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The reductive dimerization of some 1,3-dienes and of 1,3,5-cycloheptatriene in the presence of trimethylchlorosilane: a DFT investigation

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ABSTRACT

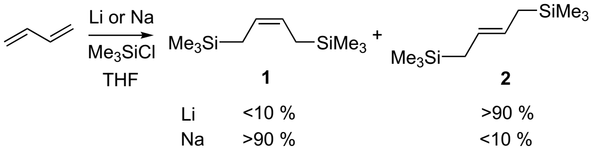
Treatment of 1,3-dienes and 1,3,5-cycloheptatriene by chlorotrimethylsilane in the presence of wire of lithium led mainly to reductive dimerization with formation of bis(allylsilane) derivatives. Bis-silyl compounds obtained: from 1,3-butadiene, 1,8-bis(trimethylsilyl)-2,6-octadiene (70%); from isoprene, (*Z*,*Z*)-2,7-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene (44%) and 2,6-dimethyl-1,8-bis(trimethylsilyl)-2,6-octadiene (19%); from butadiene–isoprene mixture (1:1), 3-methyl-1,8-bis(trimethylsilyl)-2,6-octadiene (55%); from 2,3-dimethylbutadiene, (*E*,*E*)-2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)-2,6-octadiene (36%), from 1,3-cyclohexadiene, 4,4′-bis(trimethylsilyl)-bicyclohexyl-2,2′-diene (48%); from 1,3,5-cycloheptatriene, 1,1′-bi[(*S**,*S**)-6-(trimethylsilyl)cyclohepta-2,4-dien-1-yl] (53%). The structure of the various intermediates (radical anion, dianion, silylated radical, silylated anion) has been established by calculations at the B3LYP/6-311++G(d,p) level of theory with zero-point energy correction. These results are in accordance with a pathway including the formation of a radical anion, its silylation furnishing to a γ-silylated allylic radical followed by a dimerization reaction in the head to head manner.

1. Introduction

In connection with the production of synthetic rubber, metalations of 1,3-dienes (butadiene and isoprene) with sodium metal are known as far back as 1912.[1] Anionic polymerization of butadiene by alkali metal bulk was described by Ziegler in 1938 (Buna rubbers).[2] Since the polymerization of butadiene by sodium is so rapid, its mechanism has been studied by analogy by replacing butadiene by substituted dienes, which react more slowly and by replacing sodium by lithium.[3] The industrial interest of the polymerization of butadiene in the presence of lithium is due to the structure of polymer (92.8% *cis*-1,4), which then vulcanized in either gum or a reinforced stock gives tensile strengths comparable to Hevea rubber.[4]

Frank and Foster have shown that it is possible to block the sodium-diene reaction at the dimer stage by using sodium dispersion in diglyme at −30 °C with *p*-terphenyl as sodium 'carrier' followed by carboxylation. Hydrogenation of the resultant unsaturated diacid mixture yielded three major products, sebacic acid, 2-ethylsuberic acid and 2,5-diethyladipic acid in the ratio 3.5:5:1.[5]

In order to end-capping the polymerization of butadiene with alkali metals, Nelson and his co-workers used dispersed lithium (lithium sand) or pieces of sodium in THF in the presence of trimethylchlorosilane.[6] Major products were 1,4-bis(trimethylsilyl)-2-butene *cis* **1** and *trans* **2** in quite different isomers ratios (Scheme 1). All conditions other than lithium metal in THF gave a *cis*-1,4-addition (except for lithium metal in diethyl ether and lithium naphthalenide in THF, which gave mainly a *cis*-1,4-addition).



Scheme 1.

To explain the dramatic effects of metal and solvents on the course of the reaction, Nelson proposed a sequence of reactions involving the initial formation of the *cis*-anion radical **3**, which would allow the gegenion to neutralize the partial charge on both the C(1) and C(4) atoms (Scheme 2).[7]

According to Nelson, in the presence of lithium metal in a polar solvent as THF, the radical anion **3*cis*** is quickly reduced ($k_{\text{but.1}} > k_{\text{but.2}}$) in dianion **4*trans***, which is trapped by trimethylchlorosilane to give

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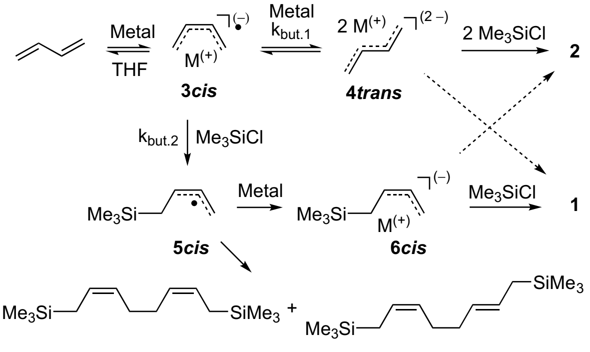


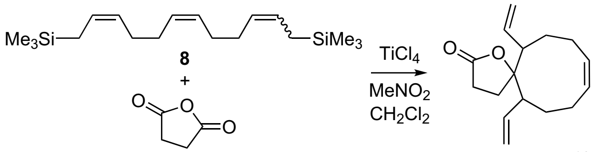
7, 1.5:1 (Metal: Li)

Scheme 2.

