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Preliminary communication

SELECTIVE SYNTHESIS OF MONO-ALKYLDICHLOROSILANES VIA THE REACTION OF OLEFINS WITH DICHLOROSILANE CATALYZED BY GROUP VIII METAL PHOSPHINE COMPLEXES

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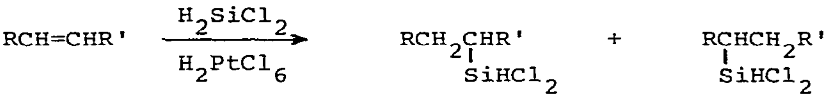
Summary

In the hydrosilylation of 1-hexene with dichlorosilane, many phosphine complexes of Group VIII metals, Ni, Ru, Rh, Pd and Pt, were found to be active catalysts, giving n-hexyldichlorosilane exclusively. Tris(triphenylphosphine)chlororhodium was found to be the most convenient and effective catalyst for the selective synthesis of mono-organodichlorosilanes.

Extensive investigations of the hydrosilylation of olefins have been carried out and a variety of effective catalysts has been found, e.g., benzoyl peroxide, tributylamine, platinum, chloroplatinic acid, etc. [1]. Chloroplatinic acid is by far the most commonly used catalyst. Recently, Group VIII metal-phosphine complexes of nickel [2], rhodium [3], palladium [4], platinum [4a,5] and iridium [4a] have been shown to be effective catalysts for the hydrosilylation of olefins. However, hydosilylation with dichlorosilane (H_2SiCl_2) in the presence of these metal complexes, except for one case of a palladium complex [4b], has received little attention and only few reports are available on the chloroplatinic acid catalyzed reaction of this hydrosilane. Thus, it was reported that hydrosilylation of terminal olefins with dichlorosilane gave a mixture of mono- and dialkyldichlorosilanes [6] or dialkyldichlorosilanes [7] (eq. 1). Recently, Benkeser and co-worker also reported that the hydrosilylation of internal olefins with H_2SiCl_2 gives a mixture of two internally substituted monoalkyldichlorosilane [8] (eq. 2).

$$RCH{=}CH_2 \xrightarrow[H_2PtCl_6]{H_2SiCl_2} RCH_2CH_2SiHCl_2 + (RCH_2CH_2)_2SiCl_2 \qquad (1)$$



$$RCH{=}CHR' \xrightarrow[H_2PtCl_6]{H_2SiCl_2} RCH_2\underset{\displaystyle SiHCl_2}{\underset{|}{CH}}R' + R\underset{\displaystyle SiHCl_2}{\underset{|}{C}}HCH_2R' \qquad (2)$$

Reactions of this type are of great importance, since they may provide a convenient route to various organodichlorosilanes which are precursors of alkylhydropolysiloxanes and, also, they can be converted to other organosilicon compounds by reactions of either their Si-H or their Si-Cl functions. We now report that with judicious choice of triphenylphosphine complexes of Group VIII metals (Ni, Ru, Rh, Pd and Pt), monoalkyldichlorosilanes can be prepared in excellent yield by the hydrosilylation of olefins using dichlorosilane under mild conditions (eq. 3).

In order to find out an effective and convenient catalyst for

$$RCH{=}CH_2 + H_2SiCl_2 \xrightarrow{\text{Catalyst}} RCH_2CH_2SiHCl_2 \qquad (3)$$

eq. 3, the catalytic activities of these complexes were examined employing 1-hexene as substrate. In a typical experiment, a 50 ml stainless steel bomb was charged with 1-hexene (54 mmol) and

$RhCl(PPh_3)_3$ (2.39×10^{-2} mmol; 0.1 mol% relative to the silane used), cooled in a liquid nitrogen bath and then evacuated. Dichlorosilane (21 mmol, 1.7 ml), condensed in a calibrated tube at -20° (ice-salt bath), was distilled into the bomb through the inlet valve and then the bomb was allowed to warm to room temperature. Subsequently, it was heated at 70° (oil bath) for 15 h. After cooling, GLC analysis (1m × 4mm Teflon column, 20% silicone KF-96 on Celite 545-AW; column temp. 156°) of the reaction mixture showed that the product was n-hexyldichlorosilane [*] in 99% yield, based on the dichlorosilane used. A similar reaction carried out at elevated temperature (120°) formed n-hexyl- and di(n-hexyl)-dichlorosilane in 94 and 6% yield, respectively.

