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Further Observations on the Stereochemistry of the Addition of Dihydrogen to Some Iridium(I) Complexes

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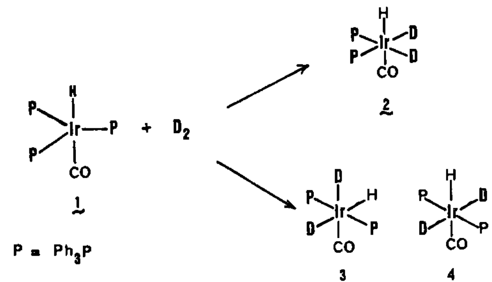
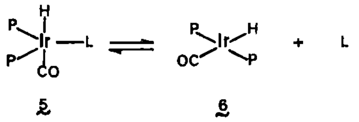
In an earlier communication the reaction depicted in (1)



(1)

was reported,[1] together with its isotopic conjugate. One of the more interesting speculations arising from these results was the possibility that the isotopomer **4** could arise from the unprecedented trans addition of deuterium to a square-planar intermediate. The evidence did not allow a distinction between the latter possibility and the more plausible alternative of **3** being the primary product, which, under the reaction conditions, then transforms into **4** by an H/D interchange. The observation that **3** and **4** always appeared to be in a 2:1 ratio suggested that they were possibly in equilibrium, and the existence of such an equilibrium greatly complicates the question as to whether **3** or **4** or both are primary products.

It has been our belief,[1-3] although there exists a claim to the contrary,[4] that reaction (1) proceeds by loss of a phosphine ligand from **1** to yield a very reactive planar intermediate **6**[5] (eq 2, L = PPh_3). The relatively high activation energy for



(2)

the loss of a phosphine from **1** leads to a rapid fall in the rate of (1) with decreasing temperature. This in turn vitiates the possibility of producing **6**, and therefrom the trihydrides, at a low temperature where equilibration between **3** and **4** might be substantially slowed down. We therefore sought a new reactant, **5**, which would lose L at a much lower temperature than **1** loses triphenylphosphine. An appealing candidate for L was an olefinic ligand, since we knew that the complex L = ethylene was not stable, yet strongly electron-withdrawing olefinic ligands (e.g., NCCH=CHCN) give the very stable complexes **5**.[6] We therefore synthesized a number of new vinyl complexes using reaction (3)[7] and established that the styrene complex exhibited more or less optimum properties.

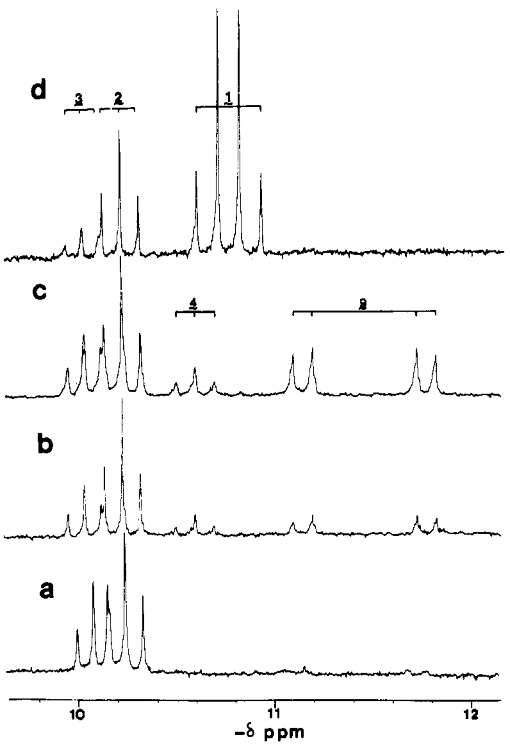
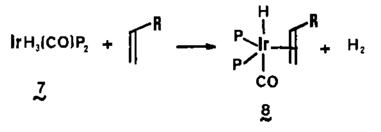


Figure 1. ^1H NMR spectra in the hydride region for the products of reacting D_2 with (a) the styrene complex at -30 °C for 16 h, (b) the styrene complex at -30 °C for 16 h, with the sample allowed to warm to room temperature for 1 h, (c) the styrene complex at 20 °C for 90 min, and (d) the tris(phosphine) complex at 20 °C for 30 min. Spectrum a was recorded at -30 °C; the others were recorded at 20 °C.



