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Reaction of Allylsilanes and Allylstannanes with Alkynes Catalyzed by Electrophilic Late Transition Metal Chlorides

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The intramolecular reaction of allylsilanes and allylstannanes with alkynes proceeds catalytically in the presence of Pt(II), Pd(II), Ru(II), and Au(III) chlorides. Although more limited, AgOTf also catalyzes the cyclization. Usually, $PtCl_2$ as the catalyst in methanol or acetone gives the best results. The reaction proceeds by exo attack of the allyl nucleophile on the alkyne to form five- or six-membered ring carbocycles. The reaction generally proceeds with anti stereoselectivity. However, a terminally substituted trimethylsilyl derivative reacts by a syn-type addition. The intermediate alkenylpalladium complex has been trapped with allyl chloride to form an allylated derivative with an additional carbon−carbon bond.

Introduction

Metal-promoted carbocyclization reactions of α,ω-enynes are of great interest due to the highly functionalized carbo- and heterocycles that can be prepared.[1] In particular, electrophilic metal complexes or halides catalyze a variety of cyclization reactions in which all atoms included in the starting materials end up in the reaction products.[2−6] We have shown that coordination of $PtCl_2$ to an enyne through the alkyne (**I**, Scheme 1) promotes the intramolecular reaction of the alkene to form a cyclopropyl Pt-carbene intermediate **II** ($MX_n = PtCl_2$).[7] Subsequent attack of the nucleophile (alcohol or water) at the cyclopropyl carbons labeled **a** and **b** of intermediate **II** then presumably gives rise to the formation of five- (**III**) or six-membered (**IV**) intermediates, which evolve under catalytic conditions to afford carbo- or heterocycles **V** or **VI**. Theoretical studies suggest that intermediates similar to **II** are also involved in the intramolecular reaction of furans with alkynes catalyzed by Pt(II).[8] Alternatively, coordination of both functional groups of the enyne to MX_n may form **VII**, which undergoes an oxidative metalacycloaddition to give metalacyclopentene **VIII**.[7b] This metalacycle then evolves by β-hydride elimination to give cycloisomerization products **IX** and **X**.[7b,9]

The transition-metal-promoted cyclizations by intramolecular attack of mild nucleophilic reagents such as allylsilanes[10] or allylstannanes[11] (**XI**) onto alkynes has been less explored.[12,13] This reaction could proceed in a concerted manner through **XII**, or via cyclopropylmetalcarbene **XIII**,[7b] to form alkenylmetal complex **XIV** (Scheme

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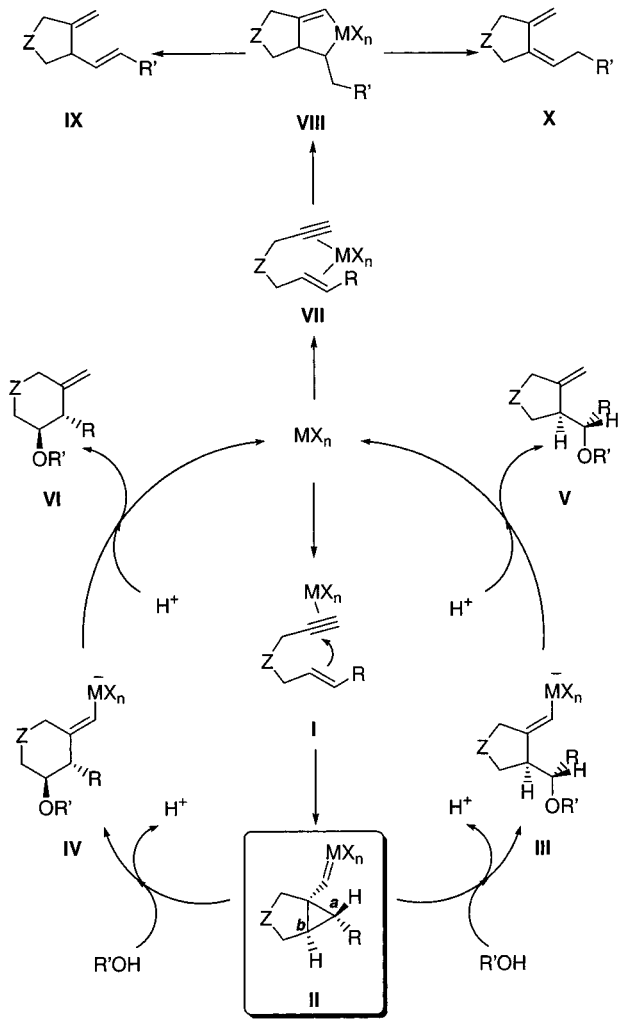
SCHEME 1



