JOC Article

Highly β-(*E*)-Selective Hydrosilylation of Terminal and Internal Alkynes Catalyzed by a (IPr)Pt(diene) Complex

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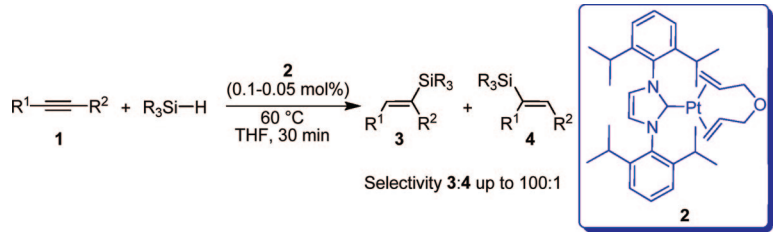

The regioselective hydrosilylation of terminal and internal alkynes catalyzed by the novel (IPr)Pt(AE) (**7**) (IPr = bis(2,6-diisopropylphenyl)imidazo-2-ylidene, AE = allyl ether) complex is presented. The (IPr)Pt(AE) catalyst displays enhanced activity and regioselectivity for the hydrosilylation of terminal and internal alkynes with low catalyst loading (0.1 to 0.05 mol %) when compared to the parent (IPr)Pt(DVDS) complex (**6**) (DVDS = divinyltetramethyldisiloxane). The reaction leads to exquisite regioselectivity in favor of the cis-addition product on the less hindered terminus of terminal and internal alkynes. The solvent effects were examined for the difficult hydrosilylation of benzylpropargyl ether. In light of the observed product distribution and kinetic data, a mechanistic scheme is proposed involving two competing catalytic cycles. One cycle leads to high regioselectivities while the other, having lost the stereodirecting IPr carbene ligand, displays low regiocontrol and activities. The importance of this secondary catalytic cycle is either caused by the strong coordinating ability of the alkyne or by the low reactivity of the silane or both.

Introduction

Over the past decades, vinylsilanes have emerged as versatile building blocks in organic synthesis.[1,2] Their low cost, high stability, and innocuous byproduct have made them attractive surrogates for their tin- and boron-derived counterparts. A significant advantage of vinylsilanes over most other vinylmetal species is their ability to be carried through many synthetic steps without decomposition. One of their most promising applications is their use as nucleophilic partners in palladium-catalyzed cross-coupling reactions.[3–5] Vinylsilanes can also act as masked carbonyl groups, being ultimately revealed by a Tamao−Fleming oxidation.[6–8] For both of these processes to readily occur, at least one heteroatom, such as F, Cl, or O, is required on the silicon atom.

The most straightforward and atom-economical manner to assemble vinylsilanes is by the regioselective hydrosilylation of alkynes. Trost et al. have reported a highly regioselective, ruthenium-based system, which promotes trans addition of silanes to terminal and internal alkynes to form the corresponding α isomers **1** and **2**, respectively.[9,10] The trans addition product (**3**, β-(*Z*)) can be accessed by rhodium[11,12] and ruthe-

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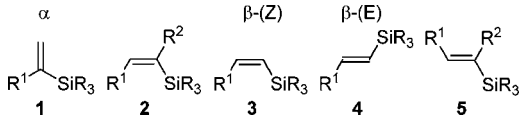
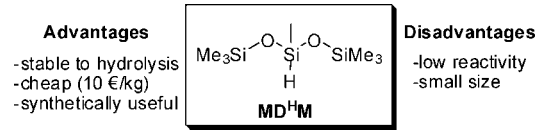
nium[13] catalyzed hydrosilylations, even though the silanes employed remained limited to Et_3SiH and Ph_3SiH, except for one notable exception reported by Hiyama and Mori.[14]



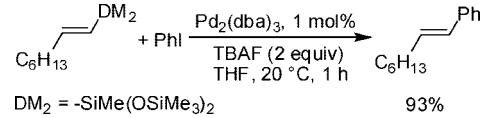
On the other hand, the platinum-catalyzed hydrosilylation of alkynes has been widely investigated and shown to proceed by the cis addition of the hydrosilane across the alkyne, forming exclusively adducts **1**, **4**, and **5**.[15,16] High selectivities in favor of the β-(*E*) isomer have been reported with use of platinum complexes bearing bulky phosphane ligands.[17–25] However, closer examination reveals that only a limited range of silanes, such as chloro-, trialkyl-, and triarylsilanes, truly offer high β-(*E*) regioselectivities. In contrast, alkoxysilanes are usually poor substrates for the Pt-catalyzed hydrosilylation of alkynes.[26] Chlorosilanes give high regioselectivites; however, they are toxic and delicate to handle, and the chlorosilyl function cannot be carried through several synthetic steps without prior modification. Finally, trialkyl- and triarylvinysilanes provide limited synthetic utility.[1] To overcome these issues, masked silanols have been introduced, such as $PhMe_2SiH$,[27] 2-thienyldimethylsilane,[28] 2-pyridyldimethylsilane,[29] and $BnMe_2SiH$,[30] but these silanes are relatively onerous. A silane, which has remained underutilized in organic chemistry, is bis(trimethylsilyloxy)methylsilane (MD^HM), an industrial compound produced on the ton-scale.[31] MD^HM combines the benefits of low cost and high hydrolytic stability (due to its siloxane linkage, Si−O−Si−O−Si). Moreover, MD^HM displays a low reactivity akin to that of dialkoxysilanes and is also less bulky than its structure would imply (e.g., smaller than Et_3SiH) (Scheme 1).

Denmark et al. have demonstrated that related disiloxanes give high yields in cross-coupling reactions[20] and preliminary results from our laboratory have shown that the high stability of the Si−O−Si bonds does not preclude its use as a nucleophilic partner in Hiyama-type cross-coupling under standard conditions (Scheme 2).

