Journal of Organometallic Chemistry, 208 (1981) 401—406
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

RHODIUM(II) COMPLEXES AS HYDROSILYLATION AND HYDROGENATION CATALYSTS

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(Received August 4th, 1980)

Summary

Two phosphine-rhodium(II) complexes, bis(tris-*o*-tolylphosphine)dichlororhodium(II) and bis(tricyclohexylphosphine)dichlororhodium(II), have been found to be active catalysts for the hydrosilylation of a variety of organic substrates, and, in conjunction with triethylaluminum, to be hydrogenation catalysts.

Introduction

In recent years a variety of rhodium(I) complexes have been utilized as catalysts for a wide variety of reactions. For example, Wilkinson's compound, $[RhCl(PPh_3)_3]$, has been used to catalyze hydrogenation [1], hydrosilylation [2], and decarbonylation [3] reactions. In view of the high catalytic activity of rhodium(I) complexes, it seems surprising that the catalytic activity of rhodium(II) complexes has not been extensively investigated. We have, therefore undertaken an investigation of the catalytic activity of these species, and report in this paper on the use of bis(tris-*o*-tolylphosphine)dichlororhodium(II), $[RhCl_2\{P(o\text{-}C_6H_4CH)_3\}_2]$ (I), and bis(tricyclohexylphosphine)dichlororhodium-(II), $[RhCl_2\{P(C_6H_{11})_3\}_2]$ (II), as hydrosilylation and hydrogenation catalysts. These complexes are readily synthesized by reaction of the appropriate phosphine with rhodium(III) chloride in ethanol [4,5].

Results and discussion

Hydrosilylation

The results of the hydrosilylation of various unsaturated species are sum-

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0022—328X/81/0000—0000/$02.50,

TABLE 1

HYDROSILYLATION USING RHODIUM (II) COMPLEXES

Unsaturated substrate	Silane	Products	Yield (%) [a] using I [b,d]	Yield (%) [a] using II [c,d]
$n\text{-}C_6H_{13}CH{=}CH_2$	$HSiEt_3$	$n\text{-}C_6H_{13}CH_2CH_2SiEt_3$	100	100
$n\text{-}C_6H_{13}CH{=}CH_2$	$HSiMe_2Ph$	$n\text{-}C_6H_{13}CH_2CH_2SiMe_2Ph$	100	100
$n\text{-}C_6H_{13}CH{=}CH_2$	$HSi(OEt)_3$	$n\text{-}C_6H_{13}CH_2CH_2Si(OEt)_3$	81	86
$n\text{-}C_6H_{13}CH{=}CH_2$	$HSiMe(OEt)_2$	$n\text{-}C_6H_{13}CH_2CH_2SiMe(OEt)_2$	86	98
$CH_2{=}C(Me)C(Me){=}CH_2$	$HSiEt_3$	$Me_2C{=}C(Me)CH_2SiEt_3$	17	28
		$CH_2{=}C(Me)CH(Me)CH_2SiEt_3$	48	64
$CH_2{=}C(Me)C(Me){=}CH_2$	$HSi(OEt)_3$	$Me_2C{=}C(Me)CH_2Si(OEt)_3$	15	22
		$CH_2{=}C(Me)CH(Me)CH_2Si(OEt)_3$	19	24
$n\text{-}C_4H_9C{\equiv}CH$	$HSiEt_3$	*cis*- and *trans*-$n\text{-}C_4H_9CH{=}CHSiEt_3$	44	56 [e]
$n\text{-}C_4H_9{\equiv}CH$	$HSiMe_2Ph$	*cis*- and *trans*-$n\text{-}C_4H_9CH{=}CHSiMe_2Ph$	46	63
$\ulcorner(CH_2)_5\urcorner C{=}O$	$HSiEt_3$	$\ulcorner(CH_2)_5\urcorner CHOSiEt_3$	74	82
$\ulcorner(CH_2)_5\urcorner C{=}O$	$HSi(OEt)_3$	$\ulcorner(CH_2)_5\urcorner CHOSi(OEt)_3$	54	78
$CH{=}C(Me)C(O)OMe$	$HSiEt_3$	$Me_2C{=}C(OMe)OSiEt_3$	[f]	75

[a] Yield based on silane and calculated by quantitative GLC. [b] Bis(tris-*o*-tolylphosphine)dichlororhodium(II). [c] Bis(tricyclohexylphosphine)dichlororhodium(II). [d] 0.064 mmol of catalyst used; 100°C for 8 h; unsaturates 6–10 mmol; silanes 5–6 mmol. [e] Small amount (2%) $n\text{-}C_4H_9C(SiEt_3){=}CH_2$ also formed. [f] Reaction not attempted.

marized in Table 1. All reactions were carried out under standard conditions, i.e., 100°C for 8 h, and no attempts were made to maximize yields.

As can be seen from Table 1, both I and II are moderate to excellent catalysts for the hydrosilylation of a wide variety of unsaturated compounds, using both alkyl- and alkoxy-silanes. The catalytic activity is comparable to that of rhodium(I) species [2]. In all cases it appears that the catalytic activity of II is greater than that of I. For example II gives a 98% yield of n-octylsilane from the hydrosilylation of 1-octene by diethoxymethylsilane, whereas I gives only a 86% yield, eq. 1.

$$n\text{-}C_6H_{13}CH{=}CH_2 + HSiMe(OEt)_2 \xrightarrow[100°C,8\,h]{} n\text{-}C_6H_{13}CH_2CH_2SiMe(OEt)_2 \qquad (1)$$

Hydrosilylation of 1-hexyne

The hydrosilylation of 1-hexyne by triethylsilane and dimethylphenylsilane using both (I) and (II) results in a mixture of *cis*- and *trans*-mono adducts, eq. 2.

$$n\text{-}C_4H_9C{\equiv}CH + HSiX_3 \xrightarrow[100°C,8\,h]{\text{(I) or (II)}} \textit{cis}\text{- and } \textit{trans}\text{-}n\text{-}C_4H_9CH{=}CHSiX_3 \qquad (2)$$

$$(X = C_2H_5, X_3 = (CH_3)_2C_6H_5)$$

Although a majority of catalysts yield only the *trans*-olefin by *cis*-addition, it is becoming apparent that many rhodium catalysts produce mixtures of *cis*- and *trans*-olefins [6,8], and that the yields and ratios of isomers are sensitive to reaction conditions. In order to gain further insight into this reaction, a more detailed investigation of the hydrosilylation of 1-hexyne by triethylsilane catalyzed by II was carried out. The variation of yield and *cis/trans* ratio was followed as a function of time and the results are summarized in Table 2. As can be seen, the ratio of *cis/trans* olefin remains approximately constant at 50/50 (±5). This implies either that addition takes place non-stereospecifically or that slow stereospecific addition takes place followed by rapid *cis-trans* isomerization. Previous work indicates that with other rhodium catalysts *cis-trans* isomerization does take place, but that it is slow compared to hydrosilylation [6,8]. The ratio of *cis/trans* adduct produced under identical conditions (100°C, 8 h) by I and II are similar (55/45 and 45/55, respectively), suggesting that elec-

TABLE 2

HYDROSILYLATION OF 1-HEXYNE BY TRIETHYLSILANE CATALYZED BY II [a]

Reaction time (h)	Yield (%) [b]	Isomer ratio (*cis/trans*)
0.5	8	49/51
1.0	41	54/56
2.0	61	53/47
4.0	73	53/47
6.0	79	51/49
8.0	91	45/55

[a] Triethylsilane, 6.3 mmol; 1-hexyne, 8.7 mmol; catalyst, 0.008 mmol; 80°C. [b] Based on silane and calculated by quantitative GLC. [c] Calculated by GLC.

TABLE 3

HYDROGENATIONS USING RHODIUM (II) COMPLEXES

Unsaturate	Product(s)	Yield (%) [b] using I	Yield (%) [b] using II
Cyclohexene	Cyclohexane	100	100
1-Octene	n-Octane	100	100
Styrene	Ethylbenzene	100	30
Cyclooctene	Cyclooctane	100	30
3-Hexyne	—	[c]	0
2-Pentyne	Pentane + 2-Pentenes (65 : 35) [d]	100 [d]	[c]

[a] 0.013 mmol of I or II and 0.75 ml of 1.0 *M* solution of Et_3Al in toluene added. 5.0 ml of unsaturate and 5.0 ml of benzene. 2—3 atm H_2 for 20—30 h. [b] Calculated by NMR by monitoring the disappearance of the olefinic resonances. [c] Reduction not attempted. [d] Estimated by GLC.

tronic differences [9] between these ligands have little effect on this ratio, which is perhaps dominated by their similar steric bulk [9].

Hydrogenation

Both I and II become catalysts for hydrogenation when activated by triethylaluminum. Under mild conditions (2—3 atm., 20°C), I-Et_3Al is extremely active and the reduction of olefins and internal acetylenes is essentially quantitative (Table 3). II-Et_3Al give quantitative reduction of cyclohexene and 1-octene, but lower yields (≈30%) with styrene and cyclooctene, and it is totally inactive for the reduction of internal acetylenes. The activity of II-Et_3Al is similar to that of polymer-bound rhodium(II) species [10].

Experimental

General procedures

All reactions were carried out under pure nitrogen, using freshly distilled dry liquids. ^1H NMR spectra were recorded on a Varian Associates T60 spectrometer. IR spectra were taken with a Perkin—Elmer 457 grating spectrophotometer as thin films. The GLC analysis of the reaction products was carried out on a Varian Aerograph A-700 "Autoprep" Gas Chromatograph, using a 6 ft. column of 10% SE 30 on Chromosorb G, using indan or dodecane as internal standards. Preparative GLC separations were carried out on the same machine using a 20 ft. column of 15% SE 30 on Chromosorb G. The silanes were purchased or prepared according to literature methods [11]. All the unsaturated organic compounds were commercial products, dried over molecular sieves and distilled prior to use, with the exception of 2,3-dimethyl-1,3-butadiene which was prepared by the dehydration of pinacol, by the literature method [12]. The rhodium(II) complexes were synthesized according to the literature methods [4,5]. Microanalyses were performed by Integral Microanalytical Laboratories, Inc. of Raleigh, North Carolina.

Hydrosilylation reactions

These reactions were carried out using the same method. The general procedure will be outlined for the hydrosilylation of 1-octene by triethoxysilane

catalyzed by I. To a mixture of 1-octene (5.7 g, 50 mmol) and triethoxysilane (4.4 g, 27 mmol) in a flask was added I (50 mg, 0.065 mmol). This mixture was heated at 100°C for 8 h. After removal of volatiles under reduced pressure at room temperature vacuum distillation yielded 1-(triethoxysilyl)octane (6.5 g, 87 based on silane), b.p. 100°C/3 mmHg. (Found: C, 61.0; H, 12.0. $C_{14}H_{32}O_3Si$ calcd.: C, 60.8; H, 11.7%). ^{1}H NMR: τ(ppm) 6.27 (6 H, quartet J 7 Hz , Si—O—CH_2—C), 8.71 (12 H, singlet, C—$(CH_2)_6$—C), 8.85 (9 H, triplet, J 7 Hz, Si—O—C—CH_3), 8.87—9.38 (5 H, broad multiplet, CH_3—C and C—CH_2—Si).

Hydrosilylation of 1-hexyne

(a) By triethylsilane. I (50 mg, 0.065 mmol) was added to a solution of 1-hexyne (4.3 g, 52 mmol) and triethylsilane (4.4 g, 38 mmol) and the mixture was heated to 100°C. The oil bath was maintained at that temperature for 8 h. The mixture was cooled and the unreacted volatiles were removed under reduced pressure and the residue was vacuum distilled yielding 1-(triethylsilyl)-1-hexenes (2.7 g, 35% based on silane), b.p. 56°C/0.5 mmHg. (Found: C, 71.9; H, 13.1. $C_{13}H_{26}Si$ calcd.: C, 72.6; H, 13.2%). The distillate was shown by GLC to be a mixture of two isomers in a 55/45 ratio which were separated by preparative GLC using a Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 20′ by 3/8″ column of 15% SE 30 Chromosorb G at 200°C. The major isomer was identified as *cis*-1-(triethylsilyl)-1-hexene from its ^{1}H NMR spectrum: τ(ppm) 3.66 (1 H, overlapping doublet of triplets; J 14 Hz, ^1J 7 Hz, C—CH=C—Si), 4.67 (1 H, doublet, J 14 Hz, C—C—CH—Si), 7.62—8.29 (2 H, broad multiplet, C=C—CH_2—C), 8.29—9.87 (22 H, complex pattern $CH_3CH_2CH_2C$—C=C—Si—CH_2CH_3. The minor component was identified as *trans*-1-(triethylsilyl)-1-hexene from its ^{1}H NMR spectrum: τ(ppm) 3.90 (1 H, doublet of triplets, J 19 Hz, ^1J 6 Hz, C—CH=C—Si; literature values [14] 4.01, J 18.7 Hz, J^1 6 Hz), 4.50 (1 H, doublet, J 19 Hz, C—C=CH—Si; literature values [14] 4.50, J 18.7 Hz), 7.61—8.14 (2 H, broad multiplet, C=C—CH_2—C), 8.14—9.71 (22 H, complex pattern $CH_3CH_2CH_2C$—C=C—Si-CH_2—CH_3).

(b) By dimethylphenylsilane. The reaction between 1-hexyne and dimethylphenylsilane was carried out in a similar fashion yielding 1-(dimethylphenylsilyl)hexenes. b.p. 72°C/0.3 mmHg. The ^{1}H NMR spectrum indicated that the product was a mixture of isomeric 1-(dimethylphenylsilyl)hexenes and no attempt was made to isolate or identify them.

Hydrogenation reactions

These reactions were carried out using the same method. The procedure will be outlined for the hydrogenation of cyclohexene using I-Et_3Al.

I (10 mg, 0.013 mmol) was placed in a pressure bottle fitted with an inlet valve. The bottle was evacuated and filled with nitrogen several times. Cyclohexene (4.0 g, 48 mmol) and benzene (5 ml) were added and the reaction mixture cooled in ice. To the stirred mixture 0.75 ml of a 1.0 M solution of triethylaluminum in toluene was added by syringe. The mixture was stirred at room temperature for 10 min, before being transferred to a Parr hydrogenator, where it was pressurized to 2 atmospheres with hydrogen and allowed to react for 24 h. At the end of the reaction period an aliquot of the reaction mixture

was removed. Its ^1H NMR spectrum showed the complete absence of peaks in the olefinic region, indicating complete hydrogenation of the cyclohexene.

Acknowledgements

We thank Dow Corning Corporation and the University of North Carolina at Greensboro Research Council for their support, the National Science Foundation for the award of an Undergraduate Research Fellowship (JPH) and Matthey Bishop, Inc. for the loan of rhodium salts.

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