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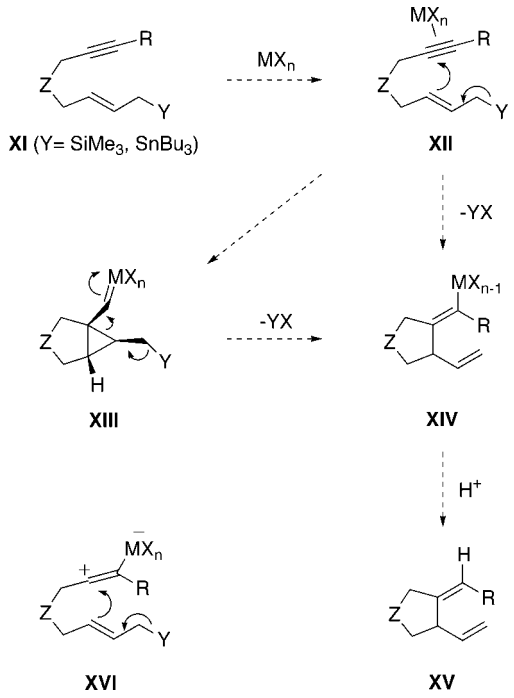

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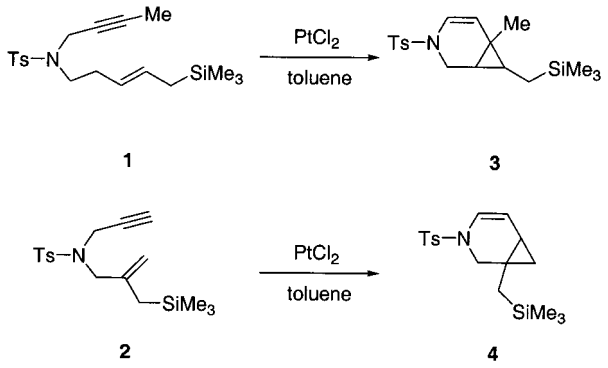

2). Cleavage of **XIV** by the protic solvent might finally give dienes **XV**. The cyclization could also be envisaged to proceed through zwitterionic complex **XVI**, resulting from the slippage of the metal toward the alkyne terminus.[14]

Under stoichiometric conditions, $HgCl_2$ promotes the intramolecular reaction of allylsilanes with alkynes in the presence of a base.[15−17] Interestingly, strong Lewis acids such as $HfCl_4$ promote the endo-dig cyclization of allylsilanes **XI** (M = SiR_3).[18] We have reported that the intramolecular attack of allylsilanes and allylstannanes on alkynes is catalyzed by a wide variety of electrophilic Pt(II), Pd(II), Ru(II), Au(III), and Ag(I) halides or complexes to form dienes **XV**.[19] However, Fürstner found different types of products in the cyclization of allylsilanes (Scheme 3).[6c] Thus, reaction of **1** and **2** in toluene in the presence of $PtCl_2$ as the catalyst gave cyclopropane derivatives **3** and **4**, respectively. Murai found a skeletal rearrangement in another case.[3b] Here we report in detail our results of the cyclization of allylsilanes and allylstannanes with alkynes to give five- and six-membered rings as a function of the substituents and length of the tether and the substitution of the alkyne.

