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# Surprising isomer preference on Ir<sup>III</sup>, favoring facile H–C(sp<sup>3</sup>) bond cleavage†

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**Species (PNP)Ir(X)(Y), where PNP = N(SiMe<sub>2</sub>CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub><sup>−1</sup> with X and Y halide, have a <sup>t</sup>Bu group C–H bond heterolytically split by addition across the Ir–N bond.**

A variety of molecules of the general type (pincer ligand) Ir(X)(Y) are known, involving X–Y pairs such as alkyl and hydride, halide and hydride and two hydrides.<sup>1–13</sup> All are 5-coordinate, and thus coordinatively unsaturated. Pincers include as their central donor sp<sup>3</sup> carbons, sp<sup>2</sup> carbons or imine nitrogens (in pyridine).<sup>14</sup> These find a variety of catalytic applications, including the especially demanding dehydrogenation of alkanes. We report here (Scheme 1) how different the potential energy landscape is for analogous new compounds where the central linking atom is a bis-silyl amide, in the pincer ligand PNP = N(SiMe<sub>2</sub>CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub><sup>−1</sup>. Surprising differences observed here center on the fact that the amide nitrogen is a highly reactive functionality, or at least that the Ir–NSi<sub>2</sub> bond is a functionality in its own right. The identity of ligands X and Y also plays a role.

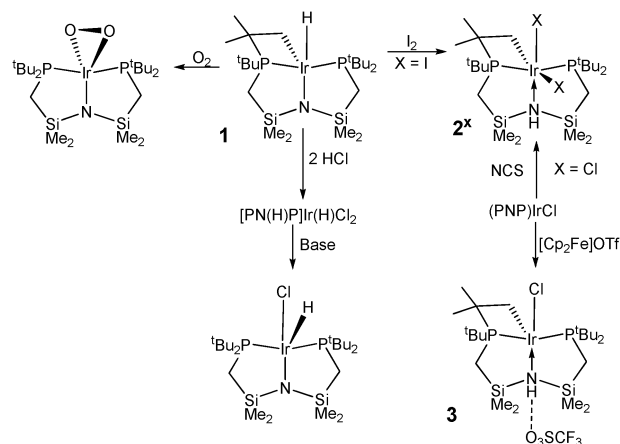
The product of reaction of [Ir(cyclooctene)<sub>2</sub>Cl]<sub>2</sub> with the Li(PNP) or (PNP)ClMg reagents of PNP in THF has structure **1**, designated (PNP\*)IrH (ESI†). This is also true of the Rh analog.<sup>15</sup> We were interested in whether the reactivity of this molecule would be exclusively that of a d<sup>6</sup>, Ir(III) center, or whether it could be a “source” of its reductive elimination product, (PNP)Ir. In this regard, a key feature of **1** is its operational unsaturation.

Reaction (1 : 1) of I<sub>2</sub> with (PNP\*)IrH in THF gives rapid and complete conversion to a single diamagnetic product **2**<sup>†</sup> with an AX <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (large J<sub>PP</sub>, indicative of *trans* phosphorus nuclei) and a <sup>1</sup>H NMR spectrum consistent with no symmetry; altogether these indicate that the Ir–C bond of **1** remains intact. However, there is no evidence of a hydride ligand. The compound has low solubility in benzene and cyclohexane, but is more soluble in CD<sub>2</sub>Cl<sub>2</sub>.†

