3. W. Vogt and H. Glaser, U. S. Patent No. 3476799 (1969).
4. D. Baldé and G. Nagy, French Patent No. 1474920 (1968).
5. F. Krüger and L. Bauer, West German Patent No. 2013372 (1976).
6. M. I. Kabachnik, T. Ya. Medved', N. M. Dyatlova, M. V. Rudomino, and N. V. Churilina, USSR Inventor's Certificate No. 684038, 1978; Byull. Izobret., No. 33 (1979).
7. M. I. Kabachnik and E. S. Shepeleva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 185 (1951).
8. R. Bannard, J. Gilpin, G. Vavasour, and A. McKay, Can. J. Chem., 31, 976 (1953).
9. S. Buc, Org. Syntheses, 36, 1 (1956).
10. K. Moedritzer, Synth. Inorg. Metallorg. Chem., 2, 317 (1972).
11. N. V. Tsirul'nikova, V. Ya. Temkina, T. M. Sushitskaya, and S. V. Rykov, Zh. Obshch. Khim., 60, 1028 (1981).
12. H. Staudinger, R. Signer, and H. Johner, Ann. Chem., 474, 254 (1929).

HYDROSILYLATION OF MONOSUBSTITUTED ACETYLENES IN THE PRESENCE OF PLATINUM(II) COMPLEXES

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A systematic investigation of the hydrosilylation reaction of acetylene and its monosubstituted derivatives in the presence of H_2PtCl_6 has permitted us to characterize quantitatively the influence of reactant structure and the nature of the solvent on the direction and rate of this process [1]. To establish the general rules for the reaction mechanisms of homogeneous hydrosilylation of acetylenes we studied the catalytic action on it of complex compounds of Pt(II). The hydrosilylation of olefins, oligomeric vinylalkylsiloxanes, and carbonyl compounds catalyzed by various compounds of Pt(II) has been studied in fair detail in [2, 3]. Recently platinum complexes of a new type $[Pt(SiR_3)(\mu\text{-}H)\text{-}P(R^1)_3]_2$ have begun to be widely used as hydrosilylation catalysts. These effectively catalyze the addition of triorganylsilanes to mono- and diolefins, styrene, vinylcyclohexane and also mono- and disubstituted acetylenes [4-7]. In the last case the yield of hydrosilylation products reacted 70-90% [5].

The stereochemistry and structural directedness of the hydrosilylation of monosubstituted acetylenes $HC{\equiv}CR$ (R = n-Bu, Ph) has been investigated by us. This reaction is catalyzed by complexes of Pt(II) containing neutral (NH_3, C_2H_5N), σ-donor (PPh_3), and π-acceptor (olefins, cycloolefins) ligands, and also acidoligands (Cl, I).

The studied neutral $Pt(C_8H_{12})Cl_2$ (C_8H_{12} is cyclooctadiene) (I), trans-$Pt(PC_6H_5)_2(H)Cl$ (II), trans-$Pt(NH_3)_2I_2$ (III) and cationic complexes $[Pt(NH_3)_2(C_8H_8)Cl]NO_3$ (C_8H_8 styrene) (IV), trans-$[Pt(NH_3)_2C_8H_{14}O_2Cl]NO_3$ ($C_8H_{14}O_2$ is tetramethylbutynediol) (V), $[Pt(NH_3)_2(C_5H_5N)Cl]NO_3$ (VI) proved to be extremely effective catalysts for the hydrosilylation of acetylenes. They provided the formation of the corresponding vinylsilane derivatives in yields up to 99% (according to GLC). The hydrosilylation reaction catalyzed by complexes (I)-(VI) was stereospecific and as in the case of the widely used Speier catalyst led to the formation of products of β-trans addition $R_3'SiCH{=}CHR$. Together with the latter the corresponding α isomers $R_3'SiC({=}CH_2)R$ were formed the amount of which depended to a significant extent on the nature of the ligands on the Pt atom, the character of the substituents on the Si atom, and the structure of the initial 1-alkyne.

The ratio of the isomeric products of hydrosilylation of $HC{\equiv}CR$ by ethyldichloro- and triethylsilane catalyzed by complexes (I)-(VI) and their overall yields are shown in Table 1. The structures of all reaction products were confirmed by IR and PMR spectra [8] and by GLC data (in comparison with standards).

