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Synthesis and characterisation of a novel mixed donor P,O,P' nixantphos ligand and its metal complex

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ABSTRACT

The complex [(NixC8OH)Ir(cod)Cl] **4** has been synthesized and structurally characterized by NMR, IR and single crystal X-ray diffraction. The synthesis and characterisation of the novel ligand NixC8OH is also presented. The coordination around Ir is trigonal bipyramidal with both P groups of the NixC8OH ligand bound in a *bis*-equatorial mode. The *bis*-chelating cod (C_8H_{12}) ligand occupies the remaining equatorial position and an axial position. This mode of bonding has resulted in a large bite angle (P1–Ir–P2) of 102.92(12)° for the title complex **4**. The IR and NMR data further support the elucidated structure. Thermal analyses of **4** indicate that it is thermally stable up to a decomposition temperature of >400 °C.

1. Introduction

The ability to control the shape of a coordination compound in catalysis has been an area of intense research interest. The pioneering work of Trofimenko in the mid 1960's introduced *tris*(-pyrazol-1-yl)borate anions (Tp) and their analogues into the field of coordination chemistry [1–4]. These ligands were characterised by their unique *fac* binding (Fig. 1a) to a metal centre and are known as scorpionate ligands. Other tridentate ligands including the pincer types preferentially coordinate to metals in a *mer* binding mode (Fig. 1b). Additionally, PCP pincer ligands due to the disposition of their donor atoms give complexes with Ir that can activate highly inert C–H bonds [5]. Based on the success of tridentate ligands we became interested in the design and complexation of a new class of xanthene based ligands.

Herein we report the synthesis of a mixed donor P,O,P' scorpionate type ligand **2** and the structure of its iridium metal complex **4** (Scheme 1). The ligand backbone nixantphos **1** belongs to the xanthene family introduced by van Leeuween and co-workers [7,8]. These ligands have been extensively reviewed for their P,P *cis*-κ^2 coordination mode to transitional metal centres [9–14] (Fig. 1c), and some fully characterised cationic and neutral complexes exhibiting *mer*–κ^3–P,O,P coordination modes via the oxygen atom of the xanthene ring have been reported (Fig. 1b) [15–22]. It is important to highlight that recently Weller and co-workers have reported the structure of the complex [Ir(κ^3(Xantphos)(H)(μ-H)]$_2$[BAr$^F{}_4$]$_2$ which also displayed the rare *fac*-κ^3–P,O,P coordination [15]. This study, therefore serves as another basis towards the unambiguous preparation of *fac* coordinating κ^3 ligands derived from nixantphos **1** where a third donor has been functionalised onto the backbone.

2. Experimental

2.1. Materials and methods

Chemicals used were of reagent grade and reactions were carried out in distilled and dried solvents using standard Schlenk tube techniques under inert and dry nitrogen atmosphere. Iridium trichloride hydrate ($IrCl_3 \cdot xH_2O$) was obtained from Johnson Matthey and used as received. The precursor (8-bromooctyloxy)(*t*-butyl) dimethylsilane was prepared by literature method [23]. The dimeric chloro bridged precursor di-μ-bis(1,5-cycloocatadiene) diiridium(I) [Ir(cod)Cl]$_2$ **2** was prepared by the reduction of $IrCl_3$ in the presence of excess 1,5-cyclooctadiene (cod) (Fluka ≥98%) in aqueous ethanol (Merck absolute ACS grade) [24]. FTIR spectra were recorded in the 4000–400 cm^{-1} region on a Perkin Elmer attenuated total reflectance (ATR) infrared spectrophotometer. ^{1}H,

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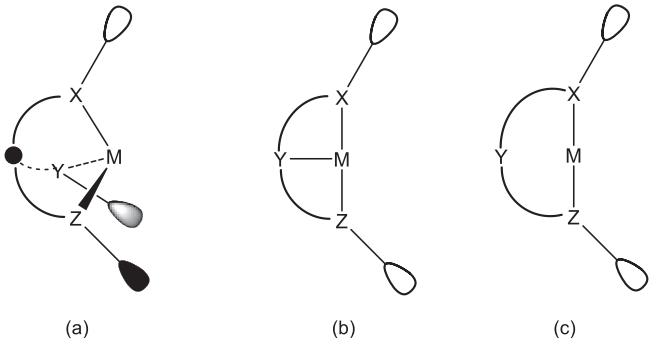
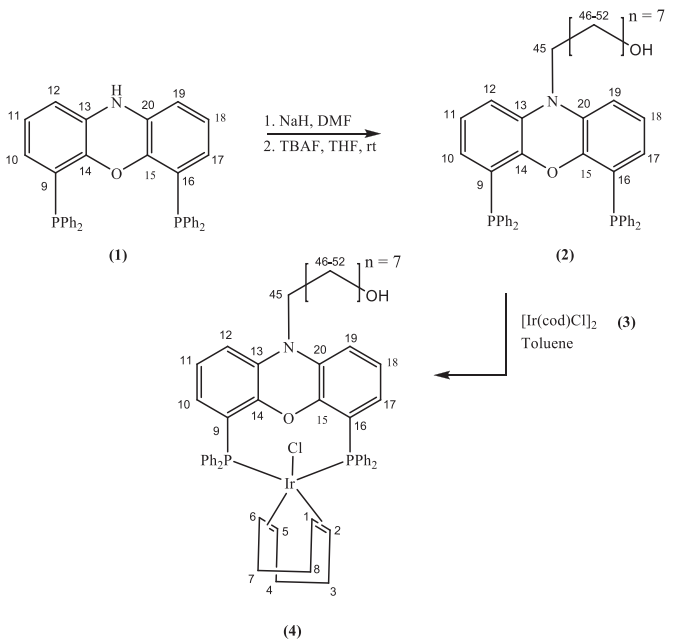


Fig. 1. Comparison between (a) the *fac* coordination of a κ^3 tripodal ligand (b) the *mer* binding of a κ^3 pincer ligand and (c) *cis*-κ^2 coordination of a bidentate ligand [6].



