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Ruthenium-Catalysed Synthesis of Functional Conjugated Dienes from Propargylic Carbonates and Silyl Diazo Compounds

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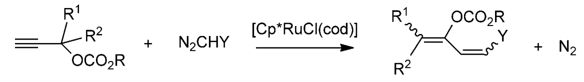
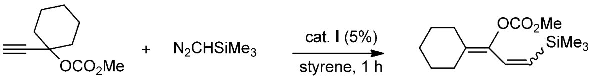
The discovery of new methods for the preparation of stereodefined and functionalised conjugated dienes remains an area of current investigation because numerous transformations,[1] such as the Diels–Alder reaction, are based on 1,3-diene building blocks and because of the presence of their recurring structure in natural products[2] and molecular materials.[3] Over the last few decades, the development of metal-catalysed reactions has led to the proposal of new and efficient syntheses of conjugated dienes.[4] Among these examples, ruthenium–carbene species have shown potential for the formation of 1,3-dienes by ene–yne, ring-closing or cross-metathesis reactions.[5] Ruthenium precatalysts are also known to activate diazo compounds, especially for the preparation of alkene-metathesis catalysts.[6] During the course of our studies on the catalytic activity of the complex [Cp*RuCl(cod)],[7] we found that this precatalyst could react with diazo compounds to form ruthenium–carbene species that were capable of activating triple bonds. Thus, functional conjugated dienes were synthesised by the addition of two carbene units to alkynes[8] or of one carbene unit to propargylic esters.[9] Carbonate derivatives are versatile compounds, owing to their utilisation as protecting groups or as synthesis intermediates,[10] as well as their applications in agrochemistry and pharmaceuticals.[11] In this respect, dienyl carbonates are interesting synthons that have appeared in various transformations, such as the Diels–Alder reaction,[12] 1,4-hydrogenation into trisubstituted allylic alcohols,[13] or asymmetric allylation.[14] However, dienyl carbonates are often obtained under drastic conditions, such as the treatment of enones with strong acids or bases.[15] Recently, a gold-catalysed rearrangement of propargylic carbonates allowed the preparation of dienyl carbonates under mild conditions.[16] Herein, we report the direct and catalytic synthesis of conjugated dienyl carbonates from the addition of a carbene unit, generated in situ from diazo compounds, to propargylic carbonates in the presence of the [Cp*RuCl(cod)] precatalyst under mild conditions (Scheme 1).



Scheme 1. Catalytic addition of diazo compounds to propargylic carbonates.

Thus, when 0.5 mmol of propargyl carbonate **1a** was reacted with 1.2 equivalents of trimethylsilyldiazomethane (2 M in Et_2O) in the presence of styrene and 5 mol % of precatalyst [Cp*RuCl(cod)] (**I**, $Cp^* = C_5Me_5$) in 0.5 mL of 1,4-dioxane at 60 °C for 1 h, the new dienyl carbonate **2a** was formed in 90 % yield (Table 1, entry 1). Great improvement came from controlling the concentration of the substrate, that is, low concentrations slowed the reaction and the best result was obtained with $[\mathbf{1a}] = 1\ \mathrm{mol\,L^{-1}}$. Two stereoisomers of compound **2a** were obtained with a Z/E ratio of 45:55 for the silylated double bond. In contrast, high stereoselectivity in favour of the Z isomer was obtained from the corresponding propargylic ester under the same conditions.[9]

Table 1. Ruthenium-catalysed reaction of propargyl carbonate **1a** with $N_2CHSiMe_3$.[a]



1a **2a**

Entry	Solvent	T [°C]	Yield [%][b]	Z/E ratio
1	1,4-dioxane	60	90	45:55
2	1,4-dioxane	80	93	45:55
3	1,4-dioxane	40	92	48:52
4	1,4-dioxane	RT	90	55:45
5[c]	1,4-dioxane	RT	92	58:42
6	*n*-hexane	RT	98	49:51
7	*n*-hexane	60	96	33:67
8	*n*-heptane	80	90	35:65
9	DCE	RT	99	66:34
10	acetone	RT	98	70:30
11	DMC	RT	98	60:40