The data of Table 1 indicate that under the studied conditions the catalytic activity of complexes (I)-(VI) in the hydrosilylation of phenylacetylene and 1-hexyne by triethylsilane

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TABLE 1. Influence of the Nature of the Platinum Catalyst on the Ratio and Yield of Products of Hydrosilylation of HC≡CR by Triethyl- and Ethyldichlorosilane $R'_{3-n}X_nSiH$ (catalyst concentration $2 \cdot 10^{-3}$ M, 100°C, 2 h, solvent THF)

Catalyst	R	$R'_{3-n}X_nSiH$	Overall yield of products, %	Content of isomeric adducts in hydrosilyation products, %		β/α
				β	α	
$Pt(C_8H_{12})Cl_2$ (I)	Ph	Et_3SiH	99	82	18	4,5
	Ph	$EtCl_2SiH$	65	67	33	2,0
	n-Bu	Et_3SiH	94	32	68	0,4
trans -$Pt(PC_6H_5)_2(H)Cl$ (II)	Ph	Et_3SiH	65	84	16	5,2
	Ph	$EtCl_2SiH$	65	70	30	2,3
	n-Bu	Et_3SiH	95	44	56	0,8
trans -$Pt(NH_3)_2I_2$ (III)	Ph	$EtCl_2SiH$	60	60	40	1,5
	n-Bu	Et_3SiH	99	29	71	0,4
$[Pt(NH_3)_2(C_8H_8)Cl]NO_3$ (IV)	Ph	Et_3SiH	70	82	18	4,5
	n-Bu	Et_3SiH	81	36	64	0,5
$[Pt(NH_3)_2C_8H_{14}O_2Cl]NO_3$ (V)	Ph	Et_3SiH	82	84	16	5,2
	Ph	$EtCl_2SiH$	65	91	9	10,1
	n-Bu	Et_3SiH	94	33	67	0,5
$[Pt(NH_3)_2(C_5H_5N)Cl]NO_3$ (VI)	Ph	$EtCl_2SiH$	53	40	60	0,7
	n-Bu	Et_3SiH	86	22	78	0,3
$Pt_2Cl_4C[CH_2CMe_3OCHMe_2]_2$ (VII)	*n*-Bu	Et_3SiH	87	13	87	0,2
	t-Bu	Et_3SiH	89	40	60	0,7
$H_2PtCl_6 \cdot 6H_2O$	Ph	Et_3SiH	85	72	28	2,6
	n-Bu	Et_3SiH	80	82	18	4,5
	t-Bu	Et_3SiH	87	90	10	9,0

was on the whole comparable with that of $H_2PtCl_6 \cdot 6H_2O$ and with rhodium complexes RhL_nX (X = Cl, Br, L = Ph_3P, Alk_3P, CO, etc.) [9]. However study of the reaction kinetics of the hydrosilylation of phenylacetylene by triethylsilane catalyzed by complex (I) (Fig. 1) showed that the rate of this process was somewhat greater than on using a freshly prepared solution of Speier catalyst (unreduced form of H_2PtCl_6). Thus for example in the case of complex (I) the yield of hydrosilylation product after 60 min (curve 1) was 76% and on using H_2PtCl_6 only 60% (curve 2). As with catalyst H_2PtCl_6 the curve reflecting the dependence of h_{su}/h_{st} on time (see Fig. 1) has a discontinuity (at a 77% conversion of initial reactants). Later some stabilization of the process was observed and the curve acquired a more regular shape. The observed slowing of the rate of the process may be due to its nonstationary nature (as in the case of H_2PtCl_6) in the initial period (together with the hydrosilylation reaction there is formation of a stable form of the catalyst which carries out the process in its stationary stage). In the initial portion of kinetic curve 1 no significant induction period was observed as also in the case of H_2PtCl_6 catalyst. This distinguishes the hydrosilylation process of acetylenes and alkenes catalyzed by H_2PtCl_6 and by Pt(II) complexes for which the presence of an induction period is characteristic, the duration of which depends to an appreciable extent on the order of mixing the catalyst with reactants and also on the nature of the solvent and the hydrosilylating reagent [10, 11]. The formation of the active catalytic complex therefore occurs much more rapidly in the case of acetylenic compounds.

