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THE HYDROSILATION OF OLEFINS CATALYZED BY SOME RHODIUM AND COBALT COMPLEXES*

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SUMMARY

A variety of homogeneous hydrogenation catalysts has been examined for the catalysis of olefin hydrosilation including $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$. The addition of phenyldimethylsilane to 2-pentene gave only n-pentyldimethylphenylsilane, although very little olefin isomerization accompanied additions to terminal olefins.

Addition of phenyldimethylsilane to acrylonitrile gave the α-adduct only. Addition of dimethylchlorosilane to acrylonitrile was catalyzed by $RhH(CO)(PPh_3)_3$ in the presence of tributylamine or by $Co_2(CO)_8$. In both cases α-adduct was formed. With methacrylonitrile, 1,4-addition occurred to give $Me_2C{=}CHN(SiMe_2Cl)_2$ with $Co_2(CO)_8$.

The addition of triethoxysilane and trichlorosilane to ethylene was catalyzed by $[RhCl(CO)_2]_2$ to give the corresponding ethyl derivatives and in the latter case excess ethylene was dimerized to butenes.

INTRODUCTION

Earlier papers have discussed the similarity between reactions of silicon hydrides and hydrogen catalyzed by Pt^{II} and $Co_2(CO)_8$[1,2]. In view of the mechanistic similarities, we have studied the use of some of the new homogeneous hydrogenation catalysts for the hydrosilation reaction. While this work was in progress, preliminary reports on the subject appeared by two other groups[3,4]. These papers thoroughly investigated the complexes formed between some rhodium complexes and silicon hydrides. However, they gave only a few examples of catalyzed hydrosilation and some of these raised further questions. This paper, therefore, deals with scope of a number of the new catalysts and investigates some of the possible differences between these and the more traditional chloroplatinic acid used by Speier**.

One of the most thoroughly investigated homogeneous hydrogenation catalysts is $RhCl(PPh_3)_3$[6]. It is unusual in giving very little isomerization, and Wilkinson's work on the subject led him to the tentative conclusion that both

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** For a detailed listening of reactions catalyzed by "Speier's Catalyst" see ref. 5.

hydrogens add to the olefin in a concerted fashion. Olefin isomerization accompanying the hydrosilation reaction has been attributed to a transition metal alkyl–hydride intermediate. If the silicon hydride addition were concerted, no isomerization would be expected. These considerations led us to examine the degree of isomerization that accompanied hydrosilation of 1-olefins and to look for the formation of branched products from 2-olefins. This would be unusual since chloroplatinic acid gives principally terminal products in the hydrosilation of internal olefins[7].

A further question raised by earlier work was the formation of 20% $C_{12}H_{25}SiCl_3$ in the reaction of 1-hexene with trichlorosilane using $[RhCl(CO)_2]_2$ as catalyst[4]. If this catalyst is capable of dimerizing 1-hexene, it would be interesting to see its effect on the more readily polymerizable ethylene.

A final question which we sought to investigate was the ability of phosphine-substituted catalysts to catalyze the hydrosilation of compounds such as acrylonitrile. Thus platinum has been found to catalyze the addition of methyldichlorosilane to acrylonitrile only with great difficulty. Speier *et al.*[8] were unable to effect the addition using either platinum on charcoal or chloroplatinic acid and Goodman *et al.*[9] achieved a 25% yield of the α-adduct after 26 h at 75° using the former catalyst. Since acrylonitrile forms strong complexes with transition metals one would expect it to inhibit catalysis of olefin hydrosilation and it has in fact been used for this purpose[10].

Phosphines have also been used to inhibit olefin hydrosilation by platinum catalysts[11] so the fact that certain phosphine complexes are active hydrosilation catalysts raised the possibility that they might act rather like the "poisoned" heterogeneous hydrogenation catalysts such as that due to Lindlar[12].

The direction of addition of silicon hydrides to acrylonitrile is also of interest here. Silicon hydrides normally add to olefins containing electronegative groups in the sense Si^+H^- so that addition to acrylonitrile would give α-adducts. With sufficiently strong electronegative groups on silicon, however, the Si–H bond is polarized in the sense Si^-H^+ and cuprous chloride–amine catalysts have been used to add chlorosilanes to acrylonitrile to give the more commercially desirable β-adducts[13,14]. The ease of addition of chlorosilanes to acrylonitrile to give the β-adduct with this basic catalyst is in the order $Cl_3SiH > MeSiCl_2H > Me_2SiClH$[14]. The last reaction has not yet been accomplished. This series suggests the decreasing polarization of the Si–H bond in the sense Si^-H^+, in agreement with the mode of addition (β).

