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Hydrosilylation of phenylacetylene catalyzed by [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]

Miguel A. Esteruelas *, Montserrat Oliván, Luis A. Oro, José I. Tolosa

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

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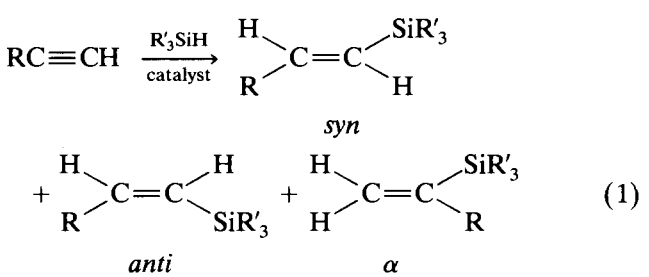
Abstract

In the presence of the complexes [Ir(diolefin)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$NMe$_2$)][BF$_4$] (diolefin = 1,5-cyclooctadiene (COD) (**1**) or tetrafluorobenzobarrelene (TFB) (**2**)) and [Ir(diolefin)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] (diolefin = COD (**3**) or TFB (**4**)), phenylacetylene undergoes reaction with triethylsilane. In all experiments carried out PhCH=CH$_2$, PhC≡CSiEt$_3$, *cis*-PhCH=CH(SiEt$_3$), *trans*-PhCH=CH(SiEt$_3$) and Ph(SiEt$_3$)C=CH$_2$ were obtained. An investigation in detail for the catalyst **3** suggests that, under catalytic conditions, the complexes [IrH(C$_2$Ph)(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**5**) and [IrH(SiEt$_3$)(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (**6**) are formed. Complex **5** is the key intermediate for the formation of PhC≡CSiEt$_3$, while **6** is the species leading to *cis*-PhCH=CH(SiEt$_3$). The isomer *trans*-PhCH=CH(SiEt$_3$) is formed by isomerization of *cis*-PhCH=CH(SiEt$_3$). The mechanisms of formation of these compounds are discussed.

Keywords: Iridium; Hydrosilation; Acetylenes; Catalysis; Mechanism

1. Introduction

Hydrosilylation of carbon–carbon multiple bonds is one of the most important laboratory and industrial methods of forming silicon–carbon bonds. In the hydrosilylation of terminal alkynes, both the normal *syn* and the unusual *anti* addition products are formed, as well as the α isomer [1]:



The formation of the *anti* addition product is interesting because the *cis* isomer is a result of the *trans* addition of the silane to the alkyne. From a mechanistic point of view, it has been proposed that the *anti* addition product is formed when the reaction involves the intervention of radical-like species as an intermediate or transition state [2]. Non-radical pathways have been also reported. Dickers et al. [3] have found a *trans*-to-*cis* isomerization in the addition of triethylsilane to 1-hexyne catalyzed by [RhCl(PPh$_3$)$_3$]. Brady and Nile [4] have reported that, in the presence of some phosphine–rhodium(I) complexes, the hydrosilylation of 1-pentyne with triethylsilane affords the *cis* product as the major species. They proposed a mechanism involving the initial insertion of the alkyne into the Rh-H bond of a Et$_3$Si–Rh–H intermediate to give Et$_3$Si–Rh((*E*)-CH=CHR) species, which isomerizes to Et$_3$Si–Rh((*Z*)-CH=CHR) via a zwitterionic carbene complex. Subsequently, the reductive elimination of the *anti* addition product regenerates the catalyst.

In 1990, Ojima et al. [5] found that the addition of triethylsilane to 1-hexyne gives *cis*-1-(triethylsilyl)-1-hexene (major), *trans*-1-(triethylsilyl)-1-hexene (minor) and 2-(triethylsilyl)-1-hexene (minor) as reaction products. The proposed mechanism for the formation of the *anti* addition product includes the insertion of the alkyne into the silicon–rhodium bond in the first place to form a (*Z*)-1-silyl-1-alkene-2-yl–Rh intermediate,

* Corresponding author.

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instead of the previously proposed insertion into the Rh–H bond. Thus this intermediate undergoes isomerization to the sterically more favoured (*E*)-1-silyl-alkene-2-yl–Rh complex, via a zwitterionic carbene compound, which is somewhat similar to the mechanism proposed by Brady and Nile.

