Note

On the Electronic Nature of Bis((*Z*)-1-(benzo[*d*]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ate)palladiumKathleen L. May,^a Genki Watanabe,^b Ryosuke Saijo,^b Masami Kawase,^b and Robert A. Gossage^{*,a}^aDepartment of Chemistry & Biology, Ryerson University; 350 Victoria Street, Toronto ON M5B 2K3, Canada; and^bFaculty of Pharmaceutical Sciences, Matsuyama University; Matsuyama, Ehime 790–8578, Japan.

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The electronic nature of the recently reported complex, bis((*Z*)-1-(benzo[*d*]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ate)palladium, is re-investigated by a combination of spectroscopy (NMR, IR, magnetic moment, etc.) and Density Functional Theory (DFT: B3LYP 6–31G*/LANL2DZ). In contrast to the recent report, the title complex displays all the properties of diamagnetism and hence retains the properties of a formally Pd(II) square planar complex with a bis- κ^2 -*N,O*-donor ligand set. A modified synthetic route is also presented which improves the yield of the compound.

Key words palladium complex; fluorinated benzoxazole; diamagnetic; density functional theory

Introduction

Group 10 transition metal (TM) complexes have played a key role in our development and understanding of the many aspects of structure and bonding within inorganic systems. Many of the most common structural geometries have a vast number of examples within the Ni, Pd and Pt group. These motifs include octahedral, square planar, tetrahedral, trigonal bipyramidal and square pyramidal compounds.¹⁾ These parameters are an important contributor to both the catalytic (e.g., Ni-catalysed polymerisation, Pd-mediated C–C bond formation) and biological activity (e.g., cisplatin) of such TM species.^{2–13)} It was recently reported that the benzoxazole derivative **1** (i.e., (*Z*)-1-(benzo[*d*]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ol; Chart 1) is a useful precursor to metal derivatives (i.e., Mg, Zn, Pd, Ni, Cu, Ag) of the corresponding enolate.¹⁴⁾ These complexes display potent anti-bacterial activity against a number of Gram-positive and Gram-negative bacterial strains. Of these compounds, the Pd complex bis((*Z*)-1-(benzo[*d*]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ate)palladium (**2**; Chart 1), was found to be “NMR-silent” and was thus presumably displaying paramagnetic behaviour.¹⁴⁾ This situation is virtually unknown in mononuclear Pd(II) complexes regardless of the ligand donor set. This observation has been attributed to the stabilization acquired by the spin pairing of all eight (i.e., d^8) metal-based valence electrons. The highest energy of these residing in an orbital derived from the d_{z^2} atomic orbital (i.e., the highest occupied molecular orbital (HOMO)). This situation thus dictates the square planar conformation. Indeed, analysis of **2** by single crystal X-ray diffraction studies clearly display the square planar configuration with a typical *trans*-bis- κ^2 -*N,O* ligand donor set ($\tau_4 = 0.00$).^{14–24)} In this Note, we re-examined the synthesis and properties of **2** using a combination of Density Functional Theory (DFT) and spectroscopic techniques (IR, UV-Vis., NMR, etc.). This work demonstrates that the title complex is, in fact, diamagnetic and hence NMR spectra (¹H, ¹³C, ¹⁹F) of the compound can be measured. This suggests that the presence of a trace of paramagnetic impurity in **2** during spectroscopic identification may be the cause of the unusual observed

molecular spin characteristics.