[a] Reaction conditions: compound **1a** (0.5 mmol) was treated with $N_2CHSiMe_3$ (1.2 equiv) in the presence of catalyst **I** (5 mol %) and styrene (5 equiv) in solvent (0.5 mL) for 1 h. [b] Yield of isolated product obtained after purification by column chromatography on silica gel. [c] Reaction without styrene

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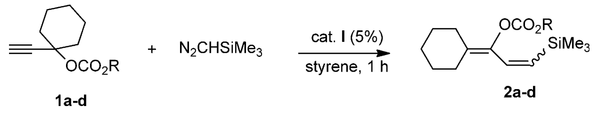
Then, we investigated the influence of the solvent and temperature on this reaction to improve the stereoselectivity (Table 1). The reaction of compound **1a** afforded excellent yields (>90%) in various solvents, nonpolar solvents, such as *n*-hexane, or more-polar solvents, such as 1,2-dichloroethane (DCE) and acetone. Interestingly, the reaction proceeded well in a “greener” solvent; that is, compound **2a** was obtained in 98% yield after 1 h at room temperature in dimethyl carbonate (DMC; Table 1, entry 11).[17] The stereoselectivity of the reaction that led to compound **2a** was strongly dependent on the nature of the solvent: Non-polar solvents favoured *E* stereochemistry (Table 1, entries 7–8), whereas more-polar solvents led to the *Z* isomer (Table 1, entries 9 and 10). The reaction temperature (from RT to 80 °C) had no significant influence on the yield of the reaction, but played an important role in determining the stereoselectivity: Increasing the temperature favoured the *E* isomer (Table 1, entry 7 versus entry 6 and entries 1–3 versus entry 4). The reaction of carbonate **1a** in the absence of styrene gave similar results in terms of yield and stereoselectivity (Table 1, entry 5 versus entry 4). However, the presence of styrene was beneficial for other substrates; thus, five equivalents of styrene were added to the solution. The coordination of styrene to the ruthenium centre may temporarily protect the intermediate species during the catalytic process. From these experiments, we determined the optimal reaction conditions to be *n*-hexane, 60 °C for the formation of the *E* isomer and acetone, RT for the formation of the *Z* isomer.

With our optimised conditions in hand, we first examined the influence of the carbonate substituent (R) on the spiro-cyclohexylpropargyl carbonates **1a–d** (Table 2). In all cases, the reactions proceeded smoothly, thereby affording excellent yields. The benzyl substituent in compound **1d** led to similar stereoselectivities to those produced with the methyl substituent in compound **1a**, but with slightly lower yield, especially in acetone. When the methyl substituent was changed to a bulkier substituent (Et, *t*Bu), the ratio of the *Z* isomer increased in acetone or *n*-hexane. In each case, the use of the more-polar solvent (acetone) favoured *Z* stereoselectivity. A very good result was obtained with R = *t*Bu in acetone because compound **2c** was produced in 97% yield with a *Z*/*E* ratio of 95:5. In *n*-hexane at 60 °C, the *E* isomer was only favoured for compounds **2a** and **d**. When the substituent was bulkier (**2b** and **c**), the *Z* isomer remained the major one.

Table 2. Ruthenium-catalysed reactions of propargyl carbonates **1** with $N_2CHSiMe_3$.[a]

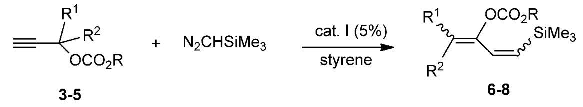


Diene **2**	Acetone, RT		*n*-Hexane, 60 °C	
R	Yield [%][b]	*Z*/*E* ratio	Yield [%][b]	*Z*/*E* ratio
Me (**2a**)	98	70:30	96	33:67
Et (**2b**)	94	81:19	92	65:35
*t*Bu (**2c**)	97	95:5	99	87:13
CH_2Ph (**2d**)	87	65:35	94	37:63

[a] Reaction conditions: compounds **1a–d** (0.5 mmol) were treated with $N_2CHSiMe_3$ (1.2 equiv) in the presence of catalyst **I** (5 mol%) and styrene (5 equiv) in solvent (0.5 mL) for 1 h. [b] Yield of isolated product obtained after purification by column chromatography on silica gel.

