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COMMUNICATION

Iridium complexes bearing a PNP ligand, favoring facile C(sp^3)–H bond cleavage†

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Hydrogen iodide is lost upon reaction of PNP with IrI_3, where PNP = 2,6-*bis*-(di-*t*-butylphosphinomethyl)pyridine to give crystallographically characterized Ir(PNP)*$(I)_2$, which reacts with H_2 to give Ir(PNP)(H)$(I)_2$. Ir(PNP)$(Cl)_3$ is relatively inert towards the intramolecular C–H activation of the *tert*-butyl's of the PNP ligand.

New synthetic routes to stable d^6 transition-metal complexes containing the PNP {2,6-*bis*-(di-*t*-butylphosphinomethyl)pyridine} ligand have emerged in recent years.[1] PNP complexes of transition metals have also been shown to act as catalysts for hydrogenation of CO_2 (Ir),[2] di-hydrogen and C–H bond activation *via* ligand–metal cooperativity (Ir),[3] dehydrogenation of secondary alcohols to ketones and primary alcohols to esters (Ru),[4] selective activation of the *ortho* C–H bonds of haloarenes and the sp^3 C–H bonds of ketones at the β position (Ir),[5] addition of amines to acrylic acid derivatives (Pd),[6] aryl C–H activation (Rh).[7] Previous C–H activation systems that our groups have investigated involved electrophilic catalysts that operated in strongly acid media. Our groups have been developing new systems that could potentially operate in weakly acidic media or non-acidic media.[8] We recently reported that the Ir(III) complex, Ir(NNC)(Et)(C_2H_4)(TFA), where NNC = 6-phenyl-4,4′-*di-tert*-butyl-2,2′-bipyridine catalyzes H/D exchange between CH_4 and DTFA.[9] In search of an air-stable Ir(III) catalyst that could make use of D_2O, CF_3CO_2D or CH_3CO_2D as the deuterium source, we elected to study the behaviour of Ir(PNP)$(X)_3$ where, X = Cl, I, TFA. We were hopeful that the aqueous/acidic medium would render the halide ligands labile and lead to a catalytically active Ir species. Complexes of iridium are expected to be less electrophilic for C–H activation and more tolerant of mildly acidic conditions as compared to Pd(II), Pt(IV), Au(III), *etc.*[9] In order to test whether replacing the NNC motifs with the PNP ligand could lead to more efficient C–H activation chemistry we synthesized new iridium complexes. In this contribution we report the synthesis, structure, and reactivity of these new complexes.

Herein, we report the synthesis and characterization of Ir(PNP)-$(Cl)_3$ (**2**) and Ir(PNP)*$(I)_2$. The reaction of $Ir(Cl)_3(CH_3CN)_3$, (**1a**) with the PNP[10] ligand in *N*,*N*-dimethylacetamide afforded complex **2** in good yields as a yellow–orange micro-crystalline solid.§ $Ir(Cl)_3(CH_3CN)_3$ was synthesized from $IrCl_3.nH_2O$ using the procedure of Tessore and coworkers.[11] The resulting *tri*-chloride complex was characterized by multinuclear NMR techniques. The compound has low solubility in ether, and benzene, but is more soluble in CH_2Cl_2, HTFA and CH_3COOH.

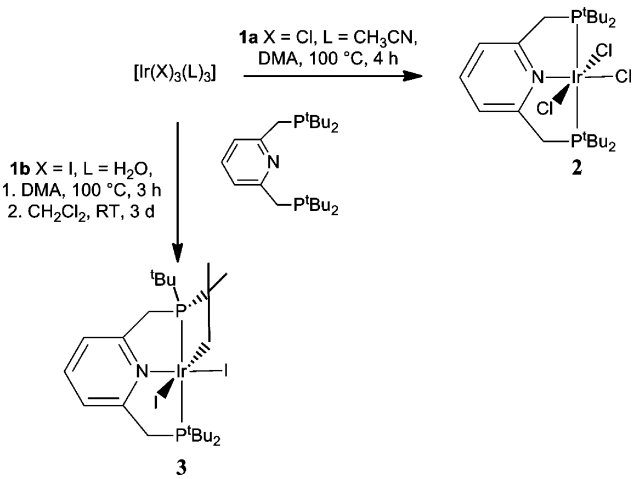

Fig. 1 Synthesis of the complexes **2** and **3**.