These observations suggest that **2** is a polar compound. This is further supported by the presence of a <sup>1</sup>H NMR resonance at 4.4 ppm attributed to an N–H functionality; this was identified as an exchangeable proton by adding a trace of D<sub>2</sub>O in CD<sub>2</sub>Cl<sub>2</sub>; the resonance at 4.4 ppm disappears within 1 h. The CI mass spectrum of this compound shows the ion of mass (PNP)IrI<sup>+</sup>. The X-ray structure of crystals grown by

vapor diffusion of pentane into benzene shows two independent molecules of (PN(H)P\*)IrI<sub>2</sub> in the asymmetric unit, but structural parameters in each are very similar and only one will be discussed here (Fig. 1). The structure is consistent with the conclusions from spectroscopic data, in that the species is molecular, with a metallated <sup>t</sup>Bu group. While the hydrogen originally on iridium was not identified in X-ray difference maps, the overall structure is consistent with this being located on the nitrogen, to give a secondary amine ligand on Ir(III). The geometry around the metal is distorted octahedral, in spite of the presence of a strained four membered ring including the metallated carbon (evident especially in the angle Ir–P–C of 90.6(2)° in that 4-membered ring). The secondary amine is nonplanar with regard to the Ir and two Si substituents, as it must be for the proton being on that nucleophile. The Ir–N bond is long at 2.213(6) Å, consistent with protonation at nitrogen. The Ir–I distance *trans* to carbon is significantly longer (by 0.1596(7) Å) than the one *trans* to N.

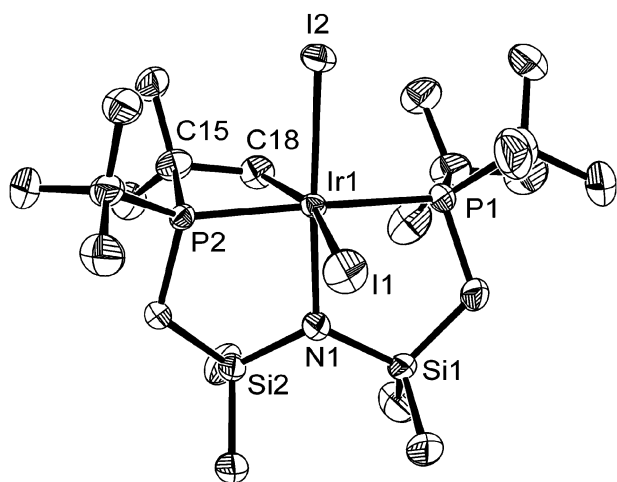
What is unusual about this result is that there has been no oxidatively induced reductive elimination<sup>16–18</sup> of H with carbon in **1**, to restore a <sup>t</sup>Bu group and form simply (PNP)IrI<sub>2</sub>, an isomer of the observed structure. The observed structure still contains trivalent Ir, so there has been reductive coupling of Ir–H with NSi<sub>2</sub>, thus avoiding Ir<sup>V</sup> from oxidant I<sub>2</sub>; transient oxidation may be what reverses the polarity of the “hydride” and makes it possible to serve as an acid, protonating amide nitrogen. Indeed, this reaction may actually occur by heterolytic splitting of I<sub>2</sub> by Ir<sup>III</sup>, to give transient [(PNP\*)IrH<sup>+</sup>][I<sup>−</sup>] whose hydride is now sufficiently acidic that it protonates the amide nitrogen. If this proton is *cis* to N, then migration of H to N is facile. If this proton is *trans* to N, then the intimately ion paired I<sup>−</sup> can shuttle this proton to N before that iodide



Scheme 1

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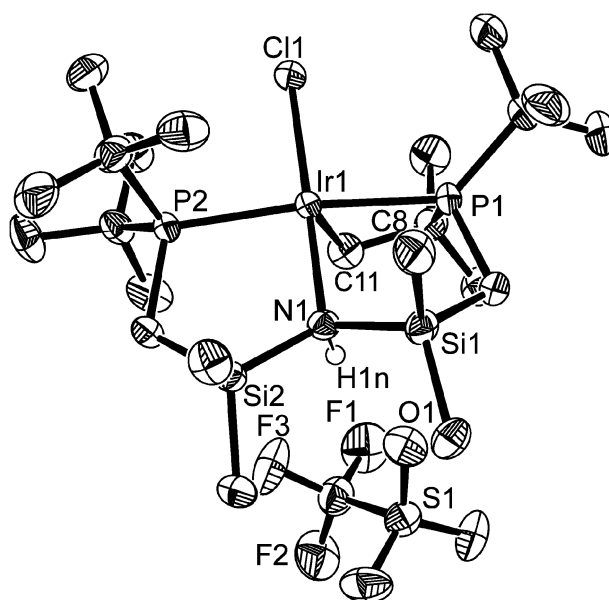


