C–H and H–H Bond Activation: Dissociative *vs.* Nondissociative Binding to Iridium

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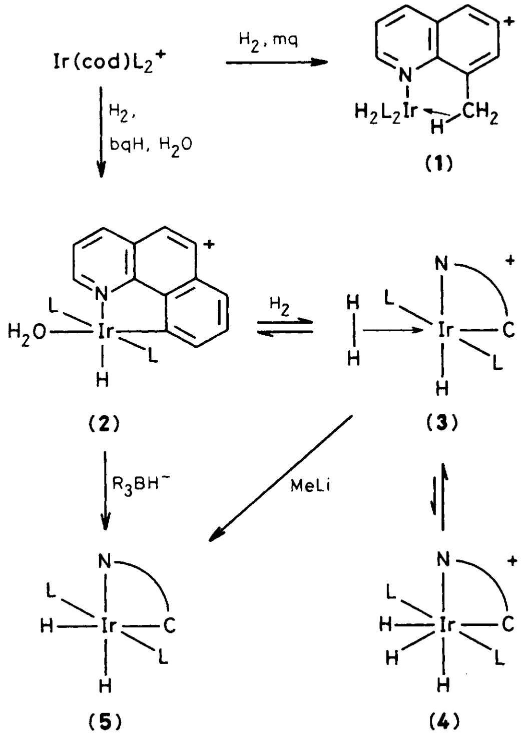
$[IrH(H_2)(PPh_3)_2(C_{13}H_8N)]^+$, a complex of molecular hydrogen, is formed reversibly from the corresponding aquo complex.

We have previously shown[1] that a C–H bond of the methyl group in the 8-methylquinoline (mq) complex $[IrH_2(mq)L_2]A$ (**1**, L = PPh_3, A = SbF_6) is nondissociatively bound to Ir *via* a 2-electron 3-centre C–H–Ir bridge. Such 'agostic' structures[2] have been proposed as intermediates on the way to C–H activation, so it is significant that the related complex $[IrH_2S_2L_2]A$ (S = Me_2CO) activates alkanes.[3] We now report an extension of this work to the related case of 7,8-benzoquinoline (bqH), which gives $[IrH(H_2O)(bq)L_2]A$ (**2**) under the same conditions {$[Ir(cod)L_2]A$ in CH_2Cl_2 under H_2 (1 atm) at 0 °C in the presence of mq or bqH (1—2 equiv.) and of a trace of water} previously used to obtain (**1**). Structure (**2**) was deduced by analytical and spectroscopic data [^1H n.m.r. δ -16.0 (t, $^2J_{P,H}$ 15 Hz, Ir–*H*), 2.54 (br. s, Ir–OH_2); i.r. ν 3550, (O–H), 2179 (Ir–H) cm^{-1}] and confirmed by an *X*-ray crystallographic study, to be published separately.[4] As shown in Scheme 1 a C–H bond of the bqH ligand is bound dissociatively, while the corresponding C–H bond of mq in (**1**)



Scheme 1. Some reactions of the dihydrogen complex. (L = PPh_3, mq = 8-methylquinoline, bqH = 7,8-benzoquinoline, cod = cyclo-octa-1,5-diene.)

was bound nondissociatively. This result illustrates the more ready cleavage of aromatic compared to aliphatic C–H bonds. Preco-ordination of the arene *via* the ring has previously been proposed to account for this effect,[5a] but here both mq and bq probably preco-ordinate *via* nitrogen; more likely, thermodynamic rather than kinetic factors are implicated. The bond dissociation energy of M–Ar bonds seems to exceed that of M–R bonds,[5b] presumably in part because the donation from metal d_π orbitals into aryl π^* orbitals is possible only for the M–Ar case.

