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Quaternary onium chlorometallates as hydrosilylation catalysts

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Sixteen triethylbenzylammonium chlorometallates $[Et_3NCH_2Ph]^+_m[MCl_n]^{m-}$ (M = transition metal, m = 1–3, n = 3–6) and nine anchored ionic metal complexes $[Ⓟ\text{–}CH_2PBu_3]^+_m[MCl_n]^{m-}$ derived from 'polymer-bound tributylmethylphosphonium chloride' have been prepared. All the complexes were studied as catalysts in the hydrosilylation of phenylacetylene with triethylsilane. The homogeneous Rh^{III}, Pt^{IV}, Ir^{III}, Cu^{II}, Zn^{II}, Fe^{III} and anchored Pt^{IV}, Rh^{III}, Os^{IV} complexes were found to be active in this reaction. The regio- and stereoselectivity of the following catalyst types is determined by the metal atom involved, being a weak function of the chemical environment; neutral chloride (MCl_{n-m}); acid (H_2MCl_6); salt containing the lipophilic organic cation ($[Et_3NCH_2Ph]^+_m[MCl_n]^{m-}$); polymer-supported metallate anion ($[Ⓟ\text{–}CH_2PBu_3]^+_m[MCl_n]^{m-}$).

Keywords: Hydrosilylation, quaternary onium chlorometallates, polymer-bound metal catalysts

INTRODUCTION

The catalysts commonly used for hydrosilylation of alkenes and alkynes are mainly limited to the platinum and rhodium complexes. The compounds containing Pd, Os, Ni, Fe are applied more rarely, most in the form of poorly accessible and sometimes unstable complexes.[1–4] Until recently there had been no systematic studies of how the metal affects the activity of complexes used for hydrosilylation. The purpose of the present work was to find new hydrosilylation catalysts containing metal complexes, to study the role of the metal in the activity of several transition metal (non-noble metals included) complexes closely related both structurally and compositionally.

EXPERIMENTAL

^1H NMR spectra were obtained on a Bruker WH-90/DS spectrometer (90 MHz). Tetramethylsilane was used as internal standard. Mass spectra were registered on a Kratos MS-25 GC MS apparatus (70 eV). GC analysis was performed using a Chrom-4 instrument equipped with a flame-ionization detector, glass column (1.2 m × 3 mm) packed with 5% OV-17 on Chromosorb W-HP (60–80 mesh). Helium was used as carrier gas (60 $cm^3\,min^{-1}$). Analyses were run at 150°C. Thermogravimetric analysis was carried out on an OD-102 instrument (MOM, Hungary). The yields of hydrosilylation products were determined using absolute calibration. The starting metal chlorides (except for $IrCl_3$), $H_2PtCl_6 . 6H_2O$ and $H_2OsCl_6 . 6H_2O$ were of the *purum* or *puriss* grade (Reakhim). $IrCl_3$, K_2PdCl_4, K_3RhCl_6, triethylbenzylammonium chloride, 'polymer-bound tributylmethylphosphonium chloride' (0.78 mmol $Cl\,g^{-1}$), and Et_3SiH were purchased from Fluka. Phenylacetylene was distilled *in vacuo* before use.

Synthesis of triethylbenzylammonium chlorometallates (Table 1) and polymer-bound ionic complexes (Table 4)

Method A

Metal chloride ($MnCl_2 . 4H_2O$, $FeCl_2$, $FeCl_3 . 6H_2O$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $RhCl_3 . 4H_2O$, $PdCl_2$, $InCl_3$, $SnCl_4$, $SbCl_3$, $SbCl_5$, $IrCl_3$; 0.5 mmol) was dissolved in a minimum amount of absolute ethanol (20–200 cm^3) at 20–60°C. To this solution a stoichiometric amount (0.5–1.5 mmol) of triethylbenzylammonium chloride dissolved in 20 cm^3 of absolute ethanol was added. The mixture was stirred for 0.5 h, evaporated if necessary, followed by addition of

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diethyl ether to achieve precipitation of a crystalline solid. The precipitate was recrystallized from water. During the preparation of the palladium complex **9** an ethanolic solution of $PdCl_2$ was acidified to prevent $PdCl_2$ reduction to metallic palladium.

