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THE STEREOCHEMISTRY OF Si—D ADDITION TO HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE)IRIDIUM(I)

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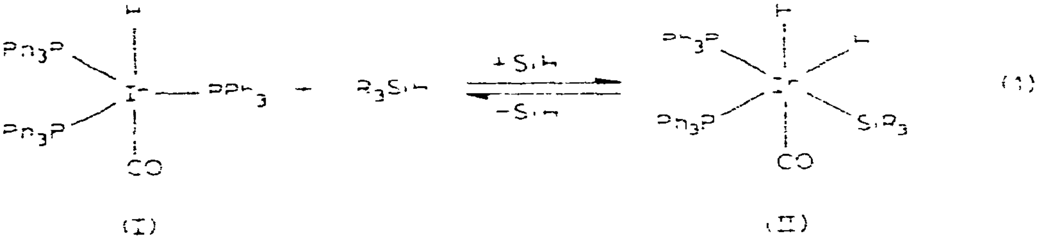
Summary

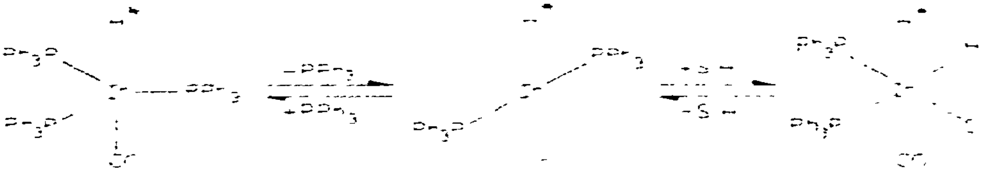
Triphenyldeuteriosilane adds to hydridocarbonyltris(triphenylphosphine)-iridium(I) to give *a*-hydrido-*b*-deuterido-*c*-triphenylsilyl-*d*,*e*-bis(triphenylphosphine)carbonyliridium(I). In the presence of excess Ph_3SiD, the latter compound undergoes rapid H/D exchange at the hydride position.

A number of years ago it was established that the stereochemistry of the addition of silicon hydrides to hydridocarbonyltris(triphenylphosphine)iridium-(I) (I) was that depicted in II [1] (eq. 1).



Although II establishes that addition occurs in a *cis* fashion, it does not establish which of the two hydrogens on the product arises from the silane, or whether in fact the silane hydrogen may end up in either of the two positions. The answer to this question has some importance in relation to a recently proposed, detailed mechanism for reaction 1 which requires either a highly stereospecific addition in which the silane hydrogen appears *cis* to CO in the product, or an explanation for the scrambling of the two hydrogens in the product [2].

It was reported earlier that the product II isolated after the addition of $(EtO)_3SiH$ to the deuterio analogue of I contained deuterium roughly equally distributed between the two hydride positions [1]. We originally considered this observation to be a serious objection to our proposed mechanism, which involved predissociation of phosphine groups from I, followed by *cis* addition of Si—H with complete restoration of the stereochemistry of the residual ligands to the positions they occupied in I, as depicted in eq. 2.



II

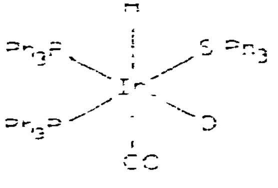
(2)

As later pointed out by Kaesz and Saillant [3], the scrambling of the two hydrogen positions might be rationalized by assuming dynamic stereoisomerization in either I or III, or both. The possibility of isomerization of I can be ruled out following the observation of Yagupsky and Wilkinson that I does not undergo fluxion up to temperatures at which phosphine dissociation occurs rapidly on the NMR time scale [4].

We wish to report some new observations, using deuterium labelling, which remove misleading ambiguities from the earlier experiments and also eliminate the need for a hypothesis that intramolecular H/D scrambling occurs in order to justify the highly stereospecific addition required by the proposed mechanism.

An experiment was performed in which a solution of I (0.005 *M*) in methylene chloride was injected into a liquid sample infrared cell (1 mm path length, capacity 0.5 ml). This solution was rapidly withdrawn into a 1 ml syringe containing a solution of Ph_3SiD (0.1 ml, 0.23 *M*) and the mixed solutions were immediately reinjected into the infrared cell. The spectrum of the mixture was scanned immediately and at several times after mixing. The results are shown in Fig. 1. Spectra were recorded with a Perkin—Elmer Model 257 Grating Spectrometer in the slow-scan mode.

The spectra in Fig. 1 are interpreted in the following manner. The first measured spectrum corresponds almost entirely to compound IV, with ν(Ir—H) 2070 cm^{-1}, and ν(CO) (*trans* to H) 1960 cm^{-1}. This compound results from the fast and complete reaction of I with Ph_3SiD under the concentration conditions used. Subsequent spectra show the rapid appearance of a band at ~1995 cm^{-1} due to ν(CO) (*trans* to D), the disappearance of ν(Ir—H) and the appearance of a band at ~2120 cm^{-1}, the frequency at which ν(Si—H) for Ph_3SiH occurs.



