Synthesis, characterization, and structure determination of Cp*Ir(dpms)Cl

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Graphical Abstract:



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Dedication: We dedicate this paper to Professor R. Bruce King for his foundational and lifelong contributions to organometallic chemistry

ABSTRACT: Bipyridyl ligands are commonplace in catalysis. Structurally similar to this ligand class with unique properties is the novel di-(2-pyridyl)methanesulfonate (dpms) ligand, which is prepared and reacted with $[Cp*IrCl_2]_2$ to afford Cp*Ir(dpms)Cl (1) in high yield. Its single-crystal X-ray structure indicates an *exo*-(κ^2) conformation of the ligand, with the sulfonate group directed away from the iridium center. Halogen exchange by treatment of 1 with NaI gives the iodide derivative, Cp*Ir(dpms)I (2). Abstraction of the halogen from 1 using AgPF₆ generates $[Cp*Ir(dpms)]PF_6$ (3), which was not found to activate the C-H bonds of benzene.

1. Introduction

Direct cleavage of strong C–H bonds is a useful technique for generating reactive intermediates with the potential for enhanced synthetic utility. Platinum(II) complexes have shown activity in activation of $C(sp^3)$ –H bonds [1-3]. What began merely as an observation of H–D exchange facilitated by a Pt-halide complex led to advancements in strong bond activation. Shortly after this initial observation, Shilov et al. reported Pt^{II}Cl₄^{2–} catalyzed oxidation of methane to methanol in aqueous media via hydrolysis of chloromethane. However, it was found that the transformation necessitates stoichiometric quantities of Pt^{IV}Cl₆^{2–} (Scheme 1).



Scheme 1. Generalized mechanism of the Shilov cycle.

This mechanism is thought to be general for related electrophilic ligand systems. In 1994, Labinger and Bercaw investigated the oxidative step using Zeiss' salt [4]. Rather than the alkyl group transfer suggested by Shilov, their findings indicated that the necessity for stoichiometric $Pt^{IV}Cl_6^{2-}$ is its role as oxidizing agent, implying there is "no inherent mechanistic reason why Pt^{IV} could not be replaced by another suitable oxidant" [4]. Indeed, such replacements have since been attempted. Notably, in the work of Periana et al. a bypyrimidine complex of Pt^{II} , (bpym) $Pt^{II}Cl_2$, was found to oxidize methane to methyl bisulfate in excellent yields (>80%) using H₂SO₄ as oxidant [5]. Similar successes

with the Shilov system have encouraged further research into related systems with different metals and ligands [6].

One refinement reported by Vedernikov was focused on the development of a new ligand for Pt coordination, di-(2pyridyl)methanesulfonate (dpms), shown in Scheme 2 [7]. The dpms ligand is distinct from other (2,2')-bipyridyl ligands in that it contains a methinyl carbon bridge bearing a sulfonate group. NOE and X-ray experiments suggest that this sulfonate group coordinates in a hemi-labile manner which may be conformationally affected by solvent polarity [7]. Dissolution of L_nPt(dpms) in polar MeOH gave a 7:1 exo-(κ^2) to endo-(κ^2) configuration owing to greater solvent-ligand interactions in polar media. Aerobic methanol formation was later reported using а $Pt^{II}(dpms)Me_2$ system, where (κ^2)–dpms binding in the first step produces a reactive species and later (κ^3)-binding in the second step stabilizes the octahedral hydroxo-adduct (Scheme 2) [8].



Scheme 2. Formation of methanol in aqueous media by Pt^{II}(dpms)Me₂.

Other metals have also been probed for their utility in C-H bond activation, including rhodium and iridium [9,10]. Fagnou demonstrated the activity of Rh^{III} in electrophilic intramolecular C-H activation and functionalization using [Cp*RhCl₂]₂ and Cu(OAc)₂ [11] and Ellman has developed extensive synthetic methods with this chemistry [12]. Since Ir has similar 2-electron gaps in its oxidation states with stable and accessible M^{n+} (n = 1, 3, 5). Ir catalysts might participate in similar 2-electron cycling as observed in the Pt system described above. Bergman et al. demonstrated this activity in the strong C-H bond activation of benzene and methane by Ir^{III}Cp*(PMe₃)(OTf) [10,13]. Interested in the versatility of the dmps ligand and the ability of Ir to participate in similar two electron cycling as Pt, we investigated Ir-catalyzed C-H activation of benzene by a dpms compound.

2. Results and discussion

2.1. Ligand synthesis

K(dpms) was synthesized in three steps using a modified procedure from that described in the literature (see Supporting Information) [7,10]. An overview is shown in Scheme 3. The workup for step three is non-trivial and requires elaboration.



Scheme 3. Synthesis of K(dpms).