The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits a broad singlet at 15.89 ppm, indicating the existence of an N–Ir–Cl plane of symmetry. Complex **2** has also been structurally characterized and an ORTEP representation is shown in Fig. 2. Single crystals suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2 at −35 °C. The crystal contains two independent, structurally analogous molecules in the asymmetric unit. Fig. 2 also shows selected bond lengths and bond angles for one of the two independent molecules.¶ The Ir–Cl, Ir–N, and Ir–P distances are typical at 2.3643(14), 2.052(5) and 2.3775(15) Å, respectively.

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† Electronic supplementary information (ESI) available. CCDC reference numbers 820458 and 820459. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10577a

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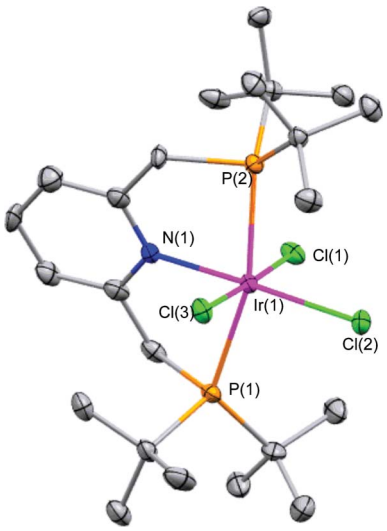


Fig. 2 ORTEP representation (50% probability level) of the molecular structure of complex **2** (only 1 of the 2 molecules in the asymmetric unit is shown). Solvent molecules as well as hydrogen atoms were omitted for clarity. Selected structural parameters: Ir(1)–N(1), 2.052(5); Ir(1)–P(1), 2.4049(15); Ir(1)–P(2), 2.3775(15); Ir(1)–Cl(1), 2.3643(14); N(1)–Ir(1)–Cl(1), 87.50(13); N(1)–Ir(1)–Cl(3), 89.91(13); Cl(3)–Ir(1)–Cl(1), 177.26(5); N(1)–Ir(1)–Cl(2), 178.06(14); Cl(1)–Ir(1)–Cl(2), 91.36(5); Cl(3)–Ir(1)–Cl(2), 91.26(5); N(1)–Ir(1)–P(2), 82.04(14); P(2)–Ir(1)–Cl(1), 91.56(5); P(2)–Ir(1)–Cl(3), 88.95(5); P(2)–Ir(1)–Cl(2), 96.42(5); N(1)–Ir(1)–P(1), 82.72(14); P(2)–Ir(1)–P(1), 164.74(5).

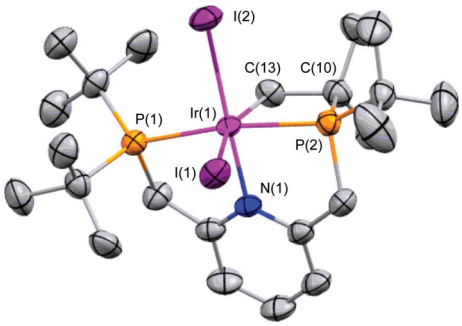


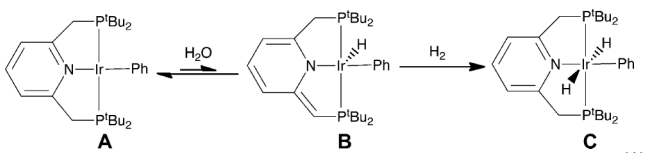
Fig. 3 ORTEP representation (50% probability level) of the molecular structure of complex **3**. Hydrogen atoms were omitted for clarity. Selected structural parameters: Ir(1)–N(1), 2.072(4); Ir(1)–C(13), 2.124(5); Ir(1)–P(2), 2.2901(14); Ir(1)–P(1), 2.3794(13); Ir(1)–I(1), 2.8789(6); Ir(1)–I(2), 2.6757(6); N(1)–Ir(1)–C(31), 81.89(17); N(1)–Ir(1)–P(2), 82.39(11); C(13)–Ir(1)–P(2), 69.38(14); N(1)–Ir(1)–P(1), 83.28(11); C(13)–Ir(1)–P(1), 97.57(14); P(2)–Ir(1)–P(1), 161.83(4).