(3)

Results and Discussion

Preparation and Properties of the Styrene Complex. When the reaction (3) is carried out in pure styrene as solvent, at slightly above ambient temperature, the styrene complex can be recovered as a relatively pure solid by rapid vacuum evaporation of the solvent. The solid can be recrystallized from styrene/heptane at low temperature (≤-20 °C) but decomposes rapidly in solution at ca. 0 °C and above. The existence of an equilibrium between the two isomers of **8a** (R = Ph) at temperatures near 0 °C was evident from a spin saturation transfer between their hydride resonances.[7] At -20 °C the spin saturation transfer was no longer evident. Above 0 °C, all resonances of free and coordinated styrene, and of coordinated hydride, broaden and collapse. All of this evidence indicated that, for the case of styrene, equilibrium 2 was still significantly fast as temperatures well below ambient.

In the absence of other ligands, **8a** decomposes by a number of different reactions, including loss of styrene to give **6**[8] and transfer of hydride from iridium to styrene to produce ethylbenzene. The styrene is readily displaced by PPh_3 and CO at temperatures down to -30 °C. The complex also reacts with H_2 to give a mixture of the *fac* and *mer* trihydrides **7**.[9]

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(1) Harrod, J. F.; Hamer, G.; Yorke, W. *J. Am. Chem. Soc.* **1979**, *101*, 3987.

(2) Harrod, J. F.; Yorke, W. *Inorg. Chem.* **1981**, *20*, 1156.

(3) Much of the work reported in ref 2 is corroborated by the earlier studies in: Werneke, M. F. Ph.D. Thesis, Clarkson College of Technology, Potsdam, NY, 1971.

(4) De Waal, D. J. A.; Gerker, T. I. A.; Louw, W. J. *J. Chem. Soc., Chem. Commun.* **1982**, 100.

(5) The geometry of this intermediate is not known since it never achieves a sufficiently high concentration to be detected without disproportionating to **1** and an uncharacterized hydride-free complex with ν_{CO} at 1980 cm^{-1}.

(6) Fraser, M. S.; Baddeley, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 3661; *J. Organomet. Chem.* **1972**, *36*, 377.

(7) The synthesis and detailed properties of these compounds will be reported elsewhere.

(8) This conclusion is based on the appearance of the disproportionation products of **6**. See ref 5.

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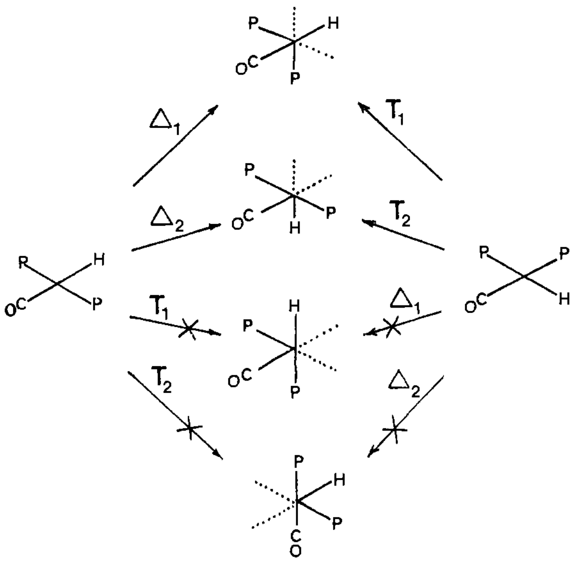
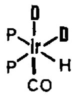
Scheme I



Most significantly, the complex was found to react with H_2, albeit slowly, at temperatures as low as −30 °C.

Reaction of the Styrene Complex with D_2. Treatment of a solution of **8a** with a stream of D_2 at −30 °C for 24 h gave a product with the high-field ^1H NMR spectrum shown in Figure 1a. The only detectable hydride products of this reaction were the species **2** and **3**. When the reaction products were allowed to warm to room temperature for 1 h, the species **4** and **9** rapidly appeared (Figure 1b). After long periods at room temperature, substantial amounts of products exhibiting the small proton–proton couplings of dihydrides appeared in the mixture.