Washing with dichloromethane removes organic side products, and a methanol extraction leaves behind excess potassium salts. 2,2,2-trifluoroethanol dissolves K(dpms) and causes KBr and additional inorganic salts to precipitate for removal by filtration. In Vedernikov's procedure, the workup continues with a recrystallization from MeOH and further washes to remove impurities observed in the aromatic region of the ¹H-NMR spectrum [7]. In our hands, effective purification may also be achieved by recrystallization from EtOH.

2.2. Synthesis and characterization of Cp*Ir(dpms)Cl (1)

Formation of iridium complex **1** was optimized by screening iridium source and solvent. Both $[IrCl(COE)_2]_2$ and $IrCl_3 \cdot nH_2O$ were examined as potential iridium sources for this reaction. Solvents used include C_6D_6 , THF- d_8 , CH₂Cl₂, CDCl₃, MeOD, as well as solutions of MeOD/THF- d_8 and MeOD/CDCl₃. Each solvent and iridium source was screened with no reaction being observed. The zwitterionic nature of the K(dpms) ligand introduced challenges with solubility, which may have partially contributed to the lack

of observed product formation. Further, heating the systems either yielded no reaction or decomposition of the substrate. In consideration of McFarland and Francis' work using $[Cp*IrCl_2]_2$ to prepare substituted (2,2')-bipyridine complexes, complexation of K(dmps) with the dimer was attempted [14]. A similar procedure was followed and met with success (eq 1).



The basic structure of this complex was inferred from ¹H and ¹³C {¹H} NMR experiments, including ¹H-¹³C HSQC, which indicated 1:1 complex formation. A single crystal X-ray structure was also obtained following recrystallization from CHCl₃/pentane as shown in Figure 1. The complex was found to crystallize in the space group C2/c with one CHCl₃ molecule per iridium atom. The Cp* ring and CHCl₃ solvent molecule are modeled as disordered over two positions (50:50). The bond lengths and angles of the (dpms) portion of the complex were found to be almost identical to those of Vedernikov's (dpms)PtMe₂(OH) complex [7]. Notably, only the *exo*-conformer of Cp*Ir(dpms)Cl was observed.



Figure 1. ORTEP diagram of Cp*Ir(dpms)Cl (1). Ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected distances (Å): Ir(1)-N(1), 2.119(6); Ir(1)-N(2), 2.122(6); Ir(1)-Cl(1), 2.399(2); Ir(1)-C(6), 3.153(7); Ir(1)-H(6), 2.746.

2.3. Synthesis and characterization of Cp*Ir(dpms)I (2)

The iodo-complex Cp*Ir(dpms)I (2) was synthesized from the chloride (1) using an excess of NaI in MeCN. The product was a mixture of product 2 and some remaining starting material 1. Pure 2 was obtained by first removing chloride with AgPF₆ (*vide infra*) and then adding NaI. In contrast to 1, an *endo*-configuration of the sulfonate group is evident in the X-ray crystal structure of 2 (Figure 2).



Figure 2. Crystal structure of Cp*Ir(dpms)I, **2**. Ellipsoids are drawn at the 50 % probability level. Selected distances (Å): Ir(1)-N(1), 2.112(3); Ir(1)-N(2), 2.120(3); Ir(1)-I(1), 2.7192(4); Ir(1)-C(6), 3.429.

2.3. Generation of $[Cp*Ir(dpms)]^+$ (3⁺)

An attempt was made to determine if the (dpms) ligand system can undergo the same hemi-labile SO₃ coordination to an iridium center as it does to a platinum center [7]. The chloride ligand of 1 was abstracted with AgPF₆, producing a formally cationic species $[Cp*Ir(dpms)]^+$ (3⁺) with the sulfonate coordinated to the Ir center (eq 2). A single crystal X-ray structure was obtained, and curiously, the anion was found to be a mixture of both BF_4^- (87%) and PF_6^- (13%) (Figure 3). In another preparation, recrystallization was carried out in air, and the counterion was identified as difluorophosphate, PO2F2- and was coordinated to the iridium (eq 2, Figure 4). This anion results from hydrolysis of the PF_6^- , and has been observed previously in AgPF₆ reactions with Pd, Mn, Re, Rh, Ir, and Ru [15-21]. It was reported that PF_6^- in the presence of water and electrophilic metal ions undergoes catalytic degradation to HF and PO₂F₂-[15]. The product obtained containing a mixture of PF_6^- and BF₄⁻ anions apparently arises from reaction of HF with the borosilicate glass [22]. The X-ray structure obtained of the BF₄[−] salt indicates clean halogen abstraction, and stabilization through a κ^3 -N,N,O-dpms binding motif. Note that the 6-membered Ir-N-C-C-C-N-Ir ring must invert to permit SO₃ coordination via the endo conformation.