In our previous work on the addition of triethylsilane to phenylacetylene catalyzed by the complexes $[MHCl(CO)(P^iPr_3)_2]$ (M ≡ Ru [6] or Os [7]), we have also found predominant *anti* addition of the silane to the alkyne. On the basis of spectroscopic studies we proposed that the formation of *cis*-PhCH=CH($SiEt_3$) involves the insertion of the phenylacetylene into the M–Si bond of the intermediates $[M(SiEt_3)Cl(CO)(P^iPr_3)_2]$ (M ≡ Ru or Os) followed by the isomerization of the resulting (*Z*)-silylvinyl derivatives to the *E* isomers, in line with the Ojima et al. proposal.

Jun and Crabtree [8] have examined the hydrosilylation of terminal alkynes in the presence of the complex $[IrH(H_2O)(bq)(PPh_3)_2][SbF_6]$ (bq ≡ 7,8-benzoquinolinato). These reactions, in contrast with those catalyzed by $[MHCl(CO)(P^iPr_3)_2]$ (M ≡ Ru or Os), furthermore lead to $RC{\equiv}CSiR'_3$ according to

$$2RC{\equiv}CH + R'_3SiH \xrightarrow{\text{catalyst}} RC{\equiv}CSiR'_3 + RCH{=}CH_2 \quad (2)$$

Similar results have been obtained by us from the addition of triethylsilane to phenylacetylene catalyzed by silyl-dihydrido compounds of the type $[IrH_2(SiEt_3)(TFB)(PR_3)]$ (TFB ≡ tetrafluorobenzobarrelene; PR_3 ≡ PPh_3, PCy_3 or P^iPr_3) [9].

Jun and Crabtree have suggested that, once the (*E*)-silylvinyl intermediate has been formed, β-elimination of the *endo*-hydrogen atom of the silylvinyl group could lead to the silylation product. However, the participation of alkynyl intermediates cannot be excluded. Recent studies have shown that the reactions of some hydrido complexes with terminal alkynes afford alkynyl derivatives [10].

Recently, we reported the synthesis of the cationic compound $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$ (COD ≡ 1,5-cyclooctadiene) [11]. This complex was found to be a very active and highly selective catalyst for the hydrogenation of phenylacetylene to styrene. Kinetic and spectroscopic investigations indicate that the hydrido alkynyl complex $[IrH(C_2Ph)(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$ is the main species under catalytic conditions. In order to investigate the role played by the alkynyl compounds during the hydrosilylation of terminal alkynes, we have now studied the addition of triethylsilane to phenylacetylene in the presence of $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$. The present paper reports the results obtained in this study.

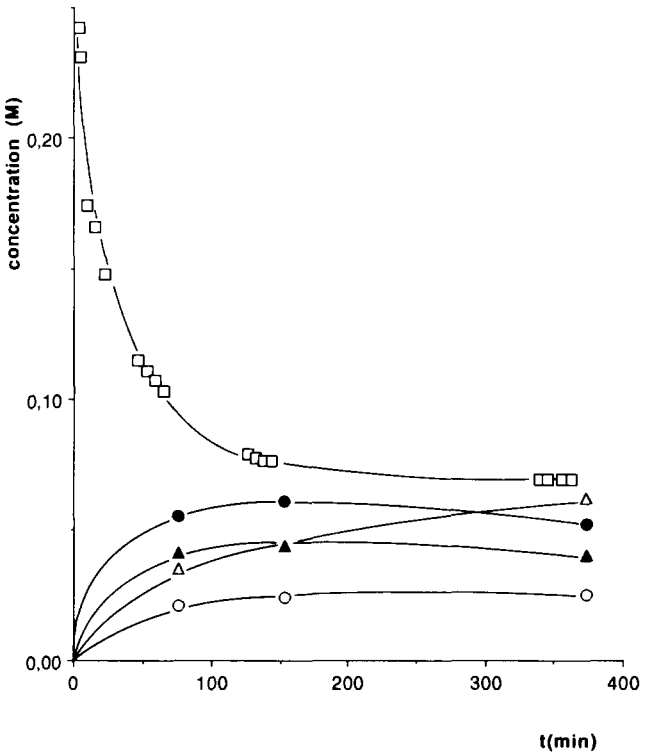


Fig. 1. Plot of the hydrosilylation of phenylacetylene catalysed by $[Ir(TFB)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$ as a function of time; initial concentration, of $HSiEt_3$ and PhC≡CH, 0.24 M (1,2-dichloroethane at 60°C; 2.4×10^{-3} M $[Ir(TFB)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$): □, $HSiEt_3$; ●, *cis*-PhCH=CH($SiEt_3$); ▲, $PhC{\equiv}CSiEt_3$; △, *trans*-PhCH=CH($SiEt_3$); ○, $Ph(SiEt_3)C{=}CH_2$.