Then, we studied the scope of this reaction with different propargylic carbonates (Table 3). The reactions proceeded smoothly with dimethylpropargyl carbonates **3a–c**, thereby leading to complete conversion after 1 h into tetrasubstituted dienes **6a–c** in good yields in acetone at RT or in *n*-hexane at 60 °C. As previously observed with propargyl carbonates **1**, the reactions in acetone at RT favoured *Z* stereoselectivity and the use of *tert*-butylpropargyl carbonate **3c** increased the quantity of the *Z* isomer. Good stereoselectivity for the *E* isomer was also obtained in *n*-hexane at 60 °C for the less-hindered carbonate **6a** (, *Z*/*E* 25:75). Diethylpropargyl carbonates **4** were less reactive, their conversions were not complete, even after 16 h, and the yield of dienes **7** decreased, particularly in acetone. With two ethyl substituents at the propargylic position, carbonates **4** led to higher *Z* ratios than those obtained from dimethylpropargyl carbonates **3** under the same reaction conditions, but these ratios were lower than those obtained from spiro-cyclohexylpropargyl carbonates **1**. The reactions with propargyl carbonates **5** with two different substituents at the propargylic position afforded dienes **8** in good yields after 1 h as mixtures of four stereoisomers. The *Z*/*E* ratios for the silylated double bond were similar to those obtained from carbonates **1** and a 65:35 ratio, as determined by ^1H NMR spectroscopy, was produced for the tetrasubstituted double bond in each case.

Table 3. Ruthenium-catalysed reactions of propargyl carbonates **3–5** with $N_2CHSiMe_3$.[a]



Carbonate	Diene	Acetone, RT		*n*-Hexane, 60 °C	
R^1, R^2, R		Yield [%][b]	*Z*/*E* ratio[c]	Yield [%][b]	*Z*/*E* ratio[c]
Me, Me, Me (**3a**)	**6a**	82	53:47	86	25:75
Me, Me, Et (**3b**)	**6b**	83	69:31	98	51:49
Me, Me, *t*Bu (**3c**)	**6c**	91	88:12	89	76:24
Et, Et, Me (**4a**)	**7a**	28[d]	61:39	63[d]	34:66
Et, Et, Et (**4b**)	**7b**	57[d]	77:23	78[d]	55:45
Et, Et, *t*Bu (**4c**)	**7c**	61[d]	93:7	71[d]	80:20
Me, *i*Bu, Me (**5a**)	**8a**	39[d]	75:25[e]	76	36:64[e]
Me, *i*Bu, Et (**5b**)	**8b**	79	83:17[e]	82	51:49[e]
Me, *i*Bu, *t*Bu (**5c**)	**8c**	95	93:7[e]	84	80:20[e]

[a] Reaction conditions: compounds **3–5** (0.5 mmol) were treated with $N_2CHSiMe_3$ (1.2 equiv) in the presence of catalyst **I** (5 mol%) and styrene (5 equiv) in solvent (0.5 mL) for 1 h. [b] Yield of isolated product obtained after purification by column chromatography on silica gel. [c] *Z*/*E* ratio for the silylated double bond. [d] The conversion was not complete after 16 h. [e] Two stereoisomers were obtained for the tetrasubstituted double bond in a 65:35 ratio.

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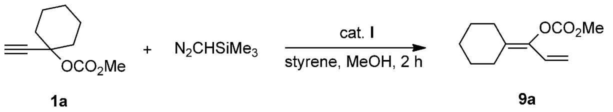
Non-silylated dienyl carbonates could also be synthesised by using this catalytic process. Indeed, the in situ formation of the desilylated double bond from $N_2CHSiMe_3$ in MeOH has already been obtained from alkynes in the presence of catalyst **I** to produce desilylated dienes.[8] Thus, when the reaction of carbonate **1a** was performed in MeOH, the formation of desilylated dienyl carbonate **9a** was observed (Table 4). However, under the preceding conditions, the reaction was not complete. To improve the efficiency of the formation of the desilylated dienyl carbonates, we screened the concentration of the substrate and the amount of catalyst. With 5 mol% of complex **I**, complete conversion of carbonate **1a** was never obtained at different concentrations of substrate, temperatures or reaction times (Table 4, entries 1–3). On the other hand, complete conversion was obtained after 2 h by using 8 mol% of the catalyst (Table 4, entries 4–7). Silylated derivatives could be obtained, along with the expected desilylated compounds, if the concentration of compound **1a** was too high (Table 4, entries 4 and 5) and the best result was observed with [**1a**] = 0.5 mol L^{-1}. Finally, 90% yield in desilylated dienyl carbonate **9a** was obtained at 60 °C or at room temperature (Table 4, entries 6 and 7).