Method B

A coloured aqueous solution of potassium metallate (K_2PdCl_4 or K_2PtCl_6; 0.25 mmol) was added to a colourless solution of $Et_3N^+CH_2Ph\ Cl^-$ (0.5 mmol) in dichloromethane (100 cm^3). The resulting mixture was stirred for 5 h at room temperature. In the meanwhile the organic layer became coloured and the aqueous layer became decolourized. The organic layer was separated, dried ($MgSO_4$) and evaporated to give the corresponding product.

Method C

A solution of acid ($H_2PtCl_6.6H_2O$ or $H_2OsCl_6.6H_2O$; 0.25 mmol) in water (15 cm^3) was added to a solution of $Et_3N^+CH_2Ph\ Cl$ (0.5 mmol) in ethanol (50 cm^3). The mixture was stirred for 1 h at 80°C, cooled to room temperature and evaporated to 30 cm^3. The addition of acetone to the residue gave a crystalline solid. It was subsequently washed with cold water and recrystallized from water.

Method D

A solution of metal chloride [$MnCl_2.4H_2O$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ (0.2 mmol) or $FeCl_3.6H_2O$, $RhCl_3.4H_2O$ (0.4 mmol)] in absolute ethanol (40 cm^3) was added to 0.5 g (0.39 mmol Cl) of polymer-bound tributylmethylphosphonium chloride (Ⓟ-$CH_2P^+Bu_3\ Cl^-$, 0.78 mmol Cl g^{-1}, Fluka) that was allowed to swell in dichloromethane (40 cm^3). The mixture was stirred for 5 h at room temperature. The solution became colourless and the polymer acquired the corresponding colour (Table 4). The polymer was filtered off, washed with CH_2Cl_2, EtOH, H_2O, acetone, ether and dried; thereby the colour and the weight remained unaltered.

Method E

$H_2OsCl_6.6H_2O$ or K_2PtCl_6 (0.2 mmol) dissolved in water (40 cm^3) was added to 0.5 g (0.39 mmol Cl) of 'polymer-bound tributylmethylphosphonium chloride' (0.78 mmol g^{-1} Cl) that was allowed to swell in dichloromethane (40 cm^3). The mixture was stirred for 5 h until decolourization of the aqueous layer was attained. The coloured polymer was filtered off, washed with CH_2Cl_2, ethanol, water, acetone, ether and dried.

Hydrosilylation of phenylacetylene with triethylsilane in the presence of soluble and polymer-bound quaternary phosphonium chlorometallates (general procedure)

A mixture of triethylsilane (1 mmol), catalyst (0.001 mmol) and phenylacetylene (1 mmol) placed in a 5 cm^3 'reacti-vial' (Pierce) was stirred at 80°C, the reaction course being controlled by GC and GC MS analysis (see Tables 3 and 4). After termination of the reactions the ^1H NMR spectra of products were registrated to assign them and to determine the ratio of the resulting compounds. The products of the hydrosilylation reaction [1] were identified using mass and ^1H NMR spectra; the ^1H NMR spectroscopic parameters were coincident with the appropriate literature data.$^{5-7}$ The complete spectrum of β-*cis*-(triethylsilyl)styrene (**Z**), $PhCH_B{=}CH_ASiEt_3$, is not known from the literature, except for the value of $^3J(H_A, H_B)$ (15 Hz) given in ref. 7. The ^1H NMR spectra of the reaction mixture registered here are sufficient to describe the spectrum of (**Z**), $PhCH_B{=}CH_ASiEt_3$ ($CDCl_3$/TMS): δ (ppm) 0.4–1.1 (m, 15H, $SiEt_3$), 6.71 (d, 1H, $J = 15$ Hz, H_A), 7.11–7.44 (m, 5H, Ph), 7.38 (d, 1H, $J = 15$ Hz, H_B). The assignment of vinyl protons in this compound was carried out as in ref. 8 where the spectrum of (**2**) $PhCH_B{=}CH_ASiPh_3$, had been described and interpreted.