Results of hydrosilylations catalyzed by other complexes are summarized in Table 1. It will be seen from Table 1 that all the phosphine complexes tested were catalytically active to form n-hexyldichlorosilane in low to excellent yields (19-99%). In particular, $NiCl_2(PPh_3)_2$, $RuH_2(PPh_3)_4$, $RuHCl(PPh_3)_3(PhMe)$, $RuH_3(PPh_3)_3[Si(OMe)_2Ph]$, $RuH_3(PPh_3)_3[Si(OMe)_3]$, $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$ gave excellent results under the conditions employed. Significantly, use of two or more equivalents of the olefin to dichlorosilane in the presence of these complexes gave only n-hexyldichlorosilane (rather than di(n-hexyl)dichlorosilane) and this is in sharp contrast to the chloroplatinic acid-catalyzed reactions which gave a mixture of mono- and dialkyldichlorosilane [6] or dialkyldichlorosilane [7,**]. The results in Table 1 show that tris(triphenylphosphine)chlororhodium, $RhCl(PPh_3)_3$, is the catalyst of choice for the mono-hydrosilylation. Acc-

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*Identification was accomplished in the usual manner (NMR and IR spectra and the comparison of the physical data with literature values.

**In our experiment, preparation of dialkyldichorosilanes directly from H_2SiCl_2 and olefins in the presence of H_2PtCl_6 catalyst was effected in excellent yield.

Table 1

HYDROSILYLATION OF 1-HEXENE WITH DICHLOROSILANE CATALYZED BY Ni-, Ru-, Rh-, Pd- AND Pt-TRIPHENYLPHOSPHINE COMPLEXES[a]

Catalyst	Product and yield (%)[b]					
	Reaction temp., 70°			Reaction temp., 120°		
	Run	$RSiHCl_2$	R_2SiCl_2	Run	$RSiHCl_2$	R_2SiCl_2
$NiCl_2(PPh_3)_2$	1	98	0			
$RuCl_2(PPh_3)_3$	2[c]	68	"	14	96	1
$RuHCl(PPh_3)_3(PhH)$[d]	3[c,e]	85	"	15	99	"
$RuH_2(PPh_3)_4$	4[c]	91	"			
$RuHCl(PPh_3)_3(PhMe)$[d]	5[c]	96	"			
$RuH_3(PPh_3)_3[Si(OMe)_2Ph]$[d]	6[c]	94	"			
$RuH_3(PPh_3)_3[Si(OMe)_3]$[d]	7[c]	94	"			
$RuH(PPh_3)_3(SiEt_2Cl)$[d]	8	87	"			
$RhCl(PPh_3)_3$	9	99	"	16	94	6
$RhH(PPh_3)_4$	10	59	trace	17	96	2
$RhCl(CO)(PPh_3)_3$	11	46	"	18	92	"
$RhH(CO)(PPh_3)_3$	12	19	"	19	26	"
$Pd(PPh_3)_4$				20	42	6
$PdCl_2(PPh_3)_2$				21	34	5
"				22[f]	91	6
$Pt(PPh_3)_4$	13[c]	99	0			

[a] 1-Hexene: H_2SiCl_2=23-35:10-15 (mmol); reaction time, 15 h; catalyst, 0.1 mol% relative to the silane used. [b] GLC yield based on the silane used and thermal conductivity correction with an internal standard ($\underline{n}$-$C_{13}H_{28}$) was made; R= $\underline{n}$-C_6H_{13}. [c] Reaction time, 25 h. [d] See ref. 9. [e] Catalyst, 0.2 mol%. [f] Reaction temp., 170°.

