Hydrosilylation of acetylenes using a H_2PtCl_6/CO catalytic system; significantly enhanced yields of α-products [1]

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Abstract

The chloroplatinic acid-catalysed hydrosilylations of phenylacetylene, 1-heptyne, and 1-octyne by $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (I), Ph_2MeSiH and $PhMe_2SiH$ have been studied in the presence of CO. The results indicate that the normally high levels of *trans-β* addition products formed in the absence of CO are dramatically reduced in favour of the α-addition products.

Keywords: Silicon; Hydrosilylation; Iron; Cyclopentadienyl; Acetylenes; Carbon monoxide; Chloroplatinic acid

1. Introduction

Hydrosilylation continues to be much studied and reviewed, and the role of transition metal catalysts represents a key aspect of these studies [1,2]. The results of such investigations have revealed that product distributions vary considerably with the nature of the olefin or acetylene, the silane structure, the catalyst, and the specific reaction conditions. The reaction is often not well-behaved, and induction periods and erratic kinetics plague the study of the system. Chloroplatinic acid, H_2PtCl_6, continues to be the most widely-used general catalyst, although many others have specialized properties that make them attractive for specific systems. Recent studies by Lewis et al. [3] have provided considerable evidence for the formation of low valent state Pt colloids that act as the catalytic species in the reactions of H_2PtCl_6.

The addition of silanes to alkynes, e.g. phenylacetylene, using H_2PtCl_6 results in the predominant formation (80–90%) of the *trans-β*-addition products via *cis*-addition, *t*-$R_3SiCH=CHPh$, with minor formation of the α-products $R_3Si(Ph)C=CH_2$ [4]. Few *cis-β*-

products derived from *trans*-addition are observed using this catalytic system [3,4]. The *cis*-addition occurs with retention of configuration at the Si atom [5]. Other catalytic systems, for example those based upon various rhodium complexes, have been shown to result in a considerable amount of *trans*-addition products as well as increased amounts of α-products, thereby illustrating the significant range of reaction products from this simple reaction [6,7].

We recently reported that the reaction between phenylacetylene and the transition metal-substituted silane $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (FpSiPh₂H, I) with chloroplatinic acid as catalyst resulted in significantly greater amounts of the α-addition product than normally found when this catalyst is used (Eq. (1)) [8]:

$$FpSiPh_2H + PhC\equiv CH$$
$$\rightarrow t\text{-}FpSiPh_2CH = CHPh(20\%)$$
$$+ FpSiPh(Ph)C = CH_2(80\%) \qquad (1)$$
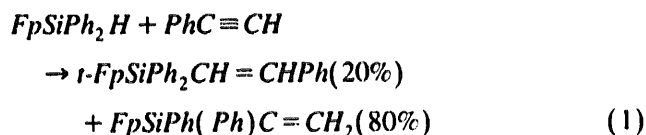
A similar product distribution was observed in the reaction between phenylacetylene and $\{\eta^5\text{-}(HSiPh_2)C_5H_4\}Fe(CO)_2Me$ (II), in which the silyl group was attached to the cyclopentadienyl ring. Therefore it seemed that the presence of a direct Fe–Si bond was not wholly responsible for the distinctive product distribution. Since the reaction was at elevated temperatures, in refluxing toluene, we attributed the result to the

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fortuitous presence of CO resulting from minor decomposition of the Fp complex.

We have further studied this system and now report that the chloroplatinic acid-catalysed hydrosilylations of the aliphatic alkynes 1-heptyne and 1-octyne by I also produce unusually high amounts of α-products and, furthermore, that when the non-metal-substituted silanes Ph_2MeSiH and $PhMe_2SiH$ are used in the same reaction mixture they also provide anomalously high yields of α-products. Identical high yields of α-products are obtained from the reactions of Ph_2MeSiH and $PhMe_2SiH$ with phenylacetylene when chloroplatinic acid is used as catalyst in an atmosphere of CO.

