Stereoselective Hydrosilylation of Terminal Alkynes Catalyzed by $[Cp^*IrCl_2]_2$: A Computational and Experimental Study

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The hydrosilylation of terminal alkynes is catalyzed by $[Cp^*IrCl_2]_2$ to afford selectively the β-(*Z*)-vinylsilanes in high yields. A catalytic cycle based on an Ir(III)−Ir(V) redox process is proposed.

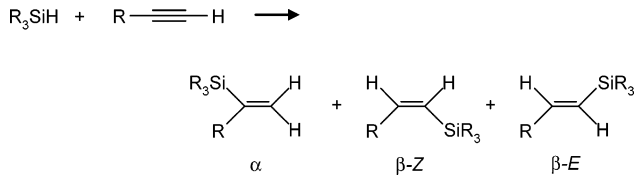
Introduction

Transition metal-catalyzed hydrosilylation of alkynes remains an area of intense research interest, as it provides a simple and direct means of producing vinylsilanes, which are widely used intermediates in organic synthesis.[1] With terminal alkynes, there are three possible products (Scheme 1).[2]

The thermodynamically more stable β-(*E*) vinylsilane is usually formed as the major product in most of the transition metal-catalyzed reactions. The most active and widely used catalysts for the selective formation of β-(*E*) vinylsilanes are platinum-based.[3] The selective formation of the β-(*Z*) vinylsilane is regarded as much more challenging, and it has considerable utility to synthetic organic chemistry.[4] Rhodium catalysts have been reported for the selective formation of both *E*- and *Z*-vinylsilanes.[5,6] High selectivity for β-(*Z*)-vinylsilanes has also been reported with ruthenium[4,7] and iridium catalysts.[8]

One of the most interesting catalysts is $[Cp^*RhCl_2]_2$, **1a**, which was reported to afford very high stereoselectivity for the β-(*Z*) vinylsilanes in the hydrosilylation of phenyl acetylene,[6] as it is fairly easily obtainable. In the course of our investigations into the chemistry of organoiridium complexes, we have discovered that $[Cp^*IrCl_2]_2$, **1**, is a very efficient catalyst for the hydrosilylation of terminal alkynes. We thought that investigations into the catalytic efficiency of the iridium analogue may be useful for mechanistic studies. Furthermore, there is also the possibility of different or improved efficiency on replacement of Rh with Ir, as exemplified by the Cativa versus the Monsanto processes.[9] We report our findings here, together with the mechanistic studies that we have carried out.

Scheme 1



Results and Discussion

The catalytic efficiency of **1** for the hydrosilylation of terminal alkynes is shown in Table 1. Catalyst **1** exhibits remarkably high β-(*Z*)-selectivity under mild reaction conditions; neither α nor β-(*E*) isomers were observed. This result was quite similar to that reported for **1a**, although we did not observe any activity for the reaction of Et_3SiH with Me_3SiCCH or that between the silane $(EtO)_3SiH$ and the alkynes PhCCH or ^{n}BuCCH. Although a trace of the other isomers was also reported in the hydrosilylation of phenyl acetylene with **1a**, we have found that this was due to subsequent isomerization of the initial product. Thus we have found that for short reaction times (<0.5 h) the initial product of the reaction between PhCCH and Et_3SiH is the β-(*Z*) vinylsilane, but over 24 h a mixture of the β-(*Z*) and β-(*E*) isomers (12% and 71%, respectively) together with the α isomer (<1%) was obtained. If the reaction was carried out at 80 °C, the main product was the β-(*E*) isomer (99%), with a trace of the other two isomers. This isomerization was not observed in all cases however; for instance, even at 80 °C the reaction between CyCCH and Et_3SiH afforded only the corresponding β-(*Z*) vinylsilane after 2.5 h.

