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Ruthenium-Catalyzed Synthesis of Functional Conjugated Dienes via Addition of Two Carbene Units to Alkynes

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Abstract: The reaction of a variety of alkynes with $N_2CHSiMe_3$, in the presence of Cp*RuCl(cod) as the catalyst precursor, leads to the general formation of functional conjugated dienes. This selective formation results from the ruthenium-catalyzed creation of two carbon−carbon double bonds in a single step under mild conditions. Terminal alkynes produce 1,4-bistrimethylsilylbuta-1,3-dienes with *Z* stereoselectivity for the less hindered double bond whereas disubstituted alkynes favor *E*-configuration for the same double bond. Diynes react also as monoalkynes, and only one triple bond is transformed to give disilylated dienynes. The reaction can be applied to the *in situ* desilylation in methanol and formation of monosilylated dienes. The catalytic formation of 1,4-bisfunctional buta-1,3-dienes can also take place with N_2CHCO_2Et and N_2CHPh. The reaction can be understood by addition of two carbene units to triple bonds. An initial [2 + 2] addition of the Ru=CHSiMe$_3$ bond with the alkyne triple bond leads to an alkenyl ruthenium-carbene species capable of coordinating a second carbene unit to produce conjugated dienes.

Introduction

Conjugated dienes are useful building blocks due to their utilization in numerous transformations[1] such as the Diels−Alder reactions and because they appear as important structural constituents in natural product chemistry and materials science.[2] Although a wide variety of methods, especially by utilizing various organometallic reagents, has been developed for the construction of 1,3-dienes,[3] the direct and efficient preparation of stereodefined substituted and functionalized conjugated dienes is not straightforward and remains an area of current investigation. The formation of several carbon−carbon bonds in a single chemical reaction represents a particularly direct and efficient approach for the synthesis of complex molecular structures using available starting materials. The metal-catalyzed addition of two carbene units across a triple bond leading to the selective construction of multisubstituted functionalized conjugated dienes does exemplify the previous concept.

In this area, metal-catalyzed reactions of diazo compounds have shown an important contribution, allowing the controlled transfer of carbene units into organic substrates.[4] Thus, ruthenium precatalysts have shown efficiency in the activation of diazo compounds allowing their dimerization[5] but especially their reactivity toward double bonds to lead to alkene metathesis,[6] ring-opening metathesis polymerization of cyclic olefins,[7] and particularly to cyclopropanation of alkenes.[5e,8] By contrast, no example of addition of diazo compounds to triple bonds, catalyzed by ruthenium-carbenoid species, has been reported to our knowledge, previous to our initial work.[9] Catalytic addition of diazo compounds to alkynes arises, however, essentially with Rh(I) catalysts[10a−d,11−13] and more recently described with copper(I) compounds.[10e,12b,c] A wide variety of cyclopropene intermediates are obtained by intermolecular

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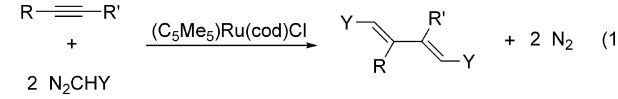
addition[10] including enantioselective reaction.[11] Intramolecular addition affords macrocyclic cyclopropenes[12] or reactive vinyl carbenoid species, which can lead to further synthetic transformations, such as cyclic enones or phenols.[13] Conjugated dienes were obtained by the stoichiometric addition of two molecules of diazocarbonyl compounds to a cobalt alkyne complex by O'Connor et al.[14]

On the other hand, ruthenium-carbene species, designed for alkene metathesis, are well-known to react with alkynes to produce vinyl carbene intermediates by intramolecular or intermolecular ene-yne metathesis,[2a,15] ring-closing or cross metathesis, respectively, leading to the formation of conjugated dienes.

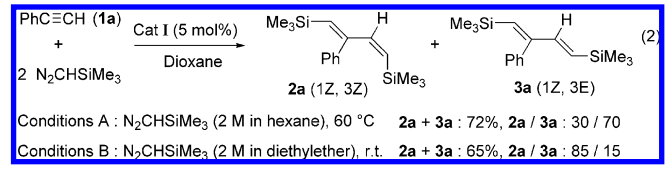
On the basis of our studies concerning the catalytic activity of the complex $(C_5Me_5)Ru(cod)Cl$[9a] and its ability to accommodate two cis carbene ligands,[16a,b] we could envisioned the formation of ruthenium-carbene species, *in situ* generated from diazo compounds, and their catalytic addition to alkynes. We describe here the synthesis of functional and stereodefined substituted conjugated dienes by the combination of two molecules of diazo compounds with an alkyne, catalyzed by the precatalyst $(C_5Me_5)Ru(cod)Cl$ (eq 1). This selective formation results from the ruthenium-catalyzed creation of two carbon−carbon double bonds in a single chemical reaction under mild conditions.



