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Catalysis of hydrosilylation.

XII *. Spectrophotometric study of the reactivity of the $[RhCl(COD)]_2$-bis(diphenylphosphinoethyl)-tetramethyldisiloxane complex with substrates of the hydrosilylation reaction

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Abstract

The reactivity of the model complex – $[RhCl(COD)]_2$ – bis(diphenylphosphineethyl)tetramethyldisiloxane (I) with the substrates of the hydrosilylation (1-hexene and triethoxysilane) has been studied spectrophotometrically at room temperature. Disappearance of the band at 24.4×10^3 cm^{-1}, characteristic for the square planar complex, I, enabled us to determine pseudo first-order rate constants (k_{obs}) for the reaction. Relative values of k_{obs} indicate that the reaction is four times faster with 1-hexene than with triethoxysilane. Inhibition by added siloxyphosphine (BPS-2) is evidence for preliminary replacement of phosphine by 1-hexene. Consequently, for silica-supported catalysts of the BPS ligand structure the anchored complex is released into solution during the reaction and catalyses the process homogeneously.

Introduction

Reaction of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with bis-(ω-diphenylphoshinoalkyl)tetramethyldisiloxy ligands of the general formula $PPh_2(CH_2)_nSi(CH_3)_2OSi(CH_3)_2(CH_2)_nPPh_2$ where n = 1-3 (BPS-1, BPS-2, BPS-3) and also with tris-(ω-diphenylphosphinoethyl)pentamethyltrisiloxane (TPS-2) in benzene solutions leads to complexes in which P : Rh = 1 : 1. Elemental analysis and spectroscopic methods as well as molecular weight measurements of the isolated complexes

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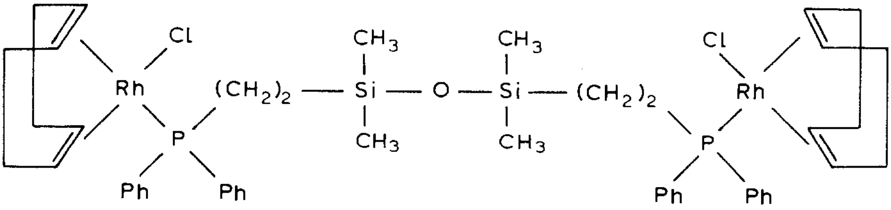
* For Part XI see Ref. 1.

allowed us to propose their molecular formulae. Coordination of the groups around the rhodium atom in these complexes is square planar and independent of the type of phosphine coordinated. The complexes appeared to be effective catalysts for the hydrosilylation of 1-hexene with triethoxysilane and show slightly lower catalytic activity compared with the Wilkinson complex, and is almost independent of the type of phosphine bound [1]. Such complexes can be regarded as soluble analogues of the silica- and silicate-supported phosphine complexes of rhodium(I) which better reflect the real surroundings of the rhodium atom in heterogenized catalysts than the monophosphine [2,3] and polyphosphine [4,5] derivatives of organosilicon ligand studied and reported previously.

The reactivity of model complex I, of the structure given below towards the substrates of hydrosilylation i.e. 1-hexene and triethoxysilane, studied by standard spectrophotometric methods is presented here.



(I)

Results

Initial stages of the hydrosilylation of 1-hexene by triethoxysilane were revealed by changes in the electronic spectra of complex I in benzene solutions when 10% by

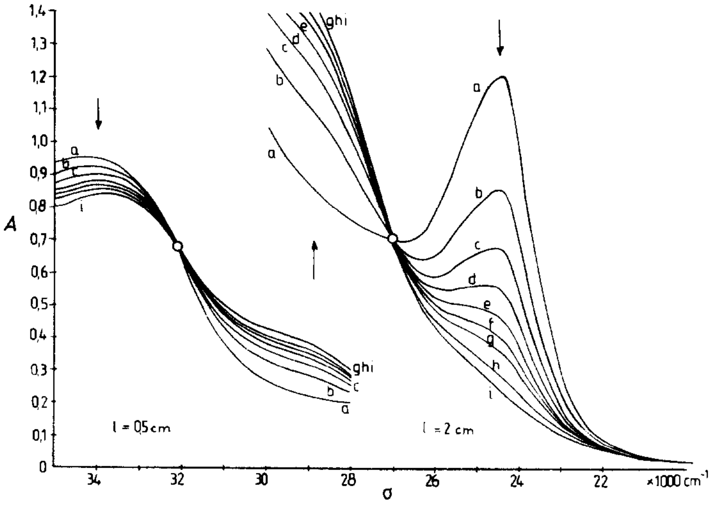


Fig. 1. Spectra of the reaction of complex I with triethoxysilane in benzene solution for various times. Reaction time: a = 0, b = 10, c = 20, d = 30, e = 40, f = 50, g = 60, h = 90, i = 270 min. *T* 20 °C, $c_{Rh} = 3.10 \times 10^{-4}$ *M*, $c_{HSi\equiv} = 0.53$ *M*.