Results and Discussion

Metal-Catalyzed Cyclizations. Certain Ru(II) complexes react with terminal alkynes to form vinylidenes.[20,21]

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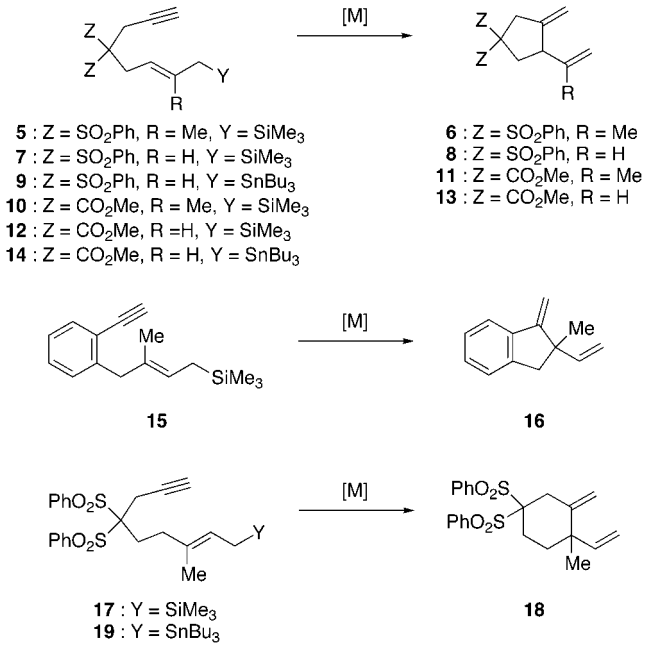
SCHEME 4



In this process, it has been proposed that Ru(II) first coordinates with the alkyne to form a η^2-alkyne complex.[22] Thus, we hypothesized that reaction of the alkyne with an electrophilic Ru(II) complex could promote the nucleophilic attack of the allylsilane or stannane (Scheme 2). In the event, heating a solution of allylsilane **5** in the presence of $CpRuCl(PPh_3)_2$ (5 mol %), and $NaPF_6$ (10 mol %) in MeOH, conditions known to readily form vinylidene ruthenium complexes with terminal akynes,[20] cleanly gave carbocycle **6** in high yield (Scheme 4 and Table 1, entry 1). This transformation was also carried out with $RuCl_3$, Pd(II), Pt(II), and Ag(I) salts under the same conditions (entries 2−9). The best results were obtained by using $PtCl_2$ or $Pt(MeCN)_2Cl_2$ as the catalyst in acetone or MeOH as the solvent (entries 6−8). It is important to remark that proton or Lewis acids could not promote the cyclization. Thus, no cyclization was observed with $BF_3{\cdot}OEt_2$, while reaction in the presence TsOH led only to decomposition of **5**. The cyclization of **5** with $Pt(MeCN)_2Cl_2$ (10 mol %) in refluxing MeOH in the presence of 2,6-di-*tert*-butylpyridine (10 mol %) as a proton scavenger afforded **6** in 59% yield. The cyclization of **5** to give **6** could be carried out in 83% yield with a catalyst prepared in situ from $Pt(MeCN)_2Cl_2$ (10 mol %) and PPh_3 (20 mol %) in refluxing MeOH for 17 h.

