N–H *vis.* C–H Activation; a Major Ligand Size Effect

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The complexes *trans*-[Ir(PR_3)$_2$(C_2H_4)]Cl (**3**, R = Et; **4**, R = Pr^i) exhibit entirely different reactivity pathways with ammonia, whereas **3** undergoes N–H oxidative addition, **4** coordinates ammonia and undergoes C–H activation of the ethylene ligand at 25 °C to yield an hydrido vinyl complex, and phosphine metallation at 80 °C.

Activation of N–H bonds by transition metal complexes is of considerable current interest.[1] Of particular importance is the activation of ammonia, which may lead to the development of selective catalysis based on this molecule.

Relatively few examples of N–H activation of ammonia by a metal centre in solution have been reported.[2] The electron-rich complex [Ir(PEt_3)$_2$(C_2H_4)$_2$]Cl, **1** is very reactive towards ammonia oxidative addition, forming the *cis*-amido-hydride complex **2** at 25 °C quantitatively.[2d]

We have observed from ^{1}H and ^{31}P NMR spectroscopy, that **1** dissociates ethylene in benzene or tetrahydrofuran (THF), leading to square planar *cis*- and *trans*-[Ir(PEt_3)$_2$(C_2H_4)]Cl.† Reaction of a THF solution of *trans*-[Ir(PEt_3)$_2$[C_2H_4)]Cl **3** (0.035 mmol in 5 ml of THF) with 50 psi (1 psi ≈ 6.894757 × 10^3 Pa) of NH_3 at room temp. proceeded at approximately the same rate as that of **1**, indicating that probably the same active species is involved and yielding complex **2** quantitatively (Scheme 1).

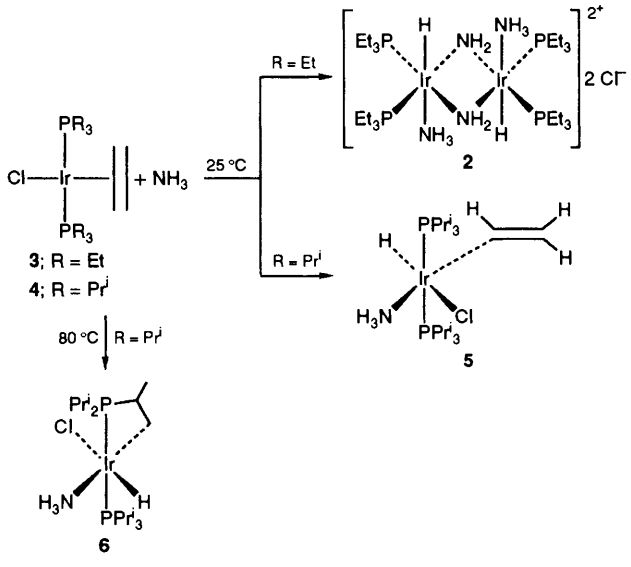
The analogous *trans*-[Ir(PPr^i_3)$_2$(C_2H_4)]Cl **4**[4] was treated with ammonia under exactly the same conditions in order to examine the effect of ligand size on the ammonia oxidative addition reaction. Surprisingly, C–H rather than N–H activation took place, leading to the hydrido vinyl compound **5**‡ (70% yield), together with some of the starting complex (30% based on ^{1}H NMR) (Scheme 1).

The hydride ligand of **5** appears as a triplet at δ −21.96 in ^{1}H NMR and absorbs at 2197 cm^{-1} in the IR. The vinyl ligand exhibits a typical AMX pattern in ^{1}H NMR, with J_{HH}, *trans* 18.0 Hz and J_{HH}, *cis* 10.5 Hz. Other hydrido-vinylbis(phosphine)iridium complexes, having very similar spectroscopic properties, were obtained very recently by photolysis of bis(phosphine)iridium ethylene complexes.[5] C–H activation of ethylene by other iridium complexes was also reported.[6]

