Inorganica Chimica Acta, 68 (1983) 103–105

New Catalysts for Hydrosilylation of Acetylenic Compounds

M. G. VORONKOV, V. B. PUKHNAREVICH, I. I. TSYKHANSKAYA, N. I. USHAKOVA

Institute of Organic Chemistry, 1 Favorsky Street, Irkutsk, 664033 U.S.S.R.

YU. L. GAFT and I. A. ZAKHAROVA*

Institute of General and Inorganic Chemistry Ac. Sci. of the U.S.S.R., 117071 Moscow-71, Leninsky propsect 31, U.S.S.R.

Received May 10, 1982

The regio- and stereo-selectivity in the homogeneous hydrosilylation of acetylene and heptene-1 monosubstituents and carbofunctional ethylene derivatives in the presence of palladium and platinum catalysts of a new type – $[Pd_2(Ph_3P)_4Cl_2]B_{10}Cl_{10}$ *(I),* $[Pd_2(Ph_3P)_4Cl_2]B_{12}Cl_{12}$ *(II),* $[Pd(Ph_3P)_3Cl]_2B_{10}Cl_{10}$ *(III),* $[Pd(Ph_3P)_3Cl]_2B_{12}Cl_{12}$ *(IV),* $[Pt(Ph_3P)_3Cl]_2B_{10}Cl_{10}$ *(V),* $[Pt(Ph_3P)_3Cl]_2B_{12}Cl_{12}$ *(VI) – have been studied. Unlike* H_2PtCl_6 *and other commonly used catalysts, their application for hydrosilylation of acetylenic compounds makes the process regiospecific, leading to formation of β-adduct exclusively. These complexes also catalyze the addition of triethylsilane to allylamine.*

Introduction

The systematic investigation of hydrosilylation of acetylene and its derivatives in the presence of platinum and rhodium complex compounds permitted us to characterize quantitatively the influence of the reagent structure, nature of the solvent and of ligands in the catalyst on the selectivity and rate of the process [1–4]. In order to establish general regularities of the mechanism of homogeneous hydrosilylation, we studied the reaction progress in the presence of a new type of catalyst, cationic triphenylphosphine complexes of palladium and platinum, containing polyhedral borane anions $B_{10}Cl_{10}^{2-}$ and $B_{12}Cl_{12}^{2-}$. The palladium complexes are known to be effective catalysts for hydrosilylation of unsaturated organic and organosilicon (vinylalkylsiloxanes) compounds, as well as 2- and 4-vinylquinoline [5–8]. At the same time the palladium catalysts give rise to some reduction side processes, reduction silylation, hydrogenolysis or hydrosilylation of azomethines [9]; interaction of alkenyl-sulphides with triethoxysilane results merely in C–S bond cleavage (in contrast with H_2PtCl_6 and $Rh(Ph_3P)_3Cl$) [10].

Until now there has been no data concerning the application of palladium complexes as the catalysts in hydrosilylation of acetylenes.

Results and Discussion

We studied the stereochemistry and structural selectivity in hydrosilylation of acetylene monosubstituents $CR{\equiv}CH$ and illustrated this on the basis of the compounds with $R = C_4H_9$ and C_6H_5, heptene-1, and carbofunctional ethylene derivatives such as acrylonitrile, allylamine, vinylbutyl ether, catalyzed by complexes I–VI.

All these complexes are found to be efficient catalysts for hydrosilylation of hexine-1 and phenylacetylene, providing formation of the corresponding vinylsilanes in yields up to 90%. Hydrosilylation by triethylsilane in the presence of complexes I–VI (as in the presence of H_2PtCl_6) is stereoselective and proceeds according to the Farmer rule to give the *cis*-additional product $(C_2H_5)_3SiCH{=}CHR$. In addition to the above mentioned products the corresponding α-adducts are formed in yields considerably dependent on the nature of the applied catalyst and substituent adding to the triple bond.

Table I lists the ratios of isomeric products of phenylacetylene and hexine-1 hydrosilylation catalyzed by H_2PtCl_6 and complexes I–VI and their reaction yields.

The structure of the reaction products was identified by PMR spectroscopy and GLC analysis (rela-

---

*Author to whom correspondence should be addressed.

