Interconversion of *cis*- and *trans*-Dihydrides derived from Chelate Biphosphine Iridium Cations

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Equilibration of *cis*- and *trans*-dihydrides derived from iridium bis chelate biphosphine complexes proceeds at room temperature or below by an intramolecular mechanism.

Little is known about the factors controlling the crucial H_2 addition step in rhodium-catalysed asymmetric hydrogenation of dehydro-amino acids, because the dihydride presumed to form in that step rearranges rapidly to an observable alkylrhodium hydride.[1] We have examined H_2 addition to chiral iridium phosphine complexes as simple models and report a surprising observation.

The orange crystalline salt bis{(*RR*)-1,2-bis-[*o*-methoxyphenyl(phenyl)phosphino]ethane}iridium tetrafluoroborate (**1**) was prepared by standard methods.[2] It reacted with H_2 (1 atm; 20 min; 0 °C; CD_3OD) to produce two diastereoisomeric *cis*-dihydrides (**2a**) and (**2b**) in unequal proportions [^1H n.m.r., major isomer δ −11.65, J_{PH} (*trans*) 113 Hz, J_{PH} (*cis*) 15—16 Hz; minor isomer δ −12.02, J_{PH} (*trans*) *ca.* 100 Hz (partly obscured), J_{PH} (*cis*) 15—16 Hz]. At this stage a further hydridic species was present and over the course of an hour at room temperature this became the major species (>90%). Four equivalent P–H couplings suggest that it is the corresponding *trans*-dihydride (**3**), this supposition being reinforced by the observation of a singlet in its ^{31}P n.m.r. spectrum [^1H n.m.r., δ −10.30; J_{PRh} 14.3 Hz, ^{31}P n.m.r. δ 35.5 p.p.m.]. The intramolecular nature of the rearrangement was established by the reaction of the complex (**1**) in methanol with HD. The solution was equilibrated for 1 h to permit rearrangement and then examined directly by field-desorption mass spectrometry. The observed isotope distributions in the molecular-ion fragment were compared with that of authentic samples of (**3**) and its dideuteride, and with computer-calculated values for the possible isotopomers (Figure 1). Furthermore, the field-desorption mass spectra of samples prepared by the reaction of (**1**) with an equimolar mixture of H_2 and D_2 which were then kept for 1 h, or by the reaction of separate samples of (**1**) with H_2 and with D_2 which were mixed and left for 1 h, showed the pattern expected for an absence of isotopic scrambling. When complex (**1**) was treated with D_2 in CD_3OD for 20 min and rearrangement then allowed to proceed under H_2, no significant metal hydride was observed in the ^1H n.m.r. spectrum after the re-

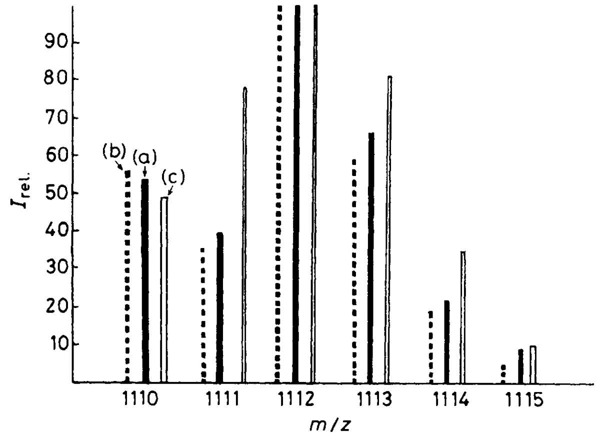
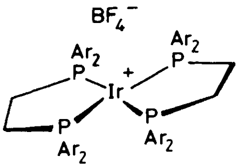


Figure 1. Field-desorption mass spectrum of a sample of (**1**) which had reacted to completion with HD in methanol at room temperature and had then been left for 1 h, to permit rearrangement (solid line, a). At the emitter current necessary for desorption (>17 mA) some (**1**) was produced by dehydrogenation and an appropriate correction was made. Theoretical ion-distributions for the HD adduct (broken lines, b) and for scrambling between H_2, HD, and D_2 adducts (open lines, c) are shown.