RESULTS AND DISCUSSION

Speier's catalyst (hexachloroplatinic acid, $H_2PtCl_6.5H_2O$, dissolved in 2-propanol) is one of the most active hydrosilylation catalysts affecting the C=C and C≡C bonds, the active species being the hexachloroplatinic anion $(PtCl_6)^{2-}$.$^{2-4}$ Our objective was to prepare and study hydrosilylation activity of a number of structurally related ionic complexes of the type $[R_4N)_m^+[MCl_n)^{m-}$ differing as to the nature of valence of the metal atom. (For general information on hydrosilylation mechanisms see References 1–4) The triethylbenzylammonium ion

Table 1 Synthesis of triethylbenzylammonium chlorometallates

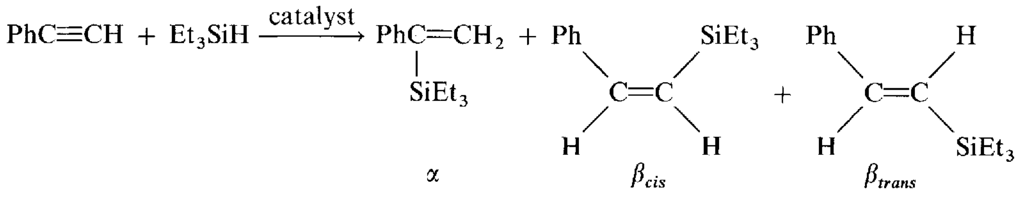
		Analytical data (%) (found/calculated)			Method of preparation[a]	
Complex	Colour	N	C	H		Starting metal compound
1 $[Et_3NCH_2Ph]_2[MnCl_4]$	White	4.64/4.82	53.56/53.70	7.67/7.57	A	$MnCl_2.4H_2O$
2 $[Et_3NCH_2Ph][FeCl_3]$	Brown	3.77/3.95	44.00/44.00	6.41/6.20	A	$FeCl_2$
3 $[Et_3NCH_2Ph][FeCl_4]$	Yellow	3.42/3.59	40.65/40.00	5.76/5.64	A	$FeCl_3.6H_2O$
4 $[Et_3NCH_2Ph]_2[CoCl_4]$	Blue	4.66/4.78	52.86/53.30	7.71/7.52	A	$CoCl_2$
5 $[Et_3NCH_2Ph]_2[NiCl_4].H_2O$	Blue	4.94/4.64	52.22/51.72	7.98/7.63	A	$NiCl_2.6H_2O$
6 $[Et_3NCH_2Ph]_2[CuCl_4]$	Bright orange	4.61/4.75	53.05/52.93	7.83/7.46	A	$CuCl_2$
7 $[Et_3NCH_2Ph]_2[ZnCl_4]$	White	4.62/4.74	52.72/52.79	7.26/7.44	A	$ZnCl_2$
8 $[Et_3NCH_2Ph][RhCl_4]$	Dark purple	3.16/3.20	34.75/35.69	5.12/5.03	A	$RhCl_3.4H_2O$
9 $[Et_3NCH_2Ph]_2[PdCl_4]$	Brick-brown	4.12/4.43	49.14/49.37	6.66/6.96	A,B	$PdCl_2$, K_2PdCl_4
10 $[Et_3NCH_2Ph]_2[InCl_5]$	White	3.88/4.13	46.11/46.08	6.50/6.50	A	$InCl_3$
11 $[Et_3NCH_2Ph]_2[SnCl_6]$	White	3.77/3.91	43.74/43.57	6.23/6.14	A	$SnCl_4$
12 $[Et_3NCH_2Ph]_2[SbCl_5]$	White	4.15/4.10	45.80/45.64	6.43/6.44	A	$SbCl_3$
13 $[Et_3NCH_2Ph][SbCl_6]$	White	2.77/2.66	29.80/29.61	4.08/4.18	A	$SbCl_5$
14 $[Et_3NCH_2Ph]_2[OsCl_6]$	Black	3.38/3.55	39.98/39.62	5.54/5.59	C	$H_2OsCl_6.6H_2O$
15 $[Et_3NCH_2Ph]_3[IrCl_6]$	Olive-coloured	4.11/4.28	47.63/47.66	6.59/6.72	A	$IrCl_3$
16 $[Et_3NCH_2Ph]_2[PtCl_6]$	Pale Orange	3.44/3.54	39.26/39.41	5.66/5.56	B,C	K_2PtCl_6, $H_2PtCl_6.6H_2O$

