Asymmetric bis-PNP pincer complexes of Zirconium and Hafnium - a measure of hemilability.

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Abstract

Asymmetrically-bound pyrrollide-based bis-PNP pincer complexes of zirconium and hafnium have been formed. The $[\kappa^2\text{-PNP}^\text{Ph}]$[$\kappa^3\text{-PNP}^\text{Ph}]\text{MCl}_2$ species are in direct contrast to previous zirconium PNP pincer complexes. The pincer ligands are fluxional in their binding and the energy barrier for exchange has been approximated using VT-NMR spectroscopy and the result validated by DFT calculations.

Introduction

Pincer ligands, tridentate ligands where a central ligating moiety is flanked by two others, occupy a privileged position in coordination chemistry. Their modular nature allows a chemist to fine-tune both the steric and electronic properties of the metal centre. Such design has allowed the development of active catalysts for a vast array of transformations. When first used by Van Koten in 1989 the term pincer ligand strictly applied to an ‘LXL’ ligand, where a central anionic carbon atom was flanked by two donors (which would force a meridional geometry). This definition has been broadened to include several different central heteroatom donors including O, Si and N. For the last, an archetypical motif is that of PNP, where a central pyridine is flanked by methylene phosphines (Figure 1, top). The non-innocence of this ‘LLL’ ligand has been exploited to accomplish difficult bond activations. A somewhat less frequently deployed PNP pincer ligand is one where the pyridine ring is replaced by a pyrrole ring, giving a formally anionic ‘LXL’ ligand ($[\text{PNP}^\text{Ph}]$, Figure 1, bottom). What we found particularly interesting is that, for both PNP congeners, the phosphorus centres are usually further substituted with alkyl substituents rather than aryl groups. Since its first synthesis in 2012 the phenyl substituted pyrrollide-PNP pincer ligand has been relatively underused, especially given both the commercial availability of the precursors and its varied reactivity.
Figure 1: The general structures of pyridine-based and pyrrollide-based PNP ligands. Emboldened [PNP\textsuperscript{R}] refers exclusively to the anionic pyrrollide-PNP, where R indicates the substituents on the phosphine.

Our interest was also piqued by the recent resurgence of early transition metal pincer chemistry. Initially pioneered by Fryzuk and others from the 1970s onwards,\textsuperscript{14} it remains remarkably underdeveloped when compared with the later transition metals. However recent work has shown rich chemistry within early transition metal pincer complexes which are capable of facilitating extremely challenging transformations, for example the activation of methane.\textsuperscript{15}

With the pyrrollide-based [PNP\textsuperscript{R}] ligand (where R represents the substituents on the phosphines), the formally anionic pyrrollide should bind strongly, however the phosphorus centres will form comparatively weaker interactions with early transition metals versus later transition metals. This provides the tantalising prospect of hemilability. Early transition metal [PNP\textsuperscript{R}] complexes have exclusively had alkyl substituents in the past. Sc[PNP\textsuperscript{R}] and Y[PNP\textsuperscript{R}] (R = Cy, 'Bu) have been shown to facilitate C-H activation, hydrosilylation and hydrogenation of olefins and support reactive methyldiene complexes.\textsuperscript{16–18} Recently Nishibayashi and co-workers have shown that Ti[PNP\textsuperscript{tBu}], V[PNP\textsuperscript{tBu}] and Zr[PNP\textsuperscript{tBu}] complexes are able to catalyse dinitrogen reduction.\textsuperscript{19,20} In order to explore the steric and electronic profile of pyrrollide-based PNP ligands we wished to investigate the synthesis and properties of the phenylated derivative [PNP\textsuperscript{Ph}] (Scheme 1).

Scheme 1: The synthesis of [PNP\textsuperscript{Ph}]\textsubscript{2}MCl\textsubscript{2}, M = Zr, Hf. (i) \textsuperscript{t}BuLi in THF, -78°C then RT for 1 hour. (ii) ZrCl\textsubscript{4}-2THF/HfCl\textsubscript{4}-2THF.

Results and Discussion

The synthesis of [PNP\textsuperscript{Ph}]H and its subsequent lithiation has been previously reported and is analogous to the alkylated congeners.\textsuperscript{11,16,19,21–29} A variety of lithium bases have been used in the literature but in our hands the conditions outlined in scheme 1 and the ESI worked best.
The lithium salt could be isolated from an Et₂O solution in very good yield (86%), but even after prolonged exposure to dynamic vacuum (16 hr, < 1 × 10⁻² mbar) one equivalent of Et₂O remained (this was not found to affect onward reactivity). Dimeric {[PNP]Li·THF}₂ was crystallised by layering a THF solution with pentane. The structure is shown in figure 2.