SCHEME 1. Advantages and Disadvantages of MD^HM as an Industrial Silan



SCHEME 2. Synthetic Relevance of the −SiMe(OSiMe$_3$)$_2$ (DM$_2$) Group in a Cross-Coupling Reaction



It thus transpires that off-the-shelf catalytic systems, which can achieve high yields of the β-(*E*) isomer with synthetically useful silanes, are still needed. Platinum(0) *N*-heterocyclic carbene (NHC) complexes are significantly more stable than their corresponding phosphine analogues and can be stored in the solid form and in solution, under ambient conditions, without significant decomposition. In our previous report on the hydrosilylation of alkynes mediated by *N*-heterocyclic carbene platinum(0) complexes, we have identified the (IPr)Pt(DVDS) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; DVDS = divinyltetramethyldisiloxane) complex (**6**) as the most active catalyst of the series investigated.[32] Thus, the hydrosilylation of 1-octyne by MD^HM, in the presence of (IPr)Pt(DVDS) (5×10^{-3} mol %; 80 °C; 6 h), yielded the β-(*E*) isomer in a 10.6:1 ratio with the α isomer, in greater than 99% yield. Although this result was promising, it was still lagging behind existing methodologies based upon bulky phosphine ligands.

Herein, we wish to report a modification of our previously described catalytic system for the hydrosilylation of alkynes which displays highly enhanced activity, superior β-(*E*) selectivity, and broader substrate scope. We also address the little developed regioselective cis-hydrosilylation of internal alkynes. A study of the initiation period has enabled us to delineate key mechanistic features and to pinpoint several deactivation pathways occurring in our system.

Results and Discussion

Optimization of Hydrosilylation Conditions with Catalyst 7. The (IPr)Pt(DVDS) complex (**6**) suffered from a lack of catalytic activity (although it was the most active among (NHC)Pt(DVDS) complexes investigated) and therefore long reaction times were required. Relatively high temperatures (80 °C) were also necessary to effect complete conversions. Our previous studies have revealed that the rate determining step in the catalyst activation is the initial decoordination of the diene ligand (Scheme 3).[33] This is due to the presence of the DVDS ligand which, being particularly strongly bound to the platinum(0) center, is difficult to displace to free the active [(IPr)Pt] species (Scheme 3, **I**).[32]

It was therefore anticipated that the replacement of the DVDS ligand by a more labile allyl ether (AE) moiety would increase

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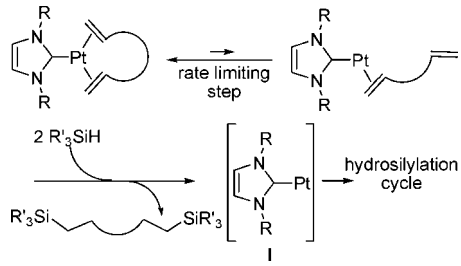
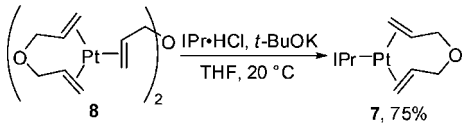
SCHEME 3. Proposed Initiation Mechanism for (NHC)Pt(diene) Complexes



SCHEME 4. Synthesis of (IPr)Pt(AE) (7)



the rate of formation of the catalytically active [(IPr)Pt] fragment (Figure 1). Similar effects of so-called "spectator" diene ligands have become widely recognized in catalysis.[34] Elegant studies on the $Pd_2(dba)_3$ (dba = *trans*,*trans*-dibenzylidene acetone) precatalysts by Fairlamb et al. have shown that electronically modified dba ligands significantly influence the overall catalytic activity in cross-coupling reactions.[35,36] The choice of the diallyl ether fragment offers a good compromise between stability and activity of the complex[37] and was inspired by studies by Pörschke et al., who first reported complex **8**.[38]

The synthesis of the (IPr)Pt(AE) complex (**7**) was accomplished by treatment of a solution of $Pt_2(AE)_3$ with the IPr carbene formed in situ (Scheme 4).[38] A direct, high-yielding synthesis of (IPr)Pt(AE) (**7**) and congeners from H_2PtCl_6 has been recently reported.[39] Complex **7** is an air-stable, off-white solid that can be stored indefinitely under ambient conditions and is stable as a toluene solution for several weeks.

With complex (IPr)Pt(AE) (**7**) in hand, we began to investigate its activity in the hydrosilylation reaction and chose, as a model transformation, the addition of MD^HM to 1-octyne (Table 1). To assess the base selectivity of this process, we employed $PtCl_2$(cod) (cod = *cis*,*cis*-1,5-cyclooctadiene) as a reference catalyst lacking any bulky regiodirecting ligands (Table 1, entry 1). Lewis et al. have shown that this platinum complex gives the same regioselectivity as the more commonly used Karstedt's catalyst[40] ([$Pt(CH_2{=}CHSiMe_2)_2O$]).[16] The optimum conditions were obtained by carrying out the reaction at 60 °C, under solventless conditions, in the presence of 0.1 mol % of **7**. A slight excess of silane (10%) was used (Table 1, entry 8) to ensure reproducibility of the reaction. Under these conditions, the reaction was essentially over within 5 min, affording the β-(*E*) isomer in high yield and with exquisite selectivity. At the onset of this transformation, the medium acquired a characteristic yellow taint, signaling the formation of a catalytically active species. Hydrosilylations, in which this yellow color did not appear, afforded low conversions and poor selectivities. The optimization study revealed that the temperature and the catalyst loading were crucial parameters. It was necessary to perform the reaction above 40 °C to maintain a good catalytic activity. This is especially true at lower catalyst loadings (0.05 mol %). In several instances, the reaction stalled when effected at 20 °C. Moreover, the hydrosilylation reaction proved to be quite sensitive to catalyst loading and a sharp decrease in activity and selectivity was observed when 0.01 mol % of **7** was employed instead of 0.05 mol % (Table 1, entries 5 and 6, respectively). This dramatic reduction in reaction rate and stereocontrol is presumably due to a specific deactivation of the catalyst (vide infra). In accord with previous observations made by Stone et al.,[17] the use of solventless conditions strikingly increased the velocity of this process, without affecting the yield or the regioselectivity of the addition (Table 1, entry 7). This is particularly useful when performing the reaction on a large scale, even though care must be exercised in controlling the ensuing exotherm (vide infra).