0020-1693/83/0000-0000/$03.00

TABLE 1. Hydrosilylation of RC≡CH (R = C_4H_9, C_6H_5) by Triethylsilane in the Presence of Complexes I–VI and H_2PtCl_6 (t = 100 °C, τ = 2 hours).

n	Catalyst	R	Total yield of α and β adducts	Ratio β:α
I	$[(Ph_3P)_4Pd_2Cl_2]B_{10}Cl_{10}$	C_4H_9	90.0	22:78
		C_6H_5	17.1	56:44
II	$[(Ph_3P)_4Pd_2Cl_2]B_{12}Cl_{12}$	C_4H_9	65.2	23:77
		C_6H_5	29.3	63:37
III	$[(Ph_3P)_3PdCl]_2B_{10}Cl_{10}$	C_4H_9	89.0	38:62
		C_6H_5	23.9	32:68
IV	$[(Ph_3P)_3PdCl]_2B_{12}Cl_{12}$	C_4H_9	86.0	25:75
		C_6H_5	32.0	53:47
V	$[(Ph_3P)_3PtCl]_2B_{10}Cl_{10}$	C_4H_9	85.4	100:0
		C_6H_5	78.5	11:89
VI	$[(Ph_3P)_3PtCl]_2B_{12}Cl_{12}$	C_4H_9	90.0	100:0
		C_6H_5	87.6	15:85
VII	H_2PtCl_6	C_4H_9	78.3	42:58
		C_6H_5	90.8	24:76

tive to standards). The PMR spectrum indicated the presence of two doublets in τ = 4.17–4.41 ppm region, which are signals typical of AX spin systems, with coupling constant J = 3.0 Hz, and are assigned to the heminal hydrogen atoms of ethylene groups. The bands in the region of the relatively weaker field are assigned to the AB spin system with J = 18.0 Hz, and indicate the *trans*- position of vicinal protons of the HC=CH fragment. In the case of phenylacetylene, hydrosilylation catalyzed by complexes I–VI is accompanied by some negligible side processes, which yield styrene (to 4%), phenyl(triethylsilyl)acetylene (to 7%) and hexaethyldisiloxane (to 10%). The latter is bound to be formed, owing to the traces of water that are difficult to be removed from the solvent.

From the data in the Table it can be seen that complexes I–VI are in general more efficient catalysts for hydrosilylation of hexine-1 than H_2PtCl_6 (under comparable conditions). At the same time the catalytic activity of studied palladium and platinum catalysts differs in the reaction of triethylsilane with phenylacetylene. The application of palladium complexes in hydrosilylation leads to much lower yields (less than 32%), while the efficiency of their platinum analogs is comparable with H_2PtCl_6 (adduct yield about 90%).

An attempt to use other palladium complexes, such as $Pd(Ph_3P)_2Cl_2$, $Pd(Ph_3P)_4$ etc. for hydrosilylation of phenylacetylene and acetylene by triethylsilane, resulted merely in polymerization of these unsaturated compounds, the polymers formed being similar to those obtained in catalysis by molybdenum and tungsten [11] halides and oxyhalides.

The specificities of regioselectivity variation in reaction, catalyzed by complexes I–IV are worth considering. When the palladium complexes I–IV are used for hydrosilylation of phenylacetylene, the prevailing product in the isomeric mixture is normally the α-adduct (in comparison with H_2PtCl_6). On the contrary, the β-adduct is predominant in the case of hexine-1 hydrosilylation.

The platinum complexes V–VI are considerably different in the regioselectivity of catalytic action from their palladium analogs III and IV. *Trans*-$(C_2H_5)_3SiCH{=}CHC_5H_6$ is predominant in hydrosilylation of phenylacetylene, catalyzed by complexes V and VI.

Hydrosilylation of hexine-1 in the presence of complexes V and VI is strictly regioselective, leading to formation of only β-adduct in high yield. These catalysts are therefore drastically different from the conventionally used hydrosilylation catalysts, such as H_2PtCl_6 and many others, whose application results in the formation of a mixture of α- and β-adducts [5].

In the light of the above results, the complexes V and VI may be recommended as selective and efficient catalysts for hydrosilylation of acetylenic compounds by trialkylsilanes, producing the corresponding β-adducts in high yields.