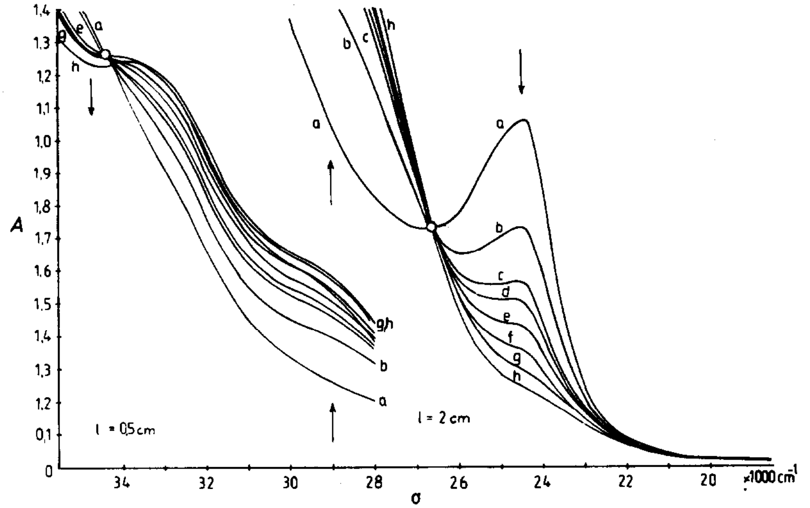


Fig. 2. Spectra of the reaction of complex I with triethoxysilane and an excess of BPS-2 in benzene solution for various times. Reaction time: a = 0, b = 10, c = 20, d = 30, e = 45, f = 60, g = 90, h = 120 min. T 20 °C, $c_{\mathrm{Rh}} = 3.10 \times 10^{-4}$ M, $c_{\mathrm{HSi}\equiv} = 0.53$ M, $c_{\mathrm{BPS-2}} = 3.16 \times 10^{-4}$ M

volume of a given substrate and/or their mixture was added. Some of the solutions also contained BPS in a two-fold excess (i.e. Rh : P = 1 : 3 in these solutions).

Figures 1–6 show the spectra obtained for various times during reaction. Most of the changes in the samples are due to disappearance of the band at 24.4×10^3 cm^{-1} which is characteristic for square planar complexes of rhodium(I) containing [RhCl(COD)(phosphine)]. Comparing the spectra of compounds of I with other

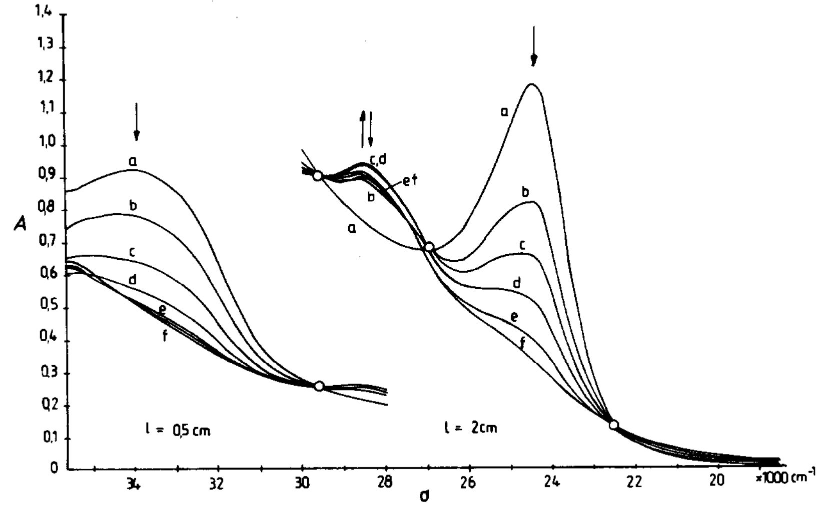


Fig. 3. Spectra of the reaction of complex (I) with 1-hexene in benzene solution for various times. Reaction time: a = 0, b = 2, c = 5, d = 10, e = 20, f = 60 min. T 20 °C, $c_{\mathrm{Rh}} = 3.10 \times 10^{-4}$ M, $c_{\mathrm{C_6H_{12}}} = 0.80$ M.