[a] See Experimental.

was chosen as a cation because of its easy availability (in the form of $Et_3N^+CH_2PhCl^-$). Moreover, this cation is known to solubilize various anions in non-polar organic media,[9–11] an important feature of homogeneous catalysts. There are numerous reports in the literature describing the synthesis of transition metal halometallates usually with symmetric organic cations (R_4Z^+, where R = Me, Et, Bu, Ph; Z = N, P, As). In this study complexes of the $[Et_3NCH_2Ph]_m^+[MCl_n]^{m-}$ type were synthesized using procedures similar to those described for halometallates with other quaternary onium ions.[12–16] For the most part, metal chlorides as well as potassium chlorometallates or the corresponding acids were used as the starting metal-containing compounds (Table 1). Analytical data for the complexes **1–16** support the given composition (Table 1). The thermogravimetric analysis performed for samples **2**, **5** and **8** shows the presence of crystallization water in the metallate **5** and its absence in samples **2** and **8**. It should be noted that Pd^{II} and Pt^{IV} complexes were each prepared by two different methods. $[Et_3NCH_2Ph]_2[PdCl_4]$ was obtained from $PdCl_2$ and K_2PdCl_4; $[Et_3NCH_2Ph]_2[PtCl_6]$ was synthesized from K_2PtCl_6 and $H_2PtCl_6.6H_2O$. Irrespective of the preparation method used, identical samples of the corresponding triethylbenzylammonium chlorometallates were obtained.

The ^1H NMR spectra of the chlorometallates **1**–**16** (Table 2) in most cases slightly differ from those of the starting $Et_3N^+CH_2Ph\ Cl^-$ except for the spectra of Mn^{II+}, Fe^{II+}, Fe^{III+}, Co^{II+}, Ni^{II+}, Cu^{II+} in which a strong broadening and sometimes a shift of signals is observed owing to the interaction of the cation protons with paramagnetic halometallate anions.[17,18]

The catalytic properties of quaternary ammonium chlorometallates **1**–**16** as hydrosilylation catalysts were assessed in the reaction of phenylacetylene with triethylsilane. This reaction permits a demonstration of the activity, regio- and stereo-selectivity of the catalysts because of the possibility of gaining two regioisomers, namely the α- and β-addition products, the formation of the *cis*- and *trans*-stereoisomers being possible in the last case (reaction [1]).



[1]

Table 2 ^1H NMR spectroscopy data for triethylbenzylammonium chlorometallates

Compound	Solvent	δ (ppm) $C\underline{H}_3CH_2$, t, $J=7$ Hz	$CH_3C\underline{H}_2N$, q, $J=7$ Hz	$PhC\underline{H}_2N$, s	Ph, s
$[Et_3NCH_2Ph]_2[MnCl_4]$	$CDCl_3$, DMSO/d_6		Very broad bands		
$[Et_3NCH_2Ph][FeCl_3]$	DMSO-d_6	1.32 (bs)	3.20 (bs)	4.47 (b)	7.49 (b)
$[Et_3NCH_2Ph][FeCl_4]$	DMSO-d_6	1.32 (bs)	3.13 (bs)	4.35 (b)	7.40 (b)
$[Et_3NCH_2Ph]_2[CoCl_4]$	DMSO-d_6	1.31 (b, distorted)	3.15 (b, distorted)	4.45	7.51 (b, distorted)
$[Et_3NCH_2Ph]_2[NiCl_4].H_2O$	$CDCl_3$	2.24 (bs)	4.02 (bs)	5.29 (b)	7.4–8.2 (m)
$[Et_3NCH_2Ph]_2[CuCl_4]$	DMSO-d_6	1.32 (distorted)	3.20 (distorted)	4.49	7.52
$[Et_3NCH_2Ph]_2[ZnCl_4]$	DMSO-d_6/$CDCl_3$	1.47	3.38	4.67	7.47
$[Et_3NCH_2Ph][RhCl_4]$	DMSO-d_6	1.33	3.18	4.49	7.53
$[Et_3NCH_2Ph]_2[PdCl_4]$	DMSO-d_6	1.31	3.15	4.44	7.49
$[Et_3NCH_2Ph]_2[InCl_5]$	DMSO-d_6/$CDCl_3$	1.47	3.38	4.67	7.47
$[Et_3NCH_2Ph]_2[SnCl_6]$	DMSO-d_6	1.31	3.18	4.49	7.51
$[Et_3NCH_2Ph]_2[SbCl_5]$	DMSO-d_6	1.31	3.19	4.52	7.52
$[Et_3NCH_2Ph][SbCl_6]$	DMSO-d_6	1.31	3.17	4.47	7.52
$[Et_3NCH_2Ph]_2[OsCl_6]$	DMSO-d_6	1.33	3.18	4.49	7.53
$[Et_3NCH_2Ph]_3[IrCl_6]$	DMSO-d_6	1.29	3.17	4.49	7.50
$[Et_3NCH_2Ph]_2[PtCl_6]$	DMSO-d_6	1.30	3.16	4.46	7.49
$[Et_3NCH_2Ph]Cl$	DMSO-d_6	1.31	3.18	4.51	7.53