(1)

Results and Discussion

Our initial attempt at transformation[9b] of phenylacetylene **1a**, in presence of 5 mol % of the precatalyst $(C_5Me_5)RuCl(cod)$ (**I**) (cod = cycloocta-1,5-diene), with 2.4 equiv of trimethylsilyldiazomethane $N_2CHSiMe_3$ (commercial solution at 2 mol L^{-1} in hexane) in 2 mL of dioxane (conditions A) gave, after 6 h at 60 °C, a 72% yield of disilylated dienes as a mixture of two isomers **2a** and **3a**, with a ratio **2a/3a** of 30/70 (eq 2). ^1H NMR and NOE experiments showed a *Z* stereoselectivity for the trisubstituted double bond, whereas the disubstituted double bond was formed with a *Z*/*E* stereoselectivity (*Z*/*E*: 30/70).



Using 2.4 equiv of a commercial solution of $N_2CHSiMe_3$ 2 mol L^{-1} in diethyl ether, the same reaction of **1a** in dioxane (conditions B) took place more rapidly, at room temperature (complete conversion in 30 min). The isolated yield was similar but the ratio **2a/3a** was reversed (85/15 instead of 30/70), the compound **2a** (1*Z*, 3*Z*) being now the major product (eq 2).

A study of the reaction conditions was carried out. First the influence of the reaction temperature and the nature of $N_2CHSiMe_3$ solution was studied in 2 mL of dioxane with 1.25 mmol of phenylacetylene and 2.4 equiv of $N_2CHSiMe_3$ (Table 1).

The species $N_2CHSiMe_3$ in solution in diethylether was more reactive than in solution in hexane. After 20 h at room temperature, only 25% of compounds **2a/3a** was produced with $N_2CHSiMe_3$ in hexane whereas 65% yield was obtained after 30 min at room temperature with $N_2CHSiMe_3$ in diethylether. Using both solutions, lower temperature favored the isomer **2a** formation which was almost exclusively obtained, up to 98%

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Table 1. Influence of the Temperature in Dioxane

$N_2CHSiMe_3$	condition reactions[a] *T*, time	isolated yield[b] **2a** + **3a**	ratio **2a/3a**
2 M in hexane	60 °C, 6 h	72%	30/70
	r.t., 20 h	25%	85/15
2 M in diethylether	60 °C, 30 min	58%	50/50
	r.t., 30 min	65%	85/15
	0 °C, 20 h	56%	95/5
	− 20 °C, 20 h	44%	98/2

[a] $N_2CHSiMe_3$ (2.4 equiv), in dioxane (2 mL), 5 mol % Cat I. [b] Isolated product yields obtained after purification by silica gel chromatography.

Table 2. Influence of the Nature of the Solvent

condition reactions[a] $N_2CHSiMe_3$, *T*, time	solvent	isolated yield[b] **2a** + **3a**	ratio **2a/3a**
2 M in hexane 60 °C, 6 h	Dioxane	72%	30/70
	THF	64%	50/50
	Hexane	52%	74/26
	DCM	15%	67/33
2 M in diethylether r.t., 30 min	Dioxane	65%	85/15
	THF	90%	85/15
	Pentane	57%	80/20
	Diethylether	52%	95/5
	DCM	38%	100/0

[a] $N_2CHSiMe_3$ (2.4 equiv), in 2 mL of solvent, 5 mol % Cat I. [b] Isolated product yields obtained after purification by silica gel chromatography.

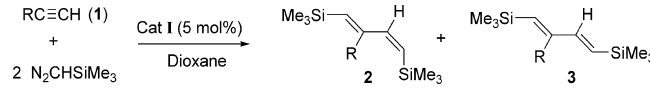
selectivity, at −20 °C. At higher temperature, the formation of **3a** was improved, becoming the main isomer using hexane solution. The best conditions, in terms of selectivity and conversion, were obtained using the diethylether solution at room temperature. The *Z*- or *E*-stereochemistry of the obtained dienes **2a/3a** did not directly result from the reaction temperature but was derived from the stability of intermediate species. Indeed, heating at 60 °C of a mixture of compounds **2a/3a** (**2a/3a**: 85/15) in dioxane in the presence, or not, of 5 mol % of precatalyst **I** did not modify, after 24 h, the ratio for **2a/3a**.

The study of the effect of the reaction solvent showed that the reaction was more efficient in polar solvents like dioxane or THF, the former giving the best results for several compounds (Table 2).

The bulky, electron-rich precursor $(C_5Me_5)RuCl(cod)$ (**I**) appeared to be a selective catalyst for this reaction whereas $RuCl_3{,}nH_2O$ $(PPh_3)_3RuCl_2$, $[(p\text{-cymene})RuCl_2]_2$, $(C_5Me_5)Ru(CH_3CN)_3PF_6$ did not catalyze it at all. The transformation of **1a**, in presence of 5 mol % of the precatalyst $(C_5H_5)RuCl(cod)$, with 2.4 equiv of $N_2CHSiMe_3$ in 2 mL of dioxane gave only, after 5 h at room temperature, 22% yield of disilylated dienes **2a** and **3a**, with a ratio **2a/3a** of 60/40. This showed the crucial role of the more electron-rich and bulky C_5Me_5 ligand.

