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Bidentate cycloimidate palladium complexes with aliphatic and aromatic anagostic bonds†

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Palladium(II) complexes of bidentate cycloimidate ligand systems with a triarylmethyl moiety exhibit exceptional downfield shifts in proton NMR spectra due to rare anagostic interactions.

The agostic interaction – a coordinatively-unsaturated transition metal coordinating to a C–H group by a three-center two-electron bond[1] – is the topic of numerous investigations and generally regarded to be mechanistically important for the key step in CH-activation processes.[2,3] The anagostic interaction, a C–H-transition metal arrangement with a bridging hydrogen, is far less established, nevertheless also demanding mechanistic interest as a prestage to the agostic binding situation. Both, agostic[4] and anagostic[5–9] complexes have been isolated, regularly being test objects for calculations in comparison with spectroscopic and structural data.[10–12] While for agostic complexes an upfield shift of the coordinated C–H-group in the proton NMR and a clearly diminished C–H coupling constant are observed,[13] in anagostic complexes the ^{1}H NMR signal of the bridging hydrogen is significantly shifted downfield,[10,14] regularly by about 2 to 3 ppm.[5–9] Herein we report on iminoisobenzofuran palladium chelate complexes with the rare situation of exhibiting anagostic interactions both with aliphatic and aromatic CH-groups, resulting in downfield shifts of up to 4.1 ppm.

Iminoisobenzofurans are important for a variety of applications either as functionalized π-systems or as synthetic building blocks for isobenzofurans and isoindolinones; *e.g.* the separation of chiral phthalides *via* their diastereomeric imidates,[15] the synthesis of spirocyclic isobenzofurans[16] and for connecting binding components of a supramolecular ligand system.[17] Only a few examples of iminoisobenzofurans as ligands are known.[18,19]

Numerous methods are known for the synthesis of iminoisobenzofurans from readily accessible substrates: (1-alkynyl)-benzamides can be cyclized to imidates either by synergetic Pd/Cu catalysis[20] or by electrophilic cyclization.[21,22] The fluoride-induced three component coupling of an isocyanate, a carbonyl compound and a TMS-substituted phenyl triflate was performed; an aryne is the reactive intermediate in this reaction.[23,24]

Our attempts to synthesize *ortho*-oxazolinyl-functionalized triarylmethyl alcohols **2** from 2-bromophenyloxazolines[16,25] **1** following established procedures[26] more or less surprisingly resulted in the isolation of the benzannulated imidoyl lactones **3** in excellent yields (Fig. 1).

Compound **3** should be thermodynamically favored due to diminished sterical crowdedness of its triarylmethyl moiety as part of the annulated 5-membered ring system, as published earlier by Mayers and Dordor.[27,28] This argument is supported

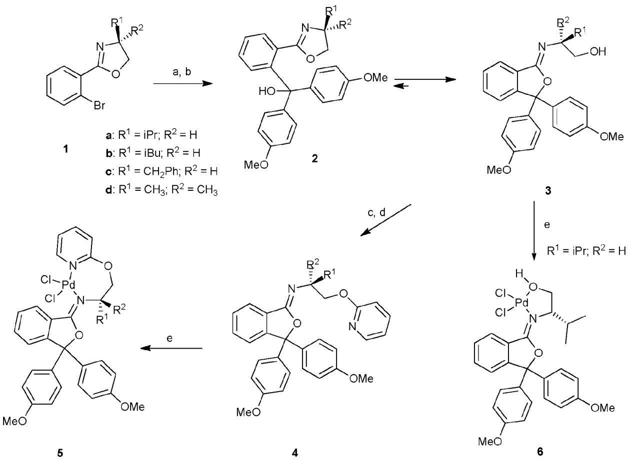

Fig. 1 Synthesis of **5a–d** (a) *n*-Buli, THF, −89 °C, 40 min; (b) 4,4′-dimethoxybenzophenone (c) NaH, THF (d) 2-fluoropyridine; and (e) $(MeCN)_2PdCl_2$, CH_2Cl_2, 1 h, RT.