Complex (V), containing NH_3 as one of the ligands, was less active in the hydrosilylation of phenylacetylene with triethylsilane than complex (I) and H_2PtCl_6 (curve 3 in Fig. 1). Lower catalytic activity was also possessed by complexes having as one of the ligands NH_3 (III), (IV) or NH_3 and C_5H_5N simultaneously (VI). This is in agreement with the inhibiting influence of nitrogen bases on the hydrosilylation reaction in the presence of H_2PtCl_6 in [12].

The overall yield of hydrosilylation products of phenylacetylene by ethyldichlorosilane in the presence of complexes (I)-(VI) proved to be appreciably lower than when using H_2PtCl_6 and rhodium complexes [13]. Thus the growth in reactivity of the hydrosilylating reagent on

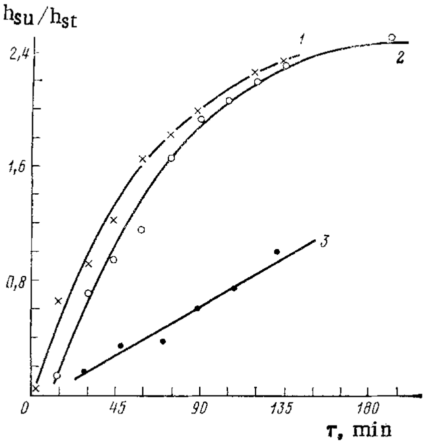

Fig. 1. Kinetic curves for the addition of triethylsilane to phenylacetylene at 60°C in the presence of 1) complex (I); 2) H_2PtCl_6; 3) complex (V). The size of h_{su}/h_{st} is proportional to the concentration of hydrosilylation products (h_{su} is the height of the substance peak, h_{st} is the height of the standard peak).

going from $EtSiHCl_2$ to Et_3SiH which was observed on using complexes (I)-(VI) did not correspond to the activity series established when hydrosilylating olefins and acetylenic compounds catalyzed by H_2PtCl_6 and by Rh (I) complexes in [13].

It follows from the data of Table 1 that the regioselectivity of the studied hydrosilylating reaction depends on the character of the substituents on the Si atom and on the triple bond. The relative content of α adduct mainly grew on going from Et_3SiH to $EtSiHCl_2$ and in the case of complexes (I) and (II) the ratio β:α remained at 2.0 and 2.3 respectively. At the same time on hydrosilylating phenylacetylene with triethylsilane in the presence of complexes (I) and (II) the fraction of α adduct proved to be significantly less (β:α = 4.5 and 5.2 respectively). In hydrosilylating 1-hexyne with triethylsilane in the presence of complexes (I)-(VI) a preferential formation of the α adduct was observed (β:α = 0.4; 0.8; 0.4; 0.5; 0.5; 0.3 respectively) which clearly distinguishes these catalysts from H_2PtCl_6 (β:α = 4.5). Complex (VI) proved to be especially active in relation to this. Complexes (I)-(VI) may be considered as selective catalysts for the hydrosilylation of 1-alkynes directing the process towards preferential formation of the α isomer $R'_3SiC(=CH_2)R$.

Previously when studying the structural directedness of the hydrosilylation of butylacetylene and tertbutylacetylene with triethylsilane catalyzed by H_2PtCl_6 and the alkoxycarbene complex of Pt(II) $Pt_2Cl_4C[CH_2CMe_3OCHMe_2]_2$ (VII) in [14] we established that on using the latter the ratio of isomers (β:α) was always displaced in favor of the α adduct. Thus in the case of H_2PtCl_6 the ratio of β and α adducts was 4.5 and 9.0 respectively, and on using complex (VII) it was 0.2 and 0.7.

The nature of the solvent (MeCN, hexametapol) proved to have no appreciable influence on the catalytic activity of complexes (I)-(VI). The overall yield of products on using these solvents reached 90%. However on hydrosilylating phenylacetylene with triethylsilane in the presence of complexes (I), (II), and (V) in MeCN the proportion of α adduct was increased (β:α = 3.0, 2.3, and 3.0 respectively).

EXPERIMENTAL

The initial phenylacetylene, 1-hexyne, triethylsilane, and ethyldichlorosilane were purified by fractional distillation. Their purity according to GLC data was 99.5%. The synthesis of platinum complexes (I)-(VI) has been described in [15-18].