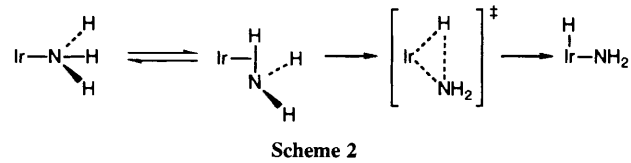
If the reaction of **4** with ammonia is carried out at higher temperature, (80 °C), a cyclometallated complex **6**§¶ is obtained in addition to **5**. The tendency of bulky alkylphosphine ligands to undergo cyclometallation has been noted before,[7] and a complex analogous to **6** (containing picoline instead of NH_3) has been prepared.[7a] On the other hand, smaller phosphines, like PEt_3, generally do not undergo metallation. We believe that in our case, **6** is obtained as a result of thermal reductive elimination of ethylene from **5** followed by ligand cyclometallation. Thus, the putative intermediate complex ClIr(NH_3)(Pr^i_3P)$_2$ prefers to undergo intramolecular C–H rather than N–H oxidative addition.

The reasons for the striking difference in reactivity of the analogous complexes **3** and **4** are not obvious. One explanation is that the N–H activation process involves the complexes Ir(PR_3)$_2$(NH_3)Cl, obtained from the 14-electron intermediate Ir(PR_3)$_2$Cl. Indications for the involvement of this 14e species in ammonia activation were obtained previously.[2d] In the Ir(I) ammonia complex, the hydrogens are not accessible to the metal, and in order to allow intramolecular N–H activation, 'slippage' of the coordinated ammonia to form an η^2-NH complex may be envisaged (Scheme 2). Alternatively, the 'slippage' could lead directly to the depicted three-centre transition state. The ease of 'slippage' and, as a result, the barrier to N–H activation will depend on the ligand *trans* to the ammine, and is expected to be more facile with *cis*-Ir(PR_3)$_2$(NH_3)Cl than with the *trans* isomer, because of the much higher *trans* effect and σ-donation of the phosphine ligand, as compared with that of the chloride. Certainly, the bulk of the PPr^i_3 ligand (θ = 160°)[8] would make formation of the *cis* complex difficult, whereas with PEt_3 (θ = 132°) this should not be a problem and, in fact, a *cis*-phosphine product **2** is formed.

These results clearly indicate that a fine balance exists between C–H and N–H oxidative addition, which is highly



Scheme 1



Scheme 2

† In pentane, however, only the *trans* isomer is present and can be isolated pure.[3]

‡ *Spectroscopic data* for **5**: ^{1}H NMR (C_6D_6): δ −21.96 (t, $J_{(P-H)}$ 16.9 Hz, 1H, IrH); 1.18 (dvt, N 13.0 Hz, J_{H-H} 6.9 Hz, 36H, PCMe, diastereotopic splitting not resolved); 2.2 (s, br, 3H, NH_3); 2.83 (m, 6H, PCHC); 5.01 (dd, $J_{(H-H)}$ 18.0, 2.8 Hz, 1H, β-H *cis* to Ir); 6.00 (dd, $J_{(H-H)}$ 10.5, 2.8 Hz, 1H, β-H *trans* to Ir); 8.02 (dd, $J_{(H-H)}$ 18.0, 10.5 Hz, 1H, α-H). All vinylic resonances are slightly broadened due to unresolved P-coupling. ^{31}P NMR (C_6D_6, ext. ref. 85% H_3PO_4 in D_2O): 10.60 (s, d in 'off-resonance'). IR ν/cm^{-1} (Nujol): 2197 (IrH), 3281, 3347, (NH).

§ This complex was prepared before: M. Schulz and H. Werner, unpublished results.

¶ **6**: ^{1}H NMR (C_6D_6) δ −23.2 (dd), J_{PH} 16.3, 12.2 Hz, IrH); 2.0 (br s, NH_3), alkyl region-complex pattern. ^{31}P {^{1}H} NMR δ 17.46 (d, J_{PP} 368 Hz, non-metallated P); −22.78 (d, J_{PP} 368 Hz, metallated P). The strong upfield shift is due to formation of a four-membered ring.

dependent on phosphine size. In general, whereas C–H activation is quite common[9] and takes place with phosphine complexes widely ranging in steric demands, N–H oxidative addition is less frequently observed and is apparently much more sensitive to the size of phosphine employed. This work demonstrates that changes in ligand size may influence not only reaction rate, as is well known, but also totally change the direction of reactivity.

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