New *in situ* Generated Ruthenium Catalyst for Enyne Metathesis: Access to Novel Cyclic Siloxanes

David Sémeril, Myriam Cléran, Christian Bruneau, Pierre H. Dixneuf*

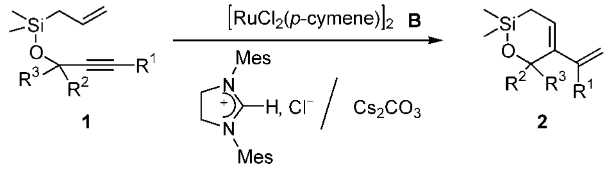
Institut de Chimie de Rennes, UMR 6509 CNRS-Université de Rennes, Organométalliques et Catalyse:
Chimie et Electrochimie Moléculaires, Campus de Beaulieu, 35042 Rennes, France
Fax: (+39) 2 99 28 69 39; e-mail: pierre.dixneuf@univ-rennes1.fr

Received October 30, 2000; Accepted December 4, 2000

Keywords: metathesis; ruthenium catalyst; unsaturated siloxanes; dihydroimidazolium salts

The intramolecular catalytic metathesis of enynes containing the O–Si linkage has the potential to afford in one step alkenyl cycloalkenes, with a 1,3-diene structure, useful not only for Diels–Alder reactions[1,2] but also as precursors for sol-gel materials[3] and fine chemistry. Indeed, cyclic siloxanes containing an allylsilyl moiety are precursors for the access to oxygenated heterocycles or polyhydroxylated olefins.[4] This potential motivates the search for very active metathesis catalysts. Initial results in the field of enyne metathesis involve the use of Grubbs-type catalysts Ru=CHR(Cl)$_2$(PCy$_3$)(L) for the intramolecular formation of O-[5] and N-[6] containing heterocycles and carbocycles and the intermolecular cross-metathesis of alkynes and alkenes to produce acyclic 1,3-dienes.[7] In addition, the salts [Ru=C=C=CR$_2$(Cl)(PR$_3$)(*p*-cymene)]X appear to be efficient in the metathesis of mixed allyl propargyl ethers and fluorine containing aminoesters.[8,9] The preparations of all these catalysts involve several steps from accessible ruthenium sources. The development of enyne metathesis requires that not only more efficient catalytic systems but also, more importantly, easy to perform routes to these catalysts are found. Only recently, the Wanzlick type carbenes,[10] possessing a 1,3-disubstituted-4,5-dihydroimidazol-2-ylidene moiety (H$_2$Im), that were shown especially by Lappert[11] to afford a large variety of electron-rich carbene-metal complexes, have been used to generate Grubbs-type catalysts Ru=CHR(Cl)$_2$(PCy$_3$)(H$_2$Im).[12] The latter are useful to promote RCM,[12,13] cross-metathesis reaction,[14] or ene-yne cross metathesis.[15] However, these catalysts are prepared via multistep metal complex synthesis.

We now report a new, simple to prepare ruthenium catalytic system for the intramolecular metathesis of O–Si containing enynes **1**. It is based on a three-component system which involves a 4,5-dihydroimidazolium salt precursor, the commercially available ruthenium source [RuCl$_2$(*p*-cymene)]$_2$, and Cs$_2$CO$_3$. This system, which easily combines only stable reagents, opens the way to novel O–Si alkenyl cyclic alkenes **2** under mild conditions (Scheme 1).



Scheme 1.