Reaction mixtures were analyzed on a Tsvet chromatograph with linear programming of temperature from 50-200°C, detector was a catharometer, column was 2 × 3 mm, 5% XE 60 on Inerton AW-HMDS silanized with HMDS. PMR spectra of ≈15% solutions of reaction mixtures in CCl_4 were obtained on a Tesla BS-487C (80 MHz) spectrometer.

Hydrosilylation of Phenylacetylene with Triethylsilane in the Presence of Complex (I). A mixture of phenylacetylene (2.04 g), triethylsilane (2.32 g), and complex (I) (0.006 mole) was heated in a sealed ampul for 2 h at 100°C. It was established by GLC that the hydrosilylation product was a mixture of α and β adducts in a ratio 18:82%. Their overall yield determined by GLC was 99%.

The hydrosilylation of phenylacetylene and 1-hexyne by triethylsilane and ethyldichlorosilane in the presence of complexes (I)-(VI) was effected in a similar manner.

CONCLUSIONS

1. Complexes of Pt(II) are active catalysts in the hydrosilylation reaction of monosubstituted acetylenes HC≡CR with triethylsilane and ethyldichlorosilane. The yield of the resulting adducts was up to 99%.

2. The reaction proceeds stereospecifically and leads to the formation of trans-β-adducts. The regioselectivity of the reaction depends to a significant extent on the character of the substituent on HC≡CR which makes it possible to direct the hydrosilylation in the direction of the preferential formation of one of the structural isomers.

LITERATURE CITED

1. M. G. Voronkov and V. B. Pukhnarevich, Izv. Akad. Nauk SSSR, Ser. Khim., 1056 (1982).
2. E. Lukevics and M. G. Voronkov, Organic Insertion Reactions of Group IVB Elements, Plenum Press, New York (1966).
3. E. Lukevics, Z. V. Belyakova, M. G. Pomerantseva, and M. G. Voronkov, J. Organometall. Chem. Library, 5, 1 (1977).
4. M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, J. Chem. Soc. Dalton Trans., 1519 (1977).
5. M. Green, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, J. Chem. Soc. Dalton Trans., 1525 (1977).
6. C. A. Tsipis, J. Organomet. Chem., 187, 427 (1980); 188, 53 (1980).
7. A. P. Barlow, M. Boag, and F. G. A. Stone, J. Organomet. Chem., 191, 39 (1980).
8. V. B. Pukhnarevich, S. P. Sushchinskaya, V. A. Pestunovich, and M. G. Voronikov, Zh. Obshch. Khim., 43, 1283 (1973).
9. V. B. Pukhnarevich, L. I. Kopylova, E. O. Tsetlina, V. A. Pestunovich, V. Khvalovskii, I. Getfleish, and M. G. Voronkov, Dokl. Akad. Nauk. SSSR, 231, 1366 (1976).
10. V. O. Reikhsfel'd and M. I. Astrakhanov, Zh. Obshch. Khim., 47, 1493 (1977).
11. V. O. Reikhsfel'd and M. I. Astrakhanov, Zh. Obshch. Khim., 47, 1497 (1977).
12. V. B. Pukharevich, L. I. Kopylova, B. A. Trofimov, and M. G. Voronkov, Zh. Obshch. Khim., 45, 2638 (1975).
13. V. B. Pukhnarevich, L. I. Kopylova, M. Chapka, I. Getfleish, É. N. Satsuk, M. V. Sigalov, V. Khvalovskii, and M. G. Voronkov, Zh. Obshch. Khim., 50, 1554 (1980).
14. M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, L. I. Kopylova, and B. A. Trofimov, Zh. Obshch. Khim., 42, 2687 (1972).
15. J. Chatt and B. L. Shaw, J. Chem. Soc., 5075 (1962).
16. M. I. Gel'fman, Dokl. Akad. Nauk SSSR, 167, 819 (1966).
17. M. I. Gel'fman, N. K. Pukhova, and V. V. Razumovskii, Zh. Obshch. Khim., 41, 892 (1971).
18. M. I. Gel'fman, N. M. Karpinskaya, and V. V. Razumovskii, Zh. Neorg. Khim., 15, 2766 (1970).