2. Results and discussion

The complexes $[Ir(diolefin)(\eta^2\text{-}^iPr_2PCH_2CH_2NMe_2)][BF_4]$ (diolefin ≡ COD (**1**) or TFB (**2**)) and

Table 1
Hydrosilylation of phenylacetylene [a]

Catalyst	*t* (h)	Products (M)				
		$PhCH{=}CH_2$	$PhC{\equiv}CSiEt_3$	$Ph(SiEt_3)C{=}CH_2$	*cis*-PhCH=CH($SiEt_3$)	*trans*-PhCH=CH($SiEt_3$)
1	24	0.017	0.018	0.013	0.053	0.045
2	21	0.015	0.015	0.010	0.046	0.029
3	5.6	0.045	0.046	0.019	0.060	0.046
4	6	0.035	0.037	0.022	0.051	0.060

[a] [Catalyst] = 2.4×10^{-3} M; [PhC≡CH] = [$HSiEt_3$] = 0.24 M. C_6H_{12} (0.125 M) is used as the internal standard.

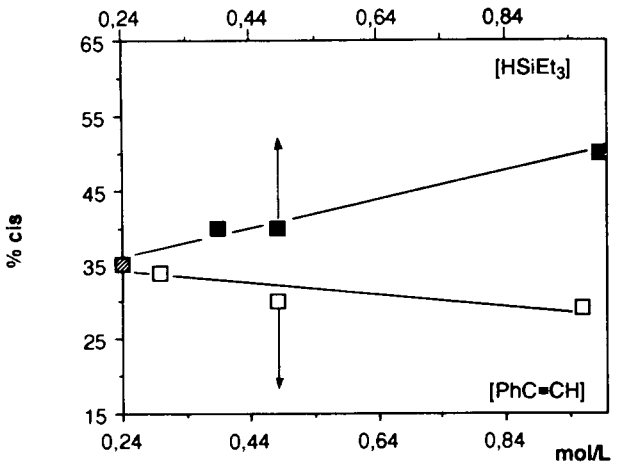


Fig. 2. *cis*-PhCH=CH(SiEt$_3$) (■) as a function of the initial concentration of HSiEt$_3$ (1,2-dichloroethane at 60°C; 0.24 M PhC≡CH; 2.4×10^{-3} M [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]; [prod]$_{tot}$ = 0.17 M), and *cis*-PhCH=CH(SiEt$_3$) ratio (□) as a function of the initial concentration of PhC≡CH (1,2-dichloroethane at 60°C; 0.24 M HSiEt$_3$; 2.4×10^{-3} M [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]; [prod]$_{tot}$ = 0.17 M).

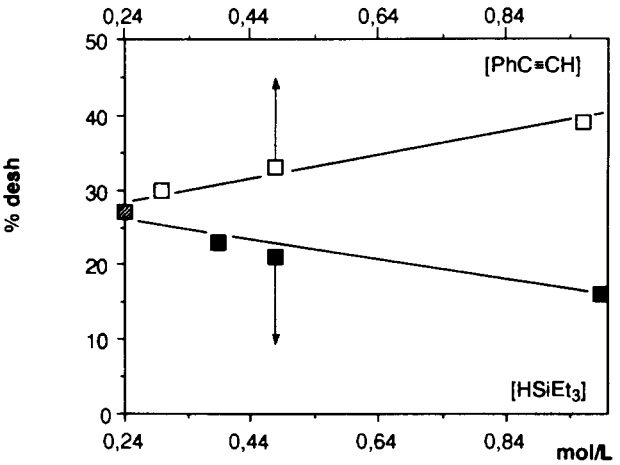


Fig. 3. PhC≡CSiEt$_3$ ratio (■) as a function of the initial concentration of HSiEt$_3$ (1,2-dichloroethane at 60°C; 0.24 M PhC≡CH; 2.4×10^{-3} M [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] [prod]$_{tot}$ = 0.17 M), and PhC≡CSiEt$_3$ ratio (□) as a function of the initial concentration of PhC≡CH (1,2-dichloroethane at 60°C; 0.24 M HSiEt$_3$; 2.4×10^{-3} M [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]; [prod]$_{tot}$ = 0.17 M).

[Ir(diolefin)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] (diolefin ≡ COD (**3**) or TFB (**4**)) efficiently catalyze the hydrosilylation of phenylacetylene with triethylsilane. Fig. 1 summarizes the course of a typical reaction with [Ir(TFB)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] as catalyst.