This selective formation of 1,4-bisfunctional buta-1,3-dienes under mild conditions constitutes an alternative route, with the advantageous presence of reactive vinylsilane moieties, to 1,3-dienes from alkynes and ethylene via intermolecular ene-yne metathesis catalyzed by Grubbs type catalysts.[17] Vinylsilanes are known to be reactive moieties and the silicon substituted

Table 3. Reaction of Terminal Alkynes with $N_2CHSiMe_3$



Alkyne **1** R =	Reaction conditions[a]	Dienes **2** + **3**	yield[c] (**2** + **3**)	ratio **2/3**
(**1a**)	A, 6 h B, 30 min B[b], 30 min	**2a/3a**	72% 65% 58%	30/70 85/15 50/50
(**1b**)	A, 6 h B, 10 min	**2b/3b**	80% 70%	11/89 30/70
NC (**1c**)	B, 30 min B[b], 30 min	**2c/3c**	40% 26%	75/25 25/75
MeO (**1d**)	B, 10 h B[b], 30 min	**2d/3d**	20% 49%	85/15 50/50
$CH_3(CH_2)_5$- (**1e**)	B, 5 h B[b], 5 h	**2e/3e**	38% 45%	95/5 50/50
$CH_3(CH_2)_3$- (**1f**)	B, 5 h	**2f/3f**	28%	95/5
Me_3Si- (**1g**)	B, 5 h	**3g**	48%	0/100
$HOCH_2$- (**1h**)	B, 5 h	**2h/3h**	70%	80/20
$BzOCH_2$- (**1i**)	B, 5 h	**2i/3i**	45%	95/5

[a] Reaction conditions: A, 2.4 equiv of $N_2CHSiMe_3$ (2 M in hexane), in dioxane (2 mL), 60 °C, 5 mol % Cat I; B, 2.4 equiv of $N_2CHSiMe_3$ (2 M in ether), in dioxane (2 mL), r.t., 5 mol % Cat I. [b] Conditions B at 60 °C. [c] Isolated product yields obtained after purification by silica gel chromatography.

1,3-dienes have become versatile building blocks in organic synthesis via Diels−Alder cycloadditions[1e,f,18] or electrophilic substitution reactions.[1e,f,19] The reaction of desilylation-bromination of silylated 1,3-butadienes affords 1,4-dibromo-1,3-butadienes[20] that are synthetically important intermediates.[3f] This synthesis potential of disilylated dienes led us to explore the scope of the reaction.

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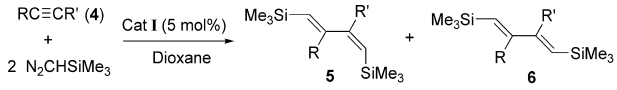
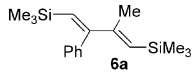
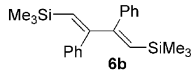
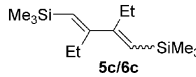
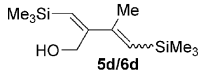
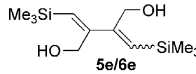
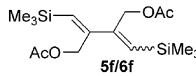
Table 4. Reaction of Disubstituted Alkynes with $N_2CHSiMe_3$



Alkyne **4**	Reaction conditions[a]	Dienes **5** + **6**	yield[c] (**5** + **6**)	ratio **5**/**6**
PhC≡CMe (**4a**)	A, 6 h B, 5 h B[b], 5 h	 **6a**	56% 74% 59%	0/100 0/100 0/100
PhC≡CPh (**4b**)	A, 6 h B, 5 h B[b], 5 h	 **6b**	30% 43% 15%	0/100 0/100 0/100
EtC≡CEt (**4c**)	A, 6 h B, 5 h B[b], 5 h	 **5c/6c**	72% 50% 57%	0/100 5/95 0/100
$HOH_2CC{\equiv}CMe$ (**4d**)	A, 6 h B, 5 h	 **5d/6d**	95% 88%	0/100 15/85
$HOH_2CC{\equiv}CCH_2OH$ (**4e**)	B, 5 h B[b], 5 h	 **5e/6e**	82% 51%	40/60 15/85
$AcOH_2CC{\equiv}CCH_2OAc$ (**4f**)	B, 5 h B[b], 5 h	 **5f/6f**	89% 95%	80/20 35/65

[a] Reaction conditions: A, 2.4 equiv of $N_2CHSiMe_3$ (2 M in hexane), in dioxane (2 mL), 60 °C, 5 mol % Cat I; B, 2.4 equiv of $N_2CHSiMe_3$ (2 M in ether), in dioxane (2 mL), r.t., 5 mol % Cat I. [b] Conditions B at 60 °C. [c] Isolated product yields obtained after purification by silica gel chromatography.

The best conditions (A and B) for the transformation of **1a** into **2a/3a**, with 5 mol % of $(C_5Me_5)RuCl(cod)$ and 2.4 equiv of $N_2CHSiMe_3$, in dioxane, were used to study the scope of the reaction with a variety of terminal alkynes (Table 3).

