REACTIONS OF $[(C_6H_5)_3P]_3RuCl_2$ WITH SOME SILICON HYDRIDES*

P.SVOBODA, R.ŘEŘICHA and J.HETFLEJŠ

Institute of Chemical Process Fundamentals
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol

Received November 13th, 1973

The reactions of the title compound with R_3SiH (R = C_2H_5, C_2H_5O, and Cl) were studied. By IR spectra measurements of solid products it was found that by the action of triethylsilane the ruthenium–phosphine complex is converted to $[(C_6H_5)_3P]RuHCl$. The analogous reaction with triethoxysilane gave a mixture of $[(C_6H_5)_3P]_3RuHCl$ and $[(C_6H_5)_3P]_3RuH[Si(OC_2H_5)_3]$, while in the case of trichlorosilane $[(C_6H_5)_3P]_3RuH(SiCl_3)$ and $[(C_6H_5)_3P]_3Ru(SiCl_3)_2$ were formed. A stepwise mechanism of the reactions was confirmed by similar experiments with $[(C_6H_5)_3P]_3RuHCl$.

In continuing our studies on hydrosilylation catalysed by transition metal complexes we investigated catalytic action of some ruthenium-phosphine complexes. While the activity of a number of complexes of the neighbouring metal, rhodium, has been authenticated, little information is available about the behaviour of similar ruthenium compounds. As found in the early stage of this work and has recently been reported[1], L_3RuCl_2 ($L = (C_6H_5)_3P$) induces the cleavage of the Si—H bond of silicon hydrides by alcohols and catalyses the addition of the hydrides across the C=O bond of various carbonyl compounds, similarly as does L_3RhCl (ref.[1-3]).

Our attempts at using several ruthenium–phosphine complexes, such as L_3RuCl_2, L_3RuHCl, and $L_3Ru(CO)HCl$, as catalysts for hydrosilylation of olefinic substrates containing terminal C=C bond (*e.g.* 1-hexene, 1,3-butadiene, styrene, allyl chloride, allylamine, vinyl ethyl ether, vinyl acetate, and acrylonitrile) by some di- and tri-substituted silicon hydrides (*e.g.* $(n\text{-}C_3H_7)_2SiH_2$, $(C_2H_5)_3SiH$, $C_6H_5(CH_3)_2SiH$, $(C_2H_5O)_3SiH$, and $HSiCl_3$) under various reaction conditions have not met, however, with success. The only reaction which we observed to take place in the presence of the ruthenium complexes, the addition of trichlorosilane to acrylonitrile, gave the unexpected product[4], 2-cyanoethyltrichlorosilane (*e.g.* 93% yield in the reaction carried out at 120°C over a period of 2 h without solvent in the presence of L_3RuCl_2 (conc. $2 \cdot 10^{-3}$ mol/l)). As confirmed by separate experiments, in this case the complexes served only as a source of the catalyst proper, triphenylphosphine, which was released by their dissociation due to the acrylonitrile. As one of the reasons of

---

* Part XXI in the series Catalysis by Metal Complexes; Part XX: This Journal *39*, 1318 (1974).

the inactivity of these ruthenium compounds might be, at least in some cases, the formation of stable ruthenium–silane complexes during hydrosilylation reaction (similar situation has already been observed in the reaction catalysed by rhodium–phosphine complexes, *cf*[5] and refs therein), it was of interest to investigate the reaction of ruthenium–phosphine complexes with silicon hydrides in more detail. The course of the reactions of L_3RuCl_2 with several silicon hydrides differing in the polarity of their Si—H bond ($(C_2H_5)_3SiH$, $(C_2H_5O)_3SiH$, and $HSiCl_3$) was followed by IR spectra of solid products.

The starting ruthenium complex, L_3RuCl_2, has in its IR spectrum the strong band due to the stretching vibration of the $RuCl_2$ group, which has already been reported[6]. In the 2000–1650 cm^{-1} region there are four overtone-combination bands of the nine phenyl groups of the complex, which are generally characteristic of monosubstituted benzene ring. These are located at 1967, 1898, 1815, and 1675 cm^{-1}. We mention them, because the highest one could eventually overlap with the Ru—H stretching band.