Whereas the preparation of {RuCl$_2$[1,3-bis(mesityl)-imidazol-2-ylidene](arene)} complexes can be carried out in good yield from [(arene)RuCl$_2$]$_2$ and the carbene generated *in situ* from an imidazolium salt,[16] the synthesis and isolation of the analogue {RuCl$_2$[1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene](*p*-cymene)} complex led to only a poor yield of the corresponding carbene complex. On the basis of previous results with imidazolium salts,[17] we attempted to produce an *in situ* generated catalytic system **A** via a three-component combination of the ruthenium(II) source [(*p*-cymene)RuCl$_2$]$_2$, 1,3-bis(mesityl)-4,5-dihydroimidazolium chloride (MesH$_2$ImCl),[18] and Cs$_2$CO$_3$ as a base, in the molar ratio 1 : 2 : 4, respectively. Thus, the reaction of 1 mmol of the silylated enyne **1 a**[19] in the presence of the catalytic system **A** {containing 2.5 mol % of [(*p*-cymene)RuCl$_2$]$_2$ **B**} in toluene (5 mL) at 80 °C for 16 h led to a complete conversion into the metathesis compound **2 a** isolated in 81% yield (Scheme 1, Table 1).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/asc/ or from the author.

Table 1. Enynes **1** metathesis with the catalytic system **A**[a]

enyne	R^1	R^2	R^3	**A** (mol % of **B**)	reaction time (h)	diene	yield (%)[b]
1 a	H	Me	Ph	2.5	16	**2 a**	81
1 b	H	$-(CH_2)_5-$		2.5	16	**2 b**	87
1c	H	Me	CH_2–$CHMe_2$	2.5	15	**2 c**	34[c]
1 d	H	Ph	Ph	2.5	15	**2 d**	70
1 e	Ph	Me	Me	2.5	48	**2 e**	75
1 f	*n*-Bu	$-(CH_2)_5-$		5	23	**2 f**	72[d]
1 g	CH_2OMe	$-(CH_2)_5-$		5	23	**2 g**	67[d]

[a] Enyne **1** (1 mmol), toluene (5 mL), 80 °C, catalytic system **A** based on a constant molar ratio of $[(p\text{-cymene})RuCl_2]_2$ **B**/Mes-H_2ImCl/Cs_2CO_3 : 1/2/4.

[b] Yields of isolated products, complete conversion.

[c] Degradation over silica during purification.

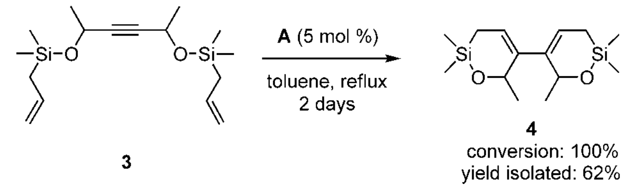
[d] In refluxing toluene.

This transformation was extended to other silylated enynes containing a terminal triple bond and various alkyl and aryl substituents as R^2 and R^3. In all cases, the complete transformation was achieved within 15 h at 80 °C and the 1,3-diene six-membered siloxanes **2 a–d** were isolated in good yields (Table 1).

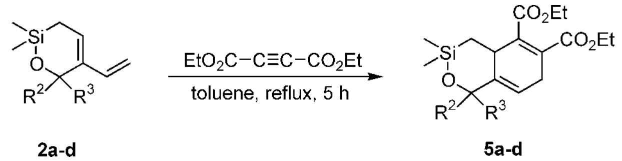
The metathesis of the enynes bearing a disubstituted triple bond **1 e–g**[20] with the catalytic system **A** required more drastic conditions. Thus, the complete conversion of **1 e** was obtained in refluxing toluene in the presence of **A** based on 2.5 mol % of **B** after 2 days and the α-styrylcycloalkene **2 e** was isolated in 75% yield. The reaction of **1 f** and **1 g** to produce **2 f** and **2 g** with **A** containing 2.5 mol % of $[(p\text{-cymene})RuCl_2]_2$ led to 73 and 70% conversion after 30 h in refluxing toluene, respectively. The use of the catalytic system **A** produced from 5 mol % of the ruthenium dimer **B** made possible the complete conversion of **1 f** in 23 h and the isolation of **2 f** in 72% yield. Under similar experimental conditions, a conversion of 86% of **1 g** was obtained after 23 h which led to the preparation of **2 g** in 67% yield (Table 1). It is noteworthy that a catalytic system analogous to system **A** but containing the 1,3-bismesitylimidazolium chloride was not as active as **A** as it transformed **1 f** into **2 f** in only 60% yield after 30 h at 80 °C.