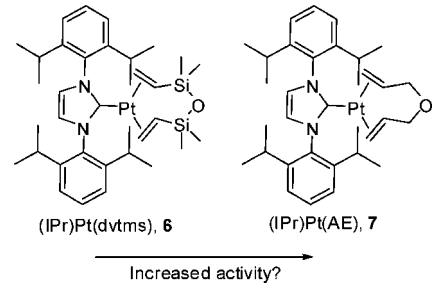


FIGURE 1. (NHC)Pt(diene) complexes **6** and **7**.

Using the optimum hydrosilylation conditions, we compared the activity of catalyst **7** with that of catalyst **6** bearing the DVDS ligand (Table 1, entries 9 and 10). Catalyst **6** displayed very little hydrosilylation activity at 25 °C and gave incomplete conversion and moderate selectivity at 60 °C. This confirms that the substitution of the DVDS ligands by the more labile allyl ether is crucial for catalytic activity.

For example, in a separate experiment, 1-octyne was reacted with MD^HM on a 50 mmol scale, at 60 °C, under solventless conditions. The addition of the catalyst **7** (5×10^{-2} mol %) caused the reaction temperature to rise to 180 °C within 1 min. After 3 min, the hydrosilylation was complete. Interestingly, even at this elevated temperature, the β-(*E*)/α ratio remained a remarkable 25:1 (Scheme 5). The product was obtained in an isolated yield of 95%, indicating the high stability of the catalytically active [(IPr)Pt] fragment and the robustness of the present catalytic system. Therefore, the regioselectivity of the addition is mostly dictated by the steric bulk of the IPr ligand and by the nature of the substrates; the temperature only plays a very marginal role. Similar observations have been reported by Yoshida et al. when they performed the hydrosilylation of 1-octyne by dimethyl(pyridyl)silane with (t-Bu_3P)Pt(DVDS) (1 mol %) at 100 °C and still achieved high regioselectivity for the β-(*E*)-vinylsilane.[21] *Obviously*, *care must be taken to avoid such strong exotherms*! The exotherm can be controlled on a large scale by performing the reaction at 30 °C with the reaction vessel immersed in a water bath or by slow addition of the alkyne to the mixture of catalyst and silane at room temperature.

Solvent Effect and Deactivation Pathway. The hydrosilylation of a more challenging substrate, benzylpropargyl ether

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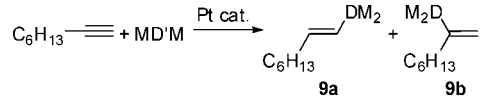
TABLE 1. Optimization of the Hydrosilylation of 1-Octyne by MD^{H}M Catalyzed by 7[a]



entry	catalyst (mol %)	solvent	*T* (°C)	*t* (min)	ratio (*β*:α)[b]	yield (%)[c]
1	$PtCl_2$(cod) (5×10^{-3})	THF	60	10	3:1	75
2[d]	**6** (5×10^{-3})	*o*-Xy	80	360	11:1	90
3	**7** (0.1)	THF	25	400	100:1	90
4	**7** (0.05)	THF	25	400	50:1	80
5	**7** (0.05)	THF	40	100	200:1	84
6	**7** (0.01)	THF	60	120	11.5:1	38
7[e]	**7** (0.1)	—[f]	25	80	100:1	95
8[e]	**7 (0.1)**	—[f]	**60**	**5**	**200:1**	**97**
9[e]	**7 (0.05)**	—[f]	**60**	**10**	**100:1**	**98**
10	**6** (0.1)	—[f]	25	12 h		<5
11	**6** (0.1)	—[f]	60	12 h	10:1	60

[a] Reaction conditions: 1-octyne (3.0 mmol, 1 equiv), MD^{H}M (3.0 mmol, 1 equiv), dodecane (internal standard), [Pt], solvent (1.0 M). [b] Ratio determined by GC analysis of the crude reaction mixture. [c] GC yield of the *β*-(*E*) isomer. [d] Results reported in ref 30. [e] 1.1 equiv of MD^{H}M used. [f] Solventless conditions. cod = *cis*,*cis*-1,5-cyclooctadiene. −DM_2: −$SiMe(OSiMe_3)_2$.