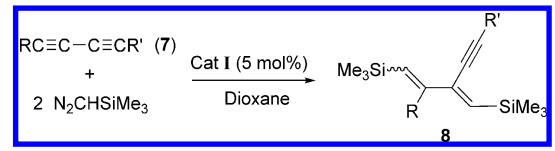
The terminal alkynes with a substituent conjugated with the triple bond (**1a**, **1b**) led to good yields in both conditions A and B. However, when the phenyl ring was substituted by a *p*-CN or a *p*-OMe group (**1c**, **1d**) the yields decreased. With an electron-withdrawing substituent, alkyne **1c** reacted rapidly but only 40% yield of products **2c/3c** was obtained. An increase of the temperature to 60 °C did not improve the yield. Alkyne with electrodonating substituent **1d** reacted more slowly at room temperature. The conversion of **1d** was not complete after 10 h (50% conversion) and the yield was low. At 60 °C, the conversion of **1d** was complete after 30 min and the yield increased with a ratio **2d/3d** of 50/50. The alkynes with an alkyl substituent (**1e**, **1f**) gave no conversion in conditions A but led to products **2/3** in conditions B, with modest yields but high selectivity at room temperature. Alkynes with functional groups reacted also in conditions B to give dienes: trimethylsilylacetylene (**1g**) led only to diene **3g** whereas propargyl alcohol (**1h**) or propargyl ester (**1i**) gave the corresponding conjugated dienes **2/3** with satisfactory yields and good selectivity toward dienes **2** (**2** ≫ **3**). From propargyl alcohol **1h**, a small quantity of a monosilylated diene (**9h**, see later Table 6) was also obtained.

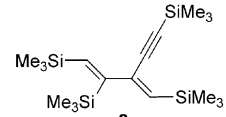
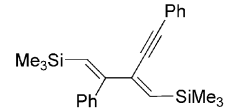
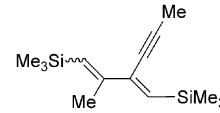
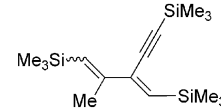
In conditions B at room temperature, the reaction favored generally the formation of isomer **2** except for the alkynes with a bulky substituent as a cyclohexenyl or trimethylsilyl group (**1b**, **1g**). In conditions A (60 °C), isomer **3** was the major product.

The reaction was then extended to various disubstituted alkynes **4**, in conditions A or B, and led to conjugated 2,3-disubstituted-1,4-bistrimethysilylbutadienes with good yields (Table 4). For both conditions, alkynes with an aryl substituent (**4a**, **4b**) led to conjugated dienes, however bulkier alkyne **4b** led to a lower yield. Alkyl disubstituted alkyne **4c** was converted in good yield to diene **6c** (72%, conditions A) whereas the corresponding terminal alkynes produced low yields. Propargylic alcohols (**4d**, **4e**) and ester (**4f**) gave the 1,4-bistrimethylsilylbutadienes **5/6d**−**f** in very good yields thus showing that the reaction tolerated hydroxy and carboxylate functional groups. However, with bulky alkynes as 1,4-dimethylbut-2-yne-1,4-diol or bistrimethylsilylacetylene, no conversion was observed. In conditions A (60 °C), only one isomer, **6**, corresponding to diene **3** structure, was obtained. Thus, the disubstituted alkynes **4a**−**d** led selectively to dienes **6a**−**d**. NOE experiments and selective ^{13}C NMR decoupling carried out on diene **6a** showed that the only isomer had both substituents in the cis position on each double bond. In conditions B, the same isomer **6** was selectively formed from alkynes with an aryl substituent (**4a**−**b**). The yields for **6a**−**b** were improved in these latter conditions. From alkynes with a methylene group linked to the triple bond (**4c**−**f**), conditions B led to a mixture of isomers **5** and **6** at room temperature. From hex-3-yne (**4c**), a small quantity of isomer **5c** was detected at room temperature. An increase of the temperature at 60 °C led only to isomer **6c**. From propargylic alcohols (**4d**, **4e**), a good yield was obtained at room temperature. A mixture of isomers **5** and **6** was formed, isomer **6** being the major isomer. From propargylic ester **4f**, the nonsymmetrical isomer **5f** became the favored isomer at room temperature (**5f/6f**: 80/20). In all cases, an increase of the temperature at 60 °C favored the formation of isomer **6**.

The reactivity of diynes was also examined to clear up the regioselectivity of the addition of diazo compounds on two triple

Table 5. Reaction of 1,3-Diynes with $N_2CHSiMe_3$



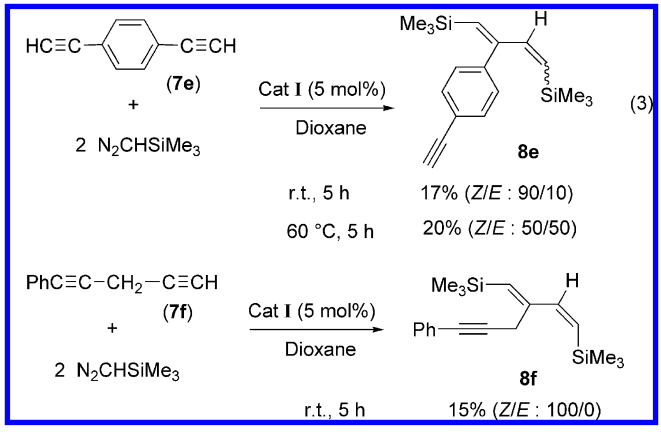
Diyne **7**	Reaction conditions[a]	Dienyne **8**	yield[b]
$Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**7a**)	A, 6 h B, 2 h	 **8a**	48% 94%
$PhC{\equiv}C{-}C{\equiv}CPh$ (**7b**)	B, 5 h	 **8b**	93%
$MeC{\equiv}C{-}C{\equiv}CMe$ (**7c**)	B, 5 h	 **8c** 2 stereoisomers: 90/10	94%
$MeC{\equiv}C{-}C{\equiv}CSiMe_3$ (**7d**)	B, 24 h	 **8d** 2 stereoisomers: 65/35	51%