Similarly, silane **7** reacted in the presence of $CpRu(PPh_3)_2Cl$ (entry 10) or $PtCl_2$ (entries 11 and 12) to give **8**. Allylstannane **9** also reacts under these conditions to furnish **8** (entry 13). Cyclization of allylsilane **10** gave **11** with similar efficiency (entries 14 and 15). Reaction of **10** also proceeded in toluene, a solvent that has been shown to favor skeletally rearranged products.[3b,6] In this case, only traces of rearranged dienes could be detected in the crude reaction mixture. This reaction was also realized using $AuCl_3$ in MeOH in 67% yield (entry 17), while reaction with $RhCl_3$ (7 mol %) in MeOH afforded only a 7% yield of **11**. The cyclization of allylsilane **12** could not be performed satisfactorily with $PtCl_2$. However, the use of $AuCl_3$ as the catalyst allowed for the formation of **13**, although in low yield. The best results were obtained with this catalyst in the presence of Me_3SiCl (entry 18). Under these conditions, no trapping of the metal intermediate by Me_3SiCl takes place. On the other hand, the reaction of allylstannane **14** was best performed with $CpRuCl(PPh_3)_2$ as the catalyst (cf. entries 19 and 20).

Formation of a quaternary center was also possible. Thus, allylsilane **15** reacted with $Pt(MeCN)_2Cl_2$ as the catalyst to furnish indan derivative **16** in 84% yield (entry 21). Cyclization of allylsilane **17** with $PtCl_2$ catalyst in refluxing MeOH proceeded rather sluggishly to give six-membered ring carbocycle **18** (entry 22). As expected, the corresponding allylstannane **19** was more reactive furnishing **18** in good yield with $PtCl_2$ as the catalyst (entry 23). The cyclization of **19** with AgOTf or $Pd(MeCN)_4(BF_4)_2$ was less efficient (entries 24 and 25).

Allylsilanes or allylstannanes substituted at C-2 of the allyl nucleophile were also examined (Scheme 5). Allylsilane **20** reacted with $Pt(MeCN)_2Cl_2$ to give symmetrical compound **21** in 87% yield (entry 26). Neither **21** nor any other malonate with this structure had been described

TABLE 1. Metal-Catalyzed Cyclization of Enynes XI (Scheme 3)[a]

entry	enyne	catalyst (mol %)	solvent	product	yield (%)
1	**5**	$CpRu(PPh_3)_2Cl$ (5)[b]	MeOH	**6**	92
2	**5**	$RuCl_3$ (5)	MeOH	**6**	53
3	**5**	$PdCl_2$ (5)	MeOH	**6**	47
4	**5**	$Pd(MeCN)_2Cl_2$ (5)	MeOH	**6**	65
5	**5**	$Pd(MeCN)_4(BF_4)_2$ (5)	MeOH	**6**	82
6	**5**	$PtCl_2$ (5)	acetone	**6**	94
7	**5**	$PtCl_2$ (5)	acetone[c]	**6**	83
8	**5**	$Pt(MeCN)_2Cl_2$ (5)	MeOH	**6**	95
9	**5**	AgOTf (5)	dioxane	**6**	54
10	**7**	$CpRu(PPh_3)_2Cl$ (20)[b]	MeOH	**8**	50
11	**7**	$PtCl_2$ (5)	MeOH	**8**	82
12	**7**	$PtCl_2$ (5)	acetone[c]	**8**	81
13	**9**	$PtCl_2$ (5)	MeOH	**8**	62
14	**10**	$PtCl_2$ (4)	MeOH	**11**	65
15	**10**	$PtCl_2$ (5)	aq acetone[d]	**11**	65
16	**10**	$PtCl_2$ (6)	toluene	**11**	93[e]
17	**10**	$AuCl_3$ (4)	MeOH	**11**	67
18	**12**	$AuCl_3$ (6)	MeOH	**13**	50[f]
19	**14**	$CpRuCl(PPh_3)_2$ (20)[b]	MeOH	**13**	81
20	**14**	$PtCl_2$ (5)	MeOH[g]	**13**	43
21	**15**	$Pt(MeCN)_2Cl_2$ (5)	MeOH	**16**	84
22	**17**	$PtCl_2$ (2)	MeOH	**18**	48
23	**19**	$PtCl_2$ (2)	MeOH	**18**	79
24	**19**	AgOTf (28)	dioxane	**18**	32
25	**19**	$Pd(MeCN)_4(BF_4)_2$ (20)	dioxane	**18**	31
26	**20**	$Pt(MeCN)_2Cl_2$ (5)	MeOH	**21**	87
27	**22**	$PtCl_2$ (5)	MeOH	**21**	43
28	**22**	$Pd(MeCN)_2Cl_2$ (5)	MeOH	**21**	24
29	**22**	$AuCl_3$ (5)	MeOH	**21**	42
30	**2**	$Pt(MeCN)_2Cl_2$ (5)	MeOH	**4** + **23**	42 + 36
31	**24**	$PtCl_2$ (5)	MeOH	**25**	87
32	**26**	$CpRu(PPh_3)_2Cl$	MeOH	**27**	79
33	**28**	$PtCl_2$ (5)	MeOH	**29** + **30**	50 + 43