SCHEME 5. Robustness of the Catalytic System at Elevated Temperatures

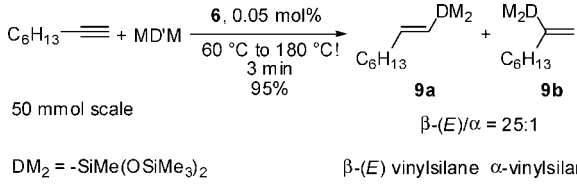
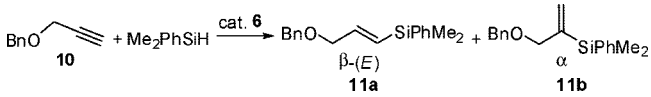


TABLE 2. Optimization of the Hydrosilylation Conditions of 10[a]



entry	**7** (mol %)	solvent	*T* (°C)	*t* (h)	ratio (*β*:α)[b]	conv (%)[c]
1	$PtCl_2$(cod) (0.1)	THF	20	1	1.5:1	92
2	0.1	—[d]	20	5 d	2.0:1	40
3	0.1	toluene	20	5 d	2.6:1	44 (47)
4	0.1	CH_2Cl_2	20	7 d	1.8:1	60 (73)
5	0.1	CH_3CN	20	7 d		0
6	0.1	acetone	20	5 d	2.3:1	40 (62)[e]
7	0.1	−PrOH	20	5 d	13.3:1	61 (88)[f]
8	**1.0**	—[d]	**20**	**0.1**	**15.7:1**	**94**[g]
9	**1.0**	**THF**	**20**	**2**	**50:1**	**98**[g]

[a] Reaction conditions: BnOP (**10**) (1 equiv), $PhMe_2SiH$ (1 equiv), dodecane (internal standard), solvent (1.0 M). [b] Ratio determined by GC analysis of the crude reaction mixture. [c] GC conversion of the alkyne (silane). [d] Solventless conditions. [e] Hydrosilylation of acetone occurred. [f] Partial silylation of −PrOH occurred. [g] Isolated yield.

(BnOP, **10**), by dimethylphenylsilane (Table 2) was next investigated. BnOP combines a coordinating ether function with a lower electronic density on the internal carbon of the alkyne, both features greatly favoring the α isomer (Figure 2).[41] Thus, the hydrosilylation of BnOP by dimethyphenylsilane, catalyzed by $PtCl_2$(cod) affords the desired adduct with an extremely low *β*-(*E*)/α ratio of 1.5:1 (Table 2, entry 1).

When the optimal conditions developed for the hydrosilylation of 1-octyne where applied to BnOP, only poor conversion and mediocre selectivities resulted, even after 5 days (Table 2, entry 2). Several solvents were screened to improve both regioselectivity and catalytic activity. While toluene, dichloromethane,

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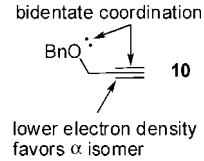
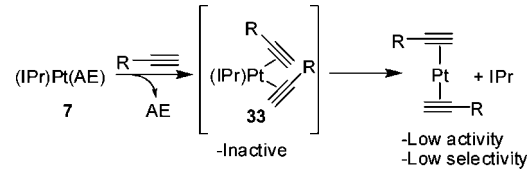


FIGURE 2. Factors making BnOP (**10**) a difficult substrate to hydrosilylate.

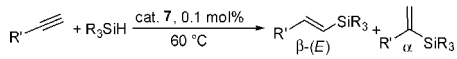
SCHEME 6. Proposed Deactivation Pathway for (IPr)Pt(AE) (7) in the Presence of Coordinating Alkynes



and acetone led to marginal improvements (Table 2, entries 3, 4, and 6, respectively), acetonitrile completely inhibited the catalyst (Table 2, entry 5), presumably due to its strong coordinating capability. However, performing the reaction in isopropyl alcohol afforded adducts **11a** and **11b** with a 13.3:1 selectivity in favor of the *β*-(*E*) isomer **11a** (Table 2, entry 7). Surprisingly, the initially fast reaction rate quickly decreased, leading to incomplete conversion even after 5 days. Concomitantly, erosion of the selectivity was also observed and some silylation of isopropyl alcohol was detected after several days. The higher selectivity obtained in isopropyl alcohol, as compared to other solvents, could be rationalized by invoking a hydrogen-bonding interaction between the alcohol and the ether function of BnOP. Such H-bonding would limit the availability of the ether lone pair for coordination to the platinum center and hence disfavor the formation of the unwanted α isomer **11b**.

Eventually, the use of 1 mol % of the (IPr)Pt(AE) (**7**) catalyst in THF gave the desired product **11a** in a 98% isolated yield and with a regioselectivity of 50:1 in favor of the *β*-(*E*) isomer (Table 2, entry 9). Although these catalyst loadings are quite high, similar loadings have been found necessary by Verkade et al. for the hydrosilylation of BnOP by triethylsilane.[23] Nevertheless, the hydrosilylation of BnOP gave us some useful information about the catalytic system. High activities and regioselectivities are achieved when the hydrosilylation occurs

TABLE 3. Hydrosilylation of Terminal Alkynes by Complex (IPr)Pt(AE) 7[a]



entry	alkyne	silane	major product	t (h)[b]	ratio (β:α)[c]	yield (%)[d]
1	n-C_6H_{13}—	Me_2PhSiH	C_6H_{13} SiMe$_2$Ph **12**	0.1	50:1	93
2		MD^HM	Ph DM_2 **13**	4	16:1	95
3		Me_2PhSiH	Ph SiMe$_2$Ph **14**	2	100:1	94
4	HO	MD^HM	HO DM_2 **15**	0.1	32:1	94
5	HO	MD^HM	HO DM_2 **16**	0.2	100:1	97
6	EtO$_2$C HO **17**	Me_2PhSiH	EtO$_2$C HO SiMe$_2$Ph **18**	0.25	>20:1[e]	94
7[f]	H_2N	MD^HM	H_2N DM_2 **19**	6	>20:1[e]	90
8	TMS—	MD^HM	TMS DM_2 **20**	0.1	25:1	96

[a] Reaction conditions: alkyne (1.0 equiv), silane (1.1 equiv), (IPr)Pt(AE) (**7**) (0.1 mol %), solventless, 60 °C. [b] Time for complete conversion by GC analysis. [c] Ratio of regioisomers determined by GC analysis. [d] Isolated yield of the mixture of regioisomers. [e] Ratio determined on the crude reaction mixture by ^{1}H NMR. [f] 0.5 mol % of catalyst was used.