The reactions were performed in 1,2-dichloroethane solutions at 60°C, under argon at 1 atm pressure. The results are listed in Table 1. In all experiments, PhCH=CH$_2$, PhC≡CSiEt$_3$, *trans*-PhCH=CH(SiEt$_3$), *cis*-PhCH=CH(SiEt$_3$) and Ph(SiEt$_3$)C=CH$_2$ were obtained. The amount of PhCH=CH$_2$ formed was very similar to that of PhC≡CSiEt$_3$. This may be rationalized in terms of a dehydrogenative silylation (Eqn. (2); R ≡ Ph; R′ ≡ Et), together with a normal hydrosilylation (Eqn. (1); R ≡ Ph; R′ ≡ Et).

Complexes **3** and **4**, which contain the ether–phosphine ligand, are more efficient catalysts than are **1** and **2**. Similar results were obtained for the hydrogenation of phenylacetylene and olefins [11].

In order to obtain information about the mechanism of these hydrosilylation reactions, a detailed study was carried out for the reaction catalyzed by **3**. In addition, the reactivity of **3** towards phenylacetylene and triethylsilane was investigated by NMR spectroscopy.

2.1. Hydrosilylation of phenylacetylene catalyzed by [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$

The rate and extent of the reaction are unaffected by the presence of hydroquinone, suggesting that participation of radical-like species as catalytic intermediates is not significant. Hydrosilylation runs were performed at different concentrations of phenylacetylene and triethylsilane.

Table 2 and Figs. 2–4 show the dependence of the relative amounts of the reaction products on the concentration of phenylacetylene and triethylsilane, when 0.17 M of reaction products were formed. As seen from Fig. 2, the relative amount of *cis*-PhCH=CH-

Table 2
Hydrosilylation of phenylacetylene catalyzed by [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] [a]

[PhC≡CH] (M)	[HSiEt$_3$] (M)	Products ratio [b] (%)			
		PhC≡CSiEt$_3$	Ph(SiEt$_3$)C=CH$_2$	*cis*-PhHC=CH(SiEt$_3$)	*trans*-PhHC=CH(SiEt$_3$)
0.24 [c]	0.24	27	11	35	27
0.24	0.39	23	11	40	26
0.24	0.48	21	12	40	27
0.24	0.99	16	8	50	26
0.30	0.24	30	12	34	24
0.48	0.24	33	12	30	25
0.96	0.24	39	8	29	24

[a] [[Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]] = 2.4×10^{-3} M; temperature, 60°C.
[b] Total concentration of silylated products was 0.17 M; concentration of PhCH=CH$_2$ was very similar to that of PhC≡CSiEt$_3$.
[c] In the presence of hydroquinone, similar results were obtained.

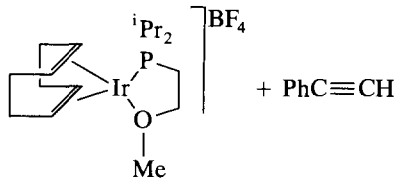
($SiEt_3$) rises as the triethylsilane concentration increases and decreases on increasing the phenylacetylene concentration. Contrary to this behaviour, the relative amount of $PhC{\equiv}CSiEt_3$ rises as the phenylacetylene concentration increases and decreases on increasing the triethylsilane concentration (Fig. 3). It can be clearly seen from Fig. 4 that the amount of *trans*-$PhCH{=}CH(SiEt_3)$ formed is independent of the concentrations of phenylacetylene and triethylsilane. This suggests that the *syn* addition product does not result from the direct addition of the silane to the alkyne.

If the *syn* addition product is not a direct consequence of hydrosilylation, its presence in the reaction mixture may be rationalized in terms of the isomerization of *cis*-$PhCH{=}CH(SiEt_3)$. In order to prove this, we have studied the behaviour of a 1,2-dichloroethane solution of *cis*-$PhCH{=}CH(SiEt_3)$ at 60°C, in the presence of **3**. Under these conditions, the treatment of a 0.12 M solution of *cis*-$PhCH{=}CH(SiEt_3)$ with 2.4×10^{-3} M of catalyst does not produce some change in the mixture composition. However, the addition of 1.2×10^{-2} M of triethylsilane gives *trans*-$PhCH{=}CH(SiEt_3)$ (Fig. 5).

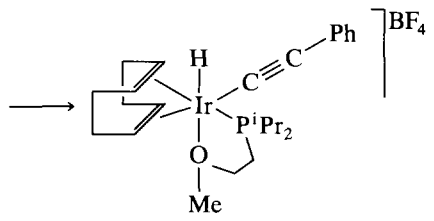
A small amount of the α isomer, $Ph(SiEt_3)C{=}CH_2$, was obtained. Consequently, its variation with the concentrations of phenylacetylene and triethylsilane could not be studied.

