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

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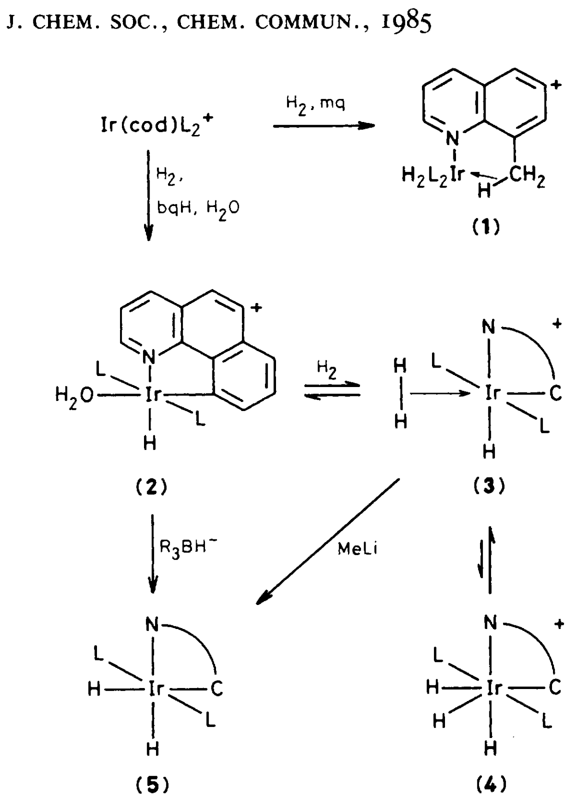
$[IrH(H_2)(PPh_3)_2(C_{13}H_8N)]^+$, a complex of molecular hydrogen, is formed reversibly from the corresponding aquo complex.

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$_3$BH 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$_2$CF$_3$)$_2$ 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.