(see Supporting Information for a more detailed description of relevant bond metrics†).

Reaction (1 : 1) of PNP with IrI_3 (**1b**) in *N*,*N*-dimethylacetamide in the presence of degassed water affords a single diamagnetic product **3** with an AX $^{31}P\{^1H\}$ NMR spectrum (with a large J_{PP}, indicative of *trans* phosphorus nuclei) and a ^1H NMR spectrum consistent with no symmetry; altogether these indicate the formation of an Ir–C bond.‖ Further, there is no evidence of a hydride ligand. The compound has low solubility in benzene, but is more soluble in CD_2Cl_2. These observations suggest that **3** is a polar compound. The mass spectrum of this compound shows the ion of mass Ir(PNP)*I^+, where PNP* = $\{NC_5H_3$-2-$(CH_2P^tBu_2)$-6-$(CH_2P^tBuC(Me)_2CH_2)\}^{-1}$.

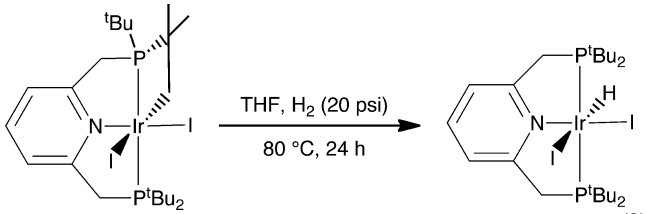
The X-ray structure of crystals grown by vapor diffusion of hexanes into CH_2Cl_2 agree with the solution NMR studies and the formation of Ir(PNP)*I_2. The geometry around the iridium metal is distorted octahedral, in spite of the presence of a strained four membered iridacycle.** The Ir–P(2)–C(10) bond angle in **3** is 90.31(18) compared with 90.6(2) and 88.05(16) in similar compounds reported by Caulton and coworkers, $Ir(PNP)^{Si}*(I)_2$ and $Ir(PNP)^{Si}*(Cl)(OTf)$ respectively, where PNP^{Si} = $N(SiMe_2CH_2P^tBu_2)_2^{-1}$.[12] Further, for complex **3** the Ir–C bond length of 2.124(5) is slightly longer as compared to 2.119(6) and 2.103(5) in $Ir(PNP)^{Si}*(I)_2$ and $Ir(PNP)^{Si}*(Cl)(OTf)$ respectively. The Ir–P(2) distance in the iridacycle of **3** is 2.2901(14) and is shorter as compared to the Ir–P(1) 2.3794(13). Also consistent with this assertion, the ^{31}P NMR resonance for P(2) is shielded significantly to –48.31 ppm from 8.36 ppm for P(1). (see Supporting Information for a more detailed description of relevant bond metrics†). Complex **2**, $Ir(PNP)Cl_3$ is relatively inert towards the intramolecular C–H activation of the *tert*-butyl's of the PNP ligand. For example, refluxing complex **2** in toluene or mesitylene at 150 °C overnight results in no reaction. Further, approximately 10% of the complex **2** eliminated HCl to form the corresponding Ir(PNP)*Cl_2 over a period of 6 months as a solid as judged by ^1H and ^{31}P NMR spectra.

Recently, Milstein and co-workers reported the addition of H_2 towards a stable Ir(I)(PNP)(Ph) (**A**) complex afforded the *trans*-dihydride complex (**C**) as the kinetic and thermodynamic product.[3] The proposed mechanism involved a dearomatized Ir(III) intermediate complex (**B**) as shown in eqn (1). Density functional theory calculations and deuterium-labelling studies agree with this proposal.[13]