2.2. Reactivity of $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$ towards phenylacetylene and triethylsilane

Complex **3** reacts with phenylacetylene to give the hydridoalkynyl derivative $[IrH(C_2Ph)(COD)(\eta^2\text{-}^iPr_2P\text{-}CH_2CH_2OMe)][BF_4]$ (**5**):



3

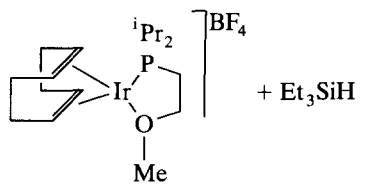


(3)

5

This is characterized, in the ^1H NMR spectrum, by a doublet at −23.34 ppm with a P–H coupling constant of 9.6 Hz, and in the $^{31}P\{^1H\}$ NMR spectrum by a singlet at 42.6 ppm [11].

Similarly to the reaction of **3** with phenylacetylene, the addition of a stoichiometric amount of triethylsilane to an NMR tube containing a chloroform-d_1 solution of **3** affords the hydridotriethylsilyl complex **6**:



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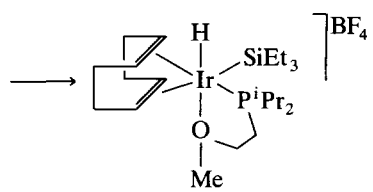


(4)

6

The ^1H NMR spectrum of this compound shows a doublet at −21.80 ppm with a P–H coupling constant of 7.6 Hz, and the $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 40.5 ppm.

The reaction of **3** with a 1:1 mixture of phenylacetylene–triethylsilane affords **5** together with traces of **6**. This suggests that, under catalytic conditions, **5** is the main species. In fact, the $^{31}P\{^1H\}$ NMR spectra of the solutions recorded during the catalysis show only one signal, at 42.6 ppm.

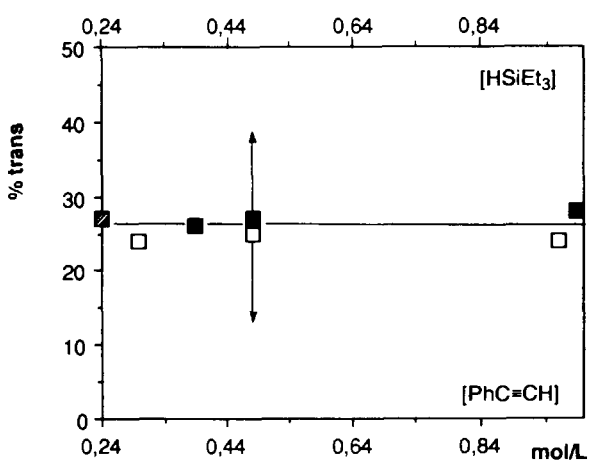


Fig. 4. *trans*-$PhCH{=}CH(SiEt_3)$ ratio (■) as a function of the initial concentration of $HSiEt_3$ (1,2-dichloroethane at 60°C; 0.24 M $PhC{\equiv}CH$; 2.4×10^{-3} M $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$; $[prod]_{tot} = 0.17$ M), and *trans*-$PhCH{=}CH(SiEt_3)$ ratio (□) as a function of the initial concentration of $PhC{\equiv}CH$ (1,2-dichloroethane at 60°C; 0.24 M $HSiEt_3$; 2.4×10^{-3} M $[Ir(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)][BF_4]$; $[prod]_{tot} = 0.17$ M).

2.3. Mechanism of the hydrosilylation

From the results of the spectroscopic studies, we conclude that, although the hydridoalkynyl **5** is the

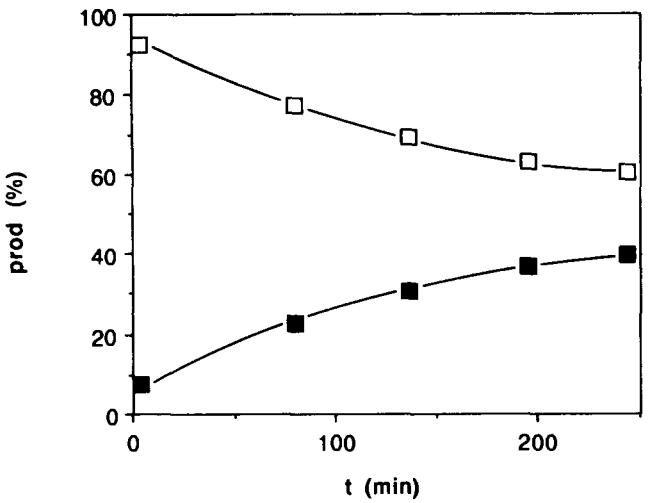
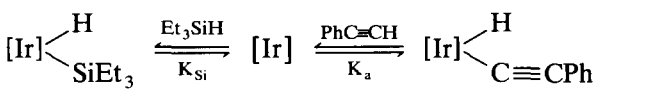