For a transition metal hydride to catalyze β-addition, it too must add in the sense M^-H^+. This consideration suggests the use of $HCo(CO)_4$ which is one of the most acidic metal hydrides known[15]. β-Cyanopropionaldehyde is the product of the hydroformylation of acrylonitrile[16] indicating β-addition of $HCo(CO)_4$[17].

EXPERIMENTAL

Materials

$Co_2(CO)_8$, $[RhCl(CO)_2]_2$ and $HRhCO(PPh_3)_3$ were obtained from Strem Chemicals Inc. Other catalysts were made according to the literature: $RhCl(PPh_3)_3$[6], $Pt(PPh_3)_4$[18], $RhCOCl(PPh_3)_2$[6], $Co_2(CO)_6(PBu_3)_2$[19] and $RuCl_2(CH_2{=}CHCN)_4$[20].

Hydrosilation reactions

Hydrosilation reactions were followed in the IR by the disappearance of the band due to ν(Si–H) stretch. Reactions were carried out at toom temperature or under reflux conditions as indicated in Table 1. No attempt was made to optimize product yields. Products were isolated by a simple distillation where possible or by preparative GLC. A two fold excess of olefin was used, except for acrylonitrile where equimolar amounts of the reactants were employed.

The following was typical. To 5.0 g ($3.7 \cdot 10^{-2}$ moles) of phenyldimethylsilane and 5.1 g of 1-pentene ($7.3 \cdot 10^{-2}$ moles) was added 0.5 ml of a 4×10^{-3} molar solution of $ClRh(PPh_3)_3$ in benzene and the mixture was refluxed under nitrogen. After 20 min no silicon hydride was detectable by IR. GLC analysis indicated the formation of a single product in nearly quantitative yield. The unconverted olefin was removed on a rotary evaporator and the remaining liquid distilled over on a vacuum transfer line to give 6 g of phenyldimethylpentylsilane.

Reactions of ethylene were carried out in a 300 ml rocking autoclave provided with a glass liner. The catalyst was added at 0° and immediately pressurized with at least a two fold excess of ethylene. The reaction was then followed by change in pressure.

RESULTS

1. *Simple olefins*

Some results are given in Table 1. $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$ all were found to be active catalysts. In catalyzing hydrosilation, $RhCl(PPh_3)_3$ gave rise to relatively little isomerization. Thus in expt. 2 in which an excess of 1-pentene was used, after all the silane had reacted, 80% of the unreacted olefin remained as 1-pentene, the remaining olefin being mainly *trans*-2-pentene.

Reaction with 2-pentene was very much slower than with 1-pentene. Thus, while 1-pentene reacted completely within 20 min at reflux, *cis*-2-pentene reacted with 10% of the silane after one h at reflux and commercial 2-pentene (which is largely the *trans* isomer) showed virtually no reaction after 2.5 h at reflux.

In spite of the high selectivity for hydrosilation over isomerization, $RhCl(PPh_3)_3$ gave only the n-pentylproduct from the reaction of 2-pentene with phenyldimethylsilane. This was confirmed by NMR examination which would easily distinguish the various isomers.

The excess olefin, on completion of expt. 5, was solely ethylene, whereas that from expt. 6 was solely a mixture of butenes, largely 2-butene.

2. *Unsaturated nitriles*

Rhodium complexes readily catalyzed addition of phenyldimethylsilane to acrylonitrile (Table 1). Addition of dimethylchlorosilane was more difficult however. A variety of catalysts were tried (see experimental) but with the rhodium phosphine catalysts the products included dimethyldichlorosilane and what appeared to be $(CH_3)_2Si(H)CH(CH_3)CN$, *i.e.* the product of the addition of dimethylsilane to acrylonitrile.