The efficiency of the catalytic system **A** for disubstituted C≡C bond containing enynes led us to explore the possibility to produce bicyclic Si-containing derivatives. The symmetrical compound **3** possesses a structure which is compatible with an yne-diene metathesis cascade reaction. Indeed, compound **3** in the presence of **A** (5 mol % of ruthenium dimer **B**) was completely converted after 2 days in refluxing toluene and the conjugated bicyclic diene **4** was isolated in 62% yield as a mixture of two diastereoisomers in the ratio 62 : 38 (Scheme 2).

The O–Si containing six-membered rings **2** obtained in these metathesis reactions were much more stable than the five-membered vinyldihydrofurans prepared via metathesis of the corresponding allyl propargyl ethers.[8] Their structures are very well adapted for the preparation of fused silicon-containing heterocycles via Diels–Alder reactions. Thus, treatment of **2 a–d** with 2 equivalents of diethyl acetylenedicarboxylate (DEAD) in refluxing toluene for 5 h led to a complete conversion of the starting dienes and formation of the bicyclic compounds **5 a–d** in 41, 79, 70 and 61% yield, respectively (Scheme 3, Table 2).



Scheme 2.



Scheme 3.

The formation of these fused rings led to the creation of a stereogenic carbon center and, from the ^1H NMR spectrum of **5 a**, it appeared that the two diastereoisomers were formed in the ratio 72 : 28. By contrast, the enynes **2 e–g** containing a phenyl, *n*-butyl,

Table 2. Synthesis of bicyclic compounds from alkenyl cycloalkenes **2**[a],[b]

Diene	Diels-Alder adduct[a]		Aromatic compound[b]	
2 a	**5 a**	79%[c]	**6 a**	86%
2 b	**5 b**	41%	**6 b**	90%
2 c	**5 c**	70%[c]	**6 c**	80%
2 d	**5 d**	61%	**6 d**	85%

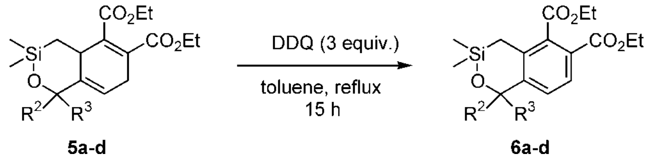
[a] Diene **2** (1 mmol, 1 equiv.), DEAD (2 equiv.), refluxing toluene, 5 h.

[b] DDQ (3 equiv.), refluxing toluene, 15 h.

[c] Without isolation of **2 a** or **2 c** (yield based on **1 a** or **1 c**).

or methoxymethyl-substituted double bond were reluctant to react with DEAD for the [2+4] addition reaction.

The oxidation of substrates **5 a–d** to form an aromatic ring from the non-conjugated intracyclic diene structure was attempted with 2,3-dichloro-5,6-dicyanoquinone (DDQ) as the oxidant.[21] The treatment of **5 a–d** in refluxing toluene with an excess of DDQ (3 equivalents) for 15 h gave a complete conversion of the dienes and afforded the functional aromatic siloxanes **6 a–d** in 60, 86, 80 and 85% yields, respectively (Scheme 4, Table 2).



Scheme 4.

The utilization of the easy to prepare efficient catalytic system **A**, from the commercially available, and easy to prepare in large scale, ruthenium precursor [(*p*-cymene)RuCl$_2$]$_2$ associated to both a 4,5-dihydroimidazolium salt and Cs$_2$CO$_3$ represents a simple, but important, contribution in catalysis and enyne metathesis. The O–Si containing enynes provide an efficient access to novel cyclic siloxanes with potential reactivities due to the presence of two conjugated double bonds and C–Si linkages in the allylic position.

