Exclusive Formation of *cis*-PhCH=CH(SiEt$_3$) by Addition of HSiEt$_3$ to PhC≡CH Catalyzed by RuHCl(CO)(P*i*Pr$_3$)$_2$

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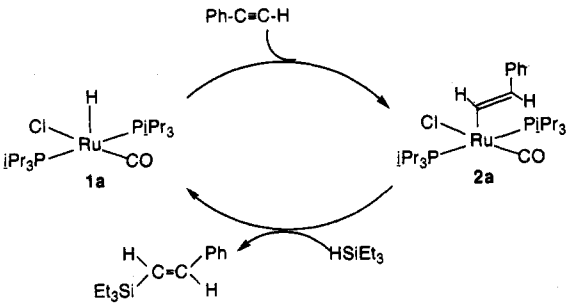
Summary: RuHCl(CO)(PiPr$_3$)$_2$ is found to be very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene. The reaction leads to cis-PhCH=CH(SiEt$_3$) with a selectivity of 100%. Although the vinyl compound Ru((E)-CH=CHPh)Cl(CO)(PiPr$_3$)$_2$ is the main species under hydrosilylation conditions, the catalysis proceeds via the initial interaction of the catalyst with the silane.

Introduction

Vinylsilanes have been shown to be versatile intermediates in organic synthesis.[1] They usually are prepared from olefins by catalytic dehydrogenative silylation[2] or from alkynes by catalytic addition of silanes.[3] Both processes lead to mixtures of *trans*- and *cis*-vinylsilanes. The hydrosilylation of terminal acetylenes generally tends to proceed through cis addition, resulting in trans adducts as main products of the reactions.

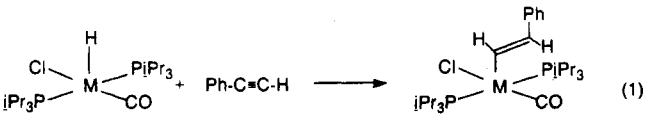
The complexes MHCl(CO)(P*i*Pr$_3$)$_2$ (M = Ru (**1a**), Os (**1b**)) in the presence of NaBH$_4$ or KOH catalyze hydrogen-transfer reactions from 2-propanol to cyclohexanone, acetophenone,[4] benzylideneacetone,[5] and phenylacetylene.[6] Under a hydrogen atmosphere, they are very active homogeneous hydrogenation catalysts for styrene,[4] cyclohexene, cyclohexadienes,[5] phenylacetylene,[7] diphenylacetylene,[8] and benzylideneacetone.[9] Recently, we have observed that **1b** is also an active catalyst for the addition of triethylsilane to phenylacetylene.[10] As a continuation of our work in this field, we now describe the addition of triethylsilane to phenylacetylene catalyzed by **1a**.

Scheme I



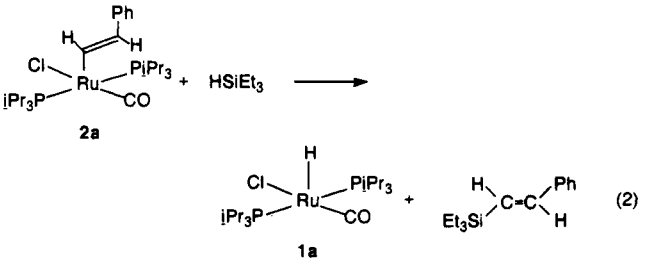
Results and Discussion

It was previously reported that the complexes **1a** and **1b** react with phenylacetylene to give the vinyl derivatives M((*E*)-CH=CHPh)Cl(CO)(P*i*Pr$_3$)$_2$ (M = Ru (**2a**), Os (**2b**))[11] (eq 1).



(1)

We have now found that **2a** reacts with triethylsilane to give **1a** and *trans*-PhCH=CH(SiEt$_3$)[12] (eq 2).



(2)

The chemical transformations collected in eqs 1 (M = Ru) and 2 can be summarized in Scheme I, which shows a stoichiometric addition of triethylsilane to phenylacetylene in the presence of **1a**. The elementary steps involved

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(12) ^{1}H NMR in CDCl$_3$: δ 7.40-7.16 (Ph), 6.82 (dd, PhC*H*=, J_{H-H} = 19.35, 1.00 Hz), 6.34 (dd, =C*H*(SiEt$_3$), J_{H-H} = 19.35, 1.00 Hz), 0.91 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.80 Hz), 0.58 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.80 Hz).

