Journal of Organometallic Chemistry, 382 (1990) 185–189
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20302

Synthesis of ruthenium and iridium polyhydride complexes under conditions of phase transfer catalysis *

V.V. Grushin, A.B. Vymenits and M.E. Vol'pin
Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow (U.S.S.R.)

(Received May 9th, 1989)

Abstract

The chlorohydrido complexes of ruthenium $(Ph_3P)_3Ru(H)Cl$ and iridium $(Pr^i_3P)_2Ir(H)Cl_2$ react smoothly with H_2 (1 atm, 20 °C) in a 50% NaOH/benzene two-phase system in the presence of triethylbenzylammonium chloride as a phase transfer catalyst to form polyhydride complexes $(Ph_3P)_3Ru(H_2)(H)_2$ (**1**) and $(Pr^i_3P)_2IrH_5$ (**2**), respectively, in quantitative yields.

Introduction

Considerable attention of many chemists is focussed on transition metal polyhydride complexes owing to their interesting structural features and fluxional behaviour as well as their chemical properties and catalytic activity [1,2]. Only a few preparative methods for the transition metal polyhydride complexes are known. Hydridometallate (e.g. $NaBH_4$, $LiAlH_4$) reduction of various transition metal derivatives is the most often used method [1]. In addition, rare examples of hydrogen transfer from alcohols, THF, and some other solvents are known [1]. Finally, some procedures are based on the action of molecular hydrogen on metal complexes including the following: (a) active metal reduction under H_2; (b) hydrogenolysis of metal–carbon σ-bonds; (c) displacement of π-bound olefins or labile donor ligands, such as N_2 [1].

Recently we reported some reactions of α-elimination of HCl from chlorohydrido complexes of platinum and iridium under phase transfer catalysis [3–5]. In the present paper application of this approach to the preparation of ruthenium and iridium polyhydride complexes is reported. It should be noted that phase transfer catalysis, which has already successfully been used in synthesizing of various transition metal complexes and organo-element compounds [6–10 **], has not previously been used for the preparation of transition metal polyhydrides.

---

* Dedicated to Professor Dr. Günther Wilke on the occasion of his 65th birthday.

** Reference number with asterisks indicates a note in the list of references.

0022-328X/90/$03.50

Results and discussion

We have found that the well-known and readily available chlorohydrido complex of ruthenium $(Ph_3P)_3Ru(H)Cl$, easily reacts with H_2 in a benzene/50% NaOH two-phase system in the presence of triethylbenzylammonium chloride as phase transfer catalyst, to give the polyhydride **1**, which has been recently reformulated as a η^2-H_2 complex [11].

$$(Ph_3P)_3Ru(H)Cl + H_2 \xrightarrow[-HCl;\ 1\ atm\ H_2,\ 20\,^\circ C;\ 1\text{–}2\ h]{50\%\ NaOH/C_6H_6,\ Et_3\overset{+}{N}CH_2Ph\ Cl} (Ph_3P)_3Ru(H_2)(H)_2$$

(**1**, 90%)

The reaction of the chlorohydrido complex of iridium under similar conditions leads to the pentahydride complex **2** in quantitative yield.

$$(Pr^i_3P)_2Ir(H)Cl_2 + H_2 \xrightarrow[-2HCl;\ 1\ atm\ H_2,\ 20\,^\circ C;\ 5\text{–}30\ min]{50\%\ NaOH/C_6H_6,\ Et_3\overset{+}{N}CH_2Ph\ Cl} (Pr^i_3P)_2IrH_5$$

(**2**, 95%)

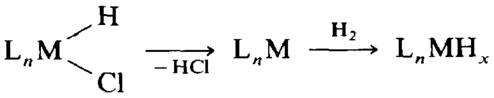
In the preliminary communication on the latter reaction [4] the initial monohydridoiridium complex was erroneously identified as a dihydride because of the coincidence of ^1H NMR spectra and crystallographic parameters for the dihydrido complex [12,13] and the compound we have obtained. A single crystal X-ray diffraction study, which will be published elsewhere, showed the presence of a *trans*-$(Pr^i_3P)_2IrCl_2$ square planar fragment; the hydrido ligand was not found. However, our compound was subsequently found to be diamagnetic, and its IR and ^{31}P NMR spectra are also in agreement with the monohydride structure reported by Werner, Wolf and Höhn [14].

The presence of the phase transfer catalyst is necessary in both procedures for the preparation of polyhydrides **1** and **2**. Thus, in the absence of triethylbenzylammonium chloride, no formation of iridium pentahydride **2** is observed. The reaction of the initial ruthenium compound in the absence of phase transfer catalyst leads to the complex mixture of products containing minor amounts of **1**, according to ^{31}P NMR data.