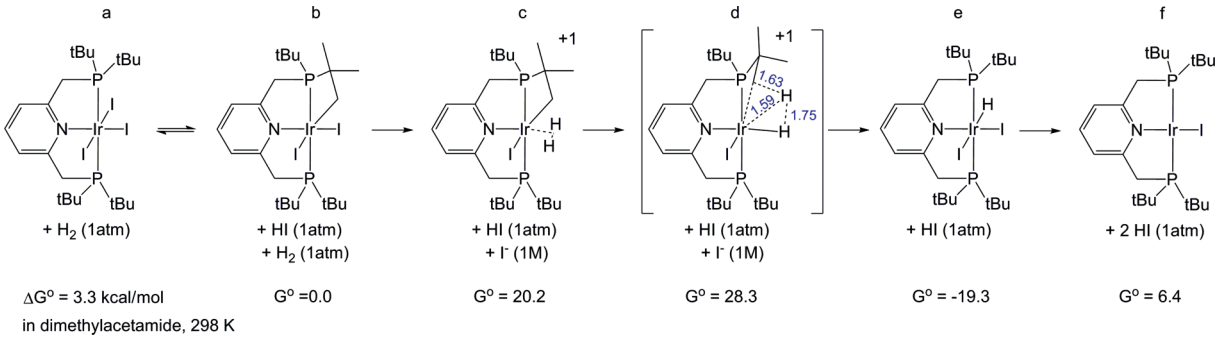


(1)

We were interested in whether complex **3** would react with H_2 and provide an alternative pathway towards an operational H_2 addition pathway as shown in eqn (2). Subsequently, treating solutions of complex **3** with H_2 resulted in formation of a yellow product; the product was identified as $Ir(PNP)(H)(I)_2$ by NMR spectroscopy.[14] The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits a doublet at 40.53 ppm, indicating the existence of an N–Ir–I plane of symmetry. The hydride ligand of **4** appears as a triplet at –21.90 ppm in the ^1H NMR spectrum.†† Unlike the reaction with H_2, complex **3** does not react with benzene to afford the corresponding Ir(III)(Ph) $(PNP)(I)_2$.



(2)

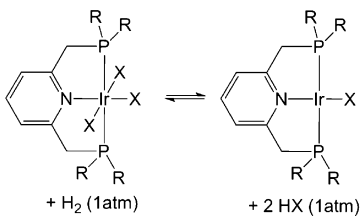


Scheme 1 Reaction free energies for the cyclometallation of the iridium(III) *tri*-iodide complex.

Reaction free energies were computed for the cyclometallation of the iridium(III) tri-iodide complex *via* extrusion of HI and hydrogenation of the Ir–C bond (Scheme 1). The Poisson–Boltzmann polarizable continuum solvation model was combined with M06//B3LYP DFT calculations.[15] Assuming a gaseous HI product, the cyclometallation was found to be 3.3 kcal mol^{-1} exergonic in the iodide case. In contrast, cyclometallation in the tri-chloride case was computed to be 8.4 kcal mol^{-1} uphill.

A pathway for the hydrogenation of the Ir–C bond following dissociation of one iodide ligand poses a calculated barrier of 28.3 kcal mol^{-1}. A dihydrogen complex **c** with a 0.94 Å H–H bond was found to lie 20.2 kcal mol^{-1} above **3**. In the oxidative hydrogen migration transition state **d** the H–H bond is broken and both Ir–H bond lengths are 1.59 Å. In this manner the hydrogenation can be accomplished without taking advantage of the ligand's acidic methylene hydrogens.

In order to probe the influence of sterics on the relative stability of octahedral and square planar geometries, the reaction free energy for reduction of tri-iodide, tri-chloride and tri-hydroxide complexes by dihydrogen was computed for the *t*-butyl and methyl derivatives of the PNP ligand (Fig. 4).



X	R	ΔG° (kcal/mol)
I	t-Bu	3.1
I	Me	46.9
Cl	t-Bu	13.3
Cl	Me	40.5
OH	t-Bu	-28.1
OH	Me	-12.8

Fig. 4 Influence of sterics on relative stability of octahedral and square planar geometries.

When the steric congestion of the *t*-butyl groups and three iodide ligands is relieved in the dimethyl analogue, the higher oxidation state is stabilized a remarkable 44 kcal mol^{-1}. For the smaller anions the destabilizing effect of the *t*-butyl groups decreases. But even for ligands as small as hydroxide access to both axial sites is severely inhibited.