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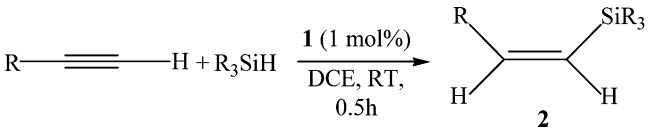
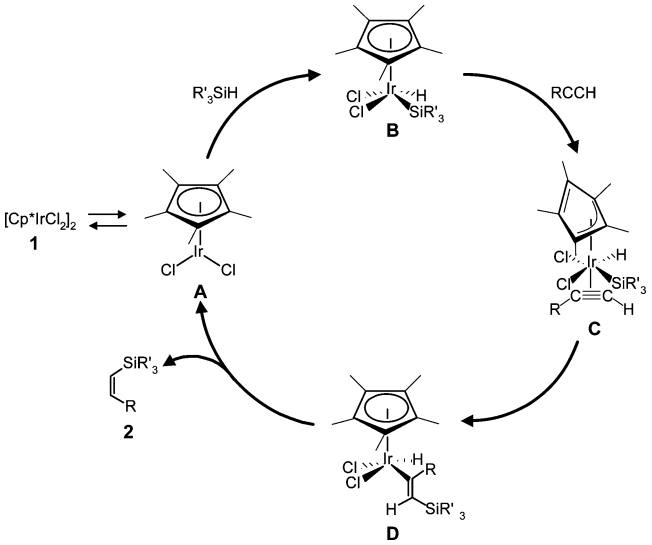
Table 1. Hydrosilylation of Terminal Alkynes Catalyzed by 1



S/no.	alkyne	silane	yield of **2** (%)[a]	isomerization[b]
1	Ph−C≡C−H	$HSiEt_3$	96 (92)	y
2	Cy−C≡C−H	$HSiEt_3$	93 (91)	n
3	^{n}Bu−C≡C−H	$HSiEt_3$	92 (89)	y
4	^{t}Bu−C≡C−H	$HSiEt_3$	13 (11)	y
5[c]	Ph−C≡C−H	$HSiPh_3$	97 (94)	n
6[c]	Cy−C≡C−H	$HSiPh_3$	97 (93)	n
7[c]	^{n}Bu−C≡C−H	$HSiPh_3$	91 (89)	n

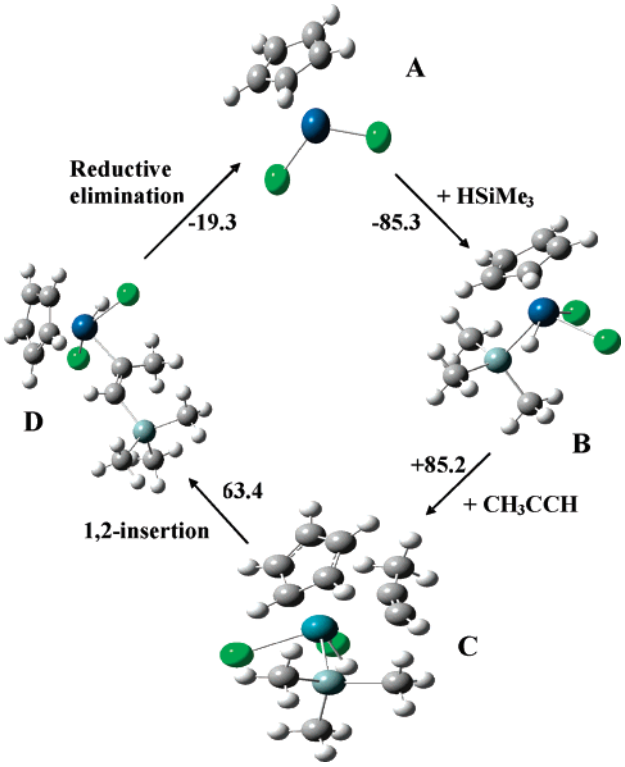
[a] Determined by NMR; isolated yields in parentheses. [b] A mixture of isomers was formed on prolonged standing. [c] Comparable yields were obtained with 1:2 alkyne:silane ratio.