Table 3 presents the results of studying reaction [1] ($PhC\equiv CH:Et_3SiH=1:1$) at 80°C in the presence of complexes **1**–**16** and (for comparison) some other metal compounds (chlorides, potassium chlorometallates, acids). The activity and selectivity of catalysts strongly depends on the metal involved. All three possible products of reaction [1] were detected as confirmed by GC, GC MS and ^1H NMR data.

GC MS analysis revealed three chromatographic bands in the mass spectra corresponding to molecular ion peaks with m/z 218. ^1H NMR spectra of the mixtures of hydrosilylation products also indicated the presence of three isomers. The α- and β-adducts were identified by the coincidence of their spectral parameters with those given in the literature.[5–7]

The Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Pd^{II}, In^{III}, Sb^{III}, Sb^{V} complexes demonstrate only insignificant hydrosilylation activity under given conditions. A somewhat higher activity is observed for the tin(IV) and osmium(IV) complexes although the

Table 3 Hydrosilylation of phenylacetylene with triethylsilane (1:1) in the presence of various catalysts (0.1 mol%) at 80°C

Catalyst	Products (isomers)	Products yield (%) (GC data) Reaction time (h) 1	2	3	4	5	6	7
$[Et_3NCH_2Ph]_2[MnCl_4]$	α	0	—	0.3	—	1	—	2
	β_t			1		2		4
$[Et_3NCH_2Ph][FeCl_3]$	α	0	-	0	—	0	—	0.3
	β_t			1		2		2
$[Et_3NCH_2Ph][FeCl_4]$	α	0	1	1.5	—	4	—	34
	β_t		1	2		8		29
$FeCl_3.6H_2O$	α	0.5	1	2	—	4	14	22
	β_c	1	1	1		2	4	7
	β_t	1.5	2.5	3.5		9	18	25

Table 3 (Continued)