Experimental Section

General Procedure for the Preparation of 2 a–g and 4

A mixture of enyne **1** or **3** (1 mmol) and catalytic system **A** {[(*p*-cymene)RuCl$_2$]$_2$, MesH$_2$ImCl (2 molar equiv.) and Cs$_2$CO$_3$ (4 molar equiv.) (5 or 10 mol % of Ru)} in toluene (5 mL) was heated at 80 °C for 16 h for terminal and at 110 °C for disubstituted alkyne derivatives. The solvent was removed in vacuum and the crude product was obtained after purification by flash chromatography (diethyl ether/pentane, 1/9).

2 a: ^{1}H NMR (CDCl$_3$, 200.132 MHz): δ = 0.17 [s, 3 H, Si(C*H*$_3$)$_2$], 0.21 [s, 3 H, Si(C*H*$_3$)$_2$], 1.56 (d, 1 H, $^3J_{\mathrm{HH}}$ = 6.5 Hz, SiC*H*$_2$), 1.60 (d, 1 H, $^3J_{\mathrm{HH}}$ = 5.6 Hz, SiC*H*$_2$), 1.72 (s, 3 H, C*H*$_3$), 4.85 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 10.3 Hz, $^2J_{\mathrm{HH}}$ = 2.0 Hz, *cis*-CH=C*H*$_2$), 5.18 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 17.0 Hz, $^2J_{\mathrm{HH}}$ = 2.0 Hz, *trans*-CH=C*H*$_2$), 6.12 (ddd, 1 H, $^3J_{\mathrm{HH}}$ = 17.0 Hz, $^3J_{\mathrm{HH}}$ = 10.8 Hz, $^4J_{\mathrm{HH}}$ = 1.1 Hz, C*H*=CH$_2$), 6.18 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 6.5 Hz, $^3J_{\mathrm{HH}}$ = 5.6 Hz, C=C*H*–CH$_2$), 7.13–7.38 (m, 3 H, Ph), 7.38–7.72 (m, 2 H, Ph); ^{13}C NMR (CDCl$_3$, 50.329 MHz): δ = 0.60, 0.80 [Si(*C*H$_3$)$_2$], 13.50 (Si*C*H$_2$), 29.71 (*C*H$_3$), 78.57 (Si-O-*C*), 113.68 (*C*H$_2$=CH), 122.73 (C=*C*H–CH$_2$), 125.97, 126.92, 128.04 (aromatic *C*H), 138.18 (CH$_2$=*C*H), 145.64 (*ipso C*), 147.32 (CH$_2$=CH–*C*).

4 (major diastereoisomer): ^{1}H NMR (CDCl$_3$, 200.132 MHz): δ = 0.04, 0.08 [s, 12 H, Si(C*H*$_3$)$_2$], 1.21–1.34 (m, 4 H, SiC*H*$_2$), 1.21 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, C*H*$_3$CH), 4.54 (q, 2 H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, CH$_3$C*H*), 5.65 (dd, 2 H, $^3J_{\mathrm{HH}}$ = 5.2 Hz, $^3J_{\mathrm{HH}}$ = 5.3 Hz, CH=C); ^{13}C NMR (CDCl$_3$, 50.329 MHz): δ = 0.78, 1.05 [Si(*C*H$_3$)$_2$], 12.73 (Si*C*H$_2$), 24.12 (*C*H$_3$CH), 70.34 (CH$_3$*C*H), 121.12 (*C*H=C), 145.92 (*C*=CH).

4 (minor diastereoisomer): ^{1}H NMR (CDCl$_3$, 200.132 MHz): δ = 0.16, 0.17 [s, 12 H, Si(C*H*$_3$)$_2$], 1.21–1.34 (m, 4 H, SiC*H*$_2$), 1.28 (d, 6 H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, C*H*$_3$CH), 4.56 (q, 2 H, $^3J_{\mathrm{HH}}$ = 6.6 Hz, CH$_3$C*H*), 5.65 (dd, 2 H, $^3J_{\mathrm{HH}}$ = 5.2 Hz, $^3J_{\mathrm{HH}}$ = 5.3 Hz, CH=C); ^{13}C NMR (CDCl$_3$, 50.329 MHz): δ = –0.63, –0.44 [Si(*C*H$_3$)$_2$], 12.66 (Si*C*H$_2$), 24.12 (*C*H$_3$CH), 71.52 (CH$_3$*C*H), 120.82 (*C*H=C), 144.79 (*C*=CH).