Experimental

General All reagents and solvents were obtained from commercially available sources. Dry tetrahydrofuran (THF) was dispensed from an *Mbraun* solvent purification system immediately before use. NMR spectroscopy (¹H: 400 MHz; ¹³C{¹H}: 101 MHz; ¹⁹F{¹H}: 376 MHz) was carried out using a Bruker Avance II AC-400 MHz spectrometer operating at 300 K and using CDCl₃ as solvent. Signals were calibrated based on solvent residual ¹H ($\delta_{\text{H}} = 7.26$ ppm; CHCl₃) and ¹³C peaks ($\delta_{\text{C}} = 77.17$ ppm; central resonance: ¹³CDCl₃). Proton and carbon assignments were made using a variety of two dimensional (2D)-NMR experiments (correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond connectivity (HMBC)). The ¹⁹F resonance is calibrated to external neat CFCl₃ ($\delta_{\text{F}} = 0.00$ ppm). IR spectra were obtained in open air from neat samples by an Agilent Cary 630 FTIR Spectrometer. UV-Vis absorption profiles were collected using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer with a 1 cm path length. Molar extinction coefficients were calculated using the Beer–Lambert law. Melting points were determined by Differential Scanning Calorimetry on a PerkinElmer, Inc. Q20 TA series in open air and are uncorrected. Magnetic susceptibility measurements were performed on a Johnson Matthey Susceptibility Balance model MSB-MK1 using Hg[Co(SCN)₄] as standard

Chart 1. Schematic Representations of Compounds **1** and **2**

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reference. The compound (Z)-1-(benz[d]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ol (**1**) was synthesised as per literature procedures.²⁵ DFT calculations were carried out using the *Spartan 16.0* suite of programs.²⁶ Initial structural minimisation was carried out *via* a semi-empirical PM6(tm) treatment followed by calculation at the DFT level of theory (6-31G*/LANL2DL level). Zero point energy (ZPE) calculations revealed no imaginary IR frequencies and hence the optimised geometry represents a stable ground state conformer on the potential energy surface.

Synthesis of 2 To a 25-mL round-bottom flask was added a sample of **1** (0.204 g, 0.890 mmol) and THF (5 mL); stirring was thereafter initiated yielding a clear pale-yellow coloured solution. Solid PdCl₂ (0.069 g, 0.39 mmol) was then added along with NEt₃ (1.00 mL, 0.726 g, 7.17 mmol). Some precipitation of an orange coloured powder was observed. The solution was then stirred at room temperature (r.t.) for 2 h. Upon completion of this time period, volatile components of the mixture were removed *in vacuo* and the resultant gum-like material was diluted with MeOH (10 mL). Complex **2** was then collected from this suspension *via* vacuum filtration, washed with cold MeOH and then recrystallized with hot, neat THF (10 mL); **2** isolated in this way is in the form of orange coloured needles (Yield: 0.219 g; 98 + %). mp = 218–220°C (lit. 200–204°C).¹⁴ High resolution (HR)-MS (DART) *m/z*: 562.96575 (Calcd for C₂₀H₁₁F₆N₂O₄Pd: 562.96578; [M + H]⁺). ¹H-NMR (CDCl₃) δ: 5.96 (2H, s), 7.30–7.34 (4H, m), 7.42–7.47 (2H, m), 8.25–8.29 (2H, m). ¹³C-NMR (CDCl₃) δ: 83.2 (q, ³J_{C-F} = 3.2 Hz), 110.3 (s), 117.3 (q, ¹J_{C-F} = 280.6 Hz), 118.5 (s), 125.1 (s), 125.3 (s), 137.9 (s), 148.6 (s), 161.0 (s), 162.4 (q, ²J_{C-F} = 34.8 Hz). ¹⁹F-NMR (CDCl₃) δ: –71.9 (s). IR (neat) cm^{–1}: 3144, 1600, 1548, 1455, 1424, 1329, 1201, 1118, 1028, 932, 893, 857, 773, 750, 723. UV λ (THF) nm (log ε): 253 (3.85), 289 (3.75), 337 (4.20), 461 (2.26).