Catalyst	Products (isomers)	Products yield (%) (GC data)						
		Reaction time (h)						
		1	2	3	4	5	6	7
$[Et_3NCH_2Ph]_2[CoCl_4]$	α	0	—	0.4	—	1.5	—	3
	β_t			1		2		4
$[Et_3NCH_2Ph]_2[NiCl_4].H_2O$	α	0	—	0.3	—	0.6	—	2
	β_t			0.6		1		2
$[Et_3NCH_2Ph]_2[CuCl_4]$	α	0	2	3	—	17	—	56
	β_t		1	2		9		37
$CuCl_2$	α	0	—	4	7	10	18	25
	β_t			4	7	10	17	23
$[Et_3NCH_2Ph]_2[ZnCl_4]$	α	0	4	8	—	52	55	55
	β_t		3	5		30	33	33
$ZnCl_2$	α	0	—	0	—	0	—	1
	β_t			1		1.5		2
$[Et_3NCH_2Ph][RhCl_4]$	α	13	23					
	β_c	15	29					
	β_t	30	48					
K_3RhCl_6	β_t	0	—	0	—	1	—	1
$RhCl_3.4H_2O$	α	10	18	16	17	16	16	15
	β_c	15	29	31	27	14	14	14
	β_t	27	35	35	42	46	47	51
$[Et_3NCH_2Ph]_2[PdCl_4]$	α	0	—	0.5	—	1	—	1
	β_c			1		1		1
	β_t			3		4		5
$[Et_3NCH_2Ph]_2[InCl_5]$	α	0	—	0.5	—	1	—	33
	β_t			1.5		2		4
$[Et_3NCH_2Ph]_2[SnCl_6]$	β_c	0	—	0.5	—	3	—	8
	β_t	1		2		5		10
$[Et_3NCH_2Ph]_2[SbCl_5]$	α	0	—	0	—	0.5	—	1
	β_c					0.7		2
	β_t					2.6		5
$[Et_3NCH_2Ph][SbCl_6]$	β_t	0	—	0	—	1	—	2
$[Et_3NCH_2Ph]_2[OsCl_6]$	β_c	0	1	1	1	2	—	3
	β_t		3	5	7	8		12
$H_2OsCl_6.6H_2O$	β_c	4	7	10	—	12	—	15
	β_t	41	50	65		69		85
$[Et_3NCH_2Ph]_3[IrCl_6]$	α	0.5	—	4.5	6	6	7	7
	β_c	2		19	25	26	26	26
	β_t	3		30	37	37	37	37
$IrCl_3$	α	1	3	4	6	7	7	9
	β_c	5	11	19	30	30	29	27
	β_t	6	12	24	35	40	46	54
	$PhC\equiv CSiEt_3$	1	2	4	5	4	4	5
$[Et_3NCH_2Ph]_2[PtCl_6]$	α	6.5	23	38	41	42	44	44
	β_t	9	30	54	55	55.5	56	56
K_2PtCl_6	α	0	—	2				
	β_t			2				
$H_2PtCl_6.6H_2O$	α	30						
	β_t	70						
Without catalyst	β_t	0	—	0	—	1	—	1

last one is significantly less active than the starting $H_2OsCl_6.6H_2O$ (the total yield of hydrosilylation products after 7 h is 15 and 100%, respectively). The complexes of Fe^{III}, Cu^{II}, Zn^{II}, Rh^{III}, Ir^{III}, Pt^{IV} were found highly active in reaction [1], the total product yields decreasing in the following order: $[RhCl_4]^- > [PtCl_6]^{2-} > [IrCl_6]^{3-} > [CuCl_4]^{2-} > [ZnCl_4]^{2-} > [FeCl_4]^-$. From the data summarized in Table 3 it is evident that some neutral metal chlorides ($FeCl_3.6H_2O$, $CuCl_2$, $RhCl_3.4H_2O$, $IrCl_3$) also display significant activity. However, in all cases (except for $IrCl_3$) the corresponding metallates containing ions $[FeCl_4]^-$, $[CuCl_4]^{2-}$, $[RhCl_4]^-$ are more active than the starting chlorides. In the case of iridium compounds the activities of the neutral chloride and the hexachloroiridate were similar. The gain in $ZnCl_2$ activity upon its transformation to $[ZnCl_4]^{2-}$ was particularly appreciable, the total product yields increasing from 3 to 88% (reaction duration 7 h).

Potassium chlorometallates (K_3RhCl_6, K_2PtCl_6) were absolutely inactive in the reaction of hydrosilylation, probably due to their insolubility in the reaction mixture. The acids ($H_2OsCl_6.6H_2O$ and $H_2PtCl_6.6H_2O$) had high activity (especially the latter) but were very hygroscopic, which made them difficult to handle and dispense precisely.

As to the regio- and stereo-selectivity of hydrosilylation in the presence of catalysts showing marked activity, the following conclusions could be drawn. In the presence of Period IV metals (Fe^{III}, Cu^{II}, Zn^{II}) α-addition prevailed; the yield of the β-addition product was lower, only the *trans*-isomer being formed. All Period V and VI metal compounds under study were more active in β-addition (in the presence of Sn^{IV} and Os^{IV} complexes no α-products were formed). In the presence of these catalysts the yield of the *trans*-isomer was greater than that of the *cis*-isomer (Pt^{IV} compounds failed to give the *cis*-product).