General Procedure for the Preparation of 5 a–d

After the metathesis reaction leading to **2 a–d**, diethyl acetylenedicarboxylate (DEAD) (2 mmol) was added to the crude reaction. The solution was heated at reflux for 5 h. The solvent was removed in vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane, 1/9).

5 a (major diastereoisomer): ^{1}H NMR (CDCl$_3$, 200.132 MHz): δ = 0.20 [s, 3 H, Si(C*H*$_3$)$_2$], 0.27 [s, 3 H, Si(C*H*$_3$)$_2$], 0.74 (dm, 1 H, $^2J_{\mathrm{HH}}$ = 13.6 Hz, C*H*$_2$Si), 0.81 (dm, 1 H, $^2J_{\mathrm{HH}}$ = 13.6 Hz, SiC*H*$_2$), 1.25 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$CH$_2$C*H*$_3$), 1.32 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$CH$_2$C*H*$_3$), 1.76 (s, 3 H, C*H*$_3$), 2.79 (d, 1 H, $^3J_{\mathrm{HH}}$ = 4.4 Hz, C*H*$_2$-CH=C), 2.88 (d, 1 H, $^3J_{\mathrm{HH}}$ = 4.5 Hz, C*H*$_2$–CH=C), 3.67–3.83 (m, 1 H, Si–CH$_2$–C*H*), 4.18 (q, 2 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$C*H*$_2$CH$_3$), 4.22 (q, 2 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$C*H*$_2$CH$_3$), 4.84 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 4.4 Hz, $^3J_{\mathrm{HH}}$ = 4.5 Hz, CH$_2$–C*H*=C), 7.15–7.42 (m, 5 H, Ph); ^{13}C NMR (CDCl$_3$, 50.329 MHz): δ = 1.19, 1.34 [Si(*C*H$_3$)$_2$], 14.07, 14.12 (CO$_2$CH$_2$*C*H$_3$), 22.87 (Si*C*H$_2$), 28.06 (C=C--*C*H$_2$–CH), 28.67 (*C*H$_3$), 32.76 (Si-CH$_2$-*C*H), 60.98, 61.17 (CO$_2$*C*H$_2$CH$_3$), 80.44 (Si–O–*C*), 119.92 (C=*C*H–CH$_2$), 125.06, 126.72, 127.76 (aromatic *C*H), 130.10 (*ipso C*), 139.34 (C=*C*–CH$_2$–CH), 143.44 (*C*=C–CH$_2$–CH), 146.40 (CH=*C*–CH), 167.77, 167.86 (*C*O$_2$CH$_2$).