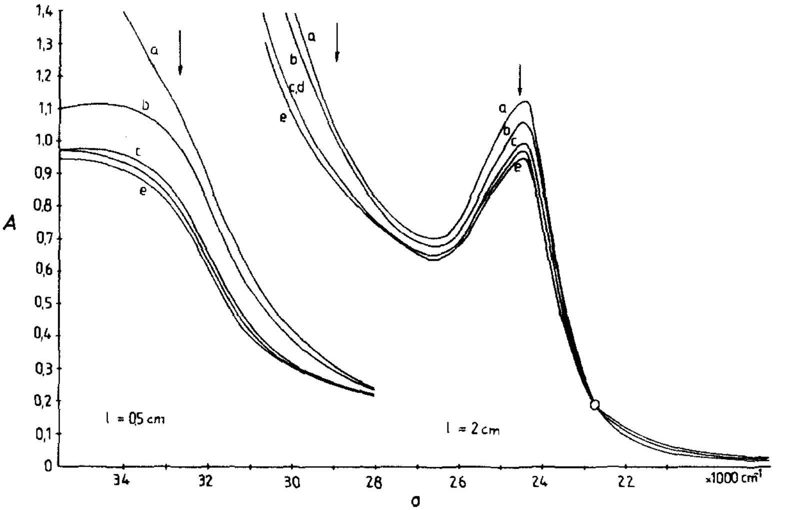


Fig. 4. Spectra of the reaction of complex I with 1-hexene and an excess of BPS-2 in benzene solution for various times. Reaction time: a = 0, b = 10, c = 20, d = 30, e = 45 min. T 20 °C, $c_{Rh} = 3.10 \times 10^{-4}$ M, $c_{C_6H_{12}} = 0.80$ M, $c_{BPS\text{-}2} = 3.16 \times 10^{-4}$ M.

square planar complexes of Rh^I containing phosphine [6,7] or COD [8,9], it is clear that the band at 24.4×10^3 cm^{-1} is attributable to metal phosphine (d_{z^2}–$\pi^\star$) transfer and their disappearance in the absence of simultaneous formation band at lower field is either due to a change in coordination number or the removal of phosphine from the coordination sphere of rhodium. No formation of new bands at

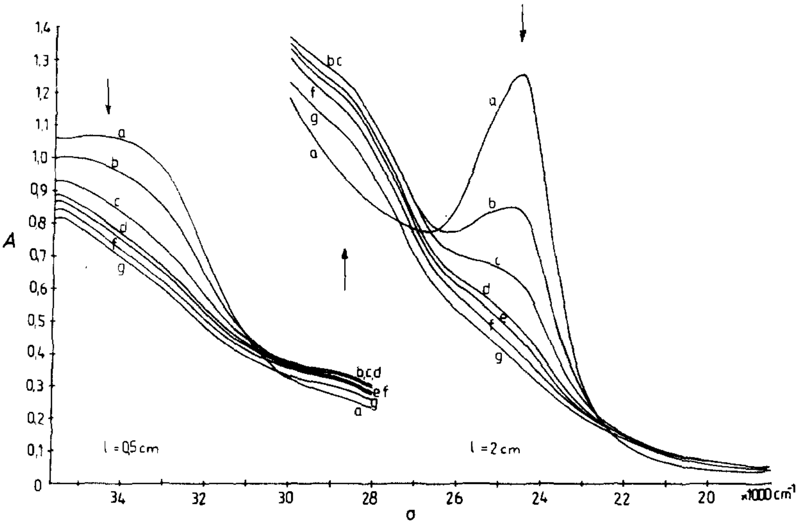


Fig. 5. Spectra of the reaction of complex I with a triethoxysilane and 1-hexene mixture in benzene solution for various times. Reaction time: a = 0, b = 3, c = 10, d = 20, e = 30, f = 60, g = 120 min. T 20 °C, $c_{Rh} = 3.10 \times 10^{-4}$ M, $c_{HSi\equiv} = 0.53$ M, $c_{C_6H_{12}} = 0.80$ M.