Figure 2: The single crystal X-ray structure of {[PNP]Li·THF}₂. Thermal probability ellipsoids at 50%, hydrogen and non-ipso phenyl carbons omitted for clarity. Symmetry related labels marked with an apostrophe. Selected bond distances (Å): Li(1)-N(1)’ 2.532(5), Li(1)-C(1)’ 2.573(6), Li(1)-C(2)’ 2.544(6), Li(1)-C(3)’ 2.453(6), Li(1)-C(4)’ 2.441(5), Li(1)-N(1) 2.042(4), Li(1)-O(1) 1.957(5), Li(1)-P(1) 2.867(4).

A dimeric structure of {Li[PNP]}₂ has been previously reported. In {Li[PNP]}₂ the Li bridges through the pyrrole nitrogens, but in {[PNP]Li·THF}₂ it preferentially binds through a π-interaction with the pyrrollide ring. This π-interaction is significantly slipped towards an η³ coordination. This may be induced by the presence of the THF donor. It is unclear whether the dimer remains in solution with both ³¹P{¹H} and ⁷Li{¹H} NMR showing broad singlets and no coupling resolved.

Anticipating a [PNP]ZrCl₃ stoichiometry in the product, initial reactions of [PNP]Li·Et₂O with ZrCl₄·2THF were carried out in a 1:1 ratio. However these reactions would give broad ³¹P{¹H} NMR spectra and complex ¹H NMR spectra. The synthesis was repeated with a 2:1 excess of [PNP]Li·Et₂O (to ZrCl₄·2THF). Curiously in the crude reaction mixture ³¹P{¹H} NMR very little [PNP]Li·Et₂O remained. Subsequent work-up yielded the product in good yield (74% with respect to ZrCl₄·2THF). Single crystals could be grown by layering a saturated THF solution with pentane and showed the structure to be an asymmetrical bis-pincer complex: [κ²-PNP]κ³-PNP)ZrCl₂, [PNP]ZrCl₂, and crystals suitable for x-ray diffraction could be grown similarly (see ESI). This complex is the first time a pyrrollide-PNP motif has been ligated onto hafnium. We have seen no evidence for a mono-[PNP] complex, even when ZrCl₄·2THF is in excess and the Li salt is added slowly and at low temperature.
The zirconium and hafnium complexes have very similar structures. Both crystallise in $P\text{-}1$ with near identical unit cells. Such similarity is common. The metal centre adopts a near-perfect pentagonal bipyramidal geometry (Cl(1)-Zr(1)-Cl(2): 170.50(4)$^\circ$; $\Sigma$ (equatorial angles) = 365.7$^\circ$). One phosphorus centre is clearly pendant. Of the remaining phosphorus centres two, P(1) and P(3), are trans to the bisector of an N-Zr-P angle and one, P(2), is trans to the P-Zr-P angle bisector. These differing phosphorus environments are reflected in the low temperature $^{31}$P{$^{1}$H} NMR studies. The individual bond lengths are similar to the comparable ones in Nishibayashi’s bis(tert-butyl)phosphinopyrrollide complex {[PNP$^{tBu}$]ZrCl$_2$(µ-Cl)}$_2$. Though unsymmetrical binding in a PNP pincer ligand is unprecedented $\kappa^2$-[PNP] binding has been observed before in the homoleptic [k$^2$-PNP$^{tBu}$]Mn complex and in a DMAP substituted Sc complex. No significant disorder is observed in the crystal structure of either [PNP$^{Ph}$]$_2$MCl$_2$ species, implying the structures to be static in crystallographic conditions.

We were curious to investigate whether the structure in the solid-state reflects the behaviour in solution. Pincer ligands often have the dissociation of a single arm of the ligand inferred in mechanistic pathways and our system could allow us to investigate experimentally the energetics of this. Variable temperature NMR studies were therefore undertaken (figure 4).
At room temperature a single $^{31}$P($^1$H) environment is observed, indicating fluxionality in the structure. However, on cooling to 203 K the $^{31}$P($^1$H) resolves into four clear environments. For both Zr and Hf congeners a high-field sharp singlet is observed at approximately $\delta$ −15.0, assigned as the free pendant phosphine ($[\text{PNP}^\text{Ph}]_2$H has a single $^{31}$P($^1$H) NMR resonance at $\delta$ −16.0). For $[\text{PNP}^\text{Ph}]_2\text{ZrCl}_2$ the remaining resonances resolve into a doublet at $\delta$ 16.3, and two remaining signals are overlapping at $\delta$ 15.0. In the case of $[\text{PNP}^\text{Ph}]_2\text{HfCl}_2$ the resonances resolve more clearly. Two of the low-field resonances appear as doublet or doublets [presumably corresponding to P(1) and P(3)] and a well-defined triplet [P(2)]. Assignments are proposed since P(2) is effectively identically trans to P(1) and P(3), therefore extremely similar coupling is expected.