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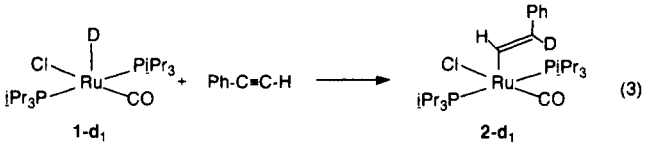
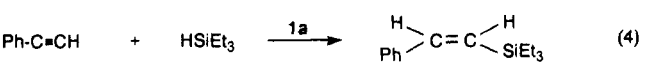
in the reaction shown in eq 1 are too rapid to be observed by spectroscopic methods. In order to obtain more information about the events involved in this process, we carried out the reaction of RuDCl(CO)(P*i*Pr$_3$)$_2$ (**1a**-d_1) with phenylacetylene. Addition of the stoichiometric amount of the alkyne to a benzene-d_6 solution of **1a**-d_1 contained in a NMR tube under argon yields **2a**-d_1 (eq 3).



(3)

The cis stereochemistry of the two substituents D and RuCl(CO)(P*i*Pr$_3$)$_2$, at the C=C bond of **2a**-d_1, suggests that the insertion of the alkyne into the Ru—H bond is a concerted process involving a four-center intermediate.

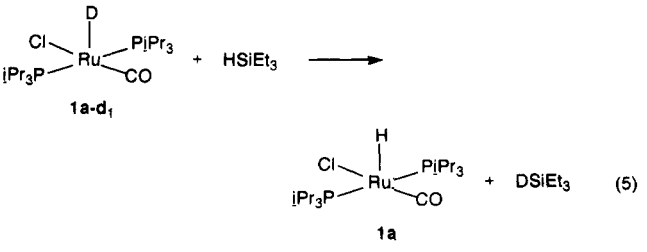
As expected from the chemistry described above, **1a** efficiently catalyzes the addition of triethylsilane to phenylacetylene to give PhCH=CH(SiEt$_3$). However, in contrast with the stoichiometric reaction (eq 2), the unexpected formation of 0.24 M *cis*-PhCH=CH(SiEt$_3$) is observed after 20 min, by treatment of 0.24 M phenylacetylene with 0.24 M triethylsilane in 1,2-dichloroethane and in the presence of 2.4×10^{-3} M **1a** at 60 °C (eq 4).



(4)

^{31}P{^{1}H] MNR spectra of the catalytic solutions show only one signal at 37.70 ppm, assigned to **2a** by comparison of these spectra with that of a pure sample. However, the exclusive formation of *cis*-PhCH=CH(SiEt$_3$) under catalytic conditions indicates that the pathway described in Scheme I does not contribute significantly to the catalytic process, because no formation of *trans*-PhCH=CH(SiEt$_3$) is observed. Therefore, **2a** represents a thermodynamic sink that causes virtually all ruthenium present in solution to be tied up in this form, but it is not an authentic catalytic intermediate.

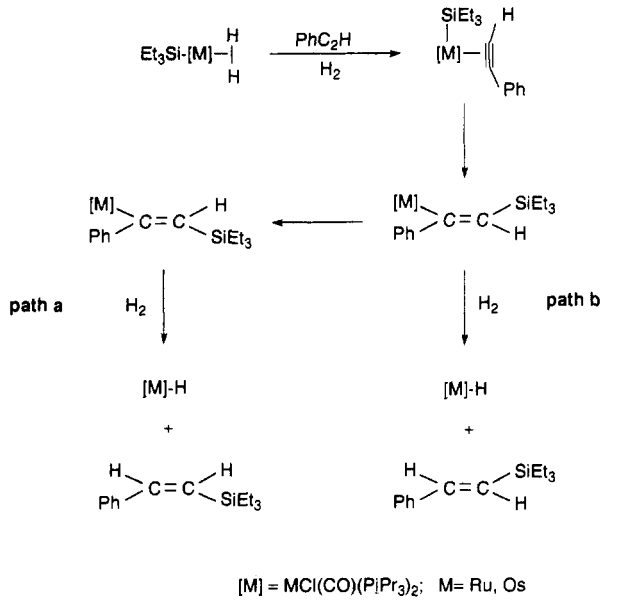
The possible participation of radical-like species as catalytic intermediates can also be rejected. The rate and extent of the reaction shown in eq 4 was unaffected by the presence of hydroquinone. Consequently, the initial interaction of **1a** with triethylsilane must be allowed as a working hypothesis. In order to corroborate this, the reaction of **1a** with triethylsilane was studied by ^{1}H NMR spectroscopy. Addition of the stoichiometric amount of the silane to a toluene solution of **1a** contained in a NMR tube at −60 °C produces the broad signal of the starting complex. However, **1a** was recovered unchanged from the solution. On the other hand, addition of triethylsilane to a benzene-d_6 solution of **1a**-d_1 yields **1a** and DSiEt$_3$ after 10 min (eq 5).