Results and Discussion

Our initial examination of complex **2** involved application of DFT to access the likelihood of a stable paramagnetic, *S* = 1, form. Our results gave quite a good structural fit with respect to the observed X-ray data using either an *S* = 0 or *S* = 1 situation (Tables 1, 2 and Supplementary Materials: .mol file).²⁷ However, ground state energies for these idealized isomers predicted that the paramagnetic *S* = 1 form was considerably higher in energy ($\Delta E > +50$ kJ/mol). This examination comes with the caveat that we are examining an isolated gas phase molecule of **2** and packing effects in the solid-state may have an influence that is not addressed by this treatment. The close similarity in structural parameters found by DFT with respect to published X-ray diffraction data promoted us to re-make this material and re-examine its spectroscopic properties.

A modified approach was taken to obtain **2** which involved the use of NEt₃ as a reaction additive to aid in the de-protonation of **1**. This further allows for a more atom economic virtually stoichiometric 2:1 ratio of ligand to PdCl₂ to be used. Removal of volatile components and addition of MeOH isolates **2** in an improved yield of 98 + %. Examination of this material gave IR data (neat; Supplementary Materials: Fig. S-7) comparable to that reported (KBr). In addition, a UV-Vis spectra was also recorded. Initial reports of the low solubility of **2** in MeOH solution prevent determination of ϵ values although a $\lambda_{\max}$ = 335.5 nm was disclosed.¹⁴ We have since

Table 1. Selected Observed^{a)} and Calculated^{b)} Bond Lengths for Complex **2** (*S* = 0)

Bond type	Bond lengths (obs.): Å	Bond lengths (calc.): Å
Pd–N	2.031	2.070
Pd–O	1.991	2.002
C=C (oxazole)	1.362(3)	1.369
C=N	1.315(3)	1.329
C–O (oxazole)	1.362(3)	1.359
C–O (enolate)	1.290(3)	1.290
C–CF ₃	1.519(4)	1.528
C–F	1.335(3), 1.333(3), 1.337(4)	1.346, 1.346, 1.351

a) CCDC #1574816; *n.b.*, the complex lies on a centre of inversion. b) Calculated by DFT (6-31G*/LANL2DZ level of theory).

Table 2. Selected Observed^{a)} and Calculated^{b)} Bond Angles for Complex **2** (*S* = 0)

Bond angle	Bond angle (obs.): °	Bond angle (calc.): °
O–Pd–O	180	175.36
N–Pd–N	180	179.36
O–Pd–N (chelate)	91.58	91.21, 91.15
O–Pd–N	88.42	88.85, 88.86
C=CH–C	121.1(2)	122.22
CH–C–CF ₃	118.9(2)	119.37
C=N–Pd–O (torsion)	17.34	9.85
C–O–Pd–N (torsion)	14.31	11.73

a) CCDC #1574816; *n.b.*, the complex lies on a centre of inversion. b) Calculated by DFT (6-31G*/LANL2DZ level of theory).

found that **2** displays superior solubility in THF and hence a $\lambda_{\max}$ value (337 nm) with $\epsilon = 1.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ is noted (Fig. S-8). Solid-state heating of this material gives a slightly higher observed mp (218–220°C; Fig. S-9) than reported (200–204°C).¹⁴ More importantly for this discussion, complex **2** isolated in the above manner gives material that provides sharp NMR resonances when examined by ¹H, ¹³C and ¹⁹F-NMR spectroscopy (Figs. S-2–S-6). Finally, measurement of the magnetic susceptibility of complex **2** reveals, including diamagnetic corrections, a χ_p value of $-6.9 \times 10^{-4} \text{ emu} \cdot \text{mol}^{-1}$ (Supplementary Materials: S-11). This situation occurs only in diamagnetic (*S* = 0) complexes.²⁸

Conclusion

Further examination of the biologically active complex bis((Z)-1-(benzo[d]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ate)-palladium (**2**) has revealed that it is diamagnetic in nature. This notion was confirmed by NMR spectroscopy and magnetic susceptibility measurements. The previously observed NMR properties of **2** may have been due to the presence of a small amount of paramagnetic impurity (hence its slightly depressed mp) or by the presence of such during spectroscopic measurement.

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Conflict of Interest The authors declare no conflict of interest.

Supplementary Materials The online version of this article contains supplementary materials.

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