When a mixture of L_3RuCl_2 and the silicon hydride was allowed to stand in the absence of solvent under the conditions similar to those described in Experimental part, in most cases the silanes reacted reluctantly and the starting complex was recovered unchanged. In benzene, the ruthenium compound reacted with triethylsilane to give a solid product, the IR spectrum of which showed no bands due to the $(C_2H_5)_3Si$-group vibration (*i.e.* the band at 780–600 cm^{-1} for the Si—C stretch and the CH_2 rocking vibration or the absorption at 1380 cm^{-1}, due to the CH_3 symmetrical deformation vibrations). Instead, the strong sharp band at 288 cm^{-1} (Ru—Cl_1 stretch) and the band at 2031 cm^{-1} (Ru—H stretch) appeared. These bands are typical for L_3RuHCl (*cf.*[6]). The identity of the product with this compound was confirmed by comparing its spectrum with the spectrum of authentic sample of the latter complex. The absence of silicon in the product excluded further the possibility that we deal here with the complex solvated by the silicon hydride. In the liquid portion of the reaction mixture we found, along with the unreacted silicon hydride and the solvent, also triethylchlorosilane, which indicates the following course of the reaction:

$$L_3RuCl_2 + (C_2H_5)_3SiH \rightarrow L_3RuHCl + (C_2H_5)_3SiCl \qquad (A)$$

The reaction of L_3RuCl_2 with $(C_2H_5)_3SiH$ led to a product whose IR spectrum showed a complex pattern in the 350–250 cm^{-1} region. At least four overlapping components could be seen in the two broad bands centered at 324 and 288 cm^{-1}. Another strong, broad band around 1070 cm^{-1} was identified as being due to the stretching vibration of the Si—O—C bonds. The more intense and broader absorption band (compared to the above described product) near 1980 cm^{-1} indicates the presence of the Ru—H bond in the product, the absorption band of which overlaps with the highest overtone-combination band of the phenyl groups. This spectral patterns may be ascribed to nonuniformity of the product which is a mixture of the starting compound, L_3RuHCl and a silyl-ruthenium species, the nature of which was clarified by experiments with L_3 RuHCl (see later). The formation of the ruthenium–silane complex is further indicated by the presence of silicon in the solid product, which cannot be ascribed to its solvation by the hydride (no band attributable to the Si—H stretching vibration was detected in the spectrum).

When L_3RuCl_2 was reacted with trichlorosilane a solid product was formed, the IR spectrum of which showed no band due to the vibrations of the Ru—Cl bond. The strong absorption around 520 cm^{-1} (superimposed on complex L_3Ru band) present in the spectrum can be ascribed to the $SiCl_3$ stretching vibration. A sharp new band at 1950 cm^{-1} excludes again the possibility of the solvation of the starting compound by trichlorosilane, because the presence of the Si—H bond should manifest itself by an absorption between 2300–2200 cm^{-1} (in the free $HSiCl_3$ at 2258 cm^{-1}; in the case of solvated rhodium-phosphine complexes near this value[7]). We ascribe this band to the Ru—H stretching vibration. On the basis of these results the silyl-ruthenium-hydride species formed may be assigned the structure of $L_3RuH(SiCl_3)$. The higher content of silicon, found by elemental analysis of the solid product, indicates that a higher silyl-substituted substance is also present, the structure of which became evident from the experiments with L_3RuHCl (see later). In the liquid portion of the reaction mixture, along with the unreacted trichlorosilane and the solvent, also tetrachlorosilane was detected by gas–liquid chromatography.

Summarizing this part of investigations it may be concluded that the band observed near 2000 cm^{-1} is in all cases due to the Ru—H bond vibration and not to the Si—H stretching vibration, which excludes a possible formation of solvated species. Moreover, the occurrence of the single band speaks against the presence of the $Ru—H_2$ species, since more bands should otherwise be observed in the solid state spectra, due to crystal field perturbation. The formation of L_3RuHCl in the reactions of L_3RuCl_2 with triethyl- and triethoxysilanes, along with a complex course of some of the described reactions, further indicated that this species might be an intermediate product of these reactions. We therefore investigated the reactions of this compound with the same silanes under the conditions employed in the previous case.

In accordance with the results mentioned above L_3RuHCl did not undergo any change by the action of triethylsilane (the recovered complex had ν(Ru—H) at 2031 cm^{-1}, and ν(Ru—Cl) at 288 cm^{-1}).

The IR spectrum of the product of the L_3RuHCl with $(C_2H_5O)_3SiH$ reaction showed one medium, broader band at 1976 cm^{-1}, belonging to the Ru—H bond, which is different from the metal–hydride bond in the starting ruthenium complex. Additional band also appeared at 805 cm^{-1} which may be assigned to the deformation vibration of the above Ru—H bond. The presence of the triethoxysilyl group in the product was manifested by absorptions near 960 cm^{-1} (the C—C stretch of the ethyl groups) and around 1100 cm^{-1} (the stretching vibrations of the Si—O—C species). The absence of a band assignable to the Si—H stretching vibration indicated that the $(C_2H_5O)_3Si$-group is attached to the ruthenium atom. Moreover, the band of the original Ru—Cl bond (288 cm^{-1}) dissapeared, leaving the 400–250 cm^{-1} region free of selective absorptions. On the basis of this spectral evidence and the elemental analysis, the product was assigned the structure of $L_3RuH[Si(OC_2H_5)_3]$. This comports with the following course of the reaction:

$$L_3RuHCl + (C_2H_5O)_3SiH = L_3RuH[Si(OC_2H_5)_3] + HCl \qquad (B)$$

This finding further allows us to ascribe the same structure to a ruthenium–silane complex formed in a similar reaction of L_3RuCl_2.