Scheme 2



We have also sought to investigate the mechanism for the reaction. Direct monitoring of the reaction by ^{1}H NMR spectroscopy was futile; the only observable resonances were those assignable to the reactants and the final vinylsilane product. We have thus resorted to studying the catalytic cycle indirectly and by computational means. The proposed mechanism is shown in Scheme 2, and our computational results, with the computed reaction free energies given in kJ mol^{-1}, are summarized in Scheme 3. The computational study was carried out at the Moeller−Plesset MP2 level of theory together with the LANL2DZ basis set. This level of theory has been shown to be of utility in studies of catalysis by organometallic systems.[10] To minimize computation time, we have chosen a model system that comprised $CpIrCl_2$ as the catalytically active species, with Me_3SiH and MeCCH as the reacting silane and alkyne, respectively. All except one step are associated with negative free energy changes.

Scheme 3



The equilibrium between **1** and its solvent-stabilized monomeric species has been suggested by earlier workers.[11] Although not shown in Scheme 3, the dimer to monomer reaction from $[CpIrCl_2]_2$ to $CpIrCl_2$ has a large $\Delta G°$ (118 kJ mol^{-1}), consistent with an equilibrium that normally lies toward the dimeric species.

The first step of the catalytic cycle probably involves metal insertion into the Si−H bond; we have found no apparent reaction between **1** and PhCCH under scrupulously dry conditions, while **1** reacted with an equimolar amount of Ph_3SiH to afford the Ir(V) species $[Cp^*Ir(Cl)(H)_2(SiPh_3)]$, **3**; this compound and its $SiEt_3$ analogue have been reported previously.[11c,12] Compound **3** is related to the catalytic intermediate $[Cp^*Ir(Cl)_2(H)(SiPh_3)]$, **B**; addition of an alkyne to **3** (formed *in situ*) regenerated **1** together with the formation of **2**. The conversion of an analogue of **B** into an analogue of **3** has recently been reported,[11c] so **3** is probably the observable form of **B**. We have ruled out **3** being the intermediate **B**, as formation of **3** requires elimination of one of the chloride ligands, but **1** is recoverable after the reaction.

What is more uncertain is how the alkyne is involved in the subsequent step (from **B** to **D**). The possibility that HCl elimination occurred prior to binding of the alkyne to the metal center was ruled out since carrying out the reaction in the presence of D_2O did not lead to any incorporation of deuterium in the product; the eliminated HCl would have to be reincorporated in subsequent steps of the cycle. That there is no HCl elimination is further corroborated by the observation that the reaction was unaffected by the presence of [PPN]Cl (5 equiv with respect to **1**). It has been suggested that for the rhodium

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analogue[6] the reaction involved the formation of a vinylidene, i.e., a Rh═C═C species, in accord with that proposed for a related iridium species.[8c] However, we deem this unlikely, as we have found that the reaction of PhCCD with Et_3SiH afforded $PhCH═CDSiEt_3$ only, indicating that there was no ≡C−H bond cleavage. The reaction of PhCCH with Et_3SiD afforded only $PhCD═CHSiEt_3$, indicating clearly the source of the benzylic hydrogen as the silane. We would therefore like to propose an intermediate such as C, involving ring slippage of the Cp*. Although relatively uncommon, ring slippage of the Cp* has been proposed previously.[13] This is also the most endoergic step; the positive free energy computed for this step is consistent with ring slippage.

The path from **C** to **D** is critical, as it accounts for the stereochemistry of the final product. It has been suggested for a related iridium system that the initial product is the isomer of **D** in which the R and SiR'_3 groups are *trans*, which then isomerized to the *cis* isomer.[8c] However, in our case, we have found by modeling that it is not possible to form a stable *trans* isomer for **D**. Instead, we believe that **C** leads directly to the proposed *cis* isomer. This proposal is essentially the same as that of Trost for the ruthenium system $[Cp^*Ru(NCCH_3)_3]^+$ [14] and is in better agreement than the alternative involving an isomerization step (see above).[15] In his computational study,[14b] Trost has found that silyl or hydrogen migration may occur. In our case, hydrogen migration to form the corresponding *anti* addition product (in which the migrated hydrogen is *trans* to the iridium) $[Cp^*Ir(Cl)_2(SiR'_3)(CH═CHR)]$, **D′**, gave rise to a steric problem similar to that for the *trans* isomer of **D** mentioned above. We therefore believe that in our system silyl migration is favored.

