Intramolecular Rearrangement Behaviour of a Dihydridoiridium(III) Complex formed by Regiospecific 'Chelate-assisted' Hydrosilylation

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Addition of $PPh_2CH_2CH_2SiMe_2{}^2H$ to $[IrH(CO)(PPh_3)_3]$ is regiospecific as evidenced by formation of a *cis* adduct $[\overline{Ir(PPh_2CH_2CH_2SiMe_2})(CO)(PPh_3)(H)(^2H)]$ in which ^2H nuclei are initially restricted to a single co-ordination position; subsequent rearrangement whereby ^2H becomes equally distributed among the two hydridic sites is intramolecular with $\Delta G^{\ddagger}_{298} = 19.3 \pm 3.2$ kcal mol^{-1} (1 kcal = 4.184 kJ).

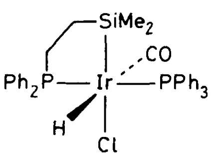
Reaction of dihydrogen with co-ordinatively unsaturated Ir^I complexes is well-established but the stereochemically labile character of the adducts so formed has only recently been recognized. Thus Brown *et al.*[1] have concluded that slow isomerization which follows H_2 addition to $[Ir(diphos)_2]^+$ [diphos = bis(diphenylphosphino)ethane] and related cations is an intramolecular process, while Drouin and Harrod[2] have suggested a bimolecular pathway involving a yet uncharacterized hydrido-bridged di-iridium intermediate to account for H/D site-exchange in deuterio-isotopomers of $[IrH_3(CO)(PPh_3)_2]$. Here we show that rearrangement of a *cis* dihydridoiridium(III) complex synthesized by an entirely different route is intramolecular.

A 'chelate-assisted' hydrosilylation reaction[3] occurred rapidly under mild conditions between the phosphinoethylsilane[4] $PPh_2CH_2CH_2SiMe_2H$ (**1**) and $[Ir(Cl)(CO)(PPh_3)_2]$ ('Vaska's complex') affording complex (**2**) which has been characterized crystallographically.[5] Subsequent treatment with $LiAlH_4$ resulted in formation in high yield of a *cis* dihydride for which structure (**3**) can be unambiguously assigned from ^1H and ^{31}P n.m.r. data; the same product may also be obtained *via* reaction of the silane (**1**) with $[IrH(CO)(PPh_3)_3]$ (**4**). The high-field region of the ^1H n.m.r. spectrum (250 MHz) for compound (**3**) showed in equal ratio H_A, δ −10.64, dd, ^2J 108.8 (to *trans* P), 16.9 Hz (to *cis* P) and H_B, δ −10.59, apparent t, ^2J 18 Hz (two *cis* P). Reaction of complex (**2**) with $LiAl^2H_4$ afforded a monodeuterio-analogue $[^2H_1]$-(**3**) with H distributed (^1H n.m.r.) equally between A and B sites. By contrast when compound (**4**) was treated with $PPh_2CH_2CH_2SiMe_2{}^2H$ {*i.e.* $[^2H_1]$-(**1**)}, initially the product $[^2H_1]$-(**3**) showed only a triplet proton resonance attributable to H_B; but after a short time a weak signal corresponding to the characteristic H_A multiplet could be resolved which slowly increased in intensity (Figure 1) to a limiting 1 : 1 H_A/H_B ratio. Complex (**3**) showed no incorporation of ^2H after 24 h/25 °C in $[^2H_8]$tetrahydrofuran (THF) solution; the isotopomer $[^2H_2]$-(**3**) which was synthesized *via* $[^2H_1]$-(**2**) using successive deuteriation steps underwent no H/D exchange with complex (**4**), also in THF solution/24 h/25 °C; and no loss in isotopic purity of complex $[^2H_2]$-(**3**) was detectable after stirring in solution (18 h/25 °C) with excess of undeuteriated (**1**).

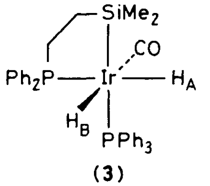
These observations are consistent with regiospecific addition of the silane (**1**) to complex (**4**) *i.e.* coplanar entry of P, Si, and H affording the dihydride (**3**); and with a subsequent slow equilibration which interconverts H_A and H_B by an intramolecular mechanism. Appropriately the rate of change in intensity of the n.m.r. signals illustrated in Figure 1 is linear, $k_{obs} = 4.30(\pm 0.20) \times 10^{-2}\,s^{-1}$ at 28 °C. Addition of a tenfold excess of free PPh_3 did not significantly affect the rate and examination of the temperature-dependence of k_{obs} yielded $\Delta G^{\ddagger}_{298} = 19.3 \pm 3.2$ kcal mol^{-1} (1 kcal = 4.184 kJ) for the rearrangement process.