In the reaction of L_3RuHCl with trichlorosilane a product was formed, the IR spectrum of which did not exhibit any absorptions due to the vibrations of the Ru—Cl, Ru—H, and Si—H bonds. Instead, a very broad absorption with the three maxima at about 565, 525 and 485 cm^{-1} appeared, indicating an increase in the number of the $SiCl_3$ groups in the product. Because of this huge absorption, which

TABLE I

The Characteristic IR Bands (cm^{-1}) and Their Assignment for the Products (in Nujol)
(s) Sharp, (br) broad; other symbols have conventional meaning.

Silicon hydride	L_3RuCl_2[a]	L_3RuHCl[b]
None	325 s, $\nu(RuCl_2)$	288 m, ν(Ru—Cl); 2 031 m (s), ν(Ru—H)
$HSiCl_3$	520 sh, $\nu(SiCl_3)$; 1 950 (s), ν(Ru—H)[d]	525 s (br); $\nu(SiCl_3)$[c,e]
$(EtO)_3SiH$	287 m (br); ν(RuCl); 325 s (br), $\nu(RuCl_2)$; 1 070 vs, ν(Si—O—C); 1 976 s (br)[f], ν(Ru—H)[g]	1 976 s (br)[b], ν(Ru—H); 2 031 w, ν(Ru—H); 1 070 vs, ν(Si—O—C)[h]
Et_3SiH	288 m, ν(Ru—Cl); 2 031 s (s), ν(Ru—H)[i]	290 m, ν(Ru—Cl); 2 031 s (s), ν(Ru—H)[i]

[a] Reported[6] one band at 315 cm^{-1} (in Nujol). [b] Reported bands[6]: 282 cm^{-1} and 2020 cm^{-1} (in Nujol). [c] Ref.[12]. [d] The yellow-brown solid containing 3·49% Si. [e] Brown solid. For $L_3Ru(SiCl_3)_2$ calculated: 4·86% Si, found: 4·38% Si. [f] Superimposed on the 1968 cm^{-1} overtone-combination band of the phenyl groups. [g] A brown solid material containing 2·29% Si. [h] Brown solid. For $L_3RuH[Si(OEt)_3]$ calculated: 2·67% Si, found: 2·81% Si. [i] Red-violet solid (Si absent). The spectrum was identical with that of an authentic sample of L_3RuHCl (ref.[6]).

masked the original L_3Ru band, the number of the phospine groups in the product became vague. In the spectrum there is further a small band at 365 cm^{-1} which we assign to the stretching vibration of the Ru—Si_2 bonds. According to the content of silicon, the compound analysed as $L_3Ru(SiCl_3)_2$. The over-all reaction may be tentatively depicted in the following way:

$$L_3RuHCl + 2\,HSiCl_3 \rightarrow L_3Ru(SiCl_3)_2 + HCl + H_2 \qquad (C)$$

Indirect support for the suggested course of the reaction follows from the fact that tetrachlorosilane was not detected by gas–liquid chromatography in the liquid portion of the reaction mixture. Although the preparative method employed did not allow to detect hydrogen evolved during the reaction, the formation of this gas is not unexpected[8]. The observed presence of the other volatile component, hydrogen chloride, is not of much significance in relation to this problem since the slight contamination of trichlorosilane by this substance can hardly be avoided during manipulations with the samples during gas–liquid chromatographical analysis. Notwithstanding, on the basis of these results it can reasonably be assumed that a higher silylated ruthenium complex, formed in the analogous reaction of L_3RuCl_2 and indicated by the higher than theoretical content of silicon (with respect to $L_3RuH(SiCl_3)$), is $L_3Ru(SiCl_3)_2$. In this reaction the structure of this product, in a mixture with L_3RuHCl, could not be recognized by IR spectra, because it is characterized only by the absence of the bands due to the Ru—H and Ru—Cl bond vibrations. In conclusion, our results indicate complex course of the studied reactions of L_3RuCl_2, which strongly depends on the structure of the silicon hydride. On the basis of the present evidence the reactions may in general be assumed to proceed in a stepwise manner, L_3RuHCl being an intermediate product. The exclusive formation of L_3RuHCl, and not a ruthenium–silane complex in the reaction of L_3RuCl_2 with triethylsilane is not surprising in view of generally low stability of related trialkylsilyl-substituted complexes of the neighbouring metal, rhodium, in the solvent used[8]. Whether the chlorine–hydrogen exchange proceeds *via* transient redox addition of the silicon hydride to the starting complex, or by a chain radical mechanism, resembling thus rather the reaction of palladium(II)–phosphine complexes with some Group IV metal hydrides[9], is not yet clear. In contrast to the reactions of silicon hydrides with L_3RhCl (ref.[7,8]), no addition products of the type $L_nRuHCl_2(SiR_3)$ have been observed even in the reactions of the ruthenium complex with triethoxy- and trichlorosilane. The results also excluded the possible formation of solvates containing coordinated silicon hydrides[7,8]. As noted earlier in this work, L_3RuHCl behaved similarly. The formation of the substitution products and not the products of the redox addition may, according to our opinion, be attributed to the instability of such, formally Ru(IV) complexes, rather than to a reluctance with which the metal might acquire this oxidation state[10].