2.4. Reaction of [Cp*Ir(dpms)]⁺ with benzene

In an attempt to observe H/D exchange cation **3** was prepared by chloride abstraction from **1** using AgPF₆ in CDCl₃. The cation was treated with a 1:1 mixture of $C_6H_6:C_6D_6$ in trifluoroethanol, and allowed to react at RT for 20 min. No H/D exchange was observed between the benzenes by GCMS. Heating to 40 °C for 24 h did not result in exchange, nor did heating at 80 °C for 24 h. Apparently, the sulfonate group is not sufficiently basic to allow for concerted metalation deprotonation to occur [23].



Figure 3. Crystal structure of $[Cp*Ir(dpms)][BF_4]$. Ellipsoids are drawn at the 50 % probability level. Selected distances (Å): Ir(1)-N(1), 2.142(3); Ir(1)-N(2), 2.133(3); Ir(1)-O1(1), 2.184(3); Ir(1)-C(6), 3.210.



Figure 4. Crystal structure of $Cp*Ir(dpms)(PO_2F_2)$. Ellipsoids are drawn at the 50 % probability level. Selected distances (Å): Ir(1)-N(1), 2.106(3); Ir(1)-N(2), 2.107(3); Ir(1)-O(4), 2.167(2); Ir(1)-C(6), 3.136(3); Ir(1)-H(6), 2.754.

3. Conclusions

Zwitterionic complexes of Ir^{III} containing the di-(2pyridyl)methanesulfonate ligand can be prepared from [Cp*IrCl₂]₂ and K(dpms). The ligand adopted either a bidentate coordination mode through its N-atoms or tridentate mode through the bipyridyl N-atoms and a sulfonate O-atom. Halogen exchange in the complex **1** was shown to occur with NaI. The halogen can be cleanly abstracted from the complex with Ag⁺ to produce a vacant Ir site stabilized by the hemi-lability of the sulfonate group of the dpms ligand. The resulting cationic species was found to be catalytically inactive in the C–H activation of benzene.

4. Experimental section

4.1. General procedures

All reagents were used directly as purchased from Aldrich, Fisher, or Acros except for CH₂Cl₂ which was used as received from Mallinckrodt. ¹H and ¹³C NMR data were recorded on 400 MHz and 500 MHz Bruker Avance NMR spectrometers. ESI-MS spectra collected on a Thermo LTQ Velos spectrometer. Elemental analyses were performed with a PerkinElmer 2400 Series II Analyzer. Potassium di-(2-pyridyl)methane-sulfonate (K(dpms)), and [Cp*IrCl₂]₂ were synthesized as described in the literature with modifications (see Supporting Information) [7,24].

4.2. Synthesis of Cp*Ir(dpms)Cl (1)

An oven-dried 2-neck 100-mL round-bottom flask was charged with [Cp*IrCl₂]₂ (425 mg, 0.50 mmol) and a Tefloncoated stir bar prior to evacuation to 200 mTorr and N₂ backfill three times. Potassium di-(2-pyridyl)methanesulfonate (300 mg, 1 mmol, 2 equiv.) was dissolved in 40 mL MeOH and added to the flask via syringe through a rubber septum. Upon completion of the addition, the mixture appeared opaque and yellow-orange. The mixture was stirred vigorously under N₂ for 67 h at 22 °C. Solvent was removed under reduced pressure and the yellow powder was dried in vacuo (708 mg, 96%). Purification was achieved by recrystallization from CH2Cl2 layered with pentane in a -40°C freezer. The product is well soluble in chlorocarbons and moderately soluble in THF and MeCN. ¹H NMR (500 MHz, CDCl₃): δ 8.95 (d, J = 7.7 Hz, 2H), 8.72 (d, J = 5.5 Hz, 2H), 7.91 (td, J = 8.0, 1.5 Hz, 2H), 7.33 (dd, J = 9.6, 3.5Hz, 2H), 5.03 (s, 1H), 1.62 (s, 15H). ¹³C NMR (126 MHz, CDCl₃): δ 156.29 (C_{Py}), 153.17 (C_{Py}), 140.58 (C_{Py}), 126.55 (C_{Pv}), 124.88 (C_{Pv}), 88.69 (C₅Me₅), 73.95 (CH), 8.83 (C₅Me₅). Anal. calcd(found) for C₂₁H₂₄ClIrN₂O₃S·³/₄CHCl₃: %C, 37.23 (37.33); %H, 3.56 (3.58); %N, 3.99 (4.14). (A single crystal X-ray structure shows CHCl₃ in the unit cell.) ESI-MS(neg. ion) m/z calcd for (1) [M]: 612.0. Found: 610.9 $(M-H^{+}).$