Only in two cases did a reaction occur fairly cleanly and in both cases (Table 1) the α-adduct was isolated by preparative GLC (Table 3). Methacrylonitrile also was examined and here only $Co_2(CO)_8$ was successful in catalyzing hydrosilation and the only isolable product was from 1,4-addition. In all cases the products were readily

TABLE 1

HYDROSILATION REACTIONS

Expt.	Silane	Olefin	Catalyst[a]	Conditions	Product	Yield (%)
1	$HSiEt_3$	$C_4H_9CH{=}CH_2$	$RhCl(PPh_3)_3$	2 h reflux	n-$C_6H_{13}SiEt_3$	80
2	$HSiPhMe_2$	$C_3H_7CH{=}CH_2$	$RhCl(PPh_3)_3$	20 min reflux	n-$C_5H_{11}SiPhMe_2$	80
3	$HSiPhMe_2$	*cis*-$C_2H_5CH{=}CHCH_3$	$RhCl(PPh_3)_3$	2 days 25°	n-$C_5H_{11}SiPhMe_2$	75
4	$HSi(OEt)_3$	$C_3H_7CH{=}CH_2$	$RhCl(PPh_3)_3$	7 days 25°	n-$C_5H_{11}Si(OEt)_3$	84
5	$HSi(OEt)_3$	C_2H_4	$[RhCl(CO)_2]_2$	65 h 20° and 60 atm	n-$C_2H_5Si(OEt)_3$	~95
6	$HSiCl_3$	C_2H_4	$[RhCl(CO)_2]_2$		n-$C_2H_5SiCl_3$	~95
7	$HSiPhMe_2$	$CH_2{=}CHCN$	$RhH(CO)(PPh_3)_3$	15 min reflux	$PhSiMe_2CH(Me)CN$	80
8	$HSiClMe_2$	$CH_2{=}CHCN$	[b]	1.5 h reflux	$ClSiMe_2CH(Me)CN$	30
9	$HSiClMe_2$	$CH_2{=}CHCN$	$Co_2(CO)_8$	24 h 25°	$ClSiMe_2CH(Me)CN$	20
10	$HSiClMe_2$	$CH_2{=}C(Me)CN$	$Co_2(CO)_8$	6 days 25°	$Me_2C{=}CHN(SiMe_2Cl)_2$	20

[a] Catalyst concentrations: $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ 10^{-4} *M*, $[RhCl(CO)_2]_2$ 10^{-2} *M*, $Co_2(CO)_8$ $5 \cdot 10^{-3}$ *M*. [b] $RhH(CO)(PPh_3)_3$ in the presence of a 10 mole excess of Bu_3N.

identified by their NMR spectra (Table 3). The α-adducts gave typical AB_3 patterns. The 1,4-addition product gave rise to quartet at τ 8.3 (CH_3) and a heptet at τ 4.4 (=CH). By irradiating with a frequency corresponding to the latter absorption, the quartet simplified to two singlets, consistent with an original allylic coupling. The structure was further confirmed by the IR spectrum which showed the absence of C≡N and the presence of a band at 1660 cm^{-1} attributable to C=N. Elemental analysis also supported the suggested structure (Table 2) which must result from initial 1,4-addition followed by the addition of a further mole of silane. Ethyltrichlorosilane and ethyltriethoxysilane (expts. 5 and 6) were identified by comparison (IR and NMR spectra) with authentic samples.

TABLE 2

ELEMENTAL ANALYSES

Compound	n_D^{20}		Analysis, found (calcd.) (%)				
	Found	Lit.	C	H	Si	N	Cl
$C_5H_{11}SiMe_2Ph$	1.490		75.44 (75.65)	10.66 (10.74)	13.99 (13.61)		
$C_6H_{13}SiEt_3$	1.442	1.4400[21]	72.25 (71.90)	14.24 (14.10)	13.95 (14.01)		
$C_5H_{11}Si(OEt)_3$	1.406	1.4059[22]	56.50 (56.36)	11.12 (11.18)	14.4[a] (13.98)		
$PhSiMe_2CH(CH_3)CN$	1.516		69.96 (69.78)	7.96 (7.99)	16.1 (14.84)	7.65 (7.40)	
$Me_2SiClCH(CH_3)CN$			41.2 (40.66)	7.1 (6.83)	20.1 (19.02)	9.6 (9.48)	22.1 (24.01)
$Me_2C{=}CHN(SiMe_2Cl)_2$			38.2 (37.5)	7.8 (7.4)	19.4 (21.9)	5.0 (5.5)	25.1 (27.7)

[a] Silicon analyses for this compound were erratic.