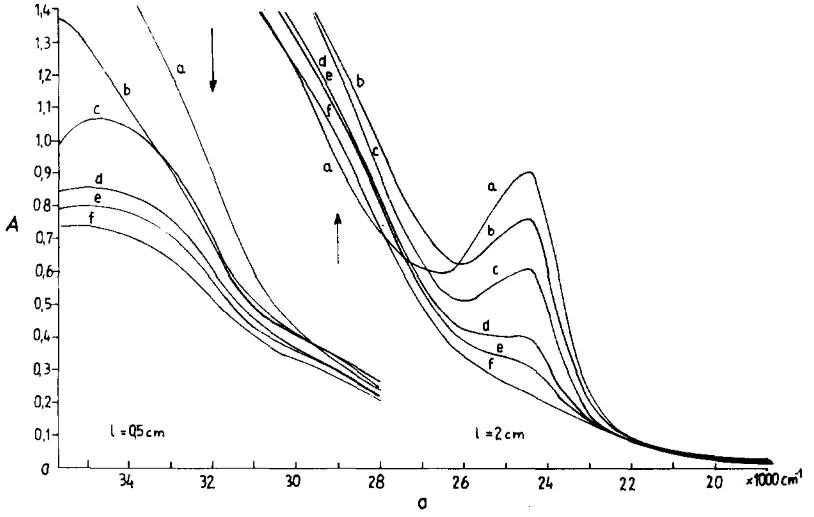


Fig. 6. Spectra of the reaction of complex I with triethoxysilane and 1-hexene as well as an excess of BPS-2 in benzene solution for various times. Reaction time: a = 0, b = 3, c = 10, d = 20, e = 30, f = 70 min. T 20 °C, $c_{\mathrm{Rh}} = 3.10\times10^{-4}$ M, $c_{\mathrm{HSi}\equiv} = 0.53$ M, $c_{\mathrm{C_6H_{12}}} = 0.80$ M, $c_{\mathrm{BPS\text{-}2}} = 3.16\times10^{-4}$ M.

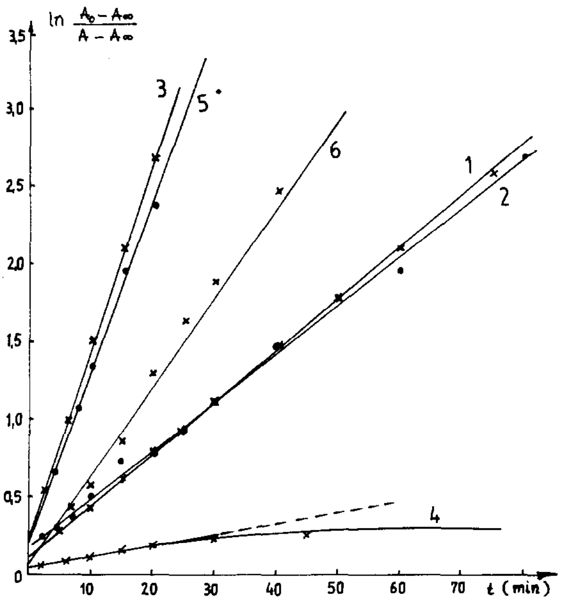


Fig. 7. Determination of the observed rate constants (k_{obs}) from the pseudo-first order kinetics (at 24.4×10^3 cm^{-1}) for reactions of the complex I with the following reagents: triethoxysilane (Fig. 1), $k_{\mathrm{obs}}(1) = 5.63\times10^{-4}$ s^{-1}; triethoxysilane + BPS-2 (Fig. 2), $k_{\mathrm{obs}}(2) = 5.26\times10^{-4}$ s^{-1}; 1-hexene (Fig. 3), $k_{\mathrm{obs}}(3) = 20.1\times10^{-4}$ s^{-1}; 1-hexene + BPS-2 (Fig. 4), $k_{\mathrm{obs}}(4) = 1.22\times10^{-4}$ s^{-1}; triethoxysilane + 1-hexene (Fig. 5), $k_{\mathrm{obs}}(5) = 18.7\times10^{-4}$ s^{-1}, triethoxysilane + 1-hexene + BPS-2 (Fig. 6), $k_{\mathrm{obs}}(6) = 9.71\times10^{-4}$ s^{-1}.