This work demonstrates that changes in the ancillary ligand size (Cl^- *versus* I^-) may influence not only reaction rates, as is well known with the PNP motif, but also change the direction of reactivity. Computational and experimental studies of the reaction mechanism, activation barriers and efforts to design complexes for RH/H_2 activation with similar ancillary ligands are in progress.

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Notes and references

§ The reaction to produce **2** was carried out using 0.24 mmol of $Ir(Cl)_3(CH_3CN)_3$. Other data for compound **2**: ^{1}H NMR (400 MHz, CD_2Cl_2): 7.55 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2 H), 3.99 (b s, 4 H, CH_2), 1.42 (s, 36 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2): 167.41, 138.81, 121.69, 40.19, 38.05, 31.68. ^{31}P NMR (282 MHz, CD_2Cl_2): 15.89. Elemental analysis. Calc. for $[C_{23}H_{43}Cl_3IrNP_2]_2{\cdot}CH_2Cl_2$ ($C_{47}H_{88}Cl_8Ir_2N_2P_4$): C, 38.32; H, 6.02; N, 1.90 found: C, 38.62; H, 5.92; N, 2.19. M.P. 245–247 °C.

¶ Crystallographic data for **2**: $(C_{23}H_{43}P_2Cl_3IrN){\cdot}0.5(CH_2Cl_2)$, M = 736.54, Triclinic, $P\bar{1}$(Z = 4), a = 13.2633(14) Å, b = 14.7326(16) Å, c = 17.4332(18) Å, α = 106.729(2)°, β = 95.934(2)°, γ = 112.653(2)°, V = 2920.8(5) Å^3, T = 100(2) K, 19155 total reflections, 13373 unique reflections [R_{int} = 0.0254]. Final R_1 = 0.0448 [$I > 2\sigma(I)$].

‖ The reaction to produce **3b** was carried out using 0.17 mmol of IrI_3. Other data for compound **3**: Assignments have been made where possible: ^{1}H NMR (400 MHz, CD_2Cl_2): 7.63 (t, J = 7.7 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 4.15 (m, 1H), 3.75 (m, 2H), 3.50 (m, 2H), 1.70 (d, J = 12.4 Hz, 3H), 1.62 (d, J = 12.4 Hz, 18H), 1.28 (d, J = 13.6 Hz, 9H), 0.98 (d, J = 12.4 Hz, 3H). ^{13}C{^{1}H} NMR (75.6 MHz, CD_2Cl_2): 166.47, 164.12, 137.1, 121.03, 120.9, 58.90, 40.68, 39.89, 39.42, 38.89, 32.52, 31.51, 30.40, 30.13, 28.60. ^{31}P NMR (282 MHz, CD_2Cl_2): 8.36 (d, J = 648.6 Hz), –48.31 (d, J = 648.6 Hz). ESI–MS (Ir(PNP)*I$^+$): 715.1537 (calc. 715.1545). M.P. 210–212 °C.

** Crystallographic data for **3b**: $C_{23}H_{42}I_2P_2IrN$, M = 840.52, Monoclinic, $P2_1/c$ (Z = 4), a = 14.348(4) Å, b = 11.993(3) Å, c = 16.442(4) Å, α = 90°, β = 90.767(3)°, γ = 90°, V = 2828.9(12), T = 296(2)K, 27266 unique reflections [R_{int} = 0.0363]. Final R_1 = 0.0350 [$I > 2\sigma(I)$].

†† The reaction to produce **4** was carried out using 0.1 mmol of **3**. Other data for compound **4**: ^{1}H NMR (400 MHz, CD_2Cl_2): 7.55 (t, J = 7.7 Hz, 1H), 7.21 (d, J = 7.7 Hz, 2H), 3.99 (m, 2 H, CH_2), 3.22 (m, 2 H, CH_2), 1.55 (t, J = 7.2 Hz, 18H), 1.25 (t, J = 7.2 Hz, 18H), –21.9 (t, J = 3 Hz, 1H). ^{13}C{^{1}H} NMR (75.6 MHz, THF-d_8): 165.90, 135.81, 119.74, 38.1, 35.37, 29.58, 28.65. ^{31}P NMR (282 MHz, CD_2Cl_2): 40.53.

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