Table 4. Ruthenium-catalysed reaction of propargyl carbonate **1a** with $N_2CHSiMe_3$ in MeOH providing desilylated dienes.[a]

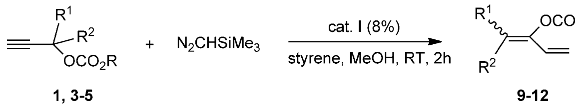


Entry	[**1a**] [mol L^{-1}]	Cat. **I** [mol%]	T [°C]	Conversion [%]	Yield [%][b]
1	1.0	5	60	70	55
2	0.67	5	60	85	79
3	0.5	5	60	90	81
4	1.0	8	60	100	58[c]
5	0.67	8	60	100	82[c]
6	0.5	8	60	100	90
7	0.5	8	RT	100	90

[a] Reaction conditions: compound **1a** (0.5 mmol) was treated with $N_2CHSiMe_3$ (1.2 equiv) in the presence of catalyst **I** and styrene (5 equiv) in MeOH (0.5–1 mL) for 2 h. [b] Yield of isolated product obtained after purification by column chromatography on silica gel. [c] 10% of silylated derivative **2a** was also obtained.

With these optimised conditions in hand, we examined the scope of the reaction with various propargylic carbonates in MeOH (Table 5). Excellent yields of the dienyl carbonates were obtained under mild conditions from propargyl carbonates **1** and **3** (Table 5, entries 1–7). Diethylpropargyl carbonates **4** were still less reactive and the conversion was stopped at 90%, even after 16 h or with a larger amount of catalyst (Table 5, entries 8–10). The reactions of carbonates **5** led to dienes **12** in good yields as a mixture of two stereoisomers for the tetrasubstituted double bond in a 65:35 ratio (Table 5, entries 11–13); this ratio was similar to that obtained for this double bond in silylated compounds **8**.

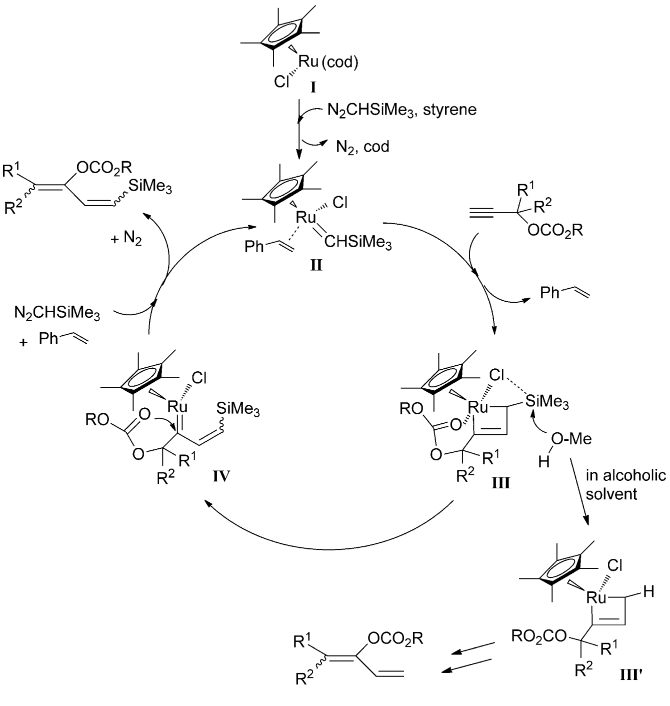
Table 5. Ruthenium-catalysed reactions of propargyl carbonates **1**, **3**–**5** with $N_2CHSiMe_3$ in MeOH, providing desilylated dienes.[a]