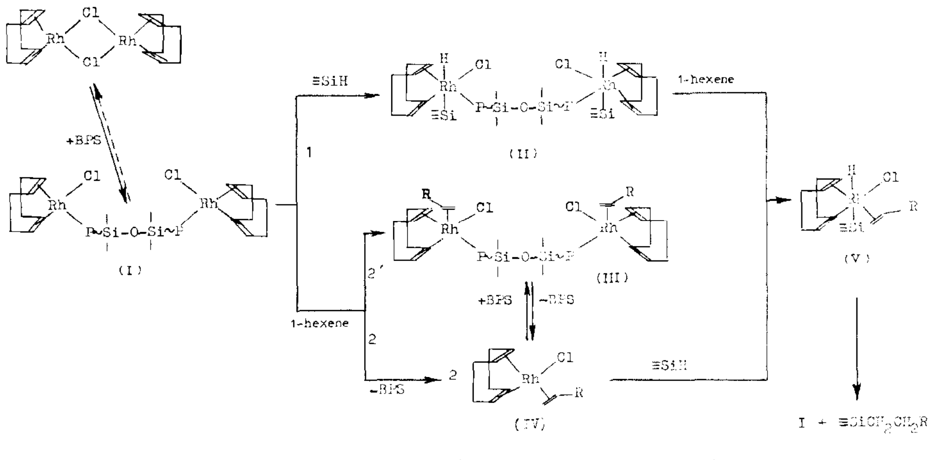
lower field except one corresponding to I was observed in the solutions examined. Disappearance of the band due to I was accompanied only by a certain decrease in absorption at 33.9×10^3 cm^{-1} and an increase in absorption at $27-31 \times 10^3$ cm^{-1}. In most spectra the presence of isosbestic points is observed.

The rate of disappearance of the band at 24.4×10^3 cm^{-1} shows a good linear correlation to pseudo first-order rate constants, therefore plots $\ln(A_0 - A_\infty)/(A_t - A_\infty) = f(t)$ (Fig. 7) enabled us to determine pseudo first-order rate constants (k_{obs}) which can be useful in characterizing the individual steps of the catalytic process.

Discussion

Complexes of $[RhCl(COD)]_2$ with BPS and TPS react with triethoxysilane, 1-hexene or their mixture with a rate that enables us to follow the reaction course by standard spectrophotometric methods. Measurement at room temperature showed no formation of the final hydrosilylation products within 4 h. In the absence of a substantial effect of the siloxyphosphine ligand on the catalytic properties of rhodium complexes [1] a detailed study was carried out only for exemplary complex I – (with the ligand BPS-2). In view of the general mechanism of the hydrosilylation [10,11] the reaction pathways can be given by Scheme 1.

The pathways proposed reflect the disappearance of the band at 24.4×10^3 cm^{-1} (found experimentally) which is either due to a change in the coordination number of the complex (the path 1, 2′) or removal of the phosphine from the coordination sphere of rhodium (path 2). The addition of triethoxysilane to a benzene solution of complex I leads to a characteristic change in the spectra (Fig. 1). Disappearance of the band at 24.4×10^3 cm^{-1} is accompanied by a relatively slight increase in absorption in the remaining regions of the spectra, but without formation of the new distinct band in the range $27-32 \times 10^3$ cm^{-1} and a decrease in absorption at 33.9×10^3 cm^{-1}. Well-shaped isosbestic points are evidence for the formation of only one compound. Addition of an excess of siloxyphosphine to this solution does



SCHEME 1. Initial pathways in the system: triethoxysilane/1-hexene/complex I (+BPS-2).