9

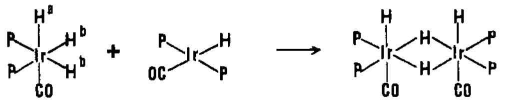
For the sake of comparison, the spectrum of the products resulting from the reaction of **1** with D_2 at room temperature is shown in Figure 1d. The complete absence of the isotopomer **9** is particularly striking, but apart from this difference the product is very similar to that given by the styrene complex, namely, a mixture of **2** and **3**. A very small amount of **4** is also evident in Figure 1d (shoulder on lowest field peak of **1**). In earlier reported spectra at 90 MHz,[1] this resonance was more obvious because it did not coincide with **1** at that frequency. It should also be noted that the reaction of Figure 1d is less advanced than the one previously reported for the same experimental conditions.[1] This difference is due to the extreme sensitivity of the rate of reaction to trace impurities of triphenylphosphine, a factor difficult to control.

Stereochemistry of Addition of Hydrogen to 6. It is not known whether **6** exists as either the trans or the cis form, or as a mixture of both, under the conditions of these experiments.[5] It is therefore necessary to consider both isomers as possible sources of the reaction products. Given the assumption that the reaction of H_2 (D_2) with **6** is a concerted cis process, the number of topochemical pathways is quite limited and they are summarized in Scheme I.

Of the four possible products shown in Scheme I, only the upper two are permitted by the experimentally observed geometric isomers or isotopomers. These two products can arise from the trans isomer of **6** by the bending operations Δ_1 and Δ_2, which bring either of the two pairs of trans ligands into a 90° relationship to each other. The same two products could arise from the cis isomer of **6** by the more elaborate operations T_1 and T_2, which require a twist of two pairs of cis ligands into orthogonal planes, followed by opening up of one of the 90° angles to 180°.[10] The latter possibility seems unlikely to us on the grounds that it contravenes the principle of least motion and that the application of the same mechanism to the reaction of Vaska's complex and its analogues would require some rather doubtful ad hoc assumptions.[11,12] We therefore conclude that **6** probably reacts predominantly in the form of its trans isomer with hydrogen, by the two concerted cis mechanisms represented by Δ_1 and Δ_2.

Difference between Reaction Products from 1 and 8a at Room Temperature. The dramatic difference between the room-temperature reactions of **1** and **8a**, with respect to production of **9**, at first led us to consider the possibility that a special reaction pathway for H/D interchange was available to the styrene complex but not to the tris(phosphine) complex. Since other evidence had indicated a free-radical pathway for the insertion reactions of **8**,[7] and since some hydrogenation of styrene was observed to accompany the reaction of hydrogen (deuterium) with **8a**, even at −30 °C, a radical-initiated hydrogen abstraction chain seemed a possible candidate. The failure of *tert*-butylphenylnitrone to have any effect on the reaction of **8a** with D_2 discounts this possibility.[13] We therefore favor the hypothesis that **6** catalyzes H/D scrambling by reversibly forming bridge dimers with the trihydride, **7**, a process which could lead to exchange of the hydride on **6** for one of those on **7**.[14] This hypothesis accounts for the facts that (a) for the styrene complex, where the equilibrium (2) lies more to the right, the rate of scrambling is much faster than for the tris(phosphine) complex and (b) scrambling produces a significant amount of dihydrides, even though the reaction occurs in the presence of D_2.[15]

A compelling piece of evidence that bridging of the kind shown in eq 4 occurs was uncovered by an attempt to convert the analogue of **7** where P = tris(4-chlorophenyl)phosphine (**7′**) to the analogue of **6** by displacing H_2 under a stream of inert gas. The evidence is illustrated in Figure 2. A solution of **7′** at ambient temperature shows resonances characteristic of the *mer* and *fac* isomers, in similar abundance. After passage of a stream of N_2 through the solution for 2 h, the resonance due to H^b (eq 4) collapses, while those due to H^a and the *mer* isomer remain sharp. Cooling the solution to −20 °C reversibly restores the H^b resonance to the form expected for a rigid molecule. This selective collapsing of the H^b resonance is interpreted as due to the formation of *small amounts* of the species **10**, where the environment of H^a has not significantly changed, while that of H^b is substantially changed. The equilibrium (4) is rapid at room temperature but slow at −20 °C, and the amount of **6′** (and therefore the amount of



7′ **6′** **10** (4)

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[9] Part of the styrene is released unchanged and part is transformed to ethylbenzene.