[a] Unless otherwise stated, all reactions were carried out under refluxing conditions for 17 h. [b] $NaPF_6$ (2 equiv on the basis of Ru) was also added. [c] Reaction temperature = 23 °C. [d] 5% aq acetone. [e] Traces of a skeletally rearranged product were detected by ^1H NMR. [f] Reaction was carried out in the presence of Me_3SiCl (10 equiv). [g] Reaction time = 48 h.

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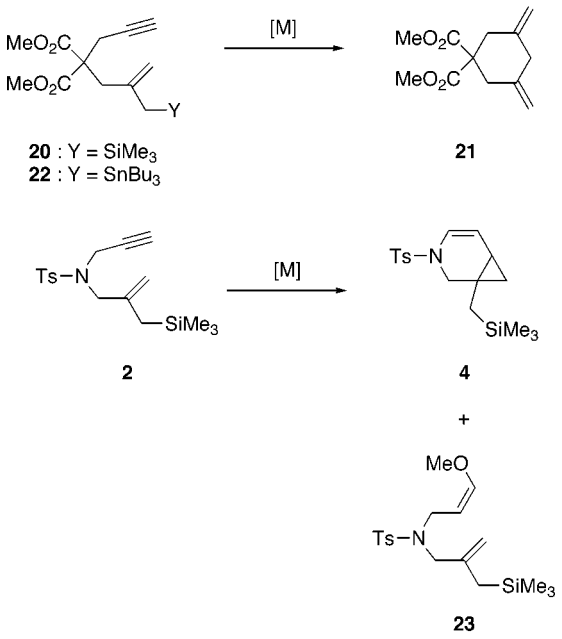
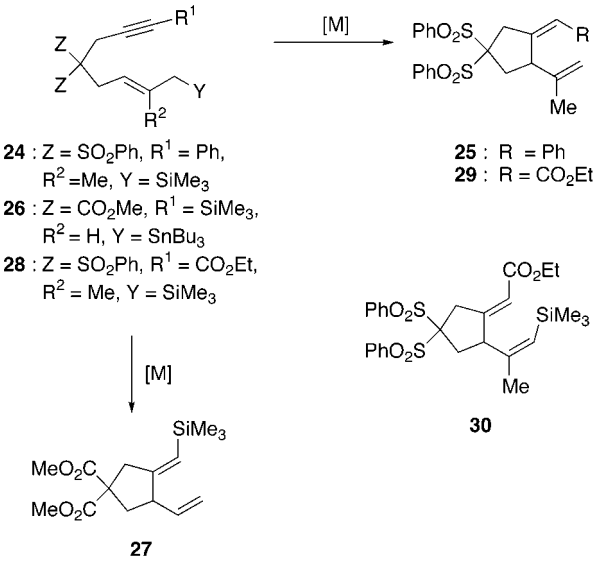
SCHEME 5