(5)

This seems to confirm that, in fact, the hydrosilylation of phenylacetylene with triethylsilane catalyzed by **1a** proceeds via the initial interaction of the catalyst with the silane, which is consistent with previous observations for the addition of triethylsilane to phenylacetylene catalyzed by **1b** and suggests furthermore that the same mechanism is operating in both cases. For the osmium system, previous experimental data support that the catalysis proceeds via the silyl dihydrogen intermediate Os(SiEt$_3$)Cl(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$, in accord with Scheme II, where the formation of *cis*-PhCH=CH(SiEt$_3$) can be rationalized in terms of a $Z \rightarrow E$ isomerization process between silylvinyl intermediates.[10]

Scheme II



The (*Z*)-vinyl derivatives shown in Scheme II could undergo an isomerization process to give the (*E*)-vinyl isomers (path a), or they could react with molecular hydrogen to give *trans*-PhCH=CH(SiEt$_3$) (path b). The fact that the catalytic solutions of **1a** lead to *cis*-PhCH=CH(SiEt$_3$) with a selectivity of 100% indicates that this system reacts exclusively by path a. Under the conditions described for eq 4, the osmium complex **1b** gives a mixture of *cis*-PhCH=CH(SiEt$_3$) and *trans*-PhCH=CH(SiEt$_3$) in a 7:3 molar ratio, showing that also in this case path a is more favored than path b.

In summary, the complex RuHCl(CO)(P*i*Pr$_3$)$_2$ catalyzes the selective formation of *cis*-PhCH=CH(SiEt$_3$) by addition of triethylsilane to phenylacetylene. Although under hydrosilylation conditions the main species is the vinyl compound Ru((*E*)-CH=CHPh)Cl(CO)(P*i*Pr$_3$)$_2$, the catalysis proceeds via the initial interaction of the catalyst with the silane. It is clear again that the observation of a species in a catalytic system is not evidence of its significance in catalysis.

Experimental Section

Complexes **1a**[13] and **2a**[11] were prepared as described in the literature.

NMR Measurements. ^{1}H NMR spectra were recorded on a Varian UNITY 300 spectrophotometer at 299.949 MHz, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL 200 spectrophotometer at 80.984 MHz; chemical shifts are expressed in parts per million upfield from Si(CH$_3$)$_4$ (^{1}H) and 85% phosphoric acid (^{31}P) as external references. Samples for recording the ^{31}P{^{1}H} NMR spectra were prepared in 5-mm-diameter tubes under the same conditions employed for the catalytic reactions. These

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samples were then introduced into 1-cm-diameter tubes containing $CDCl_3$.

Hydrosilylation of Phenylacetylene. The hydrosilylation reaction was carried out in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. In a typical procedure 4 mL of a 4.8×10^{-3} M solution of $RuHCl(CO)(PiPr_3)_2$ in 1,2-dichloroethane were added to another 1,2-dichloroethane solution (4 mL) containing 0.48 M $HSiEt_3$, 0.48 M PhC_2H, and C_6H_{12}. The flask was then immersed in a bath at 60 °C, and the reaction mixture was magnetically stirred. The reaction was followed by measuring the silane consumption as a function of time using C_6H_{12} as the internal standard with a 15% β,β'-oxodipropionitrile on Chromosorb W-HP 80/100-mesh column at 40 °C on a Perkin-Elmer 8500 gas chromatograph with a flame ionization detector. The analysis of the reaction product was carried out by using a FFAP on Chromosorb GHP 80/100-mesh column at 175 °C. *cis*-$PhCH{=}CH(SiEt_3)$ was isolated by column chromatography (Al_2O_3; hexane) and was characterized by ^1H NMR in $CDCl_3$: δ 7.45 (d, $PhCH{=}$, J_{H-H} = 15.10 Hz), 7.36–6.94 (Ph), 5.57 (d, ${=}CH(SiEt_3)$, J_{H-H} = 15.10 Hz), 0.86 (t, $SiCH_2CH_3$, J_{H-H} = 7.60 Hz), 0.58 (q, $SiCH_2CH_3$, J_{H-H} = 7.60 Hz).

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