[a] Reaction conditions: A, 2.4 equiv of $N_2CHSiMe_3$ (2 M in hexane), in dioxane (2 mL), 60 °C, 5 mol % Cat I; B, 2.4 equiv of $N_2CHSiMe_3$ (2 M in ether), in dioxane (2 mL), r.t., 5 mol % Cat I. [b] Isolated product yields obtained after purification by silica gel chromatography.

bonds. In the presence of 4.8 equiv of trimethylsilyldiazomethane, diynes **7** reacted as monoalkynes and only one C≡C bond was transformed to give disilylated dienynes. 1,4-Disubstituted-1,3-diynes (**7a**−**d**, Table 5) and diynes with a spacing group between the triple bonds (**7e**−**f**, eq 3) were reacted. The 1,3-diynes led to functional unsaturated carbon-rich molecules with good yields. The symmetrical 1,3-diynes (**7a**−**c**) afforded the corresponding dienynes **8** with excellent yields in mild conditions. Only one stereoisomer was formed except for the less bulky diyne **7c** which led to two stereoisomers in a ratio 90/10. A small quantity (5%) of tetrasilylatedtetraenes formed from a double addition of diazoalkane compound on each triple bond was also detected in this case. It was the only example of the addition of four carbene units on the two C≡C bonds of the diyne, probably due to lower steric hindrance of the methyl group.

When an unsymmetrical 1,3-diyne (**7d**) was used, only one regioisomer was obtained: the double addition of diazoalkane was carried out on the less bulky triple bond and the trimethylsilylethynyl group remained unchanged. However, two stereoisomers for **8d** were also obtained (as for **8c**) in a ratio 65/35.

When the two triple bonds of the diyne were spaced by a phenyl ring (**7e**) or a methylene group (**7f**), the conversion of the diyne decreased (eq 3). 30% of conversion was obtained at room temperature for **7e** after 5 h. The double addition of diazoalkane took place only on the terminal triple bond (**7f**) and the stereoselectivity of the obtained disubstituted double bond (*Z* favored) for both diynes was similar to the one obtained with terminal alkynes.

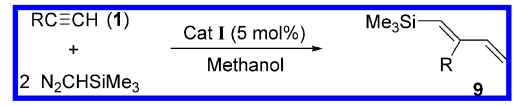


The direct desilylation of 1,4-bistrimethylsilylbuta-1,3-dienes appeared difficult to perform.[21] However, the *in situ* formation of desilylated double bond from $N_2CHSiMe_3$ in methanol has already been obtained from triple bonds of enynes, in the presence of cat **I**, to produce bicyclic compounds with desilylated vinyl groups.[9e] In the case of simple alkynes, the reaction of phenylacetylene **1a** or propargyl alcohol **1h** with a slight excess of trimethylsilyldiazomethane in methanol led to monosilylated butadienes **9** with good yields (Table 6). Only one isomer was obtained, the silylated double bond being the more substituted one.

The catalytic transformation of alkynes was performed with other diazoalkane compounds such as N_2CHCO_2Et or N_2CHPh. Ethyldiazoacetate is less reactive than trimethylsilyldiazomethane and required more drastic reaction conditions. After 24 h at 100 °C in dioxane, in the presence of 5 mol % of cat **I**, phenylacetylene **1a** or ethynylcyclohexene **1b** reacted with 2.4 equiv of ethyldiazoacetate and afforded butadienes **10** as a mixture of isomers (Table 7). No reaction was observed with disubstituted alkynes or nonactivated terminal alkynes.

(21) Xi, Z.; Song, Z.; Liu, G.; Liu, X.; Takahashi, T. *J. Org. Chem.* **2006**, *71*, 3154–3158.

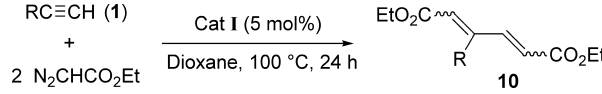
Table 6. Reaction of Alkynes with $N_2CHSiMe_3$ in MeOH



Alkyne **1**	Reaction conditions[a]	diene **9**	yield[b]
PhC≡CH (**1a**)	r.t. 60 °C	Me3Si, Ph (**9a**)	30% 82%
$HOH_2CC{\equiv}CH$ (**1h**)	r.t.	Me3Si, HO (**9h**)	58%

[a] Reaction conditions:2.4 equiv of $N_2CHSiMe_3$ (2 M in ether), in methanol (2 mL), r.t. or 60 °C, 2−5 h, 5 mol % Cat I. [b] Isolated product yields obtained after purification by silica gel chromatography.