Entry	Carbonate R^1, R^2, R	Diene	Yield [%][b]
1	$(CH_2)_5$, Me (**1a**)	**9a**	90
2	$(CH_2)_5$, Et (**1b**)	**9b**	95
3	$(CH_2)_5$, *t*Bu (**1c**)	**9c**	87
4	$(CH_2)_5$, CH_2Ph (**1d**)	**9d**	86
5	Me, Me, Me (**3a**)	**10a**	82
6	Me, Me, Et (**3b**)	**10b**	95
7	Me, Me, *t*Bu (**3c**)	**10c**	80
8	Et, Et, Me (**4a**)	**11a**	77[c]
9	Et, Et, Et (**4b**)	**11b**	80[c]
10	Et, Et, *t*Bu (**4c**)	**11c**	65[c]
11	Me, *i*Bu, Me (**5a**)	**12a**	71[d]
12	Me, *i*Bu, Et (**5b**)	**12b**	76[d]
13	Me, *i*Bu, *t*Bu (**5c**)	**12c**	90[d]

[a] Reaction conditions: compounds **1** and **3**–**5** (0.5 mmol) were treated with $N_2CHSiMe_3$ (1.2 equiv) in the presence of catalyst **I** (8 mol%) and styrene (5 equiv) in MeOH (1 mL) for 2 h. [b] Yield of isolated product obtained after purification by column chromatography on silica gel. [c] The conversion was not complete after 16 h. [d] Two stereoisomers were obtained for the tetrasubstituted double bond in a 65:35 ratio.

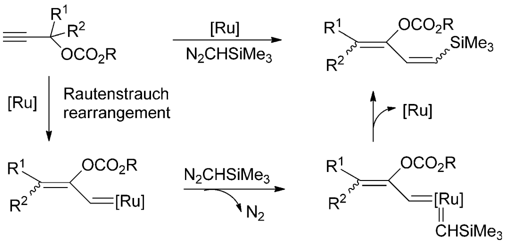
A plausible mechanism is proposed in Scheme 2. This mechanism involves the initial interaction of the catalyst with trimethylsilyldiazomethane and its stabilization with styrene, leading to ruthenium–carbene species **II**. After the displacement of styrene by the coordination of propargylic carbonates, carbene **II** can undergo a regioselective [2+2] cycloaddition[18] with the triple bond of propargylic carbonates, as in enyne metathesis,[19] thus producing ruthenacyclobutene intermediate **III** (or **III′** in MeOH), followed by the formation of the vinylcarbene–ruthenium intermediate



Scheme 2. Proposed catalytic cycle.

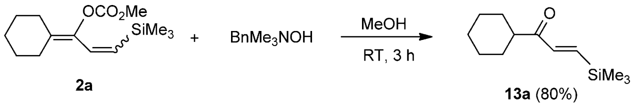
IV. As previously reported with carboxylate groups, the 1,2-shift of the carbonate group onto the carbene carbon could release dienyl carbonates.[20] However, attack of the carbonate group onto the ruthenium centre in intermediate **IV** and subsequent reductive elimination, leading to the same dienes, cannot be ruled out. A catalytic test reaction with a mixture of two different substrates (**2b** and **3a**) showed that the migration of the carbonate group was an intramolecular process. The favoured *Z* stereochemistry of the silylated double bond may arise from the interactions of the silyl group with the chloride during the ring-opening of intermediate **III**.[8,9] A possible coordination of the carbonate group on the ruthenium centre, if the R substituent is not too bulky, could disturb the Cl–Si interactions and partially lead to the *E* isomer. Similar effects with coordinated double bonds have already been proposed.[21] A more polar solvent could strengthen the Cl–Si interactions, which would then favour *Z* stereochemistry. In the same way, the Cl–Si interactions could become weaker at high temperatures and the opening of intermediate **III**, owing to steric hindrance, would increase the ratio of the *E* stereoisomer.[8b] In MeOH, desilylated dienyl carbonates were obtained. The solvent could interact with the trimethylsilyl group, because of the more-reactive Si–C bond in MeOH, to produce desilylated ruthenacyclobutene intermediate **III′**.[8b]