The transition state for this step has been computed and is shown in Figure 1. It lies ∼75 kJ mol^{-1} above **C**. The vinyl group is not planar, with the Ir−C−C−H dihedral angle at 110°. Part of the reaction coordinate is also depicted, and it corresponds to the hydrogen atom swaying (vibrating) perpendicularly to the C−H bond. There is therefore the possibility of the transition state leading to either isomer. As presented above, the *trans* product is sterically hindered; thus the reaction should proceed to form the *cis* isomer.

The final step, a reductive elimination of the vinylsilane to re-form the monomer **A**, is also energetically favorable.

Conclusion

In this study, we have reported the hydrosilylation of terminal alkynes that was efficiently catalyzed by $[Cp^*IrCl_2]_2$ to afford selectively the β-(*Z*) vinylsilanes in high yields. In some cases, the *E* isomers were also observed, which have been found to be due to subsequent isomerization. The catalytic cycle was studied with a combination of experimental and computational techniques, and we have proposed a cycle that is based on an Ir(III)−Ir(V) redox process and a direct *anti* addition of the silane.

Experimental Section

General Procedures. All reactions were performed under argon using Schlenk techniques. Solvent such as dichloroethane was purified, dried, distilled, and stored under nitrogen prior to use, except for catalytic runs, which were used as supplied. ^1H NMR spectra were recorded on a Bruker ACF300, DPX 300, or AV300 NMR spectrometer as $CDCl_3$ solutions unless otherwise stated. ^1H chemical shifts reported are referenced against the residual proton signals of the solvents. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in an NBA matrix (FAB) or a Macromass VG7035 at 70 eV (EI). $[Cp^*IrCl_2]_2$ was prepared by the literature method.[16] PhCCD (99 atom % D) and Et_3SiD (97 atom % D) were purchased from Sigma Aldrich and used as such. All other reagents are commercially available and used without further purification.

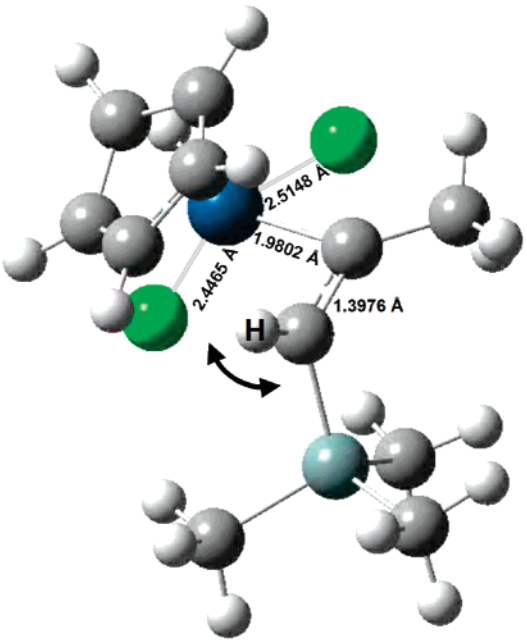

Figure 1. Structure of the computed transition state for **C** to **D**, with selected bond lengths indicated. Part of the reaction coordinate is depicted by the arrow.