Fig. 5. Plot of the isomerization of *cis*-PhCH=CH(SiEt$_3$) (□) to *trans*-PhCH=CH(SiEt$_3$) (■) catalysed by [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] in 1,2-dichloroethane at 60°C (0.12 M *cis*-PhCH=CH(SiEt$_3$); 2.4×10^{-3} M [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]; 1.2×10^{-2} M HSiEt$_3$).

main species under catalytic conditions, the hydridosilyl **6** can also be formed, but in undetectable amounts. Under catalytic conditions the following equilibrium is reached, where $K_a \geq K_{Si}$:



6 **3** **5**

(5)

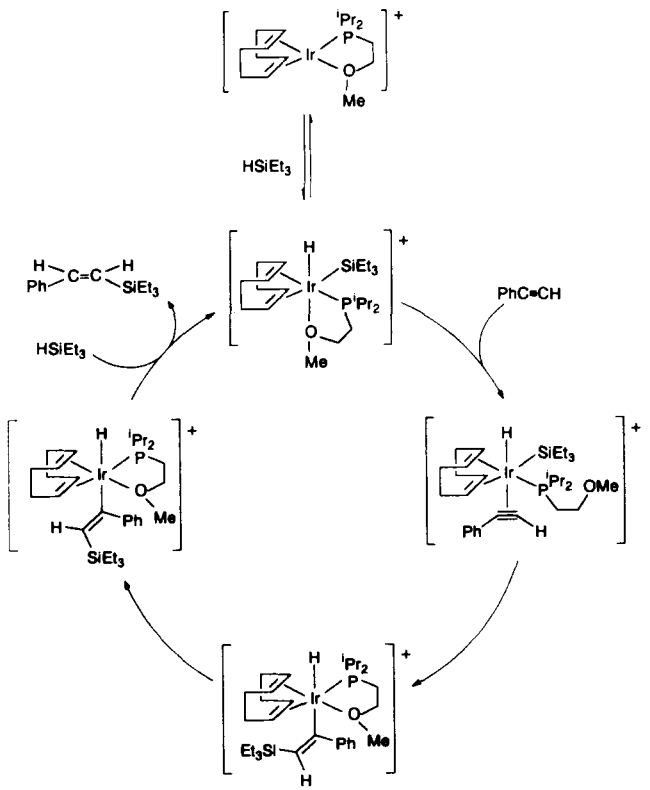
According to Eqn. (5), the concentration of the intermediate **5** must increase on increasing the phenylacetylene concentration, while it must decrease when the triethylsilane concentration increases. In contrast with **5**, the concentration of **6** must increase on decreasing the phenylacetylene concentration and must decrease when the triethylsilane concentration decreases. The dependences of the relative amounts of PhC≡CSiEt$_3$ and *cis*-PhCH=CH(SiEt$_3$) on the concentrations of phenylacetylene and triethylsilane respectively show the same trend (Figs. 2 and 3). This suggests that **5** is the key intermediate for the formation of PhC≡CSiEt$_3$, and **6** for the formation of *cis*-PhCH=CH(SiEt$_3$).

Scheme 1 shows a tentative reaction scheme for the formation of the dehydrogenative silylation product catalyzed by **3**. As **5** is coordinatively saturated, one plausible sequence of elementary steps would involve the initial dissociation of the OMe group of the ether–phosphine ligand to give a 16 e$^-$ hydridoalkynyl derivative [12] which, by oxidative addition of triethylsilane and subsequent reductive elimination of PhC≡CSiEt$_3$, could yield the dihydride [IrH$_2$(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$]. This dihydrido complex should hydrogenate phenylacetylene to styrene.