Alternatively, another mechanism (Scheme 3) would involve the initial interactions of the catalyst with the propargylic carbonate and the rearrangement of an η^2-alkyne–ruthenium species into a vinylcarbene–ruthenium intermediate, which results from 1,2-carbonate migration in a Rautenstrauch-type process.[16,20c,22] Because the ability of the Cp*RuCl moiety to accommodate two *cis*-carbene ligands is known,[8,23] the addition of the diazo compound could lead to a bis-carbene–ruthenium species, thereby affording the formation of the same dienyl carbonates.



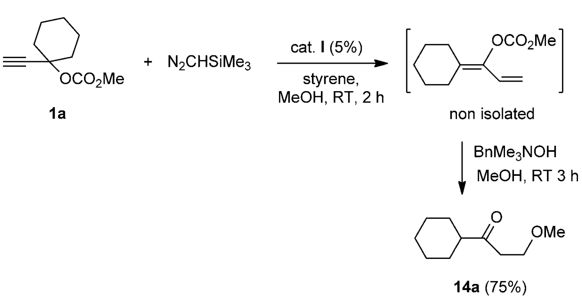
Scheme 3. Alternative mechanistic pathway.

These dienyl carbonates might be good precursors of α,β-unsaturated ketones. To test their reactivity, 0.5 mmol of dienyl carbonate **2a** was reacted with two equivalents of benzyltrimethylammonium hydroxide (as a solution in MeOH) in MeOH (1 mL) at room temperature. After 3 h, the (*E*)-α,β-unsaturated silylated ketone **13a** was isolated in 80 % yield (Scheme 4).



Scheme 4. Formation of silylated α,β-unsaturated ketone **13a**.

Because the formation of desilylated dienyl carbonates from propargylic carbonates took place in MeOH (Table 4 and Table 5), we examined the one-pot reactivity of 0.5 mmol of propargyl carbonate **1a** with 1.2 equivalents of $N_2CHSiMe_3$ in the presence of 8 mol % of precatalyst **I** in MeOH (1 mL), followed by the in situ addition of two equivalents of $BnMe_3NOH$ after 2 h. After 3 h at room temperature, compound **14a** was isolated in 75 % yield (Scheme 5). The same compound was obtained from the reaction of propargyl ethyl carbonate **1b** under the same conditions, thus showing that compound **14a** resulted from the Michael addition of MeOH onto an α,β-unsaturated desilylated ketone intermediate.



Scheme 5. Formation of saturated ketone **14a**.

In summary, we have successfully developed a direct and catalytic route to new dienyl carbonates. This one-pot [Cp*RuCl(cod)]-catalysed method proceeded in excellent yields from readily accessible propargylic carbonates under mild conditions. This transformation represents a rare example in catalysis of the 1,2-shift of a carbonate group from a propargylic carbonate under mild neutral conditions. The stereoselectivity of these reactions was found to be strongly dependent on the reaction conditions and polar solvents selectively led to the *Z* isomers of the silylated derivatives. Interestingly, the reaction could be performed smoothly in DMC as a "greener" solvent. This method provides a new approach to the synthesis of functional conjugated dienes and has potential application in further transformations.

Experimental Section

Typical procedure for the catalytic reactions: In a Schlenk tube under an inert atmosphere, styrene (2.5 mmol) and (trimethylsilyl)diazomethane (0.6 mmol, 2.0 M in Et_2O) were added to a solution of the propargyl carbonate (0.5 mmol) in degassed solvent (0.5–1.0 mL). Then, the $[(C_5Me_5)RuCl(cod)]$ precatalyst (5 mol %) was introduced and the mixture was stirred at RT for 1–2 h. The reaction was monitored by GC or TLC. After the reaction had been completed, the solvent was removed under vacuum and the dienes were separated as pure compounds by column chromatography on silica gel (Et_2O/pentane).

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Keywords: azo compounds · carbenes · carbonates · dienes · ruthenium

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