Table 2

HYDROSILYLATION OF OLEFINS WITH DICHLOROSILANE CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM AND CHLOROPLATINIC ACID

Reactants			Conditions				Product and yield		
Olefin	(mmol)	H_2SiCl_2 (mmol)	Catalyst[a]	(mol%)[b]	Temp. (°C)	Time (h)	Dichlorosilane	(%)[c]	B.p. °C (mm)
1-Butene	34[d]	13	A	0.8	110	1.5	$\underline{n}$-$C_4H_9SiHCl_2$	74	..[e]
iso-Butne	64[f]	32	"	0.1	100	16	$Me_2CHCH_2SiHCl_2$	70	"
1-Hexene	85	85	"	"	80	25	$\underline{n}$-$C_6H_{13}SiHCl_2$	70	"
cyclo-Hexene	50	50	"	"	100	24	$\underline{c}$-$C_6H_{11}SiHCl_2$	34	110-112(155)
1-Octene	54	21	"	"	"	15	$\underline{n}$-$C_8H_{17}SiHCl_2$	79	100-106(20)
1-Dodecene	68	57	"	0.25	"	35	$\underline{n}$-$C_{12}H_{25}SiHCl_2$	80	..[e]
1-Octadecene	53	55	"	0.1[g]	140	15	$\underline{n}$-$C_{18}H_{37}SiHCl_2$	72[h]	"
Styrene	55	53	"	0.1	90	10	$PhCH_2CH_2SiHCl_2$	87	67-77(3)
"	50	50	B	0.05	50	"	..[i]		
"	"	100	"	"[g]	"	15	"		
α-Methylstyrene	53	53	A	0.1	100	"	$PhMeCHCH_2SiHCl_2$	78	76-81(3)
"	"	"	B	0.005	r.t.	20	..[i]		
"	44	96	"	0.05[g]	"	15	"		

[a] A: $RhCl(PPh_3)_3$, B: $H_2PtCl_6 \cdot 6H_2O/{}^iPrOH$. [b] Relative to the silane used. [c] Isolated yield based on the silane used. [d] Mesitylene (1 ml) was added as solvent for the catalyst. [e] Known compound. [f] Mesitylene, 0.5 ml. [g] Relative to the olefin used. [h] Based on the olefin used. [i] Only polymeric high viscous liquid or solid was formed.

ordingly, the synthesis of various monoalkyldichlorosilanes from olefins was carried out using the Rh complex as catalyst. The products were readily isolated by distillation and identified in the usual manner (NMR, IR and elemental analysis, or the comparison of the spectral and physical data with those of the literature). Results listed in Table 2 show that the yields were as high as 70-90%. NMR analysis of the products gave no indication of the presence of any secondary alkyldichlorosilane and thus reactions of these olefins with dichlorosilane affords the terminal adducts only. A more striking feature was obtained in the hydrosilylation of styrene and of α-methylstyrene. The reactions of these compounds with dichlorosilane in the presence of chloroplatinic acid formed only intractable polymeric materials. On the other hand, the reactions effected in the presence of the Rh catalyst gave the corresponding adducts, β-phenylethyl- and β-methyl-β-phenylethyl-dichlorosilane, respectively, in excellent yield. Hetflejš showed that in the presence of the Rh catalyst trimethyl- and triethyl-silane added to these aryl olefins to form a mixture of the secondary and primary alkylsilane, $PhMeCHSiR_3$ and $PhCH_2CH_2SiR_3$, where R=Me or OEt [3d]. The Rh complex-catalyzed hydrosilylation of an internal olefin, cyclohexene, also could be effected, but the product yield was low.

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