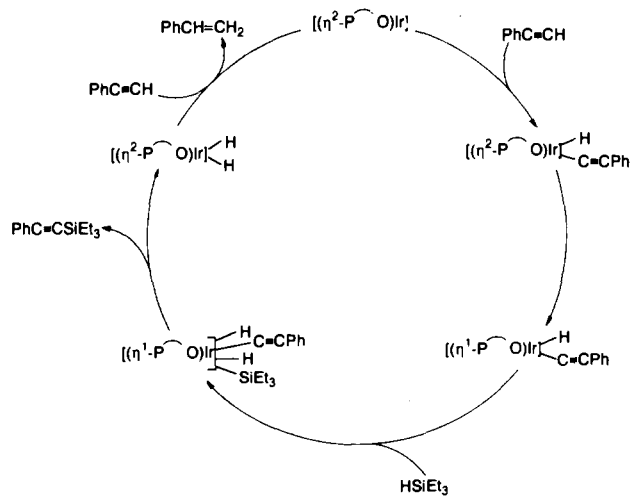
The formation of the dehydrogenative silylation product during the hydrosilylation of terminal alkynes has been previously observed [8,9,13]. In general, it is strongly favoured by increasing the alkyne-to-silane ratio. Jun and Crabtree [8] have argued that the formation of RC≡CSiR'$_3$ requires a hydrogen acceptor to remove the hydrogen formed, and so having a high concentration of alkyne is favourable. In our case, this argument is not valid. Certainly, the formation of the dehydrogenative silylation product requires a hydrogen acceptor. Furthermore, the dihydride [IrH$_2$(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] hydrogenates phenylacetylene to styrene. However, it is also true that the hydrogenation rate is independent of the phenylacetylene concentration [11]. Thus, in our case the higher concentrations of phenylacetylene favour the formation of PhC≡CSiEt$_3$, because under these conditions the intermediate **5** is favoured.

The isomer *cis*-PhCH=CH(SiEt$_3$) is formed by an *anti* addition of the Si–H bond of the silane to the C≡C bond of the alkyne. The *trans* addition of silanes to alkynes has been previously observed [14]. There is considerable agreement about how this process takes place. According to the proposal of Ojima et al., the reaction involves the initial insertion of the alkyne into the M–Si bond. On this base, Scheme 2 is a tentative reaction scheme for the formation of *cis*-PhCH=CH(SiEt$_3$) in the presence of **6**.

The formation of *cis*-PhCH=CH(SiEt$_3$) instead of



Scheme 1.



[(η²-P O)Ir] = [Ir(COD)(η²-ⁱPr₂PCH₂CH₂OMe)]⁺

Scheme 2.

trans-PhCH=CH($SiEt_3$) merits further comment. If the alkyne enters the coordination sphere of the iridium by displacing the –OMe group, the alkyne would then be *cis* to the silyl group but *trans* to the hydrido ligand. Hence, if the silyl group migrates to the alkyne, and the stereochemistry around the iridium atom does not change further, the resulting hydridosilylvinyl intermediate would have *trans* stereochemistry. This *trans* coordination would not facilitate the reductive elimination of *trans*-PhCH=CH($SiEt_3$) in the next step. Hence, the isomerization from the (*Z*)-silylvinyl intermediate into (*E*)-silylvinyl could occur, probably via a zwitterionic intermediate.

As has been previously mentioned, *trans*-PhCH=CH($SiEt_3$) seems to be formed by isomerization of *cis*-PhCH=CH($SiEt_3$). The independence of the relative amount of *trans*-PhCH=CH($SiEt_3$) of the concentrations of triethylsilane and phenylacetylene suggests that both **5** and **6** are catalyst precursors of the isomerization process. The catalytic species generated from **5** most probably also contains a silyl group. Thus, it has been observed that **5** only catalyzes the *cis–trans* isomerization in the presence of small amount of silane (about 10^{-2} M).

3. Conclusion

This study has revealed that the cationic complexes [Ir(diolefin)(η²-$^i Pr_2PCH_2CH_2NMe_2$)][BF_4] (diolefin ≡ COD, or TFB) and [Ir(diolefin)(η²-$^i Pr_2PCH_2CH_2$-OMe)][BF_4] (diolefin ≡ COD, or TFB) catalyze the reaction of phenylacetylene with triethylsilane to give $PhCH=CH_2$, $PhC{\equiv}CSiEt_3$, *cis*-PhCH=CH($SiEt_3$), *trans*-PhCH=CH($SiEt_3$) and $Ph(SiEt_3)C{=}CH_2$. Under catalytic conditions both hydridoalkynyl and hydridosilyl intermediates are formed. Hydridoalkynyl species are the key intermediates for the formation of $PhC{\equiv}CSiEt_3$, while, hydridosilyl species are the key intermediates for the formation of *cis*-PhCH=CH-($SiEt_3$). The *trans*-PhCH=CH($SiEt_3$) isomer is formed by isomerization of *cis*-PhCH=CH($SiEt_3$).

4. Experimental section

4.1. General considerations

All manipulations were conducted with rigorous exclusion of air. Solvents were dried by known procedures and distilled under argon prior to use. Phenylacetylene (Merck) was purified by distillation, and triethylsilane (Fluka) was used without further purification. Complexes **1–4** were prepared as described in the literature [11]. *cis*-PhCH=CH($SiEt_3$) was prepared by a published method [6].