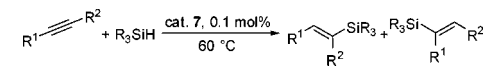
faster than the catalyst deactivation. Hence, with 1 mol % of (IPr)Pt(AE) (**7**), the reaction is extremely selective and efficient while poor regioselectivities and conversions are observed with 0.1 mol %.

The reduced regioselectivity observed with lower catalyst loading hints to the fact that a concurrent hydrosilylation cycle might be operating as a background reaction and that the active species in this cycle could presumably be lacking the bulky IPr ligand. It is thus possible that the strong coordination of BnOP to platinum may lead to the displacement of the IPr ligand, affording a Pt(η^2-alkyne)$_2$ complex that is a poor and unselective hydrosilylation catalyst.[42] To substantiate this hypothesis, (IPr)Pt(AE) was reacted with 5 equiv of BnOP (**10**) in toluene-d_8 and the reaction was monitored by ^{1}H NMR. After several hours at 40 °C, the ^{1}H NMR spectrum of the mixture displayed complete decomposition of the complex. The signals belonging to the coordinated allyl ether (3.95 and 2.44 ppm) had completely disappeared and the region of the IPr methyl groups displayed a multitude of peaks, indicating a complex mixture. More significantly, signals corresponding to the protonated IPr carbene appeared (9.9 ppm) probably due to the decoordination of the IPr carbene from the metal, followed by its protonation by residual water.

Substrate Scope and Limitation. The hydrosilylation of alkynes with dimethylphenylsilane proceeded faster and with comparable or higher selectivities than with MD^HM (Table 3, entries 1 and 3). Gratifyingly, propargyl alcohol was hydrosilylated with remarkable efficiency with use of a catalyst loading of 0.1 mol % (Table 3, entry 4). This stands in sharp contrast to the difficulties encountered in the hydrosilylation of BnOP (**10**). The transformation of pent-4-yn-ol into **16** (Table 3, entry 5) took place equally smoothly. Thus, it appears that hydrogen bonding in these systems plays a beneficial role in upholding high regioselectivities, comfirming the previous observation that higher β-(*E*)/α ratios were obtained in isopropyl alcohol. This observation also holds true for a free amine function. Hence, propargyl amine was hydrosilylated with a high regioselectivity, albeit a catalyst loading of 0.5 mol % had to be used (Table 3, entry 7). It has been previously reported that, in hydrosilylation of propargylic alcohols with (t-Bu$_3$)Pt(DVDS), the addition of a catalytic amount of Na(0) appears to be necessary to achieve high levels of regioselectivity. This additive is not necessary with the present catalyst.[43] In all these cases, no silylation of the free alcohol or the free amine was observed. Trimethylsilylacetylene, which is particularly reactive and gives poor regioselectivities with PtCl$_2$(cod) (β/α ratio of 1.5/1, due to the presence of a silicon center), was also hydrosilylated with high regioselectivity (Table 3, entry 8).

The high regioselectivities obtained for the hydrosilylation of terminal alkynes prompted us to investigate the much more challenging hydrosilylation of internal acetylenes catalyzed by complex **7** (Table 4). Therefore, we examined the ability of our system to discriminate between a simple methyl group and another substituent on the triple bond. In the case of a linear alkyl chain, the selectivity was modest with MD^HM (Table 4,

TABLE 4. Hydrosilylation of internal alkynes by complex 7[a]



entry	alkyne	silane	major product	t (h)[b]	ratio[c]	yield (%)[d]
1		MD^HM	n-C_6H_{13} DM_2 **21**	1	2:1	84
2		$BnMe_2SiH$	n-C_6H_{13} SiMe$_2$Bn **22**	0.5	3.3:1	75
3	n-C_6H_{13}—	$PhMe_2SiH$	n-C_6H_{13} SiMe$_2$Ph **23**	0.5	3.6:1	80
4		Ph_2MeSiH	n-C_6H_{13} SiMePh$_2$ **24**	0.5	4.4:1	85
5		Ph_2ClSiH	n-C_6H_{13} SiClPh$_2$ **25**	2	6.0:1	80
6		MD^HM	DM_2 **26**	0.25	9:1	87
7	Ph—	MD^HM	Ph DM_2 **27**	5	24:1	90
8	Me_3Si—	MD^HM	Me_3Si DM_2 **28**	0.75	16:1	92
9[e]	EtO EtO **29**	MD^HM	EtO OEt DM_2 **30**	4	5:1[f]	75
10	n-C_6H_{13}— SiMe$_3$ **31**	MD^HM	Me_3Si n-C_6H_{13} DM_2 **32**	6	23:1	87
11[g]	HO	Me_2PhSiH	No reaction	-	-	-

[a] Reaction conditions: alkyne (1.0 equiv), silane (1.1 equiv), (IPr)Pt(AE) (**7**) (0.1 mol %), solventless, 60 °C. [b] Time for complete conversion by GC analysis. [c] Ratio of regioisomers (major:minor) determined by GC and ^{1}H NMR analysis of the crude reaction mixture. [d] Isolated yield of the mixture of regioisomers. [e] 0.5 mol % of catalyst was used, THF (1.0 M). [f] Ratio determined on the crude reaction mixture by ^{1}H NMR. [g] 1 mol % of catalyst. $-DM_2 = -SiMe(OSiMe_3)_2$.

(42) Boag, N. M.; Green, M.; Grove, D. M.; Howard, J. A. K.; Spencer, J. L.; Stone, G. A. F. *J. Chem. Soc., Dalton Trans.* **1980**, 2170.

(43) Beresis, R. T.; Solomon, J. S.; Yang, M. G.; Jain, N. F.; Panek, J. S. *Org. Synth., Collect. Vol.* **2004**, *10*, 531.