A comparison of properties of complexes **1**–**16** with the corresponding starting compounds (chlorides, acids) has demonstrated that despite differences in their activity they possess similar regio- and stereo-selectivity. Only Fe^{III} compounds constitute an exception. The complex $[FeCl_4]^-$ catalyses α-addition to a somewhat greater extent than β-addition but $FeCl_3$ acts vice versa. Moreover, in the presence of $FeCl_3$ the *cis*-isomer is formed in up to 7% yield, whereas $[FeCl_4]^-$ fails to do so. It should be also noted that $IrCl_3$, unlike all other compounds under study, slightly catalyses the dehydrogenation process to give the acetylenic product $PhC{\equiv}CSiEt_3$ in up to 5% yield as identified by GC MS: the mass spectrum shows a molecular ion peak with *m/z* 216.

Thus, some complexes of the $[Et_3NCH_2Ph]^+_m[MCl_n]^m$ type ($M = Fe^{III}$, Cu^{II}, Zn^{II}, Rh^{III}, Ir^{III}, Pt^{IV}) exhibit an appreciably high hydrosilylation activity, the reaction direction being dependent on the metal atom present in the complex.

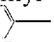
Since all the complexes in question are soluble in the reaction mixture their recovery for subsequent application is extremely cumbersome. A general method for the preparation of reusable catalytic systems is the heterogenization of soluble catalysts by their binding on to polymers.[19–22] In most cases such systems represent neutral transition-metal complexes with polymeric ligands. To obtain a recovered hydrosilylation catalyst it appears advisable to synthesize anchored ionic complexes of the type $[Ⓟ\text{-}R]^+_m[MCl_n]^{m-}$ in which the halometallate anion is bonded with the polymeric counter-ion. Literature data describing the synthesis and properties of such ionic systems in hydrosilylation reactions are limited. The following polymer-bound amines have been used as cations: a styrene–divinylbenzene copolymer (Amberlyst A-21, Ⓟ——CH_2NMe_2); poly(methacrylates), $(\text{—}CH_2\text{—}CH)_nCOO(CH_2)_mNMe_2$), both being in the anion-exchange form;[23] anion-exchanger AV-17-8 (Ⓟ-N^+Me_3);[24] and a specially prepared polymer of the type $R^1R^2R^3R^4N^+$, where R^1–R^3 = polysiloxane groups, R^4 = H, alkyl or benzyl).[25] Rhodium, platinum and iridium halometallates were chiefly used as the counter-ions of the above polymeric cations. The disadvantages of these ammonium-containing polymers include low thermal stability,[26] poor swelling in non-polar organic solvents,[27] and the necessity to devise special synthetic approaches.[25] Therefore, it appeared more convenient to use a commercially available and thermally stable polymer with anchored lipophilic quaternary onium groups for the heterogenization of $[MCl_n]^{m-}$ ions. One of the polymers meeting these requirements is the well-known phase-transfer agent, the polymer-bound tributylmethylphosphonium chloride, Ⓟ-$CH_2P^+Bu_3$ Cl^-,[27] commercially available from Fluka. The reactions of this polymeric quaternary salt with Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Rh^{III} chlorides afforded the corresponding polymer-anchored halometallates. Similar compounds of Os^{IV} and Pt^{IV} were prepared by ion-exchange

Table 4 Synthesis of anchored ionic complexes and their catalytic properties in phenylacetylene hydrosilylation with triethylsilane at 80°C ($PhC{\equiv}CH$:$HSiEt_3$:catalyst = 1:1:0.001)[a]