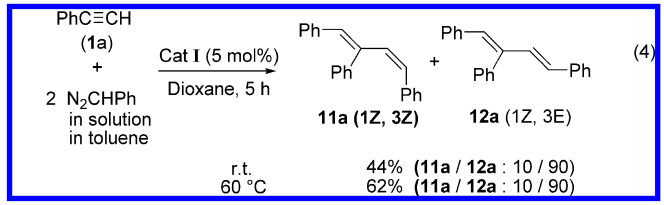
Table 7. Reaction of Terminal Alkynes with N_2CHCO_2Et



Alkyne **1**	diene **10**	yield[a]
PhC≡CH (**1a**)	EtO2C, Ph, CO2Et (**10a**)	64%
C≡CH (**1b**)	EtO2C, CO2Et (**10b**)	54%

[a] Reaction conditions: 2.4 equiv of N_2CHCO_2Et, in dioxane (2 mL), 100 °C, 5 mol % Cat I. Isolated product yields obtained after purification by silica gel chromatography.

The catalytic transformation of phenylacetylene **1a** carried out in the presence of phenyldiazomethane (in solution in toluene) led to butadienes **11a** and **12a** (eq 4).

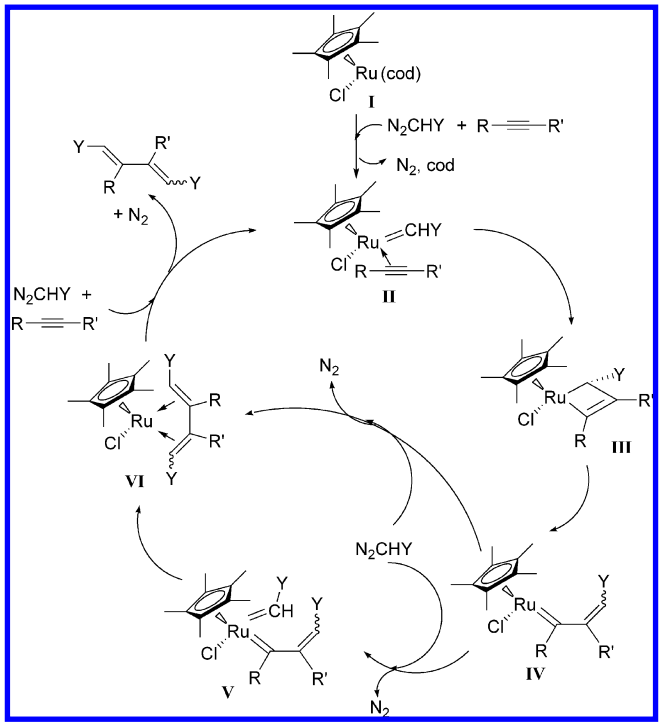


The reaction with this diazoalkane proceeded at room temperature but the diazoalkane was more reactive at 60 °C and 62% yield was obtained. A mixture of isomers **11a** and **12a** with the same ratio was formed in each case. The major isomer **12a** (1*Z*, 3*E*) was different of one obtained with trimethylsilyldiazomethane (1*Z*, 3*Z*). In this case, the selectivity was independent of the temperature.

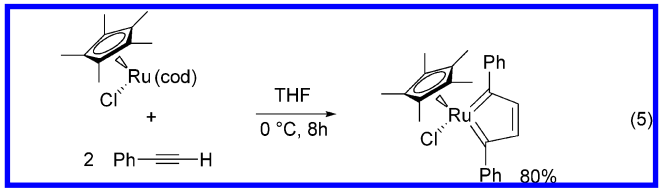
Proposed Mechanism

Catalytic Cycle. A possible mechanism for this selective formation of conjugated dienes from alkynes is shown in Scheme 1.

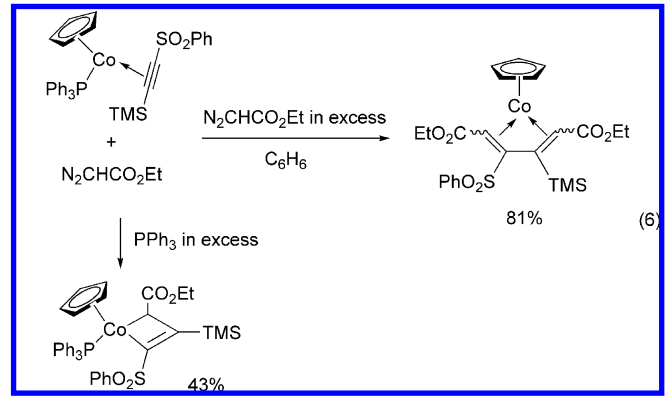
Scheme 1. Proposed Catalytic Cycle



It is known that the complex Cp*RuCl(cod) easily loses its cod ligand in the presence of unsaturated substrates, thus offering two vacant coordination sites for the activation of two unsaturated bonds.[9] Diazo compounds are expected to interact first with the precatalyst Cp*RuCl(cod) to give ruthenium-carbene species although this 16-electron species cannot be observed by NMR. Indeed, the formation of $(C_5R_5)X(PPh_3)Ru{=}CR^1R^2$ complexes has been shown by H. Werner et al.[22] They have synthesized the complexes $(C_5H_5)Cl(PPh_3)Ru{=}CHSiMe_3$ and $(C_5Me_5)Cl(PPh_3)$-$Ru{=}CHPh$ by the addition of trimethylsilyldiazomethane and phenyldiazomethane, respectively, to complexes with a (C_5R_5)-$(PPh_3)Ru$ moiety. In addition, the precatalyst Cp*RuCl(cod) **I** is known to react, in absence of diazo compound, at room temperature with phenylacetylene **1a** to give a biscarbene complex (eq 5).[16]



