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Note

A luminescent Pt-POCN pincer complex via direct cyclometalation

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ABSTRACT

We report the synthesis of the novel pincer complex $\kappa^P,\kappa^C,\kappa^N$-[2,6-(iPr$_2$PO)-(C$_6H_3$)(CH$_2$[*c*-N(CH$_2$)$_4$O])]PtBr (Pt(POCN)Br, **1a**) by direct cyclometalation of PtBr$_2$(SEt$_2$)$_2$. This represents the first report of a mixed-donor platinum pincer complex synthesized using cyclometalation. The complex is emissive in the solid state and frozen solution. Comparison of the structure of **1a** to related pincer complexes provides insights into the effect of pincer arm donor substituents on cyclometalation.

Introduction

For a number of years, chelating symmetric pincer complexes of platinum group metals have been studied, with emphasis on catalytic applications [1–6]. For example, phosphine and phosphinite pincer complexes are active catalysts for reactions ranging from CO_2 reduction [7–9], hydrosilylation [10,11], and the Kharasch addition [12] to organic carbon–carbon coupling reactions [13]. More recently, there has been growing interest in mixed-donor ligands, in which either the central carbon donor is replaced with a heteroatom [14–16] or the two pincer arms each have different donors [17–20]. These modifications influence the ligand's steric and donor properties, allowing for fine-tuning of reactivity (Scheme 1). Less attention has been given to their electronic and emission spectroscopic properties. Even among symmetric pincer ligand complexes, although NCN derivatives have been the subject of a number of such studies [21–31] (*e.g.*, Pt(pip$_2$NCN)L^{n+} complexes [29], Scheme 1), phosphorus-containing pincer complexes have received comparatively little attention. One exception is the work of Zargarian and coworkers, which focused on a charge-transfer band observed at approximately 400 nm in both nickel POCOP and POCN complexes. The effects of modifications to pincer ligand substituents, metal oxidation state, and trans-ligand were examined [12,17,32,33]. Such studies have served to deepen understanding of the influence of ligand architecture on the electronic structures of pincer complexes, which is essential for intelligent ligand design aimed at accessing multielectron catalytic properties of pincer complexes using light.

Because of the rich emission spectroscopy, long-lived excited states and photochemistry of many platinum complexes, there is particular interest in mixed-donor pincer ligand platinum complexes. Yet surprisingly little precedent exists for the synthesis of such compounds. The one platinum POCN complex previously reported was synthesized via oxidative addition [19]. However, that synthetic route requires use of a Pt^0 precursor that is prepared in low yield [34,35]. In a second strategy, lithiation of a brominated metal precursor has proven a reliable choice for synthesis of NCN complexes [36]. However, that route is problematic for synthesis of phosphinite complexes, because attack on the P–O bond by nucleophilic organolithium reagents competes with the desired metal-halide substitution chemistry. Another possible strategy is transcycloplatination, which takes advantage of the relative strength of Pt–P bonds vs. Pt–N bonds to accomplish the formal exchange of ligands, such as replacement of an NCN ligand with a PCP ligand [37]. An inconvenience of this approach is the need to prepare a cyclometalated starting material.

An attractive alternative route is direct cyclometalation, which has been employed successfully with platinum phosphine pincer complexes since the earliest days of pincer complex chemistry [38] and has been used previously in preparation of platinum

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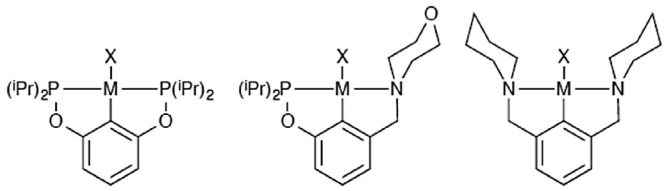