4.3. Synthesis of Cp*Ir(dpms)I (2)

A 20-mL scintillation vial was charged with 1 (20 mg, 0.033 mmol), sodium iodide (734 mg, 4.89 mmol, 150 equiv.) and a Teflon-coated stir bar. To this was added MeCN (\sim 15 mL), and the mixture was stirred under air at 22 °C for 91 h. Solvent was removed under reduced pressure, and the yellow-orange solid was dissolved in DCM and

washed with 2 × 15 mL water to remove salt. The organic layer was dried over MgSO₄ and filtered. Solvent was again removed under reduced pressure before recrystallization from CHCl₃/pentane. ¹H NMR (400 MHz, CDCl₃): δ 9.11 (dd, *J* = 5.9, 1.6 Hz, 2H), 8.90 (d, *J* = 8.1 Hz, 2H), 7.88 (td, *J* = 7.9, 1.6 Hz, 2H), 7.23 – 7.17 (m, 2H), 4.99 (s, 1H), 1.72 (s, 15H). This material was determined by ¹H NMR spectroscopy to be 80% iodide product, with 20% remaining **1**. A single crystal X-ray structure suggested 75% iodide product, 25% remaining chloride. An improved synthesis was made by reaction of **3**⁺ with excess NaI. A crystal structure of pure **2** was obtained from this material after recrystallization from CHCl₃/pentane.

4.4. Generation of $[Cp*Ir(dpms)]^+(3^+)$

In a glove box under N₂ atmosphere, a solution of 1 (25 mg, 0.04 mmol) in CDCl₃ (~10 mL) was treated with AgPF₆ (20 mg, 0.08 mmol, 2 equiv.) and stirred for 90 h. The reaction mixture was filtered and layered with hexanes (in air) to obtain yellow crystals after 2 weeks in a -20 °C freezer. ¹H NMR (500 MHz, CDCl₃): δ 9.01 (d, *J* = 8.1 Hz, 2H), 8.76 (d, *J* = 5.8 Hz, 2H), 7.98 (t, 2H), 7.46 (t, *J* = 6.7 Hz, 2H), 4.91 (s, 1H), 1.65 (s, 15H). A sample was crystallized in the drybox from chloroform/hexane, and a single-crystal X-ray structure showed a mixture of BF₄⁻/PF₆⁻ as counterion (0.87:0.13). A second crystallization was carried out in air, and a single-crystal X-ray structure showed replacement of the halogen with a coordinated PO₂F₂⁻ counteranion.

4.5. Attempted H/D Exchange with $[Cp*Ir(dpms)]^+(3^+)$

In a glove box under N_2 atmosphere, a 20-mL scintillation vial was charged with 1 (25 mg, 0.04 mmol), AgPF₆ (25 mg, 0.99 mmol, 2.4 equiv), a Teflon-coated stir bar, and fitted with a rubber septum. CDCl₃ (5 mL) was added through the septum via syringe and the solution was stirred in the dark for 145 h. A yellow precipitate formed that was collected by decantation and subsequently dried in vacuo. Outside the glovebox, N2 was bubbled through 2,2,2trifluoroethanol (TFE) for 15 minutes to degas the solvent. The yellow solid was redissolved in TFE (7 mL) before addition of equal volumes (100 µL) of C₆H₆ and C₆D₆ through the septum under positive N₂ pressure. The mixture was stirred at 22 °C under static N2. After 20 minutes, an aliquot (0.2 mL) of the reaction mixture was added to diethyl ether (2 mL), filtered, and analyzed by GC-MS: m/z (% relative intensity, ion): 76 (7.9%, $C_6H_6^+$ - 2), 77 (23.8%, $C_6H_6^+$ - 1), 78 (91.9%, $C_6H_6^+$), 79 (6.2%, $C_6H_5D^+$), 80 $(3.6\%, C_6H_4D_2^+)$, 82 $(15.9\%, C_6H_2D_4^+)$, 84 $(100\%, C_6D_6^+)$, 85 (6.5%, $C_6D_6^+$ + 1). After stirring for 21h at 22 °C, a repeat GC-MS analysis demonstrated no significant change in the relative intensities of the features at m/z = 78 and 84. Similar results were obtained after heating the mixture at 40 °C for 24.5 h and then at 80 °C for an additional 24 h. A color change from yellow to grey was noted in the reaction mixture before the temperature was increased to 80 °C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Synthetic details for the K(dpms) ligand, ¹H NMR spectra of **1**, **2**, and **3**⁺, ¹³C NMR spectrum of K(dpms) and **1**; X-ray structural details and data for **1**, **2**, **3**⁺BF₄⁻, **3**⁺PO₂F₂⁻ and di(2-pyridyl)bromomethane. The structures have been deposited in the Cambridge Crystallographic Database as CCDC# 2055322, 2193653-2193655, and 2207303. This material is available free of charge via the Internet at http://xxxxxxxxxxxx.

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