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† Electronic supplementary information (ESI) available: Experimental procedures, full characterization including NMR, MS, IR, EA and data for all new compounds and X-ray crystal structures of **5a,c–d**, **6**. CCDC 977820–977822 and 993306. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01060d

by the results of Noel *et al.*: primary oxazoline alcohols were obtained by reaction of sterically less crowded cyclic imidates with aminols.[29] Our spectroscopic proof of this finding is not only based on the chemical shift of the CH_2 group in the proton NMR as described previously,[28] but also on two-dimensional ^1H, ^{13}C-HMBC spectra: **3c** for instance exhibits only a single cross signal for the imine carbon (δ = 159.4 ppm) and the aliphatic proton at the chiral center (δ = 4.37 ppm). A correlation with the neighboring methylene group (δ = 3.67 ppm) is clearly missing, which on the other hand should be additionally registered for structures of type **2**. The sodium alcoholates of **3** undergo a subsequent nucleophilic substitution with 2-fluoropyridine, giving access to the bidentate ligands **4**, which selectively form Pd(II)-complexes with $(MeCN)_2PdCl_2$ in CH_2Cl_2 at room temperature, while failing to complex platinum salts under various conditions. Furthermore imidate **3a** was also shown to be a suitable bidentate ligand for Pd(II) salts, with the hydroxyl group as the coordination site, resulting in the formation of complex **6**. Single crystals were obtained as orange needles by slow diffusion of *n*-hexane to dichloromethane solutions of **5** and **6**.

Upon complexation with $PdCl_2$ a significant change in the proton NMR spectra was observed, since several signals were significantly shifted downfield (Fig. 2): the signal of the proton *ortho* to the pyridine nitrogen was shifted about $\Delta\delta$H = 0.8 ppm from δ = 8.14 to δ = 8.96 ppm, respectively. The signal of the *peri*-proton (H3) was registered at 11.17 ppm, resembling an astonishing downfield shift of overall 3.3 ppm. Furthermore the signal of the methylene group H24a/b splits up into two separate doublets. One signal was found at 8.55, the other at 4.25 ppm. Clearly, these downfield shifts are mainly caused by a through space interaction of the protons with the palladium ion. All complexes **5a–d** exhibit these extraordinary shifts of the selected NMR signals (Table 1).

Table 1 Chemical shifts (ppm) of the protons under the anisotropic influence of the palladium in complexes **5a–d**

R^1	δH3[a]	δH3	$\Delta(\delta$H)H3	δH24b[a]	δH24b	$\Delta(\delta$H)H24b
iPr	7.89	11.04	3.15	4.30	7.31	3.01
iBu	7.89	10.96	3.07	4.35	7.18	2.83
CH_2Ph	7.88	10.92	3.04	4.40	7.62	3.22
Me	7.82	11.17	3.35	4.45	8.55	4.10

[a] Signal of the free ligand.

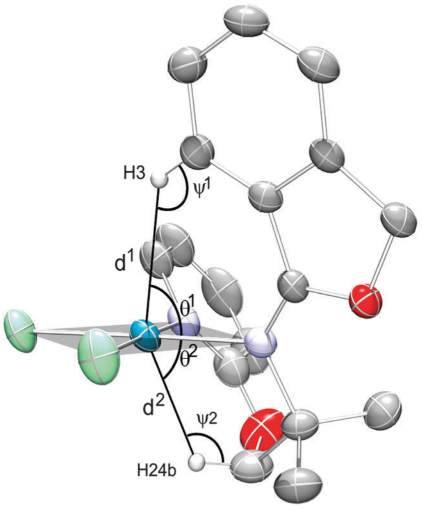

Fig. 3 Thermal ellipsoid (50% probability) plot of palladium complex **5d** with a sketched plane at the palladium atom and distances d^1, d^2 and angles ψ, θ to the shifted hydrogen atoms H3 and H24b. Other protons and the *p*-anisyl substituents are omitted for clarity.

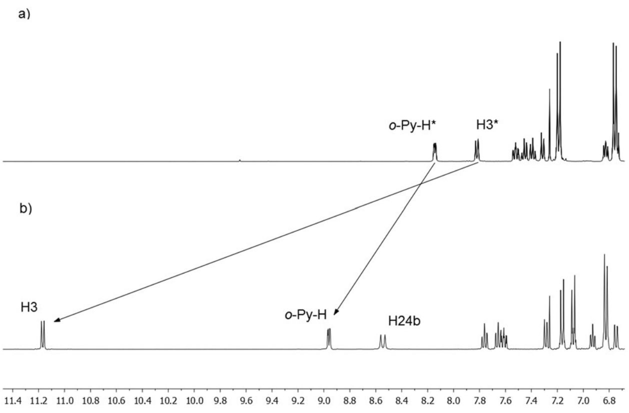

Fig. 2 Partial ^1H NMR spectra (400 MHz, $CDCl_3$) of (a) the free ligand **4d** ($R^1 = R^2 = CH_3$) and (b) its complex with $PdCl_2$ **5d**.