					Products yield (%) (GC data)					
					Reaction time (h)					
Anchored complex	Colour	Starting metal compound	Method of synthesis[b]	Isomer	1	2	3	4	5	7
[Ⓟ—CH_2PBu_3]$_2$[$MnCl_4$]	Pink	$MnCl_2.4H_2O$	D	β_c	0	0	0	0	0	1
				β_t	0	1	2	3	4	5
[Ⓟ—CH_2PBu_3][$FeCl_4$]	Yellowish green	$FeCl_3.6H_2O$	D	α	0	0	0	0	1	2
				β_c	1	2	3	4	4	4
				β_t	2	5	7	9	11	14
[Ⓟ—CH_2PBu_3]$_2$[$CoCl_4$]	Light blue	$CoCl_2$	D	β_c	0	0	1	2	2	3
				β_t	1	2	3	4	5	6
[Ⓟ—CH_2PBu_3]$_2$[$NiCl_4$]	Pale pink	$NiCl_2$	D	β_c	0	0	0	0	0	1
				β_t	0	0	1	2	3	4
[Ⓟ—CH_2PBu_3]$_2$[$CuCl_4$]	Yellow	$CuCl_2$	D	β_c	0	0	0	0	0	2
				β_t	0	0	1	2	3	4
				β_t	0	0	1	2	3	4
[Ⓟ—CH_2PBu_3]$_2$[$ZnCl_4$]	White	$ZnCl_2$	D	α	0	0	0	0	1	2
				β_t	0	1	2	3	4	5
[Ⓟ—CH_2PBu_3][$RhCl_4$]	Dark purple	$RhCl_3.4H_2O$	D	α	10	20				
				β_c	20	30				
				β_t	35	50				
[Ⓟ—CH_2PBu_3]$_2$[$OsCl_6$]	Black	$H_2OsCl_6.6H_20$	E	β_c	5	7.5	10	12	14	17
				β_t	39	46	50	56	60	66
[Ⓟ—CH_2PBu_3]$_2$[$PtCl_6$]	Orange	K_2PtCl_6	E	α	33	34				
				β_t	52	61				

[a]Quantitative formation of the polymer-bound chlorometallates was confirmed gravimetrically.[b]See Experimental.

starting from $H_2OsCl_6.6H_2O$ and K_2PtCl_6, respectively (Table 4). Polymer-bound chlorometallates (Table 4) are formed quantitatively as indicated by their gravimetric analysis data.

The data obtained by studying the hydrosilylation of phenylacetylene with triethylsilane in the presence of polymer-bound halometallates are also summarized in Table 4.

Only the catalysts containing platinum-group metals were found to be fairly active, the activity decreasing in the following order: $[PtCl_6]^{2-}$ > $[RhCl_4]^-$ > $[OsCl_6]^{2-}$. This order is somewhat different from that found for homogeneous quaternary ammonium-containing complexes. The activity of the anchored rhodium complex (Table 4) and that of the homogeneous one (Table 3) was almost the same. The heterogeneous platinum and osmium catalysts were more active than the appropriate homogeneous complexes and approached the activity of hexachloroplatinic and hexachloro-osmic acid (Table 3). A comparison of the yields of α-, β_{cis}- and β_{trans}-adducts (reaction [1], Tables 3 and 4) has shown that the heterogenization of $[PtCl_6]^{2-}$, $[RhCl_4]^-$ and$[OsCl_6]^{2-}$ ions does not influence their regio- and stereo-selectivity. Our experimental evidence gained with immobilized complexes repeatedly used for hydrosilylation (reaction [1]) indicated practically unaltered activity.

CONCLUSIONS

Triethylbenzylammonium chlorometallates $[Et_3NCH_2Ph]_m^+[MCl_n]^{m-}$ ($M = Rh^{III}$, Pt^{IV}, Ir^{III}, Cu^{II}, Zn^{II}, Fe^{III}; $m = 1$–3; $n = 4, 6$) were found to be active in the hydrosilylation of phenylacetylene with triethylsilane. This reaction was also effectively catalysed by the anchored ionic metal complexes [Ⓟ-$CH_2PBu_3]_m^+[MCl_n]^{m-}$ ($M = Pt^{IV}$, Rh^{III}, Os^{IV}; $m = 1$, 2; $n = 4, 6$) derived from the Fluka polymer-bound tributylmethylphosphonium chloride. The regio- and stereo-selectivity of the catalysts was determined by the metal atom involved.

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