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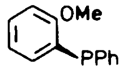
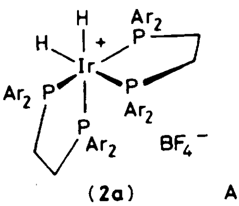
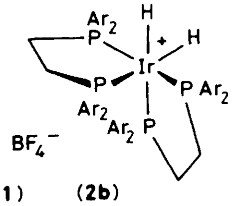
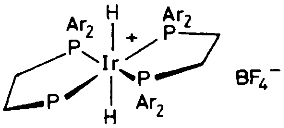






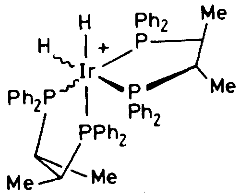
(2a) Ar_2 as for (1) (2b)

(4) $Ar_2 = Ph_2$

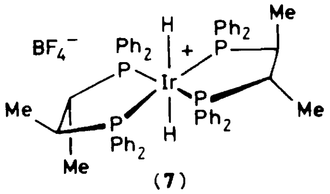


(3), Ar_2 as for (1)

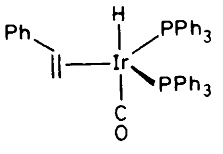
(5), Ar_2 as for (4)



(6)



(7)



(8)

arrangement. Similarly, reaction of (1) with H_2 followed by rearrangement under D_2 produced no evidence of crossover. These experiments establish that the reaction is intramolecular (excepting biphosphine dissociation pathways) but do not distinguish between six- and five-co-ordinate intermediates. The ^2H n.m.r. spectrum of a solution of [$^2H_2$]-(3) prepared by the reaction of (1) with D_2 shows signals in the Ir–H region but not the aromatic region, so that no exchange occurs with *ortho*-hydrogens.[3]

Even the well characterised[2,4] complex (4) derived from 1,2-bis(diphenylphosphino)ethane rearranges in solution to an equilibrium mixture containing *ca.* 20% of the *trans*-isomer (5) [^1H n.m.r. (CD_3OD), *cis*: δ −11.6, J_{PH}(*trans*) 113 Hz, J_{PH} (*cis*) 14—16 Hz; *trans*: δ −10.4, J_{PH} 15 Hz; ^{31}P n.m.r. (CH_2Cl_2) *cis*: δ 31.8 and 20.2 p.p.m., J_{PP} 8 Hz, *trans*: δ 38.3 p.p.m.]. Equilibration is rather slower here but it is established within 24 h at ambient temperature, and the reaction rate is insensitive to concentration, Ar or H_2 atmosphere, added NaOMe, or solvent change to CH_2Cl_2. The analogous *cis*-complex (6) derived from (*SS*)-*trans*-2,3-bis(diphenylphosphino)butane (6)[5] rearranges to the corresponding *trans*-isomer (7) over two weeks at room temperature with the latter being very strongly favoured at equilibrium.

Previous observations of *cis–trans*-isomerisation in mononuclear dihydrides H_2MP_4 have been confined to monophosphine complexes where a wider range of polytopal rearrangement pathways is permitted.[6] Harrod and co-workers[7] observed *trans*-dideuterides in the addition of deuterium to carbonylhydrido-tris(triphenylphosphine)iridium (with concomitant phosphine loss) but have shown that in the related case of complex (8) addition of deuterium occurs with *cis*-stereochemistry, and *trans*-dideuterides are the product of subsequent rearrangement. In contrast, isomerisation of related *bis*-chelate iridium complexes requires rather forcing conditions.[8]

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5 M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 1977, **99**, 6262; only one Ir–H multiplet was observed in the ^1H n.m.r. spectrum of (6) but this does not necessarily mean that reaction is stereospecific, since the Ir–H environment is very similar in the two possible diastereoisomers.

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