SCHEME 6

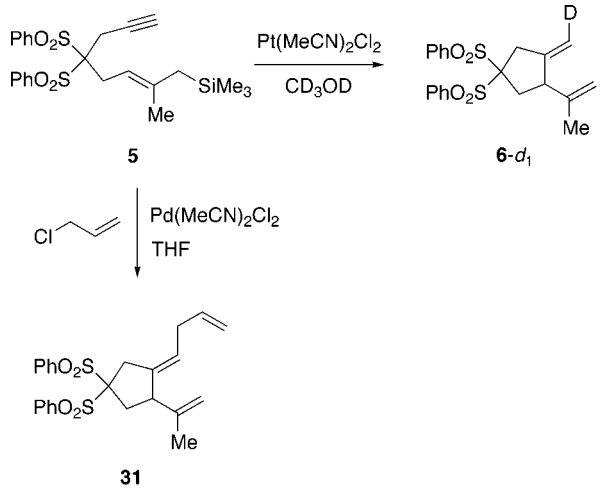


before. Carbocycle **21** was obtained in lower yields from the corresponding stannane **22** by using $PtCl_2$, $Pd(MeCN)_2Cl_2$, and $AuCl_3$ as the catalysts (entries 27−29).

Substrate **2** failed to give the usual cyclized derivatives. Instead, a 1.2:1 mixture of known cyclopropane **4**[6c] (42%) and enol ether **23** (36%) was obtained with $Pt(MeCN)_2Cl_2$ (entry 30). The cis configuration of **23** was assigned on the basis of a vicinal coupling constant of 6.6 Hz between the enol ether hydrogens. Enol ether **23** formally arises by trans-addition of methanol to the terminal alkyne in an anti-Markovnikov fashion. This result contrasts with the addition of water or alcohols to terminal alkynes catalyzed by Pt(II), which occurs at C-2.[23,24] However, the anti-Markovnikov addition of water with $CpRu(PR_3)_2Cl$ complexes as catalysts has recently been reported.[25,26]

Substituted alkynes also react with electrophilic metal catalysts to give the corresponding carbocycles (Scheme 6). Thus, phenyl-substituted alkyne **24** reacted in the presence of $PtCl_2$ to selectively give *Z*-**25** in 87% yield (Table 1, entry 31). The *E*-stereoisomer of **25** has been obtained by the cycloisomerization of the corresponding enyne with a Pt(II) catalyst.[7b] The cyclization of **26** proceeded slowly in the presence of $CpRuCl(PPh_3)_2$ (50 mol %) to give exclusively **27** (79%) with an *E*-configuration (entry 32).[15] Substrate **28**, reacted in the presence of $PtCl_2$ as the catalyst to give a 1.2:1 mixture of **29**, with the exocyclic alkene with a *Z*-configuration, and **30** (entry 33), the product of a Pt(II)-catalyzed cycloisomerization reaction.[7b]

SCHEME 7



To confirm that the cyclizations occur under kinetic conditions, the stability of **25**, **27**, and **29** was compared with that of their stereoisomers at the semiempirical PM3 level.[27] These calculations indicate that **27** is more stable than its *Z*-stereoisomer (ΔH_f = 1.6 kcal/mol). However, *Z*-derivatives **25** and **29** are indeed less stable than their *E*-isomers (ΔH_f = 1.7 and 2.2 kcal/mol, respectively). The fact that the less stable isomer **29** with an isomerizable α,β-unsaturated ester was obtained from **26** demonstrates that the carbocyclization occurs under nearly neutral conditions.

Mechanistic Insights. To ascertain the mechanism of the metal-catalyzed cyclization, the reaction of allylsilane **5** was carried out using methanol-d_4 as the solvent. Under the conditions of entry 8, **5** gave exclusively **6**-d_1 (Scheme 7). The configuration of **6**-d_1 was determined by the absence of the signal corresponding to the meth-