[10] There are in fact four T operations for each square-planar isomer, but they give only the two products shown in Scheme I.

[11] Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.

[12] Ugo, R.; Pasini, A.; Fusi, A.; Cenini, S. *J. Am. Chem. Soc.* **1972**, *94*, 7364.

[13] Janzen, E. J. *Acc. Chem. Res.* **1971**, *4*, 31.

[14] There are precedents for such bridged hydrides. See, e.g.: Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

[15] There are also trideuteride isomers, which do not show up in the ^1H NMR spectrum.

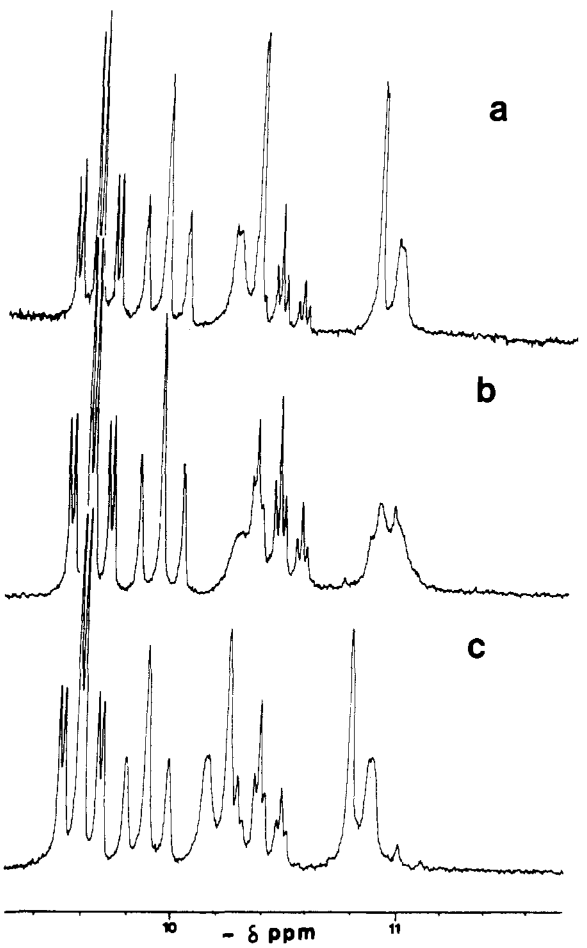

Figure 2. ^1H NMR spectra (in toluene-d_8) in the hydride region of $IrH_3(CO)[(4\text{-}ClC_6H_4)_3P]_2$: (a) at room temperature; (b) after passage of a stream of N_2 through the solution for 2 h; (c) after cooling of the solution to −20 °C.

10) is increased by purging the solution with N_2. Although the bridged intermediate **10** (or something very similar to it) is the only one whose existence is evident by NMR, others, whose exchange rate at room temperature is relatively slow, may also be present and contribute to isomerization–isotopomerization reactions.

Finally, we come to the question of the apparent trans addition of H_2 (D_2) to **6** reported previously.[1] It is clear from the reaction of the styrene complex with D_2 that no products arising from trans addition are produced at −30 °C. When the solution containing **2** and **3** is warmed to room temperature, the isotopomers **4** and **9** appear. Since the appearance of **4** parallels that of **9**, both in terms of rate and in terms of the subsequent appearance of dihydrides, it is reasonable to assume that **4** is produced by the same mechanism proposed above the production of **9**.

Experimental Section

The trihydrides **7** and **7′** were prepared by following a variation of a previously described procedure.[2] Reagent grade styrene was freshly distilled under reduced pressure of N_2 from CaH_2 immediately prior to the preparation of the styrene complex.