4.2. NMR measurements

NMR spectra were recorded on a Varian 200 XL or Varian Unity 300 spectrophotometer. Chemical shifts are expressed in parts per million upfield from Me_4Si (^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants are given in hertz.

4.3. Hydrosilylation of phenylacetylene

The hydrosilylation reaction was carried out in a double-necked flask 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. The complexes were dissolved in a 1,2-dichloroethane solution (8 ml) containing $HSiEt_3$, $PhC{\equiv}CH$ 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 products was carried out using an FFAP on Chromosorb GHP 80/100-mesh column at 175°C. Silicon-containing products were isolated by column chromatography (silica gel, 70-230 mesh; hexane) and characterized by ^1H NMR spectroscopy. ^1H NMR spectra of the Si-containing products in $CDCl_3$: *cis*-PhCH=CH($SiEt_3$), 7.49 (d, PhC*H*=, J_{H-H} = 15.4 Hz), 7.38–7.29 (Ph), 5.8 (d, =C*H*($SiEt_3$), J_{H-H} = 15.4 Hz), 0.86 (t, $SiCH_2CH_3$, J_{H-H} = 7.6 Hz), 0.58 (q, $SiCH_2CH_3$, J_{H-H} = 7.6 Hz); *trans*-PhCH=CH($SiEt_3$), 7.38–7.29 (Ph), 6.93 (d, PhC*H*=,

J_{H-H} = 19.0 Hz), 6.46 (d, =C*H*(SiEt$_3$), J_{H-H} = 19 Hz), 0.91 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.8 Hz), 0.58 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.8 Hz); Ph(SiEt$_3$)C=CH$_2$, 7.38–7.29 (Ph), 5.90 (d, one H of =CH$_2$, J_{H-H} = 3.2 Hz), 5.60 (d, one H of =CH$_2$, J_{H-H} = 3.2 Hz), 0.98 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.8 Hz), 0.75 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.8 Hz); PhC≡CSiEt$_3$, 7.38–7.29 (Ph), 1.10 (t, SiCH$_2$C*H*$_3$, J_{H-H} = 7.7 Hz), 0.75 (q, SiC*H*$_2$CH$_3$, J_{H-H} = 7.7 Hz).

In the presence of hydroquinone, the procedure was as follows: to a solution of [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] (10.80 mg, 0.019 mmol) and hydroquinone (8.46 mg, 0.076 mmol) in 4 ml of 1,2-dichloroethane was added a 1,2-dichloroethane solution (4 ml) containing HSiEt$_3$, PhC≡CH and C$_6$H$_{12}$. The flask was then immersed in a bath at 60°C, and the reaction mixture was magnetically stirred.

4.4. Isomerization of cis-PhCH=CH(SiEt$_3$)

The complex [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] (10.80 mg, 0.019 mmol) was dissolved in a 1,2-dichloroethane solution (8 ml) containing *cis*-PhCH=CH(SiEt$_3$) (209.30 mg, 0.12 M). The flask was then immersed in a bath at 60°C, and the reaction mixture was magnetically stirred. After 5 h, no isomerization was observed, and then triethylsilane was added (15.3 μl, 0.096 mmol). The isomerization reaction was followed using an FFAP on Chromosorb GHP 80/100-mesh column at 175°C.

4.5. Reaction of [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ with HSiEt$_3$

To a 5 mm NMR tube containing a CDCl$_3$ solution (1 ml) or [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]BF$_4$ (29.2 mg, 0.052 mmol) was added triethylsilane (8.5 μl, 0.052 mmol). After 1 h, the ^{1}H NMR spectrum shows, in the hydrido region, only one doublet at −21.80 ppm (J_{P-H} = 7.6 Hz). The ^{31}P{^{1}H} NMR spectrum contains a singlet at 40.5 ppm.

4.6. Reaction of [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)]-[BF$_4$] with a 1:1 mixture of PhC≡CH and HSiEt$_3$

To a 5 mm NMR tube containing a CDCl$_3$ solution (1 ml) of [Ir(COD)(η^2-^{i}Pr$_2$PCH$_2$CH$_2$OMe)][BF$_4$] (32.6 mg, 0.058 mmol) were added triethylsilane (25.4 μl, 0.23 mmol) and phenylacetylene (36.9 μl, 0.23 mmol). After 1 h, the ^{1}H NMR spectrum shows, in the hydrido region, a major doublet at δ = −23.34 ppm (J_{P-H} = 9.6 Hz) and a minor doublet at δ = −21.80 ppm (J_{P-H} = 7.6 Hz). The ^{31}P{^{1}H} NMR spectrum contains two singlets at 42.6 (major) and 40.5 ppm (minor).

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