5 a (minor diastereoisomer): ^{1}H NMR (CDCl$_3$, 200.132 MHz): δ = 0.15 [s, 3 H, Si(C*H*$_3$)$_2$], 0.16 [s, 3 H, Si(C*H*$_3$)$_2$], 1.23 (dm, 1 H, $^2J_{\mathrm{HH}}$ = 14.5 Hz, C*H*$_2$Si), 1.27 (dm, 1 H, $^2J_{\mathrm{HH}}$ = 14.5 Hz, SiC*H*$_2$), 1.19 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$CH$_2$C*H*$_3$), 1.30 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$CH$_2$C*H*$_3$), 1.56 (s, 3 H, C*H*$_3$), 2.68 (d, 1 H, $^3J_{\mathrm{HH}}$ = 4.0 Hz, C*H*$_2$–CH=C), 2.93–3.09 (m, 1 H, Si–CH$_2$–C*H*), 3.12 (d, 1 H, $^3J_{\mathrm{HH}}$ = 4.1 Hz, C*H*$_2$–CH=C), 4.13 (q, 2 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$C*H*$_2$CH$_3$), 4.27 (q, 2 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, CO$_2$C*H*$_2$CH$_3$), 5.98 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 4.0 Hz, $^3J_{\mathrm{HH}}$ = 4.1 Hz, CH$_2$–C*H*=C), 7.15–7.42 (m, 5 H, Ph); ^{13}C NMR (CDCl$_3$, 50.329 MHz): δ = 0.65, 2.34 [Si(*C*H$_3$)$_2$], 13.93, 13.97 (CO$_2$CH$_2$*C*H$_3$), 23.16 (Si*C*H$_2$), 28.01 (C=C–*C*H$_2$–CH), 31.91 (*C*H$_3$), 33.25 (Si–CH$_2$-–*C*H), 61.13, 63.00 (CO$_2$*C*H$_2$CH$_3$), 79.92 (Si–O–*C*), 118.29 (C=*C*H–CH$_2$), 125.06, 126.86, 128.00 (aromatic *C*H), 129.43 (*ipso C*), 140.25 (C=*C*–CH$_2$–CH), 142.49 (*C*=C–CH$_2$–CH), 146.88 (CH=*C*–CH), 167.72, 167.70 (*C*O$_2$CH$_2$).

General Procedure for the Preparation of 6a-d

Compound **5** (0.5 mmol) was added to a solution of 2,3-dichloro-5,6-dicyanoquinone (DDQ) (1.5 mmol) in toluene

(5 mL). The solution was heated at reflux for 15 h, the solvent was removed in vacuum and the product was isolated after purification by flash chromatography (diethyl ether/pentane, 1/9).

6 a: ^{1}H NMR ($CDCl_3$, 200.132 MHz): $\delta = -0.04$ [s, 3 H, $Si(CH_3)_2$], 0.26 [s, 3 H, $Si(CH_3)_2$], 1.34 (t, 3 H, $^3J_{HH} = 7.2$ Hz, $CO_2CH_2CH_3$), 1.38 (t, 3 H, $^3J_{HH} = 7.1$ Hz, $CO_2CH_2CH_3$), 1.44 (d, 1 H, $^2J_{HH} = 14.9$ Hz, CH_2Si), 1.87 (s, 3 H, CH_3), 1.88 (d, 1 H, $^2J_{HH} = 14.9$ Hz, CH_2Si), 4.34 (q, 2 H, $^3J_{HH} = 7.1$ Hz, $CO_2CH_2CH_3$), 4.35 (q, 2 H, $^3J_{HH} = 7.2$ Hz, $CO_2CH_2CH_3$), 7.11–7.30 (m, 3 H, Ph), 7.55 (d, 1 H, $^3J_{HH} = 8.2$ Hz, aromatic CH), 7.88 (d, 1 H, $^3J_{HH} = 8.3$ Hz, aromatic CH); ^{13}C NMR ($CDCl_3$, 50.329 MHz): $\delta = -0.56$, 0.36 [$Si(CH_3)_2$], 14.14, 14.27 ($CO_2CH_2CH_3$), 17.79 ($SiCH_2$), 33.52 (CH_3), 61.41 ($CO_2CH_2CH_3$), 80.10 (Si–O–C), 125.39, 127.10, 128.20 (aromatic CH), 127.26 (CH=C-CO_2), 128.26, 129.05 (aromatic CH), 134.97 (C=C–CO_2), 136.97 (C=C–CH_2–Si), 147.37 (ipso C), 149.04 (CH=C–C–O), 165.60, 169.50 (CO_2CH_2); anal. calcd. for $C_{23}H_{28}O_5Si$: C 65.30, H 6.74; found: C 65.20, H 6.67.

Acknowledgements

The authors wish to thank the European COST programme D12/0025/99 and the PROCOPE programme for fruitful scientific exchanges with Prof. A. Fürstner and Dr. L. Ackermann from the Max Planck Institute in Mülheim (Germany).