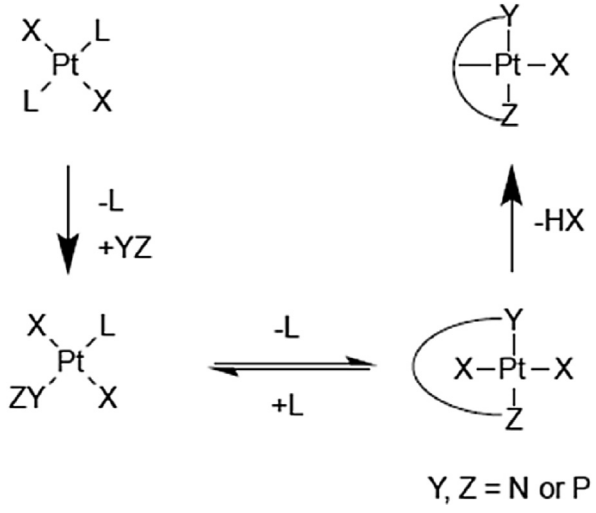
Scheme 1. Types of pincer complexes.

phosphinite pincer complexes [39]. One possible mechanism involves coordination of the pincer arms prior to C–H activation, as shown in Scheme 2; other mechanisms are possible, including those in which an amine pincer arm acts as an internal base [37]. In the case of cyclometalation, care must be taken in choice of metal precursor in order to circumvent formation of insoluble Pt^{II} and Pd^{II} oligomers [38,40,41]. Moreover, direct cyclometalation has a mixed record with respect to platinum NCN-type pincer complexes and is typically not a practical synthetic route. For example, this is not an effective approach for the synthesis of Pt(pip_2NCN)Br and related complexes [29]. Studies suggest that the bonds between the metal and aliphatic amines of the pincer arms are comparatively weak. Therefore, it is more difficult to achieve simultaneous coordination of both pincer arms, which for the mechanism shown in Scheme 2, is believed to be necessary to promote activation of the relatively inert central sp^2 C–H bond [1]. Herein, we examine the intermediate case involving a mixed-donor pincer ligand. Whereas a previous synthesis of platinum POCN-type pincer complexes has been accomplished via the oxidative addition route [19], here we report the preparation of a novel mixed-donor platinum pincer complex, Pt(POCN)Br, by direct cyclometalation (Scheme 1) of a dihalobis(-thioether) platinum precursor. Analysis of the conditions under which this cyclometalation occurs, as well as comparison of the structure of Pt(POCN)Br with other known pincer complexes, provides insight into the influence of pincer arm substituents on cyclometalation.

Experimental

General

$PtBr_2$, $NiBr_2$, 3-hydroxybenzaldehyde, chlorodiisopropylphosphine, and ethyl sulfide were purchased from Sigma Aldrich. All other reagents were purchased from Fisher. Benzene was purchased from Alfa Aesar, n-hexane was purchased from Tedia, ethyl acetate was purchased from Pharmco-Aaper, high-purity spectroscopic anhydrous methanol and ethanol were purchased from Sigma Aldrich, and all other solvents were purchased from Fisher. THF was distilled after drying over sodium metal and benzophenone. Toluene and benzene were dried over calcium hydride and distilled prior to use. Air-sensitive work was performed under an argon atmosphere using standard Schlenk and glovebox techniques. Solvents for air-sensitive reactions were degassed using three freeze-pump-thaw cycles. $PtBr_2(SEt_2)_2$ was prepared analogously to a literature procedure for the preparation of $PtCl_2(SEt_2)_2$ [42].



Scheme 2. Steps during cyclometalation of pincer complexes.