**Fig. 1** ORTEP view (50% probabilities) of the nonhydrogen atoms of molecule **A** of  $[(P'Bu_2CH_2SiMe_2)N(H)(SiMe_2CH_2P'Bu\{CMe_2CH_2\})]IrI_2$ , **2<sup>I</sup>**, showing selected atom labeling; there is a hydrogen on N1. Unlabeled atoms are carbons. Selected structural parameters: Ir1–C18, 2.119(6) Å; Ir1–N1, 2.213(5); Ir1–P2, 2.3221(14); Ir1–P1, 2.4337(15); Ir1–I2, 2.6647(4); Ir1–I1, 2.8243(5); C18–Ir1–N1, 95.3(2)°; C18–Ir1–P2, 67.62(18); C18–Ir1–I2, 89.72(18); N1–Ir1–I2, 174.94(15); C18–Ir1–I1, 160.92(18); N1–Ir1–I1, 81.58(16); C15–P2–Ir1, 90.6(2); N1–Ir1–P2, 88.02(13); C18–Ir1–P1, 102.57(18); N1–Ir1–P1, 87.92(13); P2–Ir1–P1, 168.97(5); P2–Ir1–I2, 94.63(4); P1–Ir1–I2, 90.23(4); P2–Ir1–I1, 93.41(4); P1–Ir1–I1, 96.13(4); I2–Ir1–I1, 93.945(16).

then binds to unsaturated Ir. Each mechanism leads to the observed product, containing Ir<sup>III</sup>. We have heated the observed product in THF at 60 °C to test whether it or (PNP)IrI<sub>2</sub> is thermodynamically more stable. We observe no change after 12 h. Iodine oxidation of (PNP\*)IrH is selective in that it does not halogenate the carbon–Ir bond, to form  $[(P'Bu_2CH_2SiMe_2)N(SiMe_2CH_2P'Bu\{CMe_2CH_2I\})]IrH(I)$ .

Is this preference for the metallated structure specific for iodide, or is it also true for other halides? In a synthetic approach to (PNP)IrCl<sub>2</sub> starting from *intact* <sup>t</sup>Bu groups, (Scheme 1) paramagnetic, *C*<sub>2v</sub> (PNP)IrCl reacts with equimolar *N*-chlorosuccinimide (NCS) over 10 min at 25 °C in benzene to form a diamagnetic product with no symmetry, not a hydride, and in general wholly inconsistent with the expected product, (PNP)IrCl<sub>2</sub>. Three <sup>t</sup>Bu doublets and two single methyl groups are consistent with (PN(H)P\*)IrCl<sub>2</sub>, structure **2<sup>Cl</sup>**. The N–H proton is detected at 4.47 ppm. What is most surprising is the absence of (PNP)IrCl<sub>2</sub> as the product.

We also investigated outer sphere 1-electron oxidation of *C*<sub>2v</sub> symmetric (PNP)IrCl using [Cp<sub>2</sub>Fe]O<sub>3</sub>SCF<sub>3</sub>. This reaction (Scheme 1) proceeds to completion over 12 h at 25 °C even in nonpolar benzene, to form ferrocene (detected by <sup>1</sup>H NMR) and a single product **3**, diamagnetic and with no symmetry. The phosphorus nuclei couple strongly (362 Hz) indicating they are mutually *trans* in the product. The <sup>1</sup>H NMR spectrum shows three <sup>t</sup>Bu doublets, four SiMe singlets, and two Me doublets due to a <sup>t</sup>Bu group which has had one methyl group metallated. This product is [(PN(H)P\*)IrCl](OTf), thus trivalent iridium. It is interesting and surprising that this does not have the structure (PNP)IrCl(OTf), but that instead there has been heterolytic cleavage of an H–C(sp<sup>3</sup>) bond. The detailed location of the amine H and the Cl<sup>–</sup> and triflate