Concerning the observed inactivity of the ruthenium–phosphine complexes in hydrosilylation of olefinic substrates by triethoxysilane and trichlorosilane, it can unquestionably be assigned to their conversion to stable ruthenium–silane compounds during the reaction. This was shown by hydrosilylation experiments in which solid products from the reaction of L_3RuCl_2 were employed as catalysts. They turned out to be quite inactive and were mostly recovered from the reaction mixture unchanged.

EXPERIMENTAL

The silicon hydrides were prepared in the usual way, distilled under argon prior to using. Benzene was dried by sodium, degassed, and rectified under argon. L_3RuCl_2 (ref.[11]) and L_3RuHCl (ref.[6]) were prepared by literature procedures as indicated. All the substances were stored under argon.

Hydrosilylation experiments were carried out in sealed glass ampoules. A reaction mixture, containing the appropriate olefinic compound, the silicon hydride, the catalyst (c. $5 . 10^{-3}$ mol/l) and, eventually, the solvent (benzene) was after standing for 1 day at room temperature gradually warmed up to 150°C during 5 h and kept at that temperature for another 3 h. The reaction mixtures were analysed gas–liquid chromatography. The authentic samples of the hydrosilylation products were used as reference compounds.

The reactions of L_3RuCl_2 and of L_3RuHCl with the silicon hydrides were carried out in the following way: The reaction flask was charged with 200 mg of the ruthenium complex, 2 ml of benzene and c. 200 μl of the silicon hydride (approx. tenfold molar excess with respect to the complex). The mixture was allowed to stand under argon for 4 days. The liquid portion was then removed by distillation under reduced pressure and analysed by gas–liquid chromatography. The residue was washed with ether and dried *in vacuo*. The IR spectra of the so obtained solid products were measured in Nujol mulls on a Beckmann IR-7 spectrometer (CsI / grating optics). All the manipulations with the solid samples were carried out in a dry box flushed out with nitrogen. The instrument was purged with dry air. The spectral characterization of the products is summarized in Table I; analytical data on the substances are mentioned in Notes.

REFERENCES

1. Corriu R. J. P., Moreau J. J. E.: J. Chem. Soc., Chem. Commun. *1973*, 38.
2. Ojima J., Nihonyanagi H., Nagai J.: J. Chem. Soc., Chem. Commun. *1972*, 938.
3. Chalk A. J.: J. Chem. Soc., Chem. Commun. *1970*, 847.
4. Chalk A. J.: J. Organometal. Chem. *21*, 207 (1970).
5. Svoboda P., Čapka M., Hetflejš J.: Chvalovský.: This Journal *37*, 1581 (1972).
6. Halmann P. S., Mc Garvey B. R., Wilkinson G.: J. Chem. Soc. (A) *1968*, 3143.
7. Charentenay F., Osborn J. A., Wilkinson G.: J. Chem. Soc. (A) *1968*, 787.
8. Haszeldine R. N., Parish R. V., Parry D. J.: J. Chem. Soc. (A) *1969*, 683.
9. Brooks E. H., Glockling F.: J. Chem. Soc. (A) *1967*, 1030.
10. Cotton A. E., Wilkinson G.: *Advanced Inorganic Chemistry*, 2nd Ed. Wiley, New York 1966.
11. Stephenson T. A., Wilkinson G.: J. Inorg. Nucl. Chem. *28*, 1945 (1966).
12. During J. R., Hellams K. L.: Appl. Spectrosc. *22*, 153 (1968).

Translated by the author (J. H.).