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Hydrogermylation of phenylacetylene catalyzed by onium chlorometallates

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Triethylbenzylammonium chlorometallates $[Et_3NCH_2Ph]_m^+[MCl_n]^{m-}$ (M = Pt, Pd, Rh, Ir, Fe, Co, Cu, $m = 1$–3, $n = 3$–6), polymer-anchored ionic metal complexes $[Ⓟ\text{—}CH_2PBu_3]_m^+[MCl_n]^{n-}$ and some other chlorometallates and complexes of platinum, rhodium, ruthenium and osmium were studied as catalysts in the hydrogermylation of phenylacetylene with triethylgermane. All the complexes containing platinum, palladium and rhodium were found to be effective catalysts. The *cis/trans* ratio of the products obtained is determined by the metal atom involved and decreases in the following order: Ir > Rh ≫ Pd > Pt.

Keywords: Hydrogermylation, quaternary onium chlorometallates, polymer-bound metal catalysts.

INTRODUCTION

The catalysts commonly used for the hydrogermylation of alkynes are mainly limited to the platinum and rhodium groups.[1,2] At the same time, the analogous hydrosilylation reaction can be promoted by a variety of catalysts.[3] Recently, homogeneous platinum, rhodium, iridium, copper, zinc and iron, and anchored platinum, rhodium and osmium, complexes were found to be active in this reaction.[4] The purpose of the present work was to investigate the catalytic activity of these quaternary onium chlorometallates in the hydrogermylation reaction and to study the influence of the metal on the regio- and stereo-selectivity of the addition of triethylgermane to phenylacetylene. Hexachloroplatinic acid and several rhodium, ruthenium and osmium complexes have been studied for comparison.

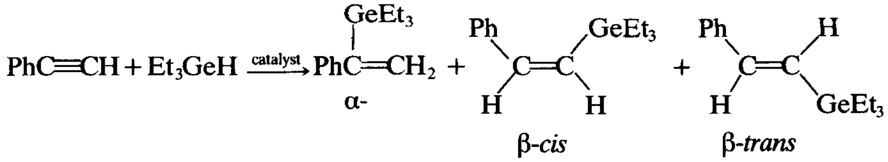
EXPERIMENTAL

^{1}H NMR spectra of the compounds synthesized were obtained on a Bruker WH-90/DS spectrometer (90 MHz). Tetramethylsilane was used as internal standard. Mass spectra were recorded on a Kratos MS-25 GC MS apparatus (70 eV). Chromatographic analysis of the mixtures was performed using a Varian instrument (model 3700, $\phi = 3$ mm) packed with 5% OV-17 on Chromosorb W-HP and on a Bruker LC 42 apparatus with a UV-detector ($\lambda = 254$ nm), with a Silasorb 600 column (4.0 mm × 250 mm) and a mobile phase of 100% hexane.

Hydrogermylation of phenylacetylene (general procedure)

Phenylacetylene (0.75 mmol), triethylgermane (0.50 mmol), tetrahydrofuran (1.7 cm^3) and 0.2 mol % of the corresponding catalyst were placed in a 5 cm^3 'reacti-vial' (Pierce) and stirred during the reaction time, the reaction course being studied by GC. The reaction time, temperature and the ratio of the compounds obtained are summarized in Tables 1 and 2.

^{1}H NMR data and mass spectra are presented in Table 3.



Scheme 1

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RESULTS AND DISCUSSION

Triethylgermane interacts with phenylacetylene in tetrahydrofuran in the presence of Speier's catalyst (hexachloroplatinic acid, $H_2PtCl_6{\cdot}6H_2O$, dissolved in 2-propanol) at 20 °C to afford a mixture of three isomers (Table 1 and Scheme 1).

The β-*trans* isomer is the main product of the reaction at temperatures up to 50 °C.

A polymer-supported hexachloroplatinate $[\text{Ⓟ}{-}CH_2PBu_3]_2[PtCl_6]$ catalyst (derived from

Table 1 Hydrogermylation of phenylacetylene with triethylgermane in tetrahydrofuran in the presence of various catalysts