Both of the polyhydride complexes **1** and **2** are known [1] and were identified by IR and ^1H and ^{31}P NMR spectra (for **1** see ref. 15,16; for **2** see ref. 17a). It should be noted that the methods of synthesis of polyhydrides **1** and **2** described here possess some advantages over literature procedures. Thus, the reaction of $(Ph_3P)_3Ru(H)Cl$ with Et_3Al gives poor yields of **1** [1], and is less convenient. The reaction between the dinitrogen complex $(Ph_3P)_3Ru(H)_2(N_2)$ and H_2 [16] leads obviously to a product of high purity, however, this way is much more laborious than our procedure. The most simple and effective preparation of **1** uses the reaction of $(Ph_3P)_3RuCl_2$ with $NaBH_4$ in a methanol/benzene mixture [15,18]; the resulting complex can be obtained either in 75% yield as white product [15], or in 83.6% yield as coloured solid [18]. In comparison with this method, our procedure requires an additional step, i.e. the transformation of $(Ph_3P)_3RuCl_2$ to $(Ph_3P)_3Ru(H)Cl$, which is a rather simple procedure leading to the product in quantitative yield [19] *. Complex **1** obtained by our method in 85–90% overall yield in two steps, is white, and its benzene solutions are either colourless or light yellow.

Reactions of triisopropylphosphine complexes of iridium with $LiAlH_4$ in THF are often used for the synthesis of pentahydride **2** [17,20]. We suppose that manipulations with aqueous alkali under H_2 are more convenient than with $LiAlH_4$ in a nitrogen or argon atmosphere. Furthermore, the THF must be purified, dried and distilled prior to use, while benzene can be used in our method without any purification.

The mechanism of the reactions described is obscure and may be complicated. However, the pathway including the generation of H^- from H_2 under the action of strong base [21] should be excluded, as it was shown by special experiments, that benzophenone is not reduced to diphenylcarbinol under the same conditions. One can conceive the polyhydrides **1** and **2** formation as being formed by reductive elimination of HCl from the transition metal atom under conditions of phase transfer catalysis [5] followed by the addition of H_2 to the coordinatively-unsaturated intermediate.



$$L_nM\begin{smallmatrix}H\\Cl\end{smallmatrix} \xrightarrow[-HCl]{} L_nM \xrightarrow{H_2} L_nMH_x$$

However such an interpretation is rather formalistic. Thus, addition of OH^- to the metal atom of the complex, and/or substitution of chloro ligand by hydroxo group may precede the reductive elimination step. For example, it is known that treatment of $(Ph_3P)_3Ru(H)Cl$ with KOH in THF leads to $(Ph_3P)_3Ru(H)OH$ [22]. On the other hand, dihydrogen may also effect on the state of the complexes $(Ph_3P)_3Ru(H)Cl$ [23] and $(Pr^i_3P)_2Ir(H)Cl_2$ [13] in solution.

Attempts were made to prepare rhodium polyhydride complexes under conditions of phase transfer catalysis. The reaction of $(Pr^i_3P)_2Rh(H)Cl_2$ with H_2 in the 50% NaOH/benzene system in the presence of $Et_3\overset{+}{N}CH_2Ph\ Cl^-$ was found to lead rapidly (3–5 min) to the dihydrido complex $(Pr^i_3P)_2Rh(H)_2Cl$ [14] in quantitative yield (based on ^1H NMR data).

$$(Pr^i_3P)_2Rh(H)Cl_2 + H_2 \xrightarrow[-HCl;\ 1\ atm\ H_2,\ 20\,^\circ C;\ 3\text{–}5\ min]{50\%\ NaOH/C_6H_6,\ Et_3\overset{+}{N}CH_2Ph\ Cl^-} (Pr^i_3P)_2Rh(H)_2Cl$$

Continuation of this reaction leads to gradual disappearance of the dihydride initially formed. Unfortunately we failed to isolate or identify the subsequent products. Attempted preparation of polyhydride from $(Cy_3P)_2Rh(H)Cl_2$ (Cy = cyclohexyl) under the same conditions was also unsuccessful.

Experimental

NMR data were obtained on a Bruker WP-200 SY spectrometer. IR spectra were obtained on a Carl Zeiss, Jena, UR-20 instrument. A magnetic stirring bar was used

---

* We failed to obtain polyhydride **1** by the reaction of $(Ph_3P)_3RuCl_2$ with H_2 under conditions of phase transfer catalysis.

for the phase transfer catalyzed reaction procedures. Benzene (Chemapol, UV grade) was used as received. Aqueous alkali and benzene were degassed by means of three freeze-pump-thaw cycles prior to the reaction procedures.

$(Ph_3P)_3Ru(H_2)(H)_2$ (1). A mixture of $(Ph_3P)_3Ru(H)Cl \cdot C_6H_6$ [19] (0.30 g, 0.30 mmol), triethylbenzylammonium chloride (0.03 g, 0.13 mmol), benzene (5 ml) and 50% NaOH (0.5 ml) was vigorously stirred at 20 °C under H_2, until the red purple colour disappeared (1–2 h). Isolation of **1** was performed under argon. A pale tan slurry was diluted with H_2 saturated methanol (20 ml). The white precipitate was filtered off, washed with degassed methanol (2 × 15 ml), degassed pentane (3 × 15 ml) and dried in vacuo; yield 0.24 g (90%). The compound is found pure by spectroscopic methods.

