N.M.R. Evidence for a Fluxional Allyl-hydride Species featuring an Aliphatic C–H . . . Ir^{III} Interaction

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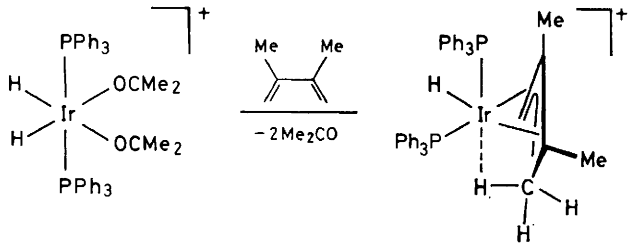
Summary The $[Ir(H)(PPh_3)_2(\eta^3\text{-}2,3\text{-dimethylbutenyl})]^+$ ion has been identified in CD_2Cl_2 solution from its ^1H, ^2H, and ^{31}P n.m.r. spectra, which reveal a novel C–H . . . Ir^{III} interaction and a fluxional process involving facile hydrogen transfer between metal and hydrocarbon.

Transfer of a hydrogen atom between metal and carbon centres is a fundamental step in many transition metal-catalysed organic reactions. Although many examples of reversible hydride transfer to hydrocarbon ligands[1] and C–H . . . M (M = metal) interactions[2] have been reported, they rarely involve catalytically active systems. We now report direct observation of a C–H . . . M interaction, and reversible hydride transfer, in species derived from (**1**). This cation is known to be an isomerisation and hydrogenation catalyst[3] and has recently been shown to activate aliphatic C–H bonds.[4]



(1) (2)

Reaction of (**1**) with 2,3-dimethylbutadiene in CD_2Cl_2 occurs at 273 K to give the butenyl-hydride (**2**). In contrast, the non-conjugated cyclo-octa-1,5-diene reacts readily with (**1**) at 243 K to give a diene-dihydride complex.[5] The ^1H n.m.r. spectrum of (**2**) in CD_2Cl_2 at 253 K (with assignments as in the Scheme) consists of a complex phenyl region (30H), three methyl singlets [δ 2·39 (3H), 1·62 (3H, Me^2, and Me^3), and –2·23 (3H, Me^1)] and two allyl singlets [δ 2·88 (1H) and 0·48 (1H, H^1 and H^2)]. In addition, there is a broad triplet assigned to the terminal iridium hydride {δ –24·65 [1H, $^2J_{PH}$ (*cis*) 19 Hz]}, with a shift which is significantly different from that expected for hydrides in a *trans*-position to an olefin (*ca.* δ –13).[5] The unusual Me^1 shift is consistent with a C–H . . . Ir interaction, rapid methyl rotation averaging both bridging and terminal C–H shifts in (**2**). It is not possible to 'freeze out' this rotation at low temperatures, although considerable broadening occurs by 153 K in CD_2Cl_2–$CFCl_3$ ($w_{\frac{1}{2}}$ 280 Hz). This interpretation of the upfield methyl resonance is supported by the observation of three Me^1 resonances for (**2**) derived from the deuterio-analogue of (**1**) at δ –2·23, –2·54, and –2·91 assigned to $-CH_3$, $-CH_2D$, and $-CHD_2$, respectively (Figure). Anomalously large shifts on deuteriation have been noted in other systems where C–H . . . M interactions occur.[6,7] These are due to zero-point-energy differences favouring residence of H rather than D in the bridging position. This is complemented by a corresponding shift to lower field of $-CH_2D$ and $-CHD_2$ [δ –1·71(br s, Me^1)] in the 61·4 MHz ^2H n.m.r. spectrum of (**2**) at 253 K.

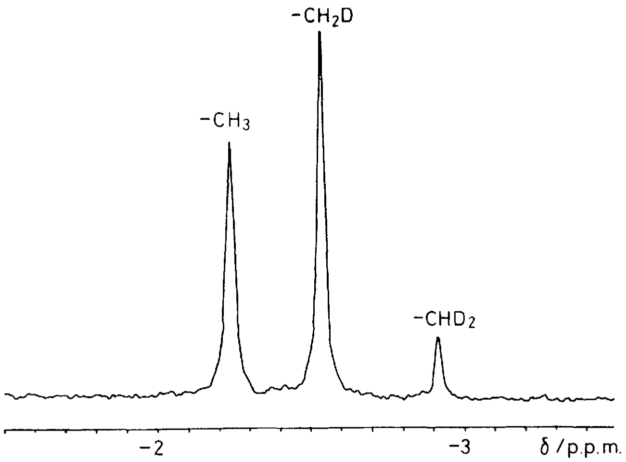
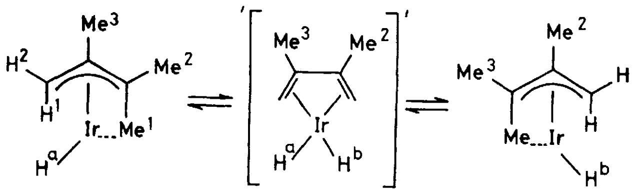


FIGURE. 400 MHz ^{1}H N.m.r. spectrum of the Me^1 region of (**2**) at 253 K.



SCHEME. Phosphine ligands are omitted for clarity.

Above 253 K the allyl and hydride resonances of (**2**) broaden with eventual collapse of the hydride signal by 273 K, while Me^2 and Me^3 clearly coalesce by 298 K (δ 2·01). ^{1}H Spin-saturation transfer experiments at 258 K show that this fluxional process does not involve H atom transfer from Me^2 or Me^3. Irradiation of Me^1 causes significant intensity reduction of the H^1, H^2, and Ir–H signals, but not of the Me^2 or Me^3 signals, while irradiation of Me^2 selectively removes Me^3 and *vice versa*. Such observations are consistent with a predominant fluxional process at 258 K involving a diene-dihydride intermediate (Scheme) analogous to that found for non-conjugated dienes such as cyclo-octa-1,5-diene.[5]

Another fluxional process must occur to allow the incorporation of two deuterium atoms at Me^1. Rapid facial rotation of the allyl-Me^1 moiety[7] in (**2**) is a likely mechanism as this would deliver the Me^1 carbon near to the iridium hydride such that either H^a or H^b can transfer to the same terminal carbon *via* the diene-dihydride intermediate (Scheme). However, other rearrangements, involving the diene dihydride intermediate in the Scheme, cannot be ruled out. ^{31}P N.m.r. spectroscopy (162 MHz) reveals two broad resonances of equal intensity (δ 10·5 and 8·2) below 253 K with no $^2J_{PP}$ coupling evident. These two resonances coalesce by 293 K. Facial rotation of the allyl-Me^1 group will not render the diastereotopic P atoms equivalent, but the onset of H atom transfer (Scheme) will do so above 253 K.

In the absence of a C–H . . . Ir interaction, (**2**) is formally a 16-electron Ir^{III} species. The 18-electron configuration may be approached by electron delocalisation from the C–H bond to the metal, as described previously.[2]

Preliminary ^{1}H n.m.r. results indicate the formation of the η^3-cyclohexenyl analogue of (**2**) from the reaction between cyclohexa-1,3- or -1,4-diene and (**1**). Attempts to isolate (**2**) as the pure solid with the exclusion of decomposition products have proved unsuccessful.

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