Scheme 1. Synthesis of the title complex **4** from ligand **2**.

^{31}P and ^{13}C NMR measurements were collected at 298 K with Bruker AVANCE III 400 MHz and 600 MHz spectrometers using 5 mm tubes and deuterated chloroform as the solvent. Coupling constants (*J*) are given in Hz. The melting point was determined using a Gallenkamp melting point apparatus and is uncorrected. High resolution mass spectroscopy was obtained with the Bruker micrOTOF-Q II instrument operating at ambient temperatures, under electron spray ionisation conditions (ESI), using a sample concentration of approximately 1 ppm. Differential scanning calorimetry (DSC) measurements (Al_2O_3 reference standard) were performed on a TA Thermo Gravimetric Analyser at a heating rate of 10 °C/min under nitrogen atmosphere. Elemental analyses were performed on a LECO CHNS-932 elemental analyser.

*2.1.1. Synthesis of compounds **2** and **4***

Synthesis of **2**. Nixantphos **1** (200 mg, 0.36 mmols) was dissolved in DMF (4 mL). To the orange reaction mixture, NaH (400 mg, 0.72 mmol) was added. (8-bromooctyloxy)(*t*-butyl)dimethylsilane (180 mg, 0.63 mmol) was slowly added, and the mixture stirred at 100 °C overnight. The reaction was worked up by the addition of water (10 mL) and the organic phase extracted with ethyl acetate (4 × 10 mL). The collective fractions were dried over anhydrous sodium sulphate and purified by column chromatography with 10% hexane/ethyl acetate elution. The resulting oil was dissolved in THF (25 mL), and tetra-*N*-butylammonium fluoride added and solution was left to stir overnight at room temperature. Thereafter, similar aqueous work-up was carried out. The crude product was purified by column chromatography with 20% ethyl acetate/hexane elution to afford **2** in 28% (38 mg oil). IR ν_{max} (cm^{-1}): 3343(m),3053(m), 2924(m), 2853(m), 1726(m), 1462(s), 1435(s), 1412(s), 1276(m), 1222(m), 743(s), 693(s); HR-MS (ESI) (*m*/*z*):$[M+H]^+$calcd. for $C_{44}H_{44}NO_2P_2$, 680.2842; found, 680.2843. Details of the NMR data are presented in Table 1.

Synthesis of **4**. Compound **3** (30 mg, 0.04 mmol) was added to $[Ir(cod)Cl]_2$ (13.4 mg, 0.02 mmol) in THF (6 mL) under an inert argon atmosphere at room temperature. Immediate discoloration was observed, and the mixture was allowed to stir overnight. The THF solvent was removed *in vacuo* and the resulting precipitate was washed with hexane (3 × 6 mL), and extracted with dichloromethane (2 × 6 mL). The dichloromethane was removed *in vacuo* and the complex **4** dried under high vacuum overnight to afford **4** in 52% (21 mg yellow powder). Melting point 504 K, DSC 513 K; IR ν_{max} (cm^{-1}):1938(s), 2920(m), 1585(m), 1489(s); HRMS (ESI) (m/z): $[M]^+$ - Cl calcd for $C_{52}H_{55}IrNO_2P_2$, 980.3332; found, 980.3333; EA: Calculated for $C_{52}H_{55}ClIrNO_2P_2$: C, 61.5; H, 5.5, N; 1.4. Found: C, 61.0; H, 5.2; N, 1.3. Details of NMR data are presented in Table 2.

2.1.2. Structure analysis and refinement

Single-crystal structure determination by X-ray diffraction was performed on a Bruker APEXII CCD area-detector diffractometer with graphite monochromated Mo K_α radiation (50 kV, 30 mA) using the APEX 2 data collection software [25]. The collection method involved ω-scans of width 0.5° and 512 × 512 bit data frames. Data reduction was carried out using the *SAINT+* software [26] and face indexed absorption corrections were made using the software *XPREP*. The crystal structure was solved by direct methods using *SHELXTL*. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*. Hydrogen atoms were first located in the difference map then positioned geometrically and allowed to ride on their respective parent atoms with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Diagrams and publication material were generated using SHELXTL [27], PLATON [28] and ORTEP-3 [29]. The n-octanol tail was found to be disordered. As a consequence it was refined over two positions with final occupancies of 0.414(14) and 0.586(14) using SADI restraints. Further details of the X-ray structural analysis are given in Table 3, while selected bond lengths and angles for **4** are listed in Table 4. The asymmetric unit was found to contain 2 molecules and 1 fragment of 2-propanol.

3. Results and discussion

3.1. Synthesis

Ligand **2** was prepared by the sodium hydride induced alkylation of nixantphos **1** with a protected tail precursor. Deprotection by standard methods of the resulting product resulted in the O-donor ligand **2**. Complex **4** was readily prepared from $[Ir(cod)Cl]_2$ metal precursor and ligand **2** at room temperature to afford 52% yield of a yellow powder. Single crystals of **4** suitable for X-ray analyses were grown by slow diffusion of 2-propanol into a dichloromethane solution of the complex.