Just as the C–H bond can bind to the metal either with or without C–H bond dissociation, so H_2 has recently been shown to behave in the same way: both nondissociative[6] and the much studied dissociative binding (oxidative addition[7]) are known. We therefore examined the behaviour of (**2**) in the presence of H_2. The ^{1}H n.m.r. evidence discussed below suggests that H_2O is rapidly and reversibly displaced to give a complex of an undissociated H_2 molecule: $[IrH(H_2)(bq)L_2]A$ (**3**). This is the first case in which H_2 displaces a ligand and the first in which a conventional hydride is present along with the co-ordinated H_2 molecule. The complex is air-stable. The ^{1}H n.m.r. spectrum of (**3**) in CD_2Cl_2 (250 MHz) shows a broad hydride resonance at 280 K but below 240 K two separate resonances are visible. A broad† absorption at δ −2.9 of intensity two is assigned to the η^2-H_2 and a triplet ($^2J_{P,H}$ 12 Hz) of unit intensity at δ −15.2 is assigned to the terminal Ir–H which, by analogy with previous work,[8] is probably *trans* to the bq nitrogen. Passing N_2 through the solution reverses the equilibrium and the spectrum of (**2**) is restored. Removing the H_2O displaced (*e.g.*, with CaH_2) shifts the equilibrium towards (**3**).

In order to characterize the bonding mode of the hydrogen, we, like Kubas *et al.*,[6] looked at the corresponding HD complex. In the range 187—220 K we were able to observe reproducible, well-resolved $^1J_{H,D}$ coupling of 29.5 Hz in the complex, similar to the value for the known example[6] (33.5 Hz), but less than that in free HD (43.2 Hz). The values are however much too large for a conventional M(H)(D) complex (<1 Hz). Exchange occurs between the Ir–H and $Ir(H_2)$ hydrogens in (**3**) as shown by the broadening and eventual coalescence of the corresponding resonances in the range 240—280 K and by spin saturation transfer studies. The most likely intermediate for this exchange is the conventional trihydride $[IrH_3(bq)L_2]A$ (**4**). No i.r. bands were observed that we could assign to an $M(H_2)$ unit, but even the terminal M–H vibration is weak and precedent[6] suggests that the $\nu(H_2)$ band may be obscured by C–H vibrations of the ligands. Raman studies were precluded by the strong fluorescence of the compound.

Other reactions of (**2**) are shown in Scheme 1, for example, $LiEt_3BH$ gives a conventional dihydride (**5**), which is also formed by reaction of (**3**) with MeLi [^{1}H n.m.r. δ −10.2 and −18.3 (t, $^2J_{P,H}$ 18.5, $^2J_{H,H}$ 4 Hz, Ir–H)]. The dihydride (**5**) can also be reprotonated with $PhCH(SO_2CF_3)_2$ to give (**2**). Methyl iodide also displaces H_2O from (**2**) and binds *via* a lone pair as an undissociated molecule [^{1}H n.m.r. δ −16.83 (br., Ir–H), 1.69 (s, Ir–I–*Me*)]. This is a type of complex we have previously observed in related Ir^I and Ir^{III} systems.[9]

The situation of the undissociated C–H bond in (**1**) is very similar to that of the analogous H–H bond in (**3**). This suggests that the reasons the X–H bonds (X = H or C) fail to break in the two cases may also be similar. The Ir–H bond strength for the postulated trihydride $[IrH_3(bq)L_2]A$ may be insufficient to compensate for H–H bond cleavage in (**3**). It is notable that (**4**) would be 7-co-ordinate and Ir^V, rather than 6-co-ordinate and Ir^{III} in (**3**) and that the high *trans*-effect aryl carbon of the bq ligand is *trans* to the dihydrogen ligand. The Kubas complex[6] is also 6-co-ordinate with H_2 *trans* to a high *trans*-effect ligand, CO. The electrophilic cationic Ir^{III} centre is content with the σ-bonding electrons of the X–H bond. Cleaving the bond would require electron donation from the metal into the X–H σ^* orbitals.

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† The broadness of the resonance, also observed in the Kubas (ref.6) example, is probably due to dipole–dipole interactions, as suggested by the smaller linewidth for the HD complex.