$(Pr^i_3P)_2Ir(H)Cl_2$. A solution of $H_2IrCl_6 \cdot nH_2O$ (4 g, 36.8% of Ir) in ethanol (40 ml) was refluxed under argon for 15 min, then treated with Pr^i_3P (8 ml, 40 mmol), then the mixture was refluxed for 15 min. The hot dark red solution was separated from the viscous black tar, and diluted with degassed ethanol (100 ml). The solution was stored under argon at room temperature for 15 days. The deep purple crystals formed were filtered off in air, washed with ethanol (3 × 10 ml) and dried in vacuo; yield 2.53 g (56%), m.p. (in air, in vacuo, or under argon) 218–220 °C (dec.). IR and ^1H and ^{31}P NMR spectra of the product are identical with those of the Werner's complex, m.p. 145 °C [14]. Anal. Found: C, 36.97; H, 7.45; Cl, 10.82. $C_{18}H_{43}Cl_2IrP_2$ calcd.: C, 36.98; H, 7.41; Cl, 12.13%. The solid complex is air stable at room temperature for at least 2.5 years.

$(Pr^i_3P)_2IrH_5$ (2). A mixture of $(Pr^i_3P)_2Ir(H)Cl_2$ (0.30 g, 0.51 mmol), triethylbenzylammonium chloride (0.03 g, 0.13 mmol), benzene (5 ml) and 50% NaOH (4 ml) was vigorously stirred under H_2 at 20 °C, until the red purple colour disappeared (5–30 min). Isolation of **2** was performed under argon. The benzene layer was separated, and the aqueous alkali layer was washed with degassed pentane (8 ml). The combined organic solutions were filtered if necessary. The solution was taken to dryness under vacuo (0.1 torr) resulting in the isolation of a yellowish-white solid; yield 0.25 g (95%). The compound is found to be pure by spectroscopic methods; it can be recrystallized without losses as described in ref. 17b.

References

1 G.G. Hlatky and R.H. Crabtree, Coord. Chem. Rev., 65 (1985) 1.
2 V.D. Makhaev and A.P. Borisov, Uspekhi Khim., 57 (1988) 2025.
3 V.V. Grushin, I.S. Akhrem and M.E. Vol'pin, Metalloorganicheskaya Khimiya, 1 (1988) 474.
4 V.V. Grushin, V.I. Bakhmutov, I.S. Akhrem and M.E. Vol'pin, Izv. Akad. Nauk SSSR. Ser. Khim., (1988) 494.
5 V.V. Grushin, I.S. Akhrem and M.E. Vol'pin, J. Organomet. Chem., 371 (1989) 403.
6 L. Cassar, Ann. N.Y. Acad. Sci., 333 (1980) 208.
7 H. Alper, Adv. Organomet. Chem., 19 (1981) 183.
8 V. Galamb, Kém. Közl., 63 (1985) 227.
9 Yu. Goldberg, V. Dirnens and E. Lukevics, J. Organomet. Chem., Library, 20 (1988) 211.
10 V.V. Grushin, V.I. Bregadze and V.N. Kalinin, J. Organomet. Chem., Library, 20 (1988) 1. See Section F in this review and references cited therein.
11 D.G. Hamilton and R.H. Crabtree, J. Am. Chem. Soc., 110 (1988) 4126.
12 P. Mura, J. Am. Chem. Soc., 108 (1986) 351.
13 P. Mura and A. Segre, Angew. Chem., Int. Ed. Engl., 25 (1986) 460.
14 H. Werner, J. Wolf and A. Höhn, J. Organomet. Chem., 287 (1985) 395.

15 R.O. Harris, N.K. Hota, L. Sadavoy and J.M.C. Yuen, J. Organomet. Chem., 54 (1973) 259.
16 D.E. Linn and J. Halpern, J. Am. Chem. Soc., 109 (1987) 2969.
17 (a) M.G. Clerici, S. DiGioaccino, S. Maspero, E. Perotti and A. Zanobi, J. Organomet. Chem., 84 (1975) 379; (b) J.W. Faller and C.J. Smart, Organometallics, 8 (1989) 602.
18 A.-R. Al-Ohaly and J.F. Nixon, J. Organomet. Chem., 202 (1980) 297.
19 P.S. Hallman, B.R. McGarvey and G. Wilkinson, J. Chem. Soc. A, (1968) 3143.
20 L. Garlaschelli, S.I. Khan, R. Bau, G. Longoni and T.F. Koetzle, J. Am. Chem. Soc., 107 (1985) 7212.
21 Z.N. Parnes and D.N. Kursanov, Hydrogen Transfer Reaction in Organic Chemistry, Nauka, Moscow, 1969 (in Russian).
22 B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1977) 1546.
23 (a) G. Strathdee and R. Given, Can. J. Chem., 53 (1975) 106; (b) A.M. Stolzenberg and E.L. Muetterties, Organometallics, 4 (1985) 1739; (c) C. Hampton, T.W. Dekleva, B.R. James and W.R. Cullen, Inorg. Chim. Acta, 145 (1988) 165.