The analysis of the solid state structures of complexes **5a,c–d**, obtained from X-ray crystallography, confirms that the relevant geometric orientation within the compounds is identical. Therefore a general explanation of the proton shifts can be given: upon chelatization of the palladium by the two nitrogen atoms of the bidentate ligand, a 7-membered ring is formed. The protons H3 and H24b are then located in an approximate axial position above and underneath the quadratic plane which is formed by the metal atom and the ligands (Fig. 3). The distances d^1 and d^2 between the palladium atom and the hydrogen atoms H3 and H24b as well as the angle ψ (Table 2) from the Pd atom to the C–H bonds are in good agreement with the definition of an anagostic interaction (d(M–H) = 2.3–2.9 Å, M–H–C = 110–170° (here ψ)).[14] The protons with shorter distances d^1 and d^2 to the palladium atom should be more deshielded (Tables 1 and 2) than those with longer distances. The dimethyl substituted complex **5d** has the shortest contacts to the metal (d^1 = 2.581 Å, d^2 = 2.299 Å) and therefore indeed exhibits the most significant downfield shifts for the protons H3 and H24b ($\Delta\delta$H = 3.35 and 4.10 ppm). Whereas the benzyl-substituted complex **5c** exhibits the longest bond for d^1 = 2.723 and the second longest for d^2 = 2.447 Å. Analogously the aromatic proton H3 experiences the smallest downfield shift of $\Delta\delta$H = 3.04 ppm, but surprisingly only an average one for H24b, although it shows a slightly shorter bond for d^2 (2.447 Å) than complex **5a**. Clearly, other factors have to be taken into account, such as the angle θ which might function as a control parameter for the anisotropic shift as suggested by Scherer *et al.*,[11] focussing on upfield shifts caused by agostic interactions. In analogy, for anagostic interactions the anisotropic downfield shift should be maximized with a perfect perpendicular angle of 90° for θ. The comparison of crystallographic data and NMR

Table 2 Contact length and angles from the palladium atom to the shifted protons in complexes **5a,c–d** and **6**

R^1	d^1	ψ^1	θ^1	d^2	ψ^2	θ^2
iPr **5a**	2.635	129.90	81.18	2.463	113.12	69.71
CH_2Ph **5c**	2.723	123.58	78.36	2.447	115.23	69.67
Me **5d**	2.581	128.83	82.55	2.299	119.14	70.40
iPr **6**	2.584; 2.586	129.33; 128.75	84.67; 83.97	—	—	—

ψ^1 = Pd–H3–C3 [°]; ψ^2 = Pd–H24b–C24 [°]; θ^1 = N1–Pd–H3 [°]; θ^2 = N1–Pd–H24b [°]; d^1, d^2 [Å].

spectra of complexes **5d** and **6** underlines this assumption (Table 2). The proton NMR of complex **6** registers a 2 : 1 equilibrium of two species in solution, both with an astonishing downfield shift of the aryl proton H3 of more than 4.1 ppm (δ = 12.06 and 12.03 ppm), interpreted as equilibrium between the chelated complex **6** and its dimeric isomer. The latter was ascertained as crystal structure, exhibiting an angle θ of about 84°, thus closer to the perpendicular angle than in the case of **5d**, but with the distance d essentially remaining the same.

Also the results of a QTAIM analysis carried out with the electron density of **5d** from a DFT/BP86/def2-TZVP calculation corroborate these results. The density exhibits bond paths with bond critical points that connect Pd with H3 and H24b. At both bond critical points the charge density is, however, only small (1.9×10^{-2} au for Pd–H3 and 2.7×10^{-2} au for Pd–H24b) and has a positive Laplacian (5×10^{-2} for Pd–H3 and 8×10^{-2} for Pd–H24b). These characteristics fit well to anagostic interactions between Pd and H3 and H24b and substantiate that in **5d** the interaction of Pd with H24b is slightly stronger than with H3, in accordance with the experimental findings and the model developed by Scherer *et al.*[11]

In summary, we have developed a bidentate ligand which exhibits rare anagostic interactions of aromatic and aliphatic protons upon complexation with a palladium salt. Astonishing downfield shifts of aliphatic and aromatic protons were correlated with geometric factors of the corresponding X-ray structures.

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