(IV)

The above observations indicate that the initial addition of Ph_3SiD to I occurs

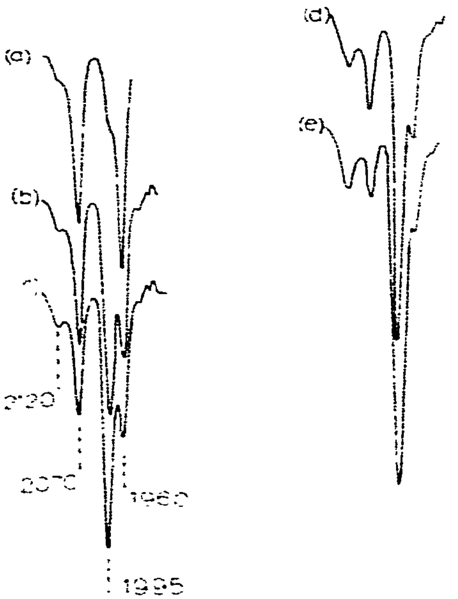
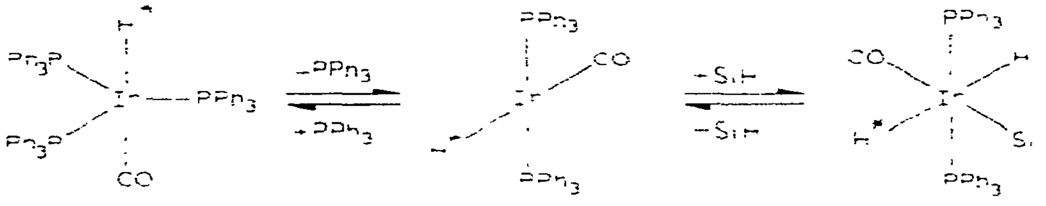


Fig. 1. Evolution of the infrared spectrum of a mixture of Ph_3SiD (ca. 0.04 *M*) and $(Ph_3P)_3CO(H)Ir^I$ (ca. 0.004 *M*) with time: (a) immediately following mixing; (b) after 5 min; (c) after 10 min; (d) after 50 min; (e) after 100 min. Reaction in dichloromethane at 25°C. Frequencies in cm^{-1}.

with a high degree of stereospecificity, but the intervention of slower secondary processes leads to H/D exchange between IV and the excess Ph_3SiD. The final spectrum indicates that, under the conditions of the present reaction, the final product is predominantly the dideuteride. The appearance of ν(Si—H) at roughly the same rate as ν(CO) (*trans* to D) strongly suggests that the secondary changes observed are due to SiD/IrH exchange and not to IrH/IrD positional scrambling. Although the present results do not exclude the possibility that the latter process is occurring to some extent, there is also no direct evidence that it is. The proton NMR spectra of II, for a range of substituents R, show no evidence of deviation from those expected for the rigid molecules up to 50°C.

The infrared spectrum measured after 10 min reaction (see Fig. 1) was almost identical to that previously observed for the product isolated from reaction of $(EtO)_3SiH$ with $(Ph_3P)_3CO(D)Ir^I$ [1]. It is now evident that the presence of nearly equal amounts of ν(CO) (*trans* to H) and ν(CO) (*trans* to D) in that case was almost certainly due to a scrambling process analogous to that producing H/D exchange in the present experiment. The same conclusion would also apply to the previously observed SiH/IrD exchange between $(EtO)_3SiH$ and the triethoxysilyl analogue of IV [1]. An experiment using equimolar Ph_3SiD and I qualitatively confirmed this conclusion. The infrared spectral results were far more complicated under these conditions (compared to those for a ten-fold excess of Ph_3SiD) because the oxidative addition reaction at equilibrium is only about 70 per cent complete. The species present at equilibrium in such a mixture are IrH_2, IrHD (2 isomers), IrD_2, SiH and SiD. Although the IR spectrum was in accord with such a mixture, it cannot discriminate between a mixture of the two IrHD isomers and a mixture of IrH_2 and IrD_2.



(3)

(V)

All of the experimental evidence concerning reaction 1 can now be accomodated by a scheme in which the principal reaction pathway is that depicted in eq. 2. The slower H/D exchange and positional interchange reactions may be rationalized by assuming a small contrubition from a number of equally possible alternative pathways. The most likely in our opinion is a pathway in which the addition results in movement of H^* and CO into a *cis* relationship to each other, leaving the phosphines *trans*, as shown in eq. 3. In fact the stereochemistry of V is far more common for adducts of bis-phosphine complexes than that of II, where the phosphines are *cis* [5,6]. The presence of a few per cent of V in the reaction product would easily escape detection but would be sufficient to account for the observed SiD/IrH exchange. Similar alternative pathways involving small amounts of the *cis* isomer of III are equally probable.

Acknowledgements

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