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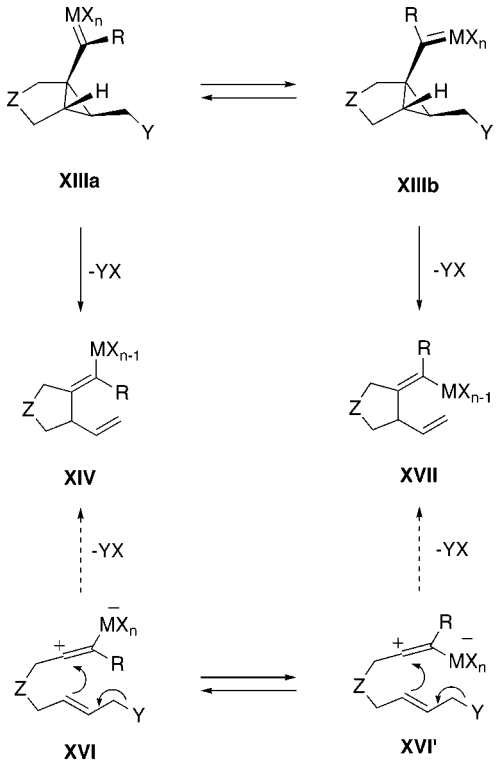
SCHEME 8



ylidene *E*-hydrogen at 4.96 ppm of **6**. This result indicates that the metal probably coordinates the alkyne as shown in **XII** (Scheme 2), thus triggering an anti attack of the allyl nucleophile. Cleavage of the carbon−metal bond of **XIV** (MX_{n-1} = PtCl) by methanol-d_4 accounts for the formation of **6**-d_1. However, monitoring by NMR the reaction of **5** with 50% $Pt(MeCN)_2Cl_2$ in methanol-d_4 at 23 °C only allowed observation of product **6** and $(CH_3)_3$-Si−O−Si$(CH_3)_3$ (δ = 1.90 in ^{13}C NMR).

Trapping of intermediate alkenyl−metal complex **XIV** by insertion of allyl chloride, followed by elimination of MX_n, could lead to the formation of an additional C−C bond.[28,29] Thus, cyclization of **5** with $Pd(MeCN)_2Cl_2$ as the catalyst (5 mol %) in THF in the presence of excess allyl chloride and 4 Å molecular sieves stereoselectively led to **31** (43%), along with **6** (19%). In the absence of 4 Å molecular sieves, **6** was obtained as the major products as a result of protodemetalation of the intermediate **XIV**. Similarly, when the reaction was carried out in MeOH, **31** was obtained in only 9% yield, along with **6** (84%). No allylation was observed when the reaction was catalyzed by Pt(II), which suggest that the intermediate alkenyl−platinum complex is more prone to protodemetalation.

The isolation of *Z*-configured **25** and **29** is also consistent with the formation of intermediates **XIV** by an overall anti attack of the allyl nucleophile and the metal on the alkyne (Scheme 2). However, formation of **27** in the cyclization of **26** can be explained by the conformational equilibrium between **XIIIa** and **XIIIb**, which could favor the rotamer **XIIIb** with the bulky $SiMe_3$ at the least sterically hindered position (Scheme 8). Alternatively, formation of **27** could also be explained by the attack of the allyl nucleophile anti to the trimethylsilyl substituent of the vinyl cation **XVI′**, which is in agreement with that proposed for a similar cyclization mediated by $HgCl_2$.[15]

Summary

The cyclization of allylsilanes and allylstannanes with alkynes proceeds catalytically in the presence of a variety of electrophilic metal salts. The use of $PtCl_2$ as the catalyst in methanol gives the best results in most cases. Products of skeletal rearrangement (metathesis-type), which are the major products in the cyclization of enynes with electrophilic metal salts,[2−4,6] are not formed in significant amounts in this metal-catalyzed cyclization. However, substrate **2** with a tosylamino functionality between the alkyne and allylsilane reacts anomalously to give a mixture of a cyclopropane derivative and the product of a formal trans addition of methanol across the triple bond. This last type of reactivity appears to be unprecedented.

This carbocyclization is particularly useful for the synthesis of five- and six-membered carbocycles, even when the C−C bond formation involves the creation of a quaternary center. This reaction is regiocomplementary to that promoted by Lewis acids,[18] which gives endocyclized products in most cases.

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Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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