**Fig. 2** ORTEP view (50% probabilities) of the nonhydrogen atoms of **3**,  $[(P'Bu_2CH_2SiMe_2)N(H)(SiMe_2CH_2P'Bu\{CMe_2CH_2\})]IrCl[O_3SCF_3]$ , showing selected atom labeling. Unlabeled atoms in the cation are carbons. Selected structural parameters: Ir1–Cl1, 2.103(5) Å; Ir1–N1, 2.176(4); Ir1–P1, 2.3331(12); Ir1–Cl1, 2.3519(12); Ir1–P2, 2.3682(12); N1–O1, 3.076(6); C11–Ir1–N1, 91.57(18)°; C11–Ir1–P1, 68.94(14); N1–Ir1–P1, 87.79(11); C11–Ir1–Cl1, 93.65(14); N1–Ir1–Cl1, 174.73(11); P1–Ir1–Cl1, 93.42(4); C11–Ir1–P2, 103.10(14); N1–Ir1–P2, 89.01(10); P1–Ir1–P2, 171.33(4); Cl1–Ir1–P2, 90.49(4); C8–P1–Ir1, 88.05(16); C8–Cl1–Ir1, 106.8(3).

ligands is not defined by the spectroscopic data, but a single crystal X-ray structure determination shows (Fig. 2) that this is a salt, with outer sphere triflate and a square pyramidal structure around Ir. The empty coordination site in this unsaturated species is *trans* to the metallated carbon, and hydrogen bonding connects the amine proton to triflate oxygen. It is noteworthy that this salt shows enough solubility in benzene to yield a useful NMR spectrum.

Is this unexpected tendency of three examples to prefer the heterolytic splitting of an H–C(sp<sup>3</sup>) bond due to the amide nitrogen functionality, or due to our being the first to explore dihalide versions of (pincer)Ir(X)(Y)? To address this latter idea, we have synthesized (PNP)IrHCl by dehydrohalogenation of (PN(H)P)IrHCl<sub>2</sub> with LiN<sup>i</sup>Pr<sub>2</sub> (Scheme 1) and find it to have *C*<sub>s</sub> symmetry, with one hydride ligand, indicating the structure to be the previously conventional one, (pincer)IrHCl. To address kinetic *vs.* thermodynamic stabilities, we have carried out DFT(PBE) calculations of both (PNP)IrCl<sub>2</sub> and the observed product **2<sup>Cl</sup>** and find **2<sup>Cl</sup>** to be more stable by 17.8 kcal mol<sup>–1</sup>. For comparison, comparable calculations show (PNP)IrHCl to be more stable than the isomeric (PN(H)P\*)IrHCl but by only 2.1 kcal mol<sup>–1</sup>; this indicates that the phosphine R groups even on (pincer)IrH(halide) are vulnerable (*e.g.* to H–D exchange). This means that the observed dihalide products **2** are thermodynamically, not merely kinetically, preferred. The DFT result indicates unexpectedly high reactivity (instability) for the (PNP)IrCl<sub>2</sub> structure, in particular that the metal complex is sufficiently reactive to attack an H–C(sp<sup>3</sup>) bond. Key to this C–H bond

scission is that it is heterolytic, and so there is no oxidation of Ir<sup>III</sup>. This requires development of nucleophilic character at the amide nitrogen,<sup>19</sup> at least at the transition state, as the C–H bond interacts with an empty iridium orbital in (PNP)IrCl<sub>2</sub>. This will clearly depend on the more numerous 4-electron repulsions<sup>20</sup> present in the (PNP)IrCl<sub>2</sub> structure than in (PNP)IrHCl.