This latter complex is not observed on reaction of **I** with phenylacetylene in presence of $N_2CHSiMe_3$, indicating that the reaction of $N_2CHSiMe_3$ with the ruthenium center is faster than the coupling of alkynes. Thus, the coordination of one molecule of diazo compound to the ruthenium center, leading to a ruthenium carbene species, and the alkyne allows the displacement of the cod ligand (species **II**, Scheme 1) and leads to a classical oxidative coupling to give the metallacyclobutene **III**. A complex analogous to this intermediate **III** has already been isolated (43%) and characterized by O'Connor et al. by reaction of ethyldiazoacetate with the η^2-alkyne complex $(C_5H_5)(PPh_3)Co(\eta^2$-$Me_3SiC{\equiv}CSO_2Ph)$ and PPh_3 in excess (eq 6).[14b]



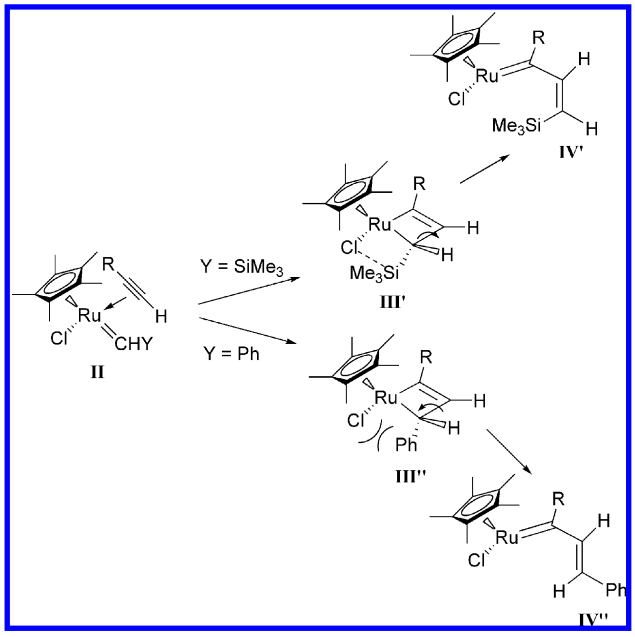
Via opening of intermediate **III**, as in enyne metathesis, the ruthenium vinyl carbene **IV** can be formed. The addition of a second molecule of diazo compound on **IV** may lead to the ruthenium biscarbene **V** as two cis carbene ligands can be accommodated on a $(C_5Me_5)RuCl$ moiety (eq 5).[16] Then the coordinated diene **VI** can be obtained by coupling of both carbene species and formation of a C=C bond. A direct interaction of the nucleophilic diazo compound with the electrophilic carbene complex (intermediate **IV**) followed by elimination of $(C_5Me_5)ClRu$ and N_2, as described for the dimerization of diazoalkanes with porphyrin ruthenium complex,[5a] is also a possible step to give coordinated diene **VI**. The displacement of conjugated dienes by coordination of alkyne and diazo compound again reactivate the catalyst. This catalytic cycle is related to the stoichiometric addition of two molecules of diazo compound to a coordinated alkyne shown by O'Connor et al.[14] Thus, the reaction of a cobalt alkyne complex has allowed to isolate a complex with a diene ligand (eq 6), analogous to the proposed intermediate species **VI**.

Stereochemistry of the Double Bonds. Simple models show that the formation of intermediate **III** requires the antiposition of the Cp* and Y groups to decrease strong steric interactions in the syn isomer. Thus, the stereochemistry of the first formed double bond results from the opening of the metallacyclobutene **III**. For monosubstituted alkynes (R′ = H), the stereochemistry depends on the nature of the substituent of diazoalkane (Scheme 2). When Y = $SiMe_3$, a *Z*-stereochemistry is favored at room temperature (**IV′**) while Y = Ph produces an *E*-stereochemistry (**IV″**), at room temperature or 60 °C. This *E*-stereochemistry is the expected configuration because of steric hindrance. For Y = $SiMe_3$, a strong interaction between $SiMe_3$ and Cl groups (**III′**) is considered and can be responsible for the opening of intermediate **III** leading to *Z* configuration (**IV′**).

This interaction leading to this *Z*-stereochemistry has already been established for the reaction of trimethylsilyldiazomethane with enynes.[9c−f] However, when the substituent R is bulky (R = cyclohexenyl (**1b**), or $SiMe_3$ (**1g**)), steric interactions become the major effect and lead to the double bond with an *E*-stereochemistry. When the reaction is carried out at a higher temperature, the Cl−Si interaction of intermediate **III′** may become weaker and the opening of **III**, according to steric hindrance, increases the ratio of *E*-stereochemistry of the double bond. For disubstituted alkynes (R′ ≠ H), steric factors become preponderant and the major obtained isomer possesses the Y and R′ groups in the cis position on the double bond. At 60 °C, the isomer controlled by steric factors is selectively formed.