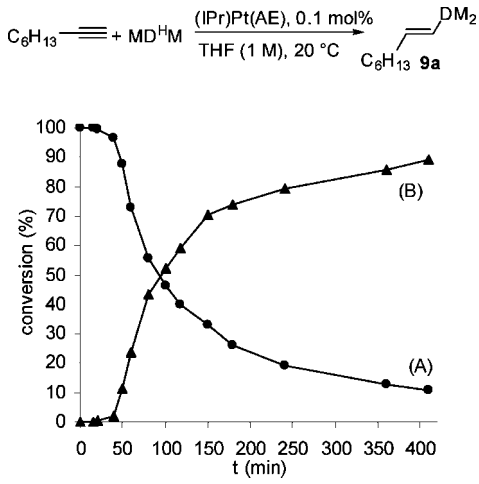


FIGURE 3. Kinetic profile of the reaction of MD^HM and 1-octyne catalyzed by (IPr)Pt(AE) (**7**). Curve A: Conversion of 1-octyne. Curve B: Formation of the *β*-(*E*) (**9a**) isomer. Reaction conditions: MD^HM (6.0 mmol, 1 equiv), 1-octyne (6.0 mmol, 1 equiv), dodecane (internal standard), (IPr)Pt(AE) (**7**, 6×10^{-3} mmol, 0.1 mol %), THF (1.0 M), 20 °C. The evolution of the reaction was followed by GC analysis.

entry 1). It increased slightly when the more hindered silane, Me_2BnSiH, was employed (Table 4, entry 2) and nearly doubled when $PhMe_2SiH$ was used as the hydrosilylating partner (Table 4, entry 3). This trend continued with the use of Ph_2MeSiH silane, which gave a 4.4:1 selectivity for the least hindered isomer (Table 4, entry 4). This level of regioselectivity is on par with the best cis hydrosilylating catalysts reported to date ([(Cp*)Y(CH_3)(THF)]).[44] Interestingly, the regioselectivity can be further increased to 6.0:1 by employing Ph_2ClSiH as a silane (Table 4, entry 5), suggesting that chloro substituent on silicon exerts a more powerful regiodirecting effect than a bulkier methyl group. From these experiments, silanes can be ranked in order of increasing steric demand against 2-nonyne: MD^HM < $BnMe_2SiH$ < $PhMe_2SiH$ < Ph_2MeSiH < Ph_2ClSiH. Therefore, MD^HM behaves as a rather small silane and thus obtaining high selectivity with this silane is a real challenge.

As might have been expected, a *tert*-butyl substituent gave useful selectivity (Table 4, entry 6). The hydrosilylation of 1-phenyl-2-propyne proceeded smoothly and efficiently (Table 4, entry 7) and so did the addition of MD^HM to trimethylsilylpropyne (Table 4, entry 8).

Interestingly, the trimethylsilyl substituent proves to be a more effective directing group than a *t*-Bu residue (Table 4, entry 8 vs entry 6) probably owing to its lower electronegativity, which results in a greater polarization of the carbon−carbon triple bond. This effect is particularly useful and can lead to excellent levels of regiocontrol (Table 4, entry 10). Whereas hydrosilylation of **29** gave a 5:1 ratio in favor of the less substituted isomer (Table 4, entry 9), we were curiously unable to effect the addition of $PhMe_2SiH$ to but-2-yn-1-ol (Table 4, entry 11) even when 1 mol % of catalyst **7** was employed.

Catalyst Activation and Deactivation Pathways. The difficulties encountered in the hydrosilylation of BnOP (vide supra) raised a number of questions on the modes of activation and deactivation of the (IPr)Pt(AE) (**7**) catalyst. The kinetic profile of our model reaction at room temperature revealed an induction period of 40 min before hydrosilylation began (Figure 3). This is the time necessary to generate a sufficient amount of active

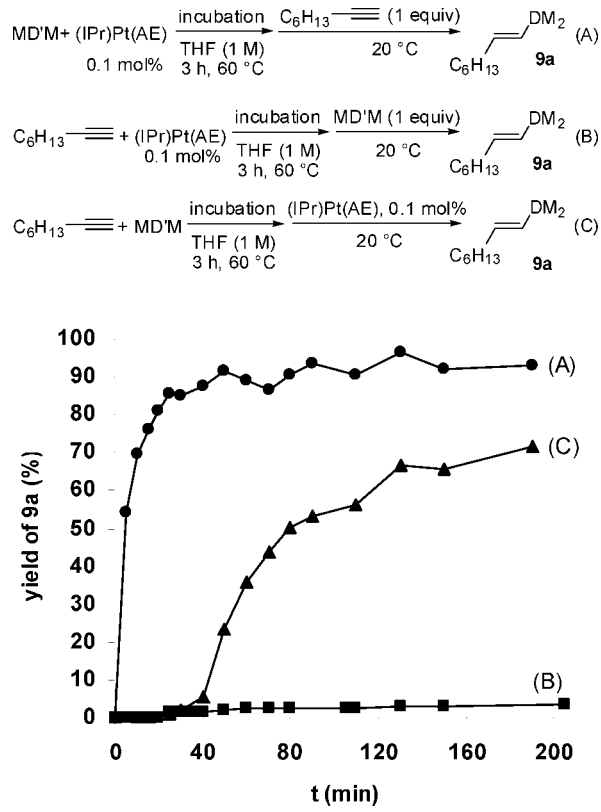


FIGURE 4. Effect of the different reaction components on the catalyst activation period. Curve A: Reaction of (IPr)Pt(AE) (**7**) and MD^HM for 3 h at 60 °C, followed by addition of 1-octyne at 20 °C. Curve B: (IPr)Pt(AE) and 1-octyne for 3 h at 60 °C, followed by addition of MD^HM at 20 °C. Curve C: MD^HM and 1-octyne, followed by addition of (IPr)Pt(AE) at 20 °C. Reaction conditions: MD^HM (6.0 mmol, 1 equiv), 1-octyne (6.0 mmol, 1 equiv), (IPr)Pt(AE) (0.1 mol %), THF (1.0 M). The evolution of the reaction was followed by GC analysis.

