On the Electronic Nature of Bis((Z)-1-(benzo[d]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ate)palladium

Kathleen L. May, Genki Watanabe, Ryosuke Saijo, Masami Kawase, and Robert A. Gossage

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. 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. It was recently reported that the benzoazole 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. 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. This situation is virtually unknown in mononuclear Pd(II) complexes regardless of the ligand donor 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

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: 400MHz; 13C(1H): 101MHz; 19F(1H): 376MHz) was carried out using a Bruker Avance II AC-400MHz spectrometer operating at 300K and using CDCl3 as solvent. Signals were calibrated based on solvent residual 1H (δH = 7.26 ppm: CHCl3) and 13C peaks (δC = 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 (δp = 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 molecular spin characteristics.

Introduction

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reference. The compound (Z)-1-(benzo[d]oxazol-2-yl)-3,3,3-trifluoroprop-1-en-2-ol (1) was synthesised as per literature procedures. DFT calculations were carried out using the Spartan 16.0 suite of programs. Initial structural minimisation was carried out via a semi-empirical PM6(tm) treatment followed by calculation at the DFT level of theory (6–31G*/LANL2DZ 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 followed by calculation at the DFT level of theory (6–31G*/LANL2DZ level). The previously observed IR bands, a UV-Vis spectrum was also recorded. Initial reports of the low solubility of 2 in MeOH solution prompted us to re-make this complex in an improved yield of 98 %. Examination of this material gave IR data (neat; Supplementary Materials: Fig. S-9) similar 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 λ₊ Max = 335.5 nm was disclosed. We have since found that 2 displays superior solubility in THF and hence a λ Max value (337 nm) with ε = 1.60 × 10⁴ M⁻¹ 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). 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 X₀ value of –6.9 × 10⁻⁵ emu mol⁻¹ (Supplementary Materials: S-11). This situation occurs only in diamagnetic (S = 0) complexes.

**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 similar 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). However, ground state energies for these idealised geometries predicted that the paramagnetic S = 1 form was considerably higher in energy (ΔE > +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 prompted 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 λ Max = 335.5 nm was disclosed. We have since found that 2 displays superior solubility in THF and hence a λ Max value (337 nm) with ε = 1.60 × 10⁴ M⁻¹ 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). 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 X₀ value of –6.9 × 10⁻⁵ emu mol⁻¹ (Supplementary Materials: S-11). This situation occurs only in diamagnetic (S = 0) complexes.

**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.

References and Notes

27) A graphing file (.mol format) for the S=1 form are available from the authors on request.