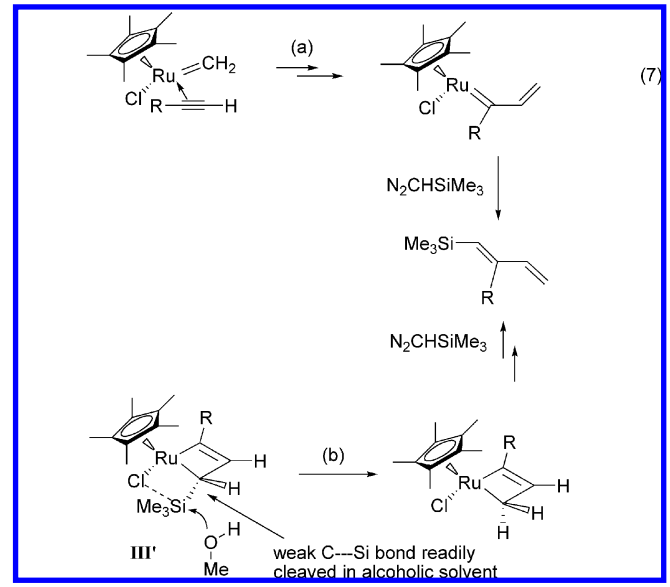
(22) Braun, T.; Münch, G.; Windmüller, B.; Gevert, O.; Laubender, M.; Werner, H. *Chem.—Eur. J.* **2003**, *9*, 2516–2530.

Scheme 2. Stereochemical Aspects of Intermediates **III** and **IV**



For mono- and disubstituted alkynes, the second double bond is formed by the coupling of two carbene units. In all cases, Y and R groups are in the cis position on the double bond, this stereochemistry being probably controlled by steric factors.

In the case of the reaction of alkynes with trimethylsilyldiazomethane in methanol, monosilylated butadienes are obtained. The *in situ* formation of diazomethane from $N_2CHSiMe_3$ could be obtained in methanol. This expected *in situ* formed diazomethane, being more reactive, may react first with ruthenium center to produce ruthenium desilylated vinyl carbene. The second addition of diazoalkane seems to be possible with trimethylsilyldiazomethane only (path a, eq 7). Another way for this transformation could occur is during the formation of intermediate **III′** (Scheme 2). The methanol solvent could interact with the trimethylsilyl group because of the weaker Si−C bond in methanol (path b, eq 7).



Conclusion

The above catalytic reaction combines, in one step, three substrates into only one diene with two N_2 eliminations to afford conjugated functionalized dienes with creation of two C═C bonds. This Cp*RuCl(cod)-catalyzed transformation constitutes an unusual formation of 1,3-dienes via addition of two carbene units to alkynes. This original synthetic method was applied, in mild conditions, to a wide range of alkynes and diynes. High stereoselectivities can be obtained depending on reaction conditions. These results allow to consider a ruthenium vinylcarbene species as a key-intermediate of the reaction, responsible of the stereoselectivity. This single-step access route to 1,4-bisfunctionalbuta-1,3-dienes, especially with the presence of vinylsilane moieties, represents an alternative synthesis for the construction of these versatile building blocks.

Experimental Section

All catalytic reactions were carried out under inert atmosphere in Schlenk tubes. The complex RuCl(COD)Cp* was prepared according to the reported method.[23] ^1H and ^{13}C NMR spectra were recorded on Bruker AM 300 WB and DPX 200 spectrometers in deuterated chloroform solutions at 298 K. IR spectra were recorded on Bruker IFS28. Mass spectra were obtained on VARIAN MATT 311 high resolution spectrometer in Centre Regional de Mesures de l'Ouest (CRMPO) of the University of Rennes1. Characterization data are presented in the Supporting Information.

Typical Procedure for Synthesis of Dienes with Trimethylsilyldiazomethane, Phenyldiazomethane, or Ethyldiazoacetate. In a Schlenk tube under inert atmosphere, to a solution of alkyne or diyne (1.25 mmol) in degazed dioxane (1.5 mL), was added 2.4 equiv of diazo compound. Five mol percent of the precatalyst RuCl(COD)Cp* was then introduced. The mixture was stirred at room temperature or at 60 °C. Reaction completion was monitored using GC or TLC techniques. The solvent was removed under vacuum and the products were obtained after purification by silica gel chromatography with ether/pentane eluting mixture.

Typical Procedure for Synthesis of Dienes with Trimethylsilyldiazomethane in Methanol. In a Schlenk tube under inert atmosphere, to a solution of alkyne (1.25 mmol) in methanol (1.5 mL) was added 2.4 equiv of the 2.0 M (trimethylsilyl)diazomethane solution in diethyl ether. Five mol % of the precatalyst RuCl(COD)Cp* was then introduced. The mixture was stirred at room temperature or at 60 °C. Reaction completion was monitored using GC or TLC techniques. The solvent was removed under vacuum and the products were obtained after purification by silica gel chromatography with ether/pentane eluting mixture.

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Supporting Information Available: Characterization data for compounds **2**−**3**, **5**−**6**, **8**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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