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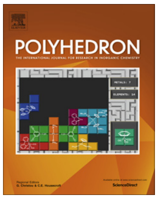

Tuning iridium (I) $PC_{carbene}P$ frameworks for facile cooperative N_2O reduction

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Dedicated to Prof. Bill Jones, a giant of organometallic chemistry, on the occasion of his 65th birthday.

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ABSTRACT

Two electron-rich PCP ligands were synthesized featuring $-C(CH_3)_2-$ and $-Si(CH_3)_2-$ functional groups linking the framework backbone. $PC_{carbene}P$–Ir–Cl complexes were prepared *via* double C–H activation protocols and the donor strengths of the new ligands were evaluated using CO stretching frequencies of monocarbonyl cations prepared from the corresponding carbene chlorides. The new tethered systems were found to be superior donors with respect to $PC_{carbene}P$ pincer complexes previously reported in our group. These carbene chloride complexes reacted readily with nitrous oxide (N_2O) to form "iridaepoxides" immune to unwanted C_{aryl}–C_{anchor} cleavage. Rates of oxygen atom transfer from N_2O to a series of $PC_{carbene}P$–Ir–Cl compounds were also measured using $^{31}P\{^1H\}$ NMR spectroscopy. Results suggested a direct positive correlation between ligand donicity and O-atom transfer rate for all *ortho*-phenylene derived systems. The sterically distinct 2,3-benzo[*b*]thiophene scaffold was found to be an outlier of this trend with a relatively high reactivity rate and ν_{CO}.

1. Introduction

Since the seminal work of Moulton and Shaw [1], metal complexes supported by pincer ligands have become important fixtures in homogeneous catalysis [2]. Participating in a large array of chemical reactivity, from alkane dehydrogenation [3] to CO_2 reduction [4], pincer complexes have shown great versatility due to easily modifiable, rigid scaffolds that exhibit great thermal stability [2,5]. Tridentate pincer ligands consist of three two-electron donor atoms – typically, but certainly not limited to, phosphorus, nitrogen and carbon – chelated in a coplanar fashion around a metal centre [2,6]. The coordinated atoms may be present in a variety of combinations and ligands are categorized by the flanking and central atoms using elemental symbols for their designation (i.e. PNP, PCP, etc.; Scheme 1) [7].

While conventional organometallic reactions take place at the metal centre, several transformations have been observed with a ligand directly participating along with the metal; this is known as metal–ligand cooperativity (MLC) [8,9]. Pincer complexes are no exception and in recent years research has indicated MLC can play a tremendous role in promoting the activation of small molecules, such as H_2, NH_3, CO_2 and H_2O [8,10,11]. More recently, there has been interest in the activation and catalytic reduction of nitrous oxide (N_2O), a relatively inert and potent greenhouse gas [12,13]. Early studies utilized the ability of N_2O to insert an oxygen atom into M–H bonds as a means of substrate activation, with subsequent reductive elimination of H_2O to complete the hydrogenation cycle [14–16]. Gianetti and co-workers similarly propose "conventional" N_2O activation in reactions that utilize nitrous oxide as a hydrogen acceptor or oxygen atom transfer agent [17,18]. In contrast, Milstein and co-workers have demonstrated the catalytic hydrogenation and hydrosilation of N_2O proceeds *via* a MLC mechanism involving ligand aromatization/dearomatization using a ruthenium PNP complex [19].

In this context, we found that iridium $PC_{carbene}P$ pincer complexes interact with N_2O *via* a distinct type of MLC. The Ir=C linkages anchoring these pincer ligands are more "Fischer-like" [20–22] and quite capably form "iridaepoxides" through the addition of an oxygen atom across an M=C bond when exposed to N_2O (**B**, Scheme 2) [23]. These iridaepoxides add hydrogen to give a dihydride species **C**, [23,24] but this thermodynamic isomer must convert to a kinetic species where the hydride ligands are *cis* to the O atom in order to release H_2O. While H_2O could be released with heating, catalytic turnover in these systems was hampered by the high barrier to water elimination from **C** and unfavorable relative kinetics of N_2O vs H_2 addition to the Ir=C bond. Furthermore, in the presence of H_2 iridaepoxides can undergo unwanted

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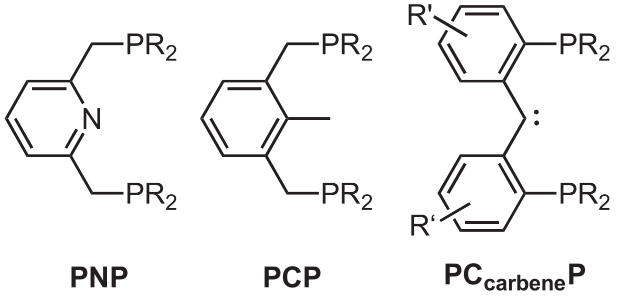


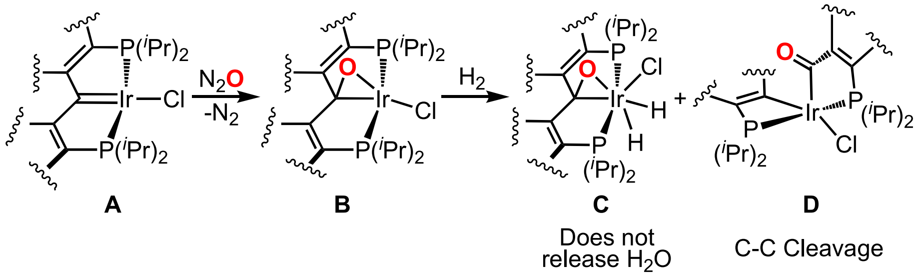
Scheme 1.