TABLE 3

NMR SPECTRA OF SOME PRODUCTS

Compound	τ values							
	Ph	CH_3–C			CH		CH_3–Si	
$PhSiMe_2CH(CH_3)CN$[a]	2.6	8.77	8.90	(D)	8.1	(Q)	9.53	(S)
$Me_2SiClCH(CH_3)CN$[a]		8.57	8.70	(D)	8	(Q)	9.4	
$Me_2C{=}CHN(SiMe_2Cl)_2$[b]		8.3			4.4		9.5	(S)

[a] 10% in CCl_4. [b] neat.

DISCUSSION

Earlier reports have stated that $RhCl(PPh_3)_3$ catalyzes the hydrosilation of 1-hexene with trichlorosilane[3], triethylsilane and triphenylsilane to give the corresponding n-hexylsilanes. The catalyst was reported to be relatively ineffective, however, and high catalyst concentrations were necessary at room temperature[3] ([catalyst]/[silane] ~ $5 \cdot 10^{-3}$ moles/mole). By contrast, under some conditions quite low catalyst concentrations are possible (Table 1, [catalyst]/[silane] ~ $4 \cdot 10^{-5}$ moles/mole).

The small extent to which excess olefin is isomerized distinguishes it from other catalysts such as $Co_2(CO)_8$ and platinum complexes where in most cases the rate of olefin isomerization exceeds that of hydrosilation[1,2]. However, the formation of terminal products from internal olefins is similar to the results obtained with the other catalysts and argues against a concerted addition of the silicon hydride across the double bond. A mechanism similar to that proposed earlier for Pt^{II} catalyzed hydrosilation[1] would seem to be sufficient to explain the results. Olefin exchange must be a relatively slow process, however, to explain the low extent of isomerization of excess olefin.

The earlier report of the formation of $C_{12}H_{25}SiCl_3$ in 20% yield from 1-hexene[4] has found no parallel in the reactions of ethylene reported here. The formation of butenes is presumably due to the catalysis of ethylene dimerization by rhodium(I) in the presence of HCl reported by Cramer[23]. Under the conditions of the experiment it was not possible to rigorously exclude traces of moisture which must have caused some hydrolysis of the trichlorosilane. The fact that no butenes were formed when using triethoxysilane (expt. 5) supports this hypothesis. No butyltrichlorosilanes were formed in expt. 6 suggesting that the hydrosilation reaction occurred very much faster or prior to the olefin dimerization.

The ease of addition of phenyldimethylsilane to acrylonitrile in expt. 7 suggests that these rhodium phosphine complexes may find application in catalyzing the hydrosilation of such strongly coordinating olefins. The direction of addition (α) is that expected from an addition of Si–H in the sense Si^+H^-.

An attempt to catalyze to addition of dimethylchlorosilane to acrylonitrile with rhodium phosphine complexes was complicated by disproportionation of the silane, *e.g.*:

$$2\ Me_2SiClH \rightleftharpoons Me_2SiCl_2 + Me_2SiH_2 \qquad (2)$$

and subsequent addition of dimethylsilane. A similar lability of hydrogen and phenyl bonded to silicon has been noted[24] in the presence of complexes such as $IrCl(CO)(PPh_3)_2$ and $PtCl_2(PBu_3)_2$, *e.g.*

$$4\ Ph_2SiH_2 \rightleftharpoons Ph_4Si + Ph_3SiH + PhSiH_3 + SiH_4 \qquad (3)$$

A vinyl–hydrogen exchange has also been reported catalyzed by platinum[25].

Surprisingly, $Co_2(CO)_8$ catalyzed only α-addition. This may result from $HCo(CO)_3$ being the true catalyst rather than $HCo(CO)_4$. Differences in the mode of addition across olefins can be controlled by the carbon monoxide pressure which controls the equilibrium between the two catalysts[17]:

$$HCo(CO)_3 + CO \rightleftharpoons HCo(CO)_4$$

However the use of CO pressure (1 atm at 25° or 20 atm at 120°) inhibited addition of dimethylchlorosilane to acrylonitrile. Further, phosphines appeared to have the same effect since $Co_2(CO)_6(PBu_3)_2$ was also ineffective as a catalyst for this reaction at 25°.

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