All NMR measurements were made on solutions in CD_2Cl_2 (99.8% minimum purity, Merck Sharp and Dohme, Canada, Ltd.) as solvent (unless specified). Spectra were recorded on a Varian XL-200 spectrometer at 200.057 MHz. All reported chemical shifts are relative to an internal $(CH_3)_4Si$ standard.

Synthesis of Hydridocarbonylbis(triphenylphosphine)(η^2-styrene)iridium(I). Freshly distilled styrene (20 mL) was added under nitrogen to $IrH_3(CO)(PPh_2)_2$ (0.35 g). The solution was stirred at 45 °C for 20 min with a constant stream of nitrogen passing through, and then the styrene solvent was rapidly stripped off under vacuum to yield a pale yellow solid. The crude product was contaminated with small amounts of the tris(phosphine) complex **1** and an unidentified hydride (^1H NMR: δ −15.4 (t)). The crude product was recrystallized from styrene/heptane at −20 °C. NMR (CD_2Cl_2, −30 °C): δ −11.52 (d) and −11.67 (d) (hydride resonance of less abundant isomer, J_{HP} = 16.5 Hz); δ −12.03 (pseudotriplet, hydride resonance of more abundant isomer, $J_{HP} \approx 19.0$ Hz); δ 2.3, 2.4, 2.6, 2.8, 3.8 (broad multiplets due to coordinated styrene). IR (Nujol mull): $\nu_{CO} = 1939\ cm^{-1}$; $\nu_{IrH} = 2059\ cm^{-1}$.

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Contribution from the Divisione Chimica, ENEA, Casaccia, Rome, Italy, and Istituto Chimica Fisica e Industriale, Università di Cagliari, Cagliari, Italy

On the Structure of Iron(III) Chloride Solutions

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The structure of iron(III) chloride solutions has been widely investigated by X-ray diffraction methods. The literature, up to 1979, has been cited in a recent work in which iron(III) chloride solutions, from 2 to 6 M, have been examined.[1] The main conclusion reached in that work was that extensive complex formation does occur in all solutions and that octahedral $Fe(H_2O)_{6-n}Cl_n^{3-n}$ (n = 1–3) or tetrahedral $FeCl_4^-$ complexes are the prevailing species at the different concentrations examined. A quantitative evaluation of the complex formation, expressed by the average number of Cl^- ions bonded per Fe^{3+} ion, n_{Cl}, was also made.

Since 1979, further papers have been published on this matter. In one of them, the structure of the undercooled hydrated $FeCl_3\cdot6H_2O$ melt was examined at room temperature.[2] Evidence of polynuclear complex formation, probably related to the presence of the bitetrahedral Fe_2Cl_6 molecule, was obtained. In two other papers, published by Wertz and his co-workers,[3,4] solutions, of concentrations approximately the same as ours,[1] were examined. The conclusions there reported, however, are dramatically different from ours. The new points claimed by Wertz and coworkers are as follows:

(a) Two solutions prepared from the hydrated $FeCl_3\cdot6H_2O$ salt (3.7 and 4.1 M), and examined by X-ray diffraction 1 week after their preparation, *do not show any complex formation.*[3] The solute species was identified as $Fe(H_2O)_6^{3+}$. The first peak of the radial curve of the two solutions occurs at 2.03/2.04 Å, which is just the sum of the Fe^{3+} (0.64 Å) and H_2O (1.40 Å) ionic radii. We have previously obtained,[1] for a 4.2 M solution also prepared with the hydrated salt, an n_{Cl} value of 3.

(b) The 3.7 M solution was reexamined after 14 months, and then an average solute species, approximately $FeCl_{1.5}(H_2O)_{4.5}^{1.5+}$, was claimed to occur.[4] The first peak of the distribution curve is centered at 2.16 Å, which is a weighted average of Fe–OH_2 (2 Å) and Fe–Cl (∼2.3 Å) interactions. In our previous work[1] we did not check the effect of time on the structure of the solutions. Usually our solutions, unless otherwise needed, are examined soon after their preparation so that our previous results are to be considered as obtained from freshly prepared solutions.

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