2.[8] With sodium metal, the corresponding very reactive radical anion ***3cis*** rapidly reacts with chlorosilane (at the beginning of the reaction, the concentration of trimethylchlorosilane is about 4 M) ($k_{but.2}>k_{but.1}$) to give the radical ***5cis***, which is further reduced in anion ***6cis*** neutralized by chlorosilane.[9]

This bis-silylation of dienic or trienic hydrocarbons constitutes a convenient route to obtain bis(silyl) unsaturated compounds that can represent useful intermediates in organic chemistry or can be used as building blocks for the organic synthesis.[10–12]

Some years ago, we have observed that by decreasing the lithium metal surface using pieces of lithium (8 mm each side) or better 3 mm wire of lithium, the rate of reduction of **3** and **5** decreases ($k_{but.2}>k_{but.1}$) making easier the dimerization of radical ***5cis*** into 1,8-bis(trimethylsilyl)-2,6-octadiene (Bistro) **7**. Fractional distillation gave **1**, **2** (1:1 mixture, 20%) and **7** obtained in 68–72% yield, which appeared as a mixture of (*Z*,*Z*)-isomer (ca. 50%), (*Z*,*E*)-isomer (ca. 40%).[13] The formation of **7** involved about 74% of radical ***5cis***. In contrast, the use of pieces of sodium leads mainly to the (*Z*,*Z*)-isomer (up to 80%). The heavy fraction of the distillation contains bis(trimethylsilyl)dodecatriene **8** (ca. 8–10%). To confirm its structure, this bis-allylsilane was added to succinic anhydride giving rise to the spiro γ-lactone **9** (33%, mixture of isomers) (Scheme 3). Taking into account the (*Z*)-geometry of the cyclic double bond, we conclude that the internal double bond of **8** is mainly similar.



9, 33%

Scheme 3.

Now we report the results concerning the reductive dimerization of isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3,5-cycloheptatriene, cyclopentadiene and 1,3-cyclooctadiene in the presence of chlorosilane.

2. Results and discussion

We have investigated the structure of the *cis* and *trans* radical anion **3**, the *cis* and *trans* dianion **4** and the *cis* and *trans* radical **5** at the B3LYP/6-311++G(d,p) level of theory with zero-point energy correction (Table 1, entries 1–10, and Supplementary data).[14]

These calculations indicate that for the radical anion **3**, the *cis* and the *trans*-isomers have similar energies ($\Delta E=-0.13$ kcal/mol), even in the absence of counter-ion (Table 1, entry 4). In contrast, in the case of the dianion **4**, and as predicted by Nelson, the *trans*-isomer is the most stable ($\Delta E=4.60$ kcal/mol) (Table 1, entry 6). Interestingly, the *cis*-isomer ***4cis*** is not plane and the structure of the two isomers looks like two vinyl anions linked by a single bond indicating that the interconversion barrier *cis–trans* is very low (see Supplementary data). However, it is well known that the stereochemical preference is the reverse in the presence of two lithium counter-ion adducts of TMEDA. These complexes prefer to adopt dibridging structures involving a delocalization of charge.[15] Finally, if the two silylated radicals **5** have comparable energies ($\Delta E=-0.71$ kcal/mol) (Table 1, entry 8), it is not the case for their corresponding anions **6**, the *cis*-isomer being the most stable ($\Delta E=2.09$ kcal/mol) (Table 1, entry 10). For silylated compounds, in each case, the C–Si bond is almost perpendicular to the allylic moiety revealing a hyperconjugation with the unsaturated system (see Supplementary data).

Table 1

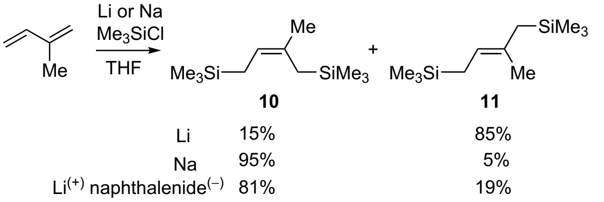