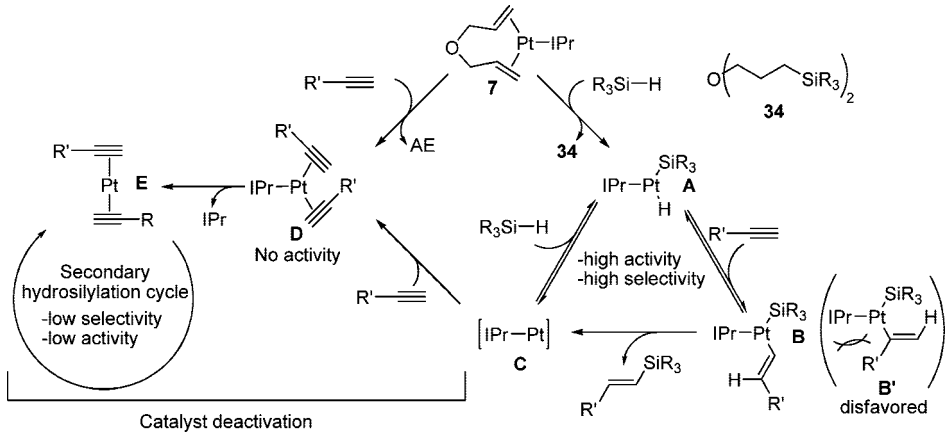
catalytic species to initiate the hydrosilylation. The addition of MD^HM to alkenes, catalyzed by (IPr)Pt(DVDS) (**6**), displayed a similar reaction profile albeit at 80 °C.[45]

To deconvolute the influence of each of the reaction components on the kinetic profile of the hydrosilylation of 1-octyne by MD^HM three separate experiments were performed. Initially, we incubated the catalyst with MD^HM at 60 °C for 3 h (Figure 4, eq A), then the catalyst and 1-octyne were allowed to react for 3 h at 60 °C (Figure 3, eq B), and finally, as a control experiment, the alkyne was treated with MD^HM under identical conditions (Figure 4, eq C). The three reactions were then brought back to 20 °C and the third component was added (the alkyne, the silane, and **7** in the first, second, and third reaction, respectively), and the kinetics were measured. The preactivation of (IPr)Pt(AE) with the silane led to a 6-fold increase in the reaction rate and this treatment completely suppressed the initial induction period (Figure 4, curve A vs curve B). On the other hand, incubation of the platinum complex with 1-octyne led to complete deactivation of the catalyst (Figure 4, curve C vs curve B). This observation reinforces our proposition, made in the case of BnOP, that the allyl ether ligand can be displaced by an alkyne to form the catalytically inactive (IPr)Pt(alkyne)$_2$ complex (Scheme 6), which can further shed

(44) Molander, G. A.; Retsch, W. H. *Organometallics* **1995**, *14*, 4570–4575.

(45) Berthon-Gelloz, G.; Brière, J. F.; Buisine, O.; Stérin, S.; Michaud, G.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D.; Markó, I. E. *J. Organomet. Chem.* **2005**, *690*, 6156–6168.

SCHEME 7. Proposed Catalytic Cycle and Deactivation Pathways for the Hydrosilylation of Alkynes Catalyzed by (IPr)Pt(AE) 7



the NHC ligand to produce an unselective hydrosilylation catalyst. Despite the generally accepted belief that carbene−metal bonds are strong and do not dissociate easily, the loss of NHC ligands has been reported in many cases.[46]

Investigations into the nature of the highly reactive intermediate formed by activation of **7** with a silane are currently underway and will be reported in due course. Preliminary results suggest the formation of a sensitive (IPr)Pt(SiR_3)$_2$ complex, which is a bright yellow compound, reminiscent of the characteristic yellow taint observed during the hydrosilylation reaction (vide supra).

The information garnered on the reactivity of (IPr)Pt(AE) enabled us to propose a reasonable catalytic cycle (Scheme 7). The (IPr)Pt(AE) complex **7** can react with a silane to form the [(IPr)Pt(H)(SiR_3)] (**A**) intermediate, which subsequently undergoes 1,2-migratory insertion of the alkyne to produce **B**. The β-(*E*) isomer is favored over the α isomer because of the steric repulsion encountered in the Pt alkenyl intermediates (**B** and **B′**). After reductive elimination of the vinylsilanes, the [IPr-Pt] (**C**) intermediate can either react with the silane, thus regenerating species **A** and thereby completing the catalytic cycle, or be coordinated by two alkyne molecules to yield a bisalkyne complex **D**, which is catalytically inactive.[32] Platinum derivative **D** can lose the IPr ligand to form the corresponding platinum bisalkyne complex **E**, which, having now lost the bulky IPr ligand, can perform the hydrosilylation reaction but with a low regioselectivity. The (IPr)Pt(alkyne)$_2$ (**E**) complex can also be generated directly from (IPr)Pt(AE) and the alkyne by displacement of the bidentate allyl ether ligand. Indeed, this was observed when 1-octyne and BnOP (**10**) were incubated with **7**. These catalyst deactivation pathways become predominant when the acetylene has a strong coordinating ability (e.g., BnOP). To compensate for the loss of the catalyst, higher loading must be used. Alternatively, the concentration of the alkyne could be kept low.