Procedure for Catalytic Runs. In a typical reaction, a 10 mL stock solution of the reactants was prepared from phenylacetylene (1.0 mL, 9.1 mmol), triethylsilane (1.5 mL, 9.4 mmol), and nonane as internal standard (0.41 mL, 2.3 mmol) and made up to the mark with dichloroethane. A stock solution of the catalyst **1** (72.5 mg, 91.2 μmol) was also prepared in dichloroethane (10.0 mL). The appropriate amounts of catalyst and reactant stock solutions (1.0 mL each for a 1.0 mol % reaction) were mixed and stirred at room temperature for 0.5 h. Aliquots (∼0.5 mL) were drawn, and $CDCl_3$ (0.1 mL) was added for NMR quantification. The yields were calculated on the basis of the limiting reagent. For reactions in which the products were isolated, the solvent and volatiles were removed under reduced pressure after the catalytic run and the residues chromatographed on silica gel TLC plates, with hexane as eluant. The products were identified by comparison with literature data.

Reaction of $[Cp^*IrCl_2]_2$ with Ph_3SiH. Compound **1** (36.8 mg, 46.2 μmol) was reacted with Ph_3SiH (24.1 mg, 92.6 μmol) in CD_2Cl_2 (0.5 mL) for 0.5 h. ^1H NMR analyses of the crude mixture showed unreacted starting materials and $[Cp^*Ir(Cl)(H)_2(SiPh_3)]$ together with some unidentified products. ^1H NMR (δ, CD_2Cl_2): 1.65 (s, Cp*, 15H), 7.31−7.48 (m, 15H, aromatic), −11.64 (s, 2H, IrH). (lit. values:[12b] ^1H NMR (δ, CD_2Cl_2): 1.62 (s, Cp*, 15H), 7.2−7.4 (m, 15H, aromatic), 7.6 (dd, 6H, aromatic), −11.65 (s, 2H, IrH). Based on the integration ratio against unreacted **1**, yield =

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24%. A FAB-MS spectrum showed a peak at *m*/*z* 775 $[M + NBA]^+$.

Deuterium Labeling Studies. Catalyst **1** (0.905 μmol), Et_3SiD (15 μL, 93.1 μmol), phenylacetylene (10 μL, 91.1 μmol), and deuterated dichloroethane (0.5 mL) were placed in an NMR tube. The reaction mixture was allowed to stand for 0.5 h. Analysis of the ^{1}H NMR mixture showed the formation of [(β-*Z*)-Ph−(D)C═C($SiEt_3$)H]. ^{1}H NMR (δ, $ClCD_2CD_2Cl$): 7.36−7.24 (m, 5H, aromatic), 5.77 (s, 1H, ═C*H*$SiEt_3$), 0.88 (t, $^3J_{HH}$ = 8 Hz, 9H, CH_3), 0.58 (q, 6H, CH_2).

A similar reaction using **1** (0.905 μmol), Et_3SiH (15 μL, 93.1 μmol), PhC≡CD (10 μL, 91.1 μmol), and deuterated dichloroethane (0.5 mL) afforded [(β-*Z*)-Ph−(H)C═C($SiEt_3$)D]. ^{1}H NMR (δ, $ClCD_2CD_2Cl$): 7.45 (s, 1H, ═C*H*Ph), 7.36−7.25 (m, 5H, aromatic), 0.87 (t, $^3J_{HH}$ = 8 Hz, 9H, CH_3), 0.58 (q, 6H, CH_2).

Computational Studies. The reaction pathways for the hydrosilylation catalysis were studied using Moeller−Plesset MP2 theory together with the LANL2DZ basis set. Spin-restricted calculations were used for determining the structures of the organic and organometallic reactants, intermediates, and products, fully optimized at the MP2/LANL2DZ level. Harmonic frequencies were calculated at the optimized geometries to characterize stationary points as equilibrium structures, with all real frequencies, and to evaluate zero-point energy (ZPE) correction. All calculations were performed using the Gaussian 03 suite of programs.[17]

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Supporting Information Available: ^{1}H NMR and mass spectroscopic data for all the vinylsilanes in this article and tables for the catalytic run with a 2:1 molar ratio of PhC≡CH:$HSiEt_3$ and for the computational study.

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