$PPh_2CH_2CH_2SiMe_2H$

(**1**)



(**2**)



(**3**)

$[IrH(CO)(PPh_3)_3]$

(**4**)

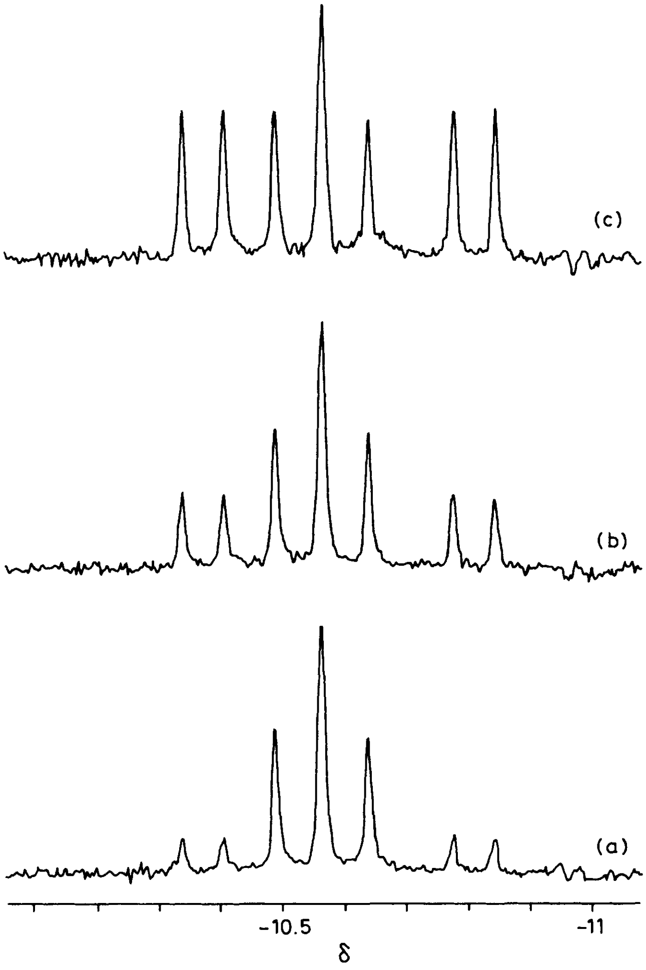


Figure 1. ^1H N.m.r. spectrum of the product $[^2H_1]$-(**3**) of reaction between silane $[^2H_1]$-(**1**) and complex (**4**) after (a) 1 h, (b) 5 h, and (c) 48 h at 28 °C.

The high stability towards intramolecular distortion of the octahedral configuration has been emphasized[6] and accounts for the rarity of stereochemically non-rigid six-co-ordinate molecules.[6,7] An important exception is provided by a family of dihydridoiron complexes,[6,7] most of which are exclusively *cis* and are fluxional, typified by $FeH_2[P(OEt_3)]_4$ for which $\Delta G^{\ddagger}_{298} = 13.7\,\mathrm{kcal\,mol^{-1}}$ for degenerate intramolecular exchange, although a few examples exist as equilibrium mixtures of *cis* and *trans* isomers which interchange with similar free energies of activation.[7] Barriers to corresponding dynamic behaviour of ruthenium analogues however are estimated[7] to be substantially higher and directly comparable with that reported here for non-degenerate rearrangement of compound (**3**).

In conclusion we suggest that metal-centred rearrangement of dihydridoiridium(III) species may not be uncommon as believed hitherto.[1] More particularly it seems to us that such an intramolecular process would adequately account for all of the experimental data described by Drouin and Harrod,[2] since an exchange similar to that we have characterized for compound (**3**) would inevitably lead to a 1:2 equilibrium distribution of ^2H (reflecting statistical axial/equatorial site-occupancy) in a trihydrido-complex formed by reaction of complex (**4**) with $^2H_2$, exactly as was observed.[2]

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