Trichloro- and triethoxysilan are far less reactive in hydrosilylation of hexine-1 and phenylacetylene, catalyzed by complexes I-IV, than H_2PtCl_6. In this case the total yield of the two adducts amounts only to 30%.

An attempt to conduct hydrosilylation of heptene-1, acrylonitrile, allylamine and vinylbutylether by triethylsilane in the presence of complex I failed: heptene-1 and vinylbutylether proved to be totally unconverted, and acrylonitrile polymerized. On hydrosilylation of allylamine the corresponding triethyl(3-aminopropyl)silan was obtained with a 53% yield.

Experimental

Materials and Methods

The initial acetylenic, ethylenic compounds and triethylsilane were purified by conventional procedures. According to GLC analysis their purity was 99%.

The investigated catalysts were prepared by literature techniques [12, 13]. PMR spectra of 30% solutions of the compounds in CCl_4 were recorded with a BS-487-C Tesla spectrometer at 80 MHz. The chemical shifts were measured relative to tetramethylsilan (internal standard) with an accuracy of 0.01 ppm.

GLC analysis of reaction mixtures was performed on a "Tsvet" chromatograph. The column temperature was programmed from 50 to 240 °C (6 °C/min). The stationary liquid phase was Apiezon L – 10% from the support weight (Chromosorb P). The carrier gas (He) flow rate was 60 ml/min.

The Reaction of Triethylsilane with Hexine-1 in the Presence of I

A mixture of hexine-1 (1.16 g), triethylsilane (2.32 g) and complex I (0.001 mol) in dry acetonitrile (6 ml) was heated in a sealed ampoule for 2 hours at 100 °C in an argon atmosphere. The GLC analysis revealed that the reaction products consisted of α and β *trans* isomers in 22 and 78% ratio (see the Table).

The hydrosilylation of phenylacetylene, hexine-1, heptene-1, vinylbutylether in the presence of complexes I–VI was carried out in a similar way.

References

1 M. G. Voronkov, S. P. Sutshinskaya, V. B. Pukhnarevich and O. I. Randin, *Zh. obtshei khimii, 49,* 1281 (1979).

2 V. B. Pukhnarevich, L. I. Kopylova, B. A. Trophimov and M. G. Voronkov, *Zh. obtshei khimii, 45,* 89 (1975).

3 V. B. Pukhnarevich, L. I. Kopylova, E. O. Tsetlina, V. A. Pestunovich, V. Khvalovskii, I. Getfleish and M. G. Voronkov, *Dokl. Acad. Nauk SSSR, 231,* 1366 (1976).

4 L. I. Kopylova, V. B. Pukhnarevich, I. I. Tsykhanskaya, E. N. Satsuk, B. V. Timokhin, V. I, Dmitriev, B. Khvalovskii, M. Chapka, A. V. Kalabina and M. G. Voronkov, *Zh. obtshei khimii, 51,* 1851 (1981).

5 E. Lukevics, Z. V. Belyakova, M. G. Pomerantseva and M. G. Voronkov, *J. Organomet. Chem. Library, 5,* 1 (1977).

6 G. Chandra, *Brit. Patent,* 1.412.257 (1975), *C.A., 84,* 50368f (1976).

7 G. Chandra, *U.S. Patent,* 3.856.837 (1974), *C.A., 83,* 10381f (1975).

8 K. Kan, K. Miki, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Japan, 51,* 733 (1978).

9 K. A. Andrianov, M. I. Filimonova and V. I. Sidorov, *J. Organomet. Chem., 142,* 31 (1977).

10 M. G. Voronkov, N. N. Vlasova, S. A. Bolshakova and S. V. Kirpichenko, *J. Organomet. Chem., 190,* 335 (1980).

11 M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkov, V. M. Annenkova and N. I. Andreeva, *J. Polym. Chem. Ed., 18,* 53 (1980).

12 Yu. L. Gaft, I. A. Zakharova and N. T. Kuznetsov, *Russ. J. Inorg. Chem., 25,* 1308 (1980).

13 Yu. L. Gaft and N. T. Kuznetsov, *Russ. J. Inorg. Chem., 26,* 1301 (1981).