$C_{aryl}–C_{cleavage}$ [25]. Since many of these problems stemmed from slow N_2O reactions with the Ir=C species **A**, we sought ways in which to increase the rate of this reaction relative to H_2 addition through ligand design. We hypothesized that more electron donating, and rigid ligand frameworks would facilitate this reaction, while slowing the addition of H_2 to the Ir=C bond to give coordinatively saturated Ir(III) hydrido chloride species [22].

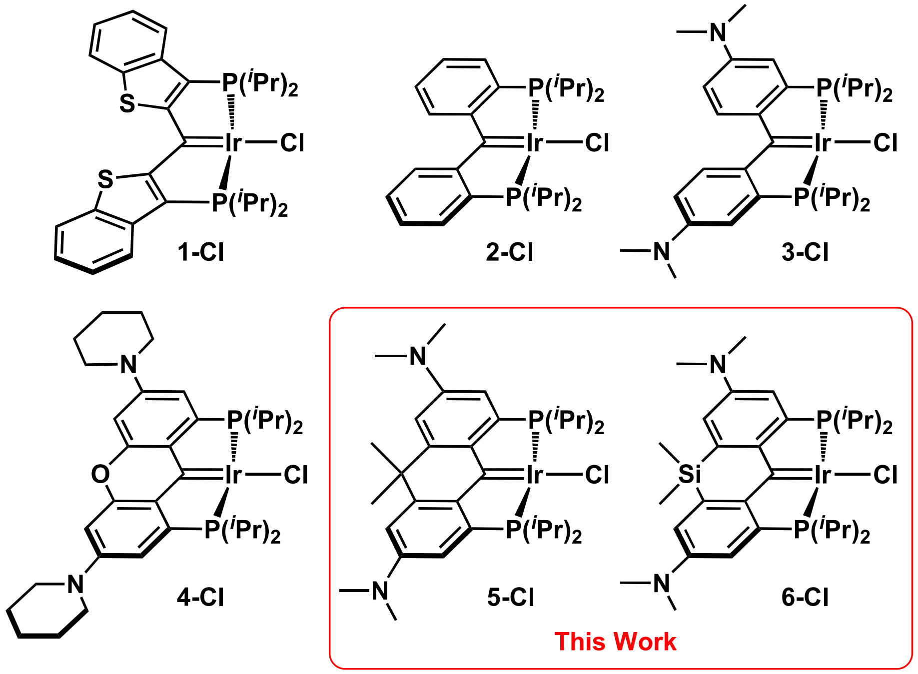
Recently our group ranked a series of iridium $PC_{carbene}P$ complexes (**1** to **4-Cl**, Scheme 3) according to ligand donor strength by preparing cationic carbonyl and dicarbonyl derivatives and cataloguing the CO stretching frequencies [26]. Among this collection was the tethered system **4-Cl**, which exhibited an intermediate ligand donor strength relative to **2-Cl** and **3-Cl**. However, preliminary experiments showed that the more rigid ligand framework in **4-Cl** rendered it immune to $C_{aryl}–C_{anchor}$ cleavage and furthermore that it reacted much more rapidly with N_2O than **2-Cl** (but slower than the more electron rich **3-Cl**). It thus appeared as though ligand donor ability could be exploited to enhance reactivity at the M=C bond, while rigid ligands prevent C–C bond cleavage deactivation pathways. Therefore, we designed similarly rigidified but more electron-rich derivatives. Herein, we report the synthesis and characterization of the two new iridium $PC_{carbene}P$ complexes, **5-Cl** and **6-Cl**. Mono- and dicarbonyl cationic derivatives are prepared and carbonyl stretching frequencies (ν_{CO}) are used to gauge ligand donicity. Reaction profiles of complexes **1** through **6-Cl** with N_2O are compared alongside their ν_{CO} to reveal any trends linking donor strength and reaction rate.

2. Results and discussion

Previously, we established a method for preparing an electron rich, rigidified iridium $PC_{carbene}P$ system **4-Cl** [26]. However, the cumbersome 14 step synthesis from 1,3,5-tribromobenzene and unexpectedly low ligand donor strength relative to **3-Cl** suggested that replacing the electronegative O linker in the ligand of **4-Cl** with a more electron donating fragment like $–C(CH_3)_2–$ or –Si



Scheme 2.



Scheme 3.