Upon slowly warming the sample coalescence phenomena for both samples were observed. Coalescence of all resonances occurs simultaneously; however it is unlikely that direct exchange of the pendant phosphorus with all three others is degenerate. A more likely alternative is that P4 exchange with P1 and P3 is of similar energy, which could undergo sequential exchange with either P2 or P4. Using this model the exchange can be modelled as single-site exchange, and therefore $\Delta G^\ddagger = +55.6$ kJ mol$^{-1}$ can be estimated (for $[\text{PNP}]_2\text{ZrCl}_2$).
In order to elucidate plausible mechanisms for the fluxional ligand exchange process, we performed DFT calculations using a truncated model complex in which Ph groups were replaced by Me groups. The geometry of the starting complex \([\text{PNP}^\text{Me}]_2\text{ZrCl}_2\) and its truncated variant \([\text{PNP}^\text{Me}]_2\text{ZrCl}_2\) optimised at the BP86/SDD/6-31G(d,p) level of theory, gave satisfactory agreement with their experimental counterparts (see ESI). Ligand exchange occurs via a dissociative mechanisms, involving initial decoordination of one phosphine arm followed by coordination of P4. In the case of P1/P4 exchange, the rate-determining step is associated with P1 decoordination (\(\Delta G^\ddagger = +11.7\) kcal mol\(^{-1}\)), while for the P2/P4 and P4/P3 exchange processes their respective overall barriers of \(\sim 16.5\) kcal mol\(^{-1}\) represent rate determining step that is associated with small rearrangement of the pyrrolidine ring. This rearrangement shifts the pyrrolidine ring onto the vacant coordination site initially coordinated by the leaving phosphine. We note that we here report energies uncorrected for London dispersion effects. Inclusion of D3 correction across a large range of tested functionals adds up to 10 kcal mol\(^{-1}\) to barrier heights (see ESI).

Obtaining accurate ligand binding energies remains a challenge for quantum chemical methods.\(^{32}\) In particular, the use of polarisable continuum models often restricts the accuracy of predictions of dissociative processes. This is due to them falling short of correctly describing intermolecular solute-solvent interactions on one hand, and both intramolecular dispersive interactions and intermolecular solvent-solvent interactions on the other. It has been argued that the solvent can significantly attenuate inter- and intramolecular dispersive interactions.\(^{33,34}\) Nonetheless, we believe that the suggested mechanism for the ligand exchange provides is plausible and gives a rationale for the experimentally observed temperature-dependence of the NMR resonances.

Finally, we were interested in investigating the derivatization of the \([\text{PNP}^\text{Ph}]_2\text{ZrCl}_2\) complex with simple alkylating and arylating agents. With all reagents investigated an equivalence (with respect to Zr) of \([\text{PNP}^\text{Ph}][\text{M}]\) was observed in the \(^{31}\text{P}\{^1\text{H}\}\) NMR (\([\text{M}] = \text{Li}^+\) or \([\text{MgBr}]^+\)). Work to isolate these derivatives and explore their chemistry is ongoing in our laboratory, as is work to isolate bis-pincer derivatives.
Scheme 2: The proposed reaction of $[\text{PNP}^{\text{Ph}}]_2\text{ZrCl}_2$ with Grignard and alkyl/aryl lithium reagents. $R = \text{Me, Ph, Bn}$, $[M] = \text{Li}^+$ or $[\text{MgBr}]^+$. 

In conclusion we have synthesised the first asymmetric bis-pincer complexes in good yield. We have shown that by simple alterations of the modular pincer ligand framework interesting binding modes can be found. We have investigated the fluxionality in these complexes and experimentally quantified the energetics of the processes involved. We also synthesised the first pyrrollide-PNP complex of hafnium. We have begun derivatizing these compounds, and are continuing to investigate this interesting chemical motif.

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