not influence the rate of its formation (Fig. 2). Observed rate constants (k_{obs}) are equal to 5.63×10^{-4} s^{-1} (without an excess of BPS-2) and 5.26×10^{-4} s^{-1} with an excess of BPS-2). Only isosbestic points in the spectra (Fig. 2) are slightly shifted, apparently due to the absorption by phosphine. The above results show that oxidative addition of silane takes place giving complex II. This is accompanied by a change in oxidation state of rhodium from +1 to +3, and by a change to octahedral geometry. The spectrum of complex I is influenced by the addition of 1-hexene (Fig. 3), which can be explained only by formation of the intermediate III or IV (Fig. 8). The spectrum (Fig. 3) shows the appearance of a new absorption band at 28.4×10^3 cm^{-1}, during reaction which is attributed to metal-COD transfer (d_{z^2}–$\pi^\star$) of complex $[RhCl(COD)]_2$ [7]. Yet, the corresponding isosbestic points in this spectrum are almost identical with those for the mixture of the complex I and $[RhCl(COD)]_2$ (at 26.9 and 26.8×10^3 cm^{-1} as well as 29.6 and 29.4×10^3 cm^{-1}, respectively [1]). However, an increase in absorption of this band is only initially proportional to the decrease of the band at 24.4×10^3 cm^{-1} (as well as the band at 33.9×10^3 cm^{-1}). As the reaction proceeds further decreases in these bands are observed, however, the band at 28.4×10^3 cm^{-1} does not change.

Reaction of complex I with 1-hexene is ca. four times faster than that of triethoxysilane. Addition of an excess of phosphine to the former causes extreme (16-fold) slowing of the reaction rate such that even after 10 h 50% conversion is not achieved Fig. 4). Synchronously, no band at 28.4×10^3 cm^{-1} is observed in such a solution and all isosbestic points disappear. The above spectrophotometric measurements appear to be clear evidence that under the reaction conditons formation of complex IV is favoured (together with replacement of phosphine by 1-hexene), which could be regarded as the active hydrosilylation intermediate. In an excess of the phosphine, however, the complex I reacts with 1-hexene yielding predominantly complex III and thus assuming the existence of the equilibrium III $\rightleftarrows$ IV (Scheme 1).

In the reaction of complex I with both substrates no isosbestic points are noted. The band appearing at 28.4×10^3 cm^{-1} (Fig. 5) shows (i) the competitive course of the two reactions described earlier and (ii) the formation in the reaction mixture of the previously-mentioned complexes, presumably II and IV. Rate constants (k_{obs}) determined graphically (Fig. 7) indicate that complex I reacts more readily and quickly with 1-hexene than with triethoxysilane. When both substrates are used 1-hexene is responsible for the rate and character of the changes in the spectra. Addition of an excess of siloxyphosphine (Fig. 6) causes considerable inhibition of the reaction with 1-hexene, so that oxidative addition also becomes rate-determining. Complexes II and IV by subsequent reaction with 1-hexene or triethoxysilane, respectively, probably form complex V which at higher temperatures leads to the hydrosilylation products and to recovery of the initial complex I. However, spectrophotometric measurements carried out at room temperature cannot confirm these pathways.

Finally, it is noteworthy that during the reaction under conditions examined, replacement of the siloxyphosphine ligand by olefin (path 2′) takes place. It can be concluded that for silica and/or silicate-supported catalysts with a ligand structure similar to BPS, the anchored complex is released into the solution under the conditions for catalysis. Accordingly, the proper catalytic cycle in the presence of such types of supported complexes occurs homogeneously in solution, and subsequently the Rh^I complex is again bound by the phosphine groups of the support.

Experimental

All experiments were carried out under purified and dried argon using syringe techniques. The spectrophotometric measurements in the visible region were made using a Specord UV-VIS spectrometer (Carl Zeiss, Jena) in glass cells hermetically sealed with silicon rubber. Benzene (POCh) and 1-hexene (Fluka AG) were distilled and stored under argon. Triethoxysilane was prepared by a published method [11] and redistilled under argon before use. Preparation of $[RhCl(COD)]_2$ with BPS-2 (complex (I)) was by a published method [1]. The kinetic examinations were carried out as follows: stock solutions of complex I (as well as BPS-2) (3.9×10^{-4} mole Rh/l) were prepared. This solution (8 ml) was diluted with benzene to 10 ml and the spectrum was recorded using glass cells (of 0.5 cm, from 30 to 20×10^3 cm^{-1}) obtaining the result for the initial absorption ($t = 0$). Subsequently, 8 parts (by volume) of stock solution were mixed with either 1 part 1-hexene and 1 part benzene, or 1 part triethoxysilane and 1 part benzene, or 1 part 1-hexene and 1 part triethoxysilane. The spectra of the above mixtures were recorded after various periods of time at 20 °C. Thus, the solutions prepared contained circa 3.1×10^{-4} mole Rh/l, 0.8 mole 1-hexene/l and 0.53 mole $HSi(OEt)_3$/l and some of them also with excess of BPS-2 such that Rh : P was 1 : 3.

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