$[IrH_2(H_2)_2L_2]^+$ {L = $P(C_6H_{11})_3$}: A Non-classical Polyhydride Complex

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$[IrH_5(PCy_3)_2]$ (Cy = cyclohexyl) is shown by n.m.r. evidence, including T_1 measurements, to undergo protonation to give the title complex, a bis(dihydrogen) dihydride, the first example of a non-classical polyhydride complex.

Recent reports of complexes of molecular hydrogen[1,2] led us to question[3] whether the classical formulation of polyhydride complexes as MH_xL_y, containing terminal M–H bonds only, always applies. We previously showed[2] that the classical dihydride $IrH_2(bq)(PPh_3)_2$ (**1**) is protonated with $PhCH(SO_2CF_3)_2$ to give the dihydrogen hydride cation $[IrH(H_2)(bq)(PPh_3)_2]^+$ (**2**). We have now protonated the polyhydride IrH_5L_2 (**3**) (L = PCy_3) in the same way and report the evidence that leads us to formulate the product as the non-classical polyhydride cation $[IrH_2(H_2)_2L_2]^+$ (**4**). Like (**2**), (**4**) is protonated without loss of H_2 and is stable at −80 °C. Both tend to lose H_2 at room temperature, but can be maintained in a dihydrogen atmosphere. MeCN displaces two molecules of H_2 to give the known $[IrH_2(MeCN)_2L_2]^+$. Deprotonation of (**4**) with NEt_3 [equation (1)] takes place in the absence of excess of H_2 to give back the original complex (**3**) quantitatively at −80 °C.

$IrH_2(bq)(PPh_3)_2$ (**1**)

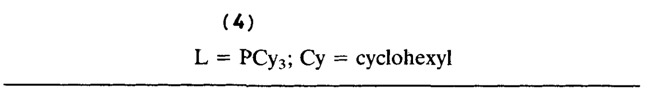
$[IrH(H_2)(bq)(PPh_3)_2]^+$ (**2**)

Hbq = benzo[*h*]quinoline

The room temperature ^1H n.m.r. spectrum of (**4**), like that of (**2**), shows a broad resonance at δ *ca.* −8.3 due to exchange between the Ir–H and $Ir(H_2)$ units. On cooling, two resonances are seen. One, at δ −5.05 [(**2**) δ −3.0], of intensity 4 is assigned to the $Ir(H_2)$ groups. It is broad, as was found for (**2**). A second and narrower resonance at δ −15.2 [(**2**) δ −15.2] and of intensity 2 is also found and assigned to the two classical Ir–H groups. Complex (**4**) is somewhat more fluxional than complex (**2**) and so the $^2J(P,H)$ of the Ir–H group and $^1J(H,D)$ coupling of the corresponding HD complex could not be observed even at the lowest accessible temperatures in CD_2Cl_2; in no other suitable solvent was (**4**) both stable and soluble. This prevented us from observing the value of $^1J(H,D)$ which had previously been shown[1,2] to be an excellent spectroscopic criterion for the existence of a dihydrogen ligand.

We therefore looked for another spectroscopic criterion, and determined the apparent T_1 values for both (**2**) and (**4**) at −80 °C by the inversion–recovery method. While the T_1 value of 350 ms for the terminal Ir–H in (**2**) is normal,[4] the value for the co-ordinate dihydrogen molecule (30 ms) is extremely short for a metal hydride, but comparable to the relaxation time for free molecular hydrogen.[5] Since the dipole–dipole contribution to T_1 depends on r^{-6}, the short H–H distance in $M(H_2)$ and in free H_2 itself is consistent with a short T_1; a spin–rotation contribution may also be involved.[5] On warming, the apparent T_1 values for the two resonances begin to average before the chemical shifts do so, owing to proton exchange between the $Ir(H_2)$ and IrH sites.

In the more fluxional case of (**4**), the T_1 values for the $Ir(H_2)$ (48 ms) and IrH (73 ms) resonances are both short.† This is consistent with the known higher rate of proton exchange between the two sites in (**4**) compared with (**2**). The weighted average of the two T_1 values observed for (**2**) at −80 °C is 43 ms, a value comparable to the observed values for (**4**). Depending, as it does, on γ^2, the dipole–dipole contribution to proton relaxation due to a second nearby nucleus is expected[5] to be much smaller if this nucleus is D rather than H.



(**4**)

L = PCy_3; Cy = cyclohexyl

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† For comparison, the apparent T_1 for $IrH_5(PCy_3)_2$ under the same conditions (500 MHz, −80 °C) is 870 ms. The field and temperature dependence of the T_1 values suggests that the slow motion regime applies.

Accordingly, we find that the apparent relaxation times for the co-ordinated dihydrogen molecule show a marked increase when HD is substituted for H_2 [(**2**): H_2, 30 ms; HD, 200 ms. *(**4**): H_2, 48 ms; HD,* 240 ms]. This confirms the formulation shown, and makes (**4**) a member of the extensive $[IrH_2S_2L_2]^+$ series[6] of cations (S = H_2O, Me_2CO, RI, olefines, and now H_2; L = PR_3). We suggest the stereochemistry shown for (**4**) on the basis of this analogy.

'$IrH_6L_2^+$' is of particular interest because, if formulated as a classical polyhydride, it would be an unprecedented example of Ir^{VII}. This work has shown that it is better thought of as a nonclassical octahedral Ir^{III} complex of the well known $[IrH_2S_2L_2]^+$ type.

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