, 0.017 mmol, 1.2 equiv) in MeCN (2 mL). The resulting solution was stirred overnight at 60 °C, then it was cooled to room temperature. A yellow precipitate was filtered off, washed with MeCN (3 × 5 mL) and dried. 11 mg (95%) of cyclopalladated dimer **6** was obtained.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.91 (d, J = 5 Hz, 1H), 7.44–7.38 (m, 1H), 7.14 (d, J = 8 Hz, 1H), 6.96–6.91 (m, 2H), 6.88–6.82 (m, 2H), 6.53–6.46 (m, 1H), 2.56–2.50 (m, 2H), 2.46–2.40 (m, 2H), 1.44–1.35 (br. m., 6H). The multiplet analysis is restricted due to the incredibly poor signal/noise ratio alongside the possible formation of a mixture of isomers.

Elemental *Anal.* Calc. for $C_{29}H_{26}N_2O_4Pd_2$: C, 51.27; H, 3.86; N, 4.12. Found: C, 51.28; H, 3.84; N, 4.12%.

2.5. Crystallography

Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and Mo Kα (λ = 0.71073 Å) radiation. The data were extracted and integrated using Crysalis RED [15]. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELX [16] Molecular graphics were generated using CrystalMaker® 8.3.5 [17]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

3. Results and discussion

3.1. Complexes with a naphthyridine ligand

As a compromise between strong interaction with palladium and oxidative stability we started our study with the investigation of nitrogen ligands. 1,8-Naphthyridine (1,8-diazanaphthalene) possesses two L-type nitrogen donor atoms in geminal positions and substituted 1,8-naphthyridines are known to be able to bind two metal atoms simultaneously [18–20]. In some cases the bound palladium atoms are also bearing a bipyridyl ligand [19,20], which is at least sterically similar to the phenyl-pyridine ligand. The direct reaction between the cyclometallated acetato-bridged dimer and naphthyridine did not lead to any conclusive results. However, when we used a chlorido-bridged dimer as the starting material we were able to isolate a new product. The NMR spectra indicated the presence of resonances assigned to both the metallacyclic fragment and a coordinated naphthyridine. However, a more detailed inspection showed that the relative ratio between the naphthyridine and phenyl-pyridine signals is 1:1. Hence only one of

Table 1
Crystal data and refinement details for compound **2**.

Formula	$C_{19}H_{14}ClN_3Pd$, 0.5 H_2O
F_w	434.18
Space group	$P2_1/n$
Crystal system	monoclinic
T (K)	293
a (Å)	8.94410(10)
b (Å)	24.2498(3)
c (Å)	16.7494(2)
β (°)	95.8110(10)
V (Å^3)	3614.15(7)
Z	8
D_{calcd} (g cm^{-3})	1.596
μ (mm^{-1})	1.182
θ-range (°)	2.438–32.523
No. reflections collected	115 373
No. of unique reflections	12 554
$R(F)$ ($I > 2(I)$)[a]	0.0440
$wR^2(F^2)$ (all data)[b]	0.1385
S[c]	1.178
R_{int}	0.0396

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$.
[c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$.