Conclusions

In summary, we have designed a new NHC−platinum(0) complex, (IPr)Pt(AE) **7**, possessing enhanced activity and displaying high regioselectivity in the hydrosilylation of terminal and internal alkynes. The reaction, which requires low catalyst loading (0.1 to 0.05 mol %), leads exclusively to the cis-addition product containing the silyl substituent on the less hindered terminus of the alkyne. Moreover, the regioselectivity of the addition appears to be independent of the temperature. Investigations into the mechanistic cycles have enabled us to pinpoint several deactivation pathways which are triggered by the alkyne. Low regioselectivities and poor activities are due to a competing secondary cycle in which a platinum species having lost the stereodirecting IPr carbene ligand catalyzed the hydrosilylation. The appearance of this undesired species is due either to the strong coordinating ability of the alkyne or to the low reactivity of the silane or to both. This situation can be remedied by performing the reaction at higher temperatures (60 °C), by increasing the catalyst loading, or by adding slowly the alkyne to the catalyst/silane mixture.

On the basis of our previous study on the structure−activity relationship of (NHC)Pt-based complexes[32] and the present study, our efforts are now being directed toward designing NHCs that would lead to even higher selectivities for internal alkynes.

Experimental Section

The general conditions employed for the hydrosilylation reactions given in Tables 3 and 4 are described below. A detailed account of the reaction conditions and the full characterization of products can be found in the Supporting Information.

Synthesis of (IPr)Pt(AE) (7). To a freshly prepared solution of $Pt_2(AE)_3$ (0.50 mmol of Pt, containing 10 equiv of excess AE) in THF (5 mL, 0.1 M) was added the IPr·HCl salt (331 mg, 0.75 mmol, 1.5 equiv) at rt, followed by *t*-BuOK (83 mg, 0.75 mmol, 1.5 equiv). The reaction was stirred at 20 °C until the reaction was judged complete by TLC (Hex/Et_2O 85:15), usually 16 h. The mixture was filtered on a pad of Celigel (SiO_2/Celite 1:1) and eluted with Et_2O. The crude complex was purified by flash chromatography (Hex/Et_2O 85:15) to yield **7** (256 mg, 75%). R_f 0.65 (SiO_2, hexanes/Et_2O, 85/15, UV, heat, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, 2H, J = 7.7 Hz), 7.20 (s, 2H, J_{Pt-H} = 9.0 Hz), 7.17 (d, 4H, J = 7.7 Hz), 3.95 (dd, 2H, J = 12.0, J = 3.5, J_{Pt-H} = 34.4 Hz), 2.97 (h, 4H, J = 6.7 Hz), 2.44 (dt, 2H, J = 10.9 Hz, J = 2.8 Hz, J_{Pt-H} = 30.0 Hz), 1.63 (tt, 2H, J = 5.6 Hz, J = 11.6 Hz), 1.32 (dd, 2H, J = 1.0, J = 8.3, J_{Pt-H} = 61.6 Hz), 1.18 (d, 12H, J = 6.9 Hz), 1.15 (d, 12H, J = 6.9 Hz), 0.83 (dd, 2H, J_{gem} = 1.0 Hz, J = 10.7 Hz, J_{Pt-H} = 60.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.5 (C), 145.9 (C), 136.8 (CH.), 129.1 (CH), 123.4 (CH), 123.2 (J_{Pt-C} = 40.8 Hz, C), 69.2 (J_{Pt-C} = 30.4 Hz, CH_2), 47.8 (J_{Pt-C} = 142.8 Hz, CH), 32.1 (J_{Pt-C} = 196.1 Hz, CH_2), 28.4 (CH), 25.7 (CH_3), 22.6

(46) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.

(CH_3). ^{195}Pt NMR (107 MHz, $CDCl_3$) −5574 ppm. IR (film, cm^{-1}) 3165 w, 3124 m, 3090 w, 3037 w, 2962 s, 2869 s, 2839 m, 1560 m, 1467 s, 1446 s, 1395 s, 1385 m, 1362 m, 1330 s, 1260 s, 1178 s, 1059 s, 929 s, 858 m, 801 s, 757 s, 697 m, 609 m. MS (ESI) *m*/*z* 681−680−599 $[M - H]^+$, 625−624−623 $[(IPr)Pt(CH_2{=}CH{-}CH_2)]^+$, 599−598−597 $[(IPr)Pt(CH_3)]^+$. Anal. Calcd for $C_{33}H_{46}N_2OPt$: C, 58.13; H, 6.80; N, 4.11. Found: C, 58.19; H, 6.82; N 4.04.

General Procedure for the Hydrosilylation of Alkynes Catalyzed by (IPr)Pt(AE) (7). A mixture of silane (1.1 equiv) and alkyne (1 equiv) was dissolved in the appropriate solvent (1.0 M, solvent can be omitted) and brought to 60 °C. To this mixture was added (IPr)Pt(AE) (**7**) (THF solution, 10 mg/mL, 0.1 mol %). The reaction was heated until judged complete by GC analysis. The β-(*E*)/α ratio of the reaction were determined by GC analysis. The solvents were removed and the residue was filtered on a pad of silica (elution with hexane) to remove the catalyst. The product obtained was pure enough for further transformations. Analytically pure samples were obtained by bulb-to-bulb distillation.

Acknowledgment. This paper is dedicated to Professor T. Hayashi on the occasion of his 60th birthday. G.B.-G. acknowledges Rhodia Corporate for a Ph.D. fellowship. We wish to thank Umicore A.G. (Dr. R. Karch and V. Raab) for a generous gift of platinum salts. Dr. B. Leroy is acknowledged for a gift of compound **17**. Dr. G. Binot is thanked for performing the hydrosilylation on compound **29**.

Supporting Information Available: Additional experimental procedures and full characterization data of all compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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