The small size of the  $\Delta G^\circ$  favoring the (PNP)IrHCl structure shows that it is easy to reverse the isomer preference for (PNP)IrX(halide) species (X = hydride or halide), yet the fact (Scheme 1) that (PNP)Ir(O<sub>2</sub>) does not show the C–H metallated structure (ESI<sup>†</sup>) is also significant. The competition between the two Ir<sup>III</sup> isomers evaluated here for X = hydride *vs.* halide cannot be attributed to ligand reducing power, nor to the *trans* influence (both structures have one high *trans* influence ligand) but may find contributions from the fact that the C–H addition structure has 18 valence electrons, while (PNP)IrHCl has 16 +  $\delta$ ,  $\delta$  being the pi donation from the amide,<sup>21–24</sup> and that hydride is clearly most compatible with the 16 +  $\delta$  configuration (no ligand *trans* to hydride).

The unusually facile H–C(sp<sup>3</sup>) bond cleavages reported here are all heterolytic in character (*i.e.* constant metal oxidation state) and thus depend on developing Brønsted basicity at amide nitrogen, and on the electron rich character of the Ir–amide bond. This is the generality to be derived from our work, and it is analogous to the heterolytic splitting of H<sub>2</sub> by d<sup>6</sup> ruthenium amides which has been widely exploited recently.<sup>25,26</sup>

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## Notes and references

† Crystal data for **2<sup>I</sup>**: orange block, 0.15 × 0.12 × 0.12 mm, C<sub>22</sub>H<sub>52</sub>I<sub>2</sub>IrNP<sub>2</sub>Si<sub>2</sub>, *M* = 894.77, monoclinic space group *P*2<sub>1</sub>/*c*, *Z* = 8, *T* = 150 K, *a* = 16.4974(9) Å; *b* = 12.9874(7) Å; *c* = 30.8640(18) Å;  $\alpha$  = 90°;  $\beta$  = 105.052(10)°,  $\gamma$  = 90°, *V* = 6386.0(6) Å<sup>3</sup>;  $\rho_{\text{calc.}}$  = 1.861 Mg m<sup>−3</sup>,  $\mu$  = 6.302 mm<sup>−1</sup>, MoK $\alpha$ , 2 $\theta_{\text{max}}$  = 55°. Total reflections collected = 81 937. 14 579 (*R*<sub>int</sub> = 0.0396) were unique. Final residues: *R*<sub>1</sub> = 0.0363, *wR*<sub>2</sub> = 0.0736 (11 532 observed reflections with *I* > 2 $\sigma$ (*I*) and 571 parameters), GOF = 1.023, largest difference peak = 4.621 eÅ<sup>−3</sup>; peak and hole are of same magnitude, located near iodine. CCDC 730042.

Crystal data for **3**: red block, 0.15 × 0.13 × 0.10 mm, C<sub>23</sub>H<sub>52</sub>ClF<sub>3</sub>–IrNO<sub>3</sub>P<sub>2</sub>SSi<sub>2</sub>, *M* = 825.49, monoclinic *P*2<sub>1</sub>/*n*, *Z* = 4, *T* = 150 K, *a* = 12.9232(9) Å; *b* = 20.6668(15) Å; *c* = 13.5066(9) Å;  $\alpha$  = 90°;  $\beta$  = 105.573(1)°;  $\gamma$  = 90°, *V* = 3474.9(4) Å<sup>3</sup>,  $\rho_{\text{calc.}}$  = 1.578 Mg m<sup>−3</sup>,  $\mu$  = 4.181 mm<sup>−1</sup>, MoK $\alpha$ , 2 $\theta_{\text{max}}$  = 51°. Total reflections collected = 28 585. 6581 (*R*<sub>int</sub> = 0.0400) were unique. Final residues were *R*<sub>1</sub> =

0.0316, *wR*<sub>2</sub> = 0.0771 (5559 observed reflections with *I* > 2 $\sigma$ (*I*) and 338 parameters), GOF = 1.026, largest difference peak = 2.462 eÅ<sup>−3</sup>; peak and hole are of the same magnitude, located near iridium. CCDC 730044.

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