^{1}H and ^{31}P NMR spectra were recorded at room temperature using a Bruker AC 400 MHz instrument. Deuterated solvents ($CDCl_3$ and C_6D_6) were purchased from Cambridge Isotope Laboratories. ^{1}H NMR spectra are reported relative to TMS, and ^{31}P NMR spectra are reported relative to 85% H_3PO_4 at $\delta = 0$. UV–visible absorption spectra were recorded using a HP8453 UV–visible diode array spectrometer. Frozen solution emission spectra were recorded using a SPEX Fluorolog-3 fluorimeter equipped with a double-emission monochromator and a single excitation monochromator. 77 K Glassy solutions were prepared by inserting a quartz EPR tube containing a 4:1 ethanol:methanol solution of the respective complex into a quartz-tipped finger dewar. Emission spectra were corrected for instrumental response. Solid-state emission spectra were collected using a Renishaw Raman Microscope using a 442 nm HeCd laser for excitation and a 20x objective lens to magnify the sample. Mass spectra were obtained by electrospray ionization (ESI) of acetonitrile solutions using a Micromass Q-TOF-2 instrument.

*Synthesis of Pt(POCN)Br (**1a**)*

The ligand precursor, POC(H)N, was prepared *in situ*. To a solution of chlorodiisopropylphosphine (1.3 mmol, 0.21 mL) in 5 mL toluene was added via cannula a solution of 3-((morpholino)methyl)phenol (1.3 mmol, 0.3455 g) and triethylamine (1.6 mmol, 195 μL) in 5 mL toluene at 10 °C and allowed to warm to room temperature while stirring. The mixture was filtered to remove precipitate, and the solvent was removed to give a pale orange oil. Next, a 2 mL toluene solution of $PtBr_2(S(CH_2CH_3)_2)_2$ (1.3 mmol, 0.6796 g) and triethylamine (1.6 mmol, 195 μL) were added to POC(H)N via cannula, and the resulting solution was refluxed for 24 h. After cooling to room temperature, the solvent was removed under vacuum. The product was purified by chromatography using a silica column and dichloromethane as the eluent. Yield: 0.1231 g, 17%. ^{1}H NMR ($CDCl_3$, δ): 1.21-1.26 (dd, $^3J_{PH} = 16$ Hz, $^3J_{HH} = 7$ Hz, 6H, $PCHC\underline{H}_3$), 1.32-1.39 (dd, $^3J_{PH} = 19$ Hz, $^3J_{HH} = 7$ Hz, 6H, $PCHC\underline{H}_3$), 2.41-2.49 (m, 2H, $PC\underline{H}$), 2.92 (d, $^3J_{HH} = 13$ Hz, 2H, $NC\underline{H}_2CH_2$), 3.88-3.98 (m, 4H, $ArC\underline{H}_2N$ and $OC\underline{H}_2CH_2$), 4.21 (t, $^3J_{HH} = 11$ Hz, 2H, $NC\underline{H}_2CH_2$), 4.49 (t, $^3J_{HH} = 12$ Hz, $OC\underline{H}_2CH_2$), 6.66 (d, $^3J_{HH} = 8$ Hz, 1H, {Ar}H^5), 6.74 (d, $^3J_{HH} = 7$ Hz, 1H, {Ar}H^3), 6.98 (t, $^3J_{HH} = 8$ Hz, 1H, {Ar}H^4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ) 160.56 ($J_{PtP} = 4655$ Hz). MS-ESI (m/z). Observed (Calculated): 582.1 (582.1), $[Pt(POCN)BrH]^+$; 605.1 (605.1), $[Pt(POCN)BrNa]^+$; 503.2 (503.1) $[Pt(POCN)]^+$.

*Synthesis of Ni(POCN)Br (**1b**)*

The product was prepared by modification of the procedure of Zargarian et al. [17]; however, the metal precursor was added directly to the ligand precursor without first isolating the ligand precursor. A solution of chlorodiisopropylphosphine (2.7 mmol, 0.45 mL) in 7.5 mL THF was added via cannula to a solution of 3-((morpholino)methyl)phenol (2.6 mmol, 0.5046 g) and triethylamine (2.8 mmol, 400 μL) in 17.5 mL THF at −10 °C and allowed to