References and Notes

[1] S. Blechert, *Pure Appl. Chem.* **1999**, *71*, 1393–1399; S. C. Schürer, S. Blechert, *Tetrahedron Lett.* **1999**, *40*, 1877–1880.

[2] S. Kotha, N. Sreenivasachary, E. Brahmachary, *Tetrahedron Lett.* **1998**, *39*, 2805–2808 .

[3] P. Chevalier, R. P. J. Corriu, P. Delord, J. J. E. Moreau, M. W. C. Man, *New J. Chem.* **1998**, 423–433.

[4] S. Chang, R. H. Grubbs, *Tetrahedron Lett.* **1997**, *38*, 4757–4760; C. Meyer, J. Cossy, *Tetrahedron Lett.* **1997**, *38*, 7861–7864; J. H. Cassidy, S. P. Marsden, G. Stemp, *Synlett* **1997**, 1411–1413; R. Stragies, S. Blechert, *Tetrahedron* **1999**, *55*, 8179–8188.

[5] W. J. Zuercher, M. Scholl, R. H. Grubbs, *J. Org. Chem.* **1998**, *63*, 4291–4298; J. S. Clark, G. P. Trevitt, D. Boyall, B. Stammen, *Chem. Commun.* **1998**, 2629–2630.

[6] A. Kinoshita, M. Mori, *Synlett* **1994**, 1020–1022; A. Kinoshita, M. Mori, *J. Org. Chem.* **1996**, *61*, 8356–8357; A. G. M. Barrett, S. P. D. Baugh, D. C. Braddock, K. Flack, V. C. Gibson, P. A. Procopiou, *Chem. Commun.* **1997**, 1375–1376.

[7] M. Mori, N. Sakakibara, A. Kinoshita, *J. Org. Chem.* **1998**, *63*, 6082–6083; J. A. Smulik, S. Diver, *Org. Lett.* **2000**, *2*, 2271–2274; L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohle, W. A. Herrmann, *Tetrahedron Lett.* **1999**, *40*, 4787–4790.

[8] M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 2249–2250.

[9] D. Sémeril, J. Le Nôtre, C. Bruneau, P. H. Dixneuf, A. F. Kolomiets, S. N. Osipov, *New J. Chem.* **2001**, 16–18.

[10] H. W. Wanzlick, H.-J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142; W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187; D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[11] D. J. Cardin, B. Çetinkaya, M. F. Lappert, *Chem. Rev.* **1972**, *72*, 545–574 ; B. Çetinkaya, P. Dixneuf, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1974**, 1827–1833.

[12] C. W. Bielawski, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906 ; M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[13] A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *112*, 3783–3784: C. W. Lee, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 2145–2147; D. L. Wright, J. P. Schulte, M. A. Page, *Org. Lett.* **2000**, *2*, 1847–1850.

[14] A. K. Chatterjee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 1751–1753.

[15] R. Stragies, U. Voigtmann, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 5465–5468.

[16] L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 3760–3763.

[17] L. Ackermann, C. Bruneau, P. H. Dixneuf, submitted.

[18] A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523–14534.

[19] The enynes **1 a–g** were prepared in more than 90% yield by reaction of $Me_2(CH_2{=}CH{-}CH_2)SiCl$ with the propargylic alcohol in the presence of 4-dimethylaminopyridine (DMAP) (10 mol %) and NEt_3 (2 equiv.) in CH_2Cl_2 at room temperature overnight.

[20] The enynes **1 f** and **1 g** were prepared in two steps from cyclohexanone: i) reaction in THF with 1-hexynyl- or 3-methoxypropynyllithium salt prepared by deprotonation of the corresponding terminal alkyne with BuLi in THF at –78 °C followed by hydrolysis, ii) etherification with allyldimethylchlorosilane in Et_3N in the presence of a catalytic amount of DMAP. The overall yields of isolated products from cyclohexanone were 81% (**1 f**) and 86% (**1 g**), respectively.

[21] S. Kotha, N. Screenivasachary, *Chem. Commun.* **2000**, 503–504.