Catalyst	Temperature (°C)	Reaction time (h)	Products ratio (%)			Conversion (%)
			α-	β-*cis*	β-*trans*	
None	50	140	8.1	58.0	33.9	<1
Ultrasound (50 KHz, 100 W)	30	40	3.5	70.0	26.5	3.5
H_2PtCl_6	20	19	11.0	6.6	82.4	100
		24	18.0	11.3	70.7	100
		39	10.5	6.4	83.1	100
	50	2	22.0	3.0	75.0	95
		15	10.3	1.4	88.3	100
$[\text{Ⓟ}{-}CH_2PBu_3]_2[PtCl_6]$	20	22	11.0	4.5	84.5	100
$[Et_3NBz]_2[PtCl_6]$	20	22	11.9	41.6	46.5	37
		30	10.2	42.2	47.6	86
		46	12.9	37.0	50.1	90
		70	12.2	28.25	59.55	98
		93	5.6	12.9	81.5	99
$[Ph_4As]_2[PtCl_6]$	20	96	10.6	51.0	38.3	1.5
	50	17	12.6	2.4	85.0	100
$[\text{Ⓟ}{-}CH_2PBu_3](RhCl_4)$	20	15	7.45	70.1	22.45	25
		40	6.2	73.6	20.2	40
		65	2.1	89.8	8.1	80
		17	6.4	80.15	13.45	90
	50	24	21.25	57.05	30.7	95
		39	11.8	58.1	30.1	100
$[Et_3NBz][RhCl_4]$	20	96	5.4	84.5	10.1	80
		144	5.8	81.4	12.7	100
	50	17	25.4	36.7	37.9	83
		65	12.2	36.6	51.2	99
		140	16.0	21.4	62.6	100
$(CO)Cl(Ph_3P)_2Rh$	20	17	6.4	81.3	12.3	90
		40	9.2	62.5	28.3	100
$(CO)H(Ph_3P)_3Rh$	20	17	6.05	82.15	11.8	100
	50	1	15.9	55.55	28.55	23
		2	6.4	82.1	11.5	61
		4.5	15.1	56.9	26.0	89
		24	6.0	83.4	10.6	100
$Cl(Ph_3P)_3Rh$	20	17	5.9	56.2	37.9	100
	50	1	7.0	77.7	15.3	62
		2	6.7	78.6	14.7	71
		4.5	10.4	54.0	35.6	99
		24	7.45	77.0	15.55	100
$Cl_2(Ph_3P)_3Ru$	20	17	5.2	76.3	18.5	<1
		40	5.9	74.1	20.0	<1
		65	5.6	73.8	20.6	<1
		114	5.8	71.4	22.8	<1
		180	4.6	72.1	23.3	<1
	50	24	5.3	71.1	23.6	95
		45	4.3	63.6	31.1	98
		72	5.3	60.5	32.2	100
		118	4.4	56.4	39.2	100
		140	3.7	61.6	34.7	100

Table 1 (*continued*)

Catalyst	Temperature (°C)	Reaction time (h)	Products ratio (%) α-	β-*cis*	β-*trans*	Conversion (%)
$(CO)_2Cl_2(Ph_3P)_2Ru$	20	17	—	80.5	19.5	<1
		40	—	93.7	6.3	<1
		65	—	93.7	6.3	<1
		114	—	75.2	24.8	<1
		180	3.35	66.65	30.0	<1
	50	24	5.7	75.1	19.2	<1
		45	5.65	74.0	20.35	1.2
		72	2.9	69.9	27.2	1.9
		118	6.15	65.25	28.6	2.7
		140	5.3	75.8	18.9	3.3
$[Et_3NBz]_2[PdCl_4]$	20	15	5.0	40.8	54.2	56
		40	3.0	45.3	51.7	95
		65	1.0	51.2	47.8	98
$(NH_4)_2[OsCl_6]$	20	17	—	87.1	12.9	<1
		40	—	82.6	17.4	<1
		65	—	80.7	19.3	<1
		114	—	80.8	19.2	<1
		180	4.6	67.5	30.0	<1
	50	24	—	87.2	12.8	<1
		45	5.9	70.65	23.45	<1
		72	10.15	59.2	30.65	<1
		118	12.05	46.0	41.95	<1
		140	13.25	44.95	41.8	<1
$[Et_3NBz]_3[IrCl_6]$	20	96	3.1	83.6	13.3	<1
		144	2.9	83.1	14.0	1
	50	24	6.5	84.4	9.4	2.6
		65	5.7	69.5	24.8	6.7
		140	—	76.2	23.8	9.1
$[Et_3NBz]_2[FeCl_4]$	50	96	4.9	73.8	21.3	1
$[Et_3NBz]_2[CoCl_4]$	20	144	2.9	78.7	18.4	<1
		24	7.7.	71.8	20.5	<1
	50	65	7.3	72.2	20.5	1.5
		140	7.6	75.8	16.6	2.5
$[Et_3NBz]_2[CuCl_4]$	50	96	15.4	55.0	29.6	<1
[Ⓟ—CH_2PBu_3][$CuCl_3$]	50	96	10.6	51.0	38.3	<1

polymer-bound tributylmethylphosphonium chloride, Fluka 90808) has comparable catalytic activity in this reaction (Table 1). The other catalysts containing platinum appeared to be less active. Thus, in the presence of triethylbenzylammonium hexachloroplatinate ($[Et_3NBz]_2[PtCl_6]$) the reaction becomes considerably slower, and for complete conversion of triethylgermane, 93 h of stirring at 20 °C was required. In the case of $[Ph_4As]_2[PtCl_6]$ used as a catalyst, the reaction takes place only at 50 °C. It is noteworthy that all the platinum-containing catalysts studied enable the formation of a mixture of three isomers, with β-*trans* being the major product (75–85 %).

Rhodium complexes [$(CO)Cl(Ph_3P)_2Rh$, $(CO)H(Ph_3P)_3Rh$, $Cl(Ph_3P)_3Rh$] are comparable in terms of their reaction rate with the polymer-supported platinum catalyst ([Ⓟ—$CH_2PBu_3]_2[PtCl_6]$), but the β-*cis* isomer is the main product of the reaction. The latter isomer dominated when triethylbenzylammonium tetrachlororhodate ($[Et_3NBz][RhCl_4]$) was used as a catalyst. However, during prolonged heating (50 °C, 140 h) the β-*trans* isomer becomes the main product (Table 1).

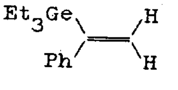
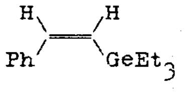
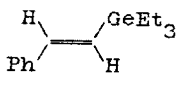
Ruthenium-containing catalysts [$Cl_2(Ph_3P)_3Ru$ and $(CO)_2Cl_2(Ph_3P)_2Ru$] appeared to be inactive during hydrogermylation of phenylacetylene with triethylgermanes at 20 °C. In the case of

Table 2 Hydrogermylation of phenylacetylene with triethylgermane in various solvents

Catalyst	Solvent	Temperature (°C)	Time (h)	Products ratio (%) α-	β-*cis*	β-*trans*	Conversion (%)
H_2PtCl_6	$C_2H_4Cl_2$	20	1.5	32.0	14.0	54.0	90
			24	28.8	9.6	61.6	100
	$CHCl_3$	20	18	42.0	3.6	54.4	82
			24	43.3	3.9	52.8	88
			48	40.2	4.1	55.7	100
	$CHCl_3$	50	17	52.7	—	47.3	95
			24	53.8	—	46.2	100
			39	54.8	—	45.2	100
	THF	20	2	22.0	3.0	75.0	95
			15	10.3	1.4	88.3	100
	THF	50	19	11.0	6.6	82.4	100
			24	18.0	11.3	70.7	100
			39	10.5	6.4	83.1	100
	$C_6H_5CH_3$	20	1	25.2	6.7	68.1	36
			24	21.4	10.8	67.8	84
			48	13.1	3.9	83.0	93
	C_6H_{14}	20	1	19.25	3.5	77.25	53
			24	9.5	1.0	89.5	99
[Ⓟ—CH_2PBu_3][$RhCl_4$]	$C_2H_4Cl_2$	20	1.5	6.8	19.3	73.9	50
			24	5.1	25.7	69.2	100
	$C_2H_4Cl_2$	50	3.5	4.3	14.3	81.4	90
	THF	20	15	7.45	70.1	22.45	25
			40	6.2	73.6	20.2	40
			65	2.1	89.8	8.1	80
	THF	50	17	6.4	80.15	13.45	90
			24	21.25	57.05	30.7	95
			39	11.8	58.1	30.1	100

tris(triphenylphosphine)ruthenium dichloride, raising the reaction temperature to 50 °C leads after 72 h to the complete conversion of triethylgermane to give β-*cis* and β-*trans* isomers as the main reaction products. Prolonged heating (140 h) of the reactive mixture does not affect much the ratio of isomers formed. Quaternary onium halometallates of iron, iridium, cobalt and copper, as well as ammonium hexachloro-osmate, were not effective in the hydrogermylation of

Table 3 NMR data and mass spectra

	^{1}H NMR σ (ppm)	*J* (Hz)	Mass spectra *m*/*z* (intensity, % from max.)
	5.42 5.87	3	235 (M^+ − Et, 100), 207(60), 179(63), 151(52), 133(29), 103(65), 77(35)
	5.91 7.43	14	235 (M^+ − Et, 100), 207(38), 177(35), 151(49), 133(15), 103(38), 77(19)
	6.55 6.89	18	235 (M^+ − Et,100), 207(45), 177(32), 151(48), 133(20), 103(40), 77(20)

phenylacetylene with triethylgermane in tetrahydrofuran at 20–50 °C (Table 1).

Thus the catalytic activity of onium metallates depends on the metal used; from their rates, the metals studied can be arranged in the order Pt > Pd > Rh ≫ Ir, and from the *cis/trans* ratio in the order Ir > Rh ≫ Pd > Pt, whilst the α/β ratio is less influenced by the metal involved.

We have treated several solvents in order to elucidate solvent influence on the rate and direction of hydrogermylation of phenylacetylene with triethylgermane in the presence of hexachloroplatinic acid (Table 2). It has been found that the solvent affects not only the regio- and stereospecificity of the reaction but also considerably changes its rate. Thus, in dichloroethane and tetrahydrofuran the reaction proceeds in 1.5–2 h, whilst in the non-polar solvents (hexane, toluene) complete conversion of triethylgermane is observed only after 24–48 h. The direction of hydrogermylation significantly depends on the nature of the solvent at higher temperature (50 °C). Thus, in chloroform a mixture of α- and β-*trans* isomers (β-*cis* isomer being absent) is formed, whilst in tetrahydrofuran a mixture of three isomers is obtained (the β-*trans* product prevailing) (Table 2).

The application of the rhodium catalyst ([Ⓟ—CH_2PBu_3][$RhCl_4$]) to the hydrogermylation reaction obviously demonstrates the effect of solvent on reaction stereospecificity: the β-*cis* isomer is the major product in tetrahydrofuran, while in dichloroethane the β-*trans* isomer prevails.

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