2. Experimental details

The synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_2H$ (FpSiPh$_2$H, I), and the hydrosilylation reaction conditions, product purification and analysis were as previously described [8]. The hydrosilylations in a CO atmosphere were performed as follows. Carbon monoxide was bubbled through a silane–acetylene mixture in toluene for 20 min, the catalyst added, and the mixture refluxed under a CO atmosphere until the reaction was complete. Analysis of the product mixtures was by GC/MS, ^{1}H, and ^{29}Si NMR spectroscopy using literature values for the chemical shifts [4,9,10]. In a typical analytical set up using a Hewlett Packard GC/MS with a column temperature of 173°C, the retention times observed for the α, trans-β and trace amounts of the cis-β products derived from the reaction of $PhMe_2SiH$ and PhC≡CH were 14, 16 and 19.7 min respectively. The fragmentation patterns for the isomeric $Ph_2MeSiC_2H_2Ph$ and $PhMe_2SiC_2H_2Ph$ compounds, which appear to be unpublished, differ as noted below. Their NMR data were in total accord with those reported by Lucevics' group [9a]. From the various analyses it was observed that the hydrosilylation products

represented more than 93% of the total materials; the nature of the other products was not investigated further at this time.

2.1. $Ph_2MeSi(Ph)C = CH_2$

$m/e = 300$ (28%), 285 (14%), 222 (10%), 197 (100%), 105 (40%), 77 (25%).

2.2. t-$Ph_2MeSiCH = CHPh$

$m/e = 300$ (25%), 285 (44%), 222 (38%), 207 (95%), 183 (40%), 105 (100%), 77 (26%).

2.3. $PhMe_2Si(Ph)C = CH_2$

$m/e = 238$ (47%), 223 (58%), 197 (16%), 145 (27%), 135 (100%).

2.4. t-$Ph_2MeSiCH = CHPh$

$m/e = 238$ (58%), 223 (88%), 145 (100%).

2.5. c-$Ph_2MeSiCH = CHPh$

$m/e = 237$ (33%), 135 (100%).

2.6. $FpPh_2Si\text{-}t\text{-}CH = CH(CH_2)_4CH_3$

^{1}H NMR (C_6D_6) 0.8–2.3 (alkyl groups), 4.68 (C_5H_5), 5.95 (d, $J_{CH=CH} = 18.2$ Hz), 6.26 (d, $J_{CH=CH} = 18.2$ Hz) (FpCH=CH), 7.3–7.8 ppm (m, Ph). ^{29}Si NMR (C_6D_6) 36.7 ppm. IR (hexane) ν(CO) = 2010, 1960 cm^{-1}.

2.7. $FpPh_2Si(C_5H_{11})C = CH_2$

^{1}H NMR (C_6D_6) 0.7–1.4, 2.10 (alkyl groups), 4.62 (C_5H_5), 5.57 (d, $J = 2.4$ Hz), 5.91 (d, $J = 2.4$ Hz) (C=CH$_2$), 7.2–7.7 ppm (Ph).

Table 1
Product distribution for the reaction $R_3SiH + R'C≡CH$ [a]

	R_3SiH	$R'C≡CH$	Catalyst	Product $\alpha : t - \beta$
1	FpPh$_2$SiH	R' = Ph	H$_2$PtCl$_6$	80:20
2	FpPh$_2$SiH	R' = C$_5$	H$_2$PtCl$_6$	60:40
3	FpPh$_2$SiH	R' = C$_6$	H$_2$PtCl$_6$	43:57
4	FpPh$_2$SiH + Ph$_2$MeSiH	R' = Ph	H$_2$PtCl$_6$	80:20 / 55:45
5	PhMe$_2$SiH	R' = Ph	H$_2$PtCl$_6$	25:75
6	PhMe$_2$SiH	R' = Ph	H$_2$PtCl$_6$/CO	66:34
7	PhMe$_2$SiH	R' = Ph	H$_2$PtCl$_6$/PPh$_3$	21:79
8	PhMe$_2$SiH	R' = C$_5$	H$_2$PtCl$_6$	12:88
9	PhMe$_2$SiH	R' = C$_5$	H$_2$PtCl$_6$/CO	60:40
10	Ph$_2$MeSiH	R' = Ph	H$_2$PtCl$_6$	18:82
11	Ph$_2$MeSiH	R' = Ph	H$_2$PtCl$_6$/CO	58:42

[a] Only trace amounts of cis-β products were observed.

^{29}Si NMR (C$_6$D$_6$) 29.1 ppm.
IR (hexane) ν(CO) = 2010, 1960 cm^{-1}.

2.8. FpPh$_2$Si-t-CH = CH(CH$_2$)$_5$CH$_3$

^{1}H NMR (C$_6$D$_6$) 0.9–1.4, 2.3 (alkyl groups), 4.60
(C$_5$H$_5$), 6.00 (d, $J_{CH=CH}$ = 17.3 Hz), 6.22 (d, $J_{CH=CH}$
= 17.3 Hz) (FpCH=CH), 7.2–7.8 ppm (m, Ph).
^{29}Si NMR (C$_6$D$_6$) 36.6 ppm.
IR (hexane) ν(CO) = 2003, 1954 cm^{-1}.

2.9. FpPh$_2$Si(C$_6$H$_{13}$C = CH$_2$)

^{1}H NMR (C$_6$D$_6$) 0.9–1.4, 2.26 (alkyl groups), 4.60
(C$_5$H$_5$), 5.65 (d, J = 2.4 Hz), 5.90 (d, J = 2.4 Hz)
(C=CH$_2$), 7.2–7.7 ppm (Ph).
^{29}Si NMR (C$_6$D$_6$) 29.0 ppm
IR (hexane) ν(CO) = 2003, 1954 cm^{-1}.

3. Results and discussion

The chloroplatinic acid-catalysed hydrosilylation of
terminal acetylenes by alkyl/aryl organosilanes nor-
mally yields a product ratio α:trans-β averaging 20:80,
with specific values ranging from 5:95 to 30:70. Either
little or no cis-β products have been observed [4]. Our
observations that the transition metal-substituted silane
FpSiPh$_2$H reacted with phenylacetylene to produce a
ratio of 80:20 was therefore quite unexpected and
warranted further study. We have now investigated the
reaction of I with both 1-heptyne and 1-octyne, and
note that the product ratios are 60:40 and 57:43 re-
spectively, Table 1. While it is clear that these values
are not as striking as those obtained with phenylacety-
lene, they still reveal a preponderance of the α-product,
an unusual situation for reactions involving chloropla-
tinic acid or other platinum-based catalysts [3,4].

We previously suggested that the increase in α-prod-
uct formation was the result of liberation of CO by
minor decomposition of the Fp complexes, which alters
the nature of the active catalyst, rather than arising from
a direct effect of the Fp substituent [8]. If this is the
case, then addition of CO to a typical chloroplatinic
acid organosilane/phenylacetylene reaction mixture
should cause a significant change in the product distri-
bution. We chose the silanes Ph$_2$MeSiH and PhMe$_2$SiH
as model silanes to test this prediction. Their hydrosily-
lation products with phenylacetylene have been spectro-
scopically well-characterized [9], and the silanes are
reported to give α : trans-β ratios of 22:78 and 31:69
respectively [4]. We have repeated these reactions and
obtained similar product distributions and spectroscopic
results. However, as noted from the data in Table 1,
addition of CO to such systems causes a significant

change in the product distribution. Under our experi-
mental conditions the chloroplatinic acid-catalysed reac-
tion between PhMe$_2$SiH and PhC≡CH in the absence
of CO resulted in an α : trans-β product ratio of 25:75,
and that in the presence of CO a corresponding ratio of
66:34. This change is less marked in the case of
Ph$_2$MeSiH, for which the presence of an extra phenyl
group (which normally increases the percentage of
trans-β product) resulted in a product ratio of 60:40.

Since the Fp substituent produces a low field shift in
the ^{29}Si NMR resonance of Si atoms directly bonded to
the Fe atom, around 40 ppm, it could be suggested that
the Fp acts as an electron-withdrawing group [11].
Indeed the related group (η^5-C$_5$H$_5$)Fe(CO) has been
shown to behave in exactly this manner in the iron
silylene systems (η^5-C$_5$H$_5$)Fe(CO)=SiR$_2$ [12]. It has
been established that electron-withdrawing substituents
on Si enhance the formation of α-products in the hy-
drosilylation of terminal acetylenes [1–4]. To confirm
that it was fortuitous that CO gave rise to the large
α-product formation in the reactions of I, we performed
an experiment in which both I and Ph$_2$MeSiH were
treated with phenylacetylene in the same flask in the
presence of H$_2$PtCl$_6$ but with no added CO. If the high
α-product yield from the reaction of I alone was due to
a simple Fp substituent effect, not to CO, then the ratio
of products derived from the non-metal-containing silane
should be equivalent to that observed when using the
chloroplatinic acid catalyst alone. The result, recorded
in Table 1 as experiment 4, is unambiguous, since the
reaction of the Ph$_2$MeSiH component of the reaction
mixture resulted in an α : trans-β product ratio of
55:45 (cf. the normal value of 18:82), confirming our
hypothesis.

The observed increases in the α-product formation
for the simple aryl/alkyl silanes are not as large as
those for the reaction of I with phenylacetylene, and
steric and electronic factors still play a significant role.
However, the increases are significant, and demonstrate
that the nature of the chloroplatinic acid system can be
modified simply by changing the atmosphere in which
the reaction is performed. It is of interest that these
increases in α-product formation in the presence of CO
are in the opposite direction to those observed for the
hydrosilylation of styrene in the presence of the chloro-
platinic acid/triphenylphosphine (or pyridine) catalyst
systems [13]. Capka et al. [13] reported that the reaction
between Cl$_3$SiH or MeCl$_2$SiH and styrene (which gave
both α- and β-products in a ratio approximately 39:59
in the absence of the Lewis base) gave only the β-prod-
uct in the presence of the Lewis base [13]. We per-
formed a single reaction between PhMe$_2$SiH and
PhC≡CH with chloroplatinic acid and PPh$_3$, and the
product ratio indicated a slight increase in β-product
formation (experiment 7, Table 1), paralleling the Capka
result.

The above findings are not in accord with the suggestion that altering the nature of Pt-based catalysts, e.g. chloroplatinic acid, Karstedt catalyst, etc., has little effect on the product distribution [3a]. The question arises as to the precise nature of the chemical transformation caused by the presence of CO in these catalysed reactions. We have no evidence for significant incorporation of CO into any reaction products, such as were observed for reaction of a mixture of silane, CO and olefin in the presence of Co, Ru and Rh carbonyl catalysts. These various silylformylation reactions noted by Seki et al. [14] and by Ojima et al. [15] are usually performed under high pressures of CO, although a single reaction with CO at ambient pressure was reported.

There is always a trace amount of H_2O from $H_2PtCl_6 \cdot 6H_2O$ in the reaction mixtures, and the reaction of CO with $[PtCl_4]^-$ in the presence of water is known to produce inter alia CO_2 and $[PtCl_3CO]^-$. Therefore, it is not surprising that in the hydrosilylations new Pt species could be present to significantly modify the outcome of the catalysis [16]. The role of CO as a reductant is probably important (the transformation $Pt(IV) \rightarrow Pt(II) \rightarrow Pt(0)$ is now known to be important for the operation of chloroplatinic acid), but so also will be its ability to coordinate to low oxidation state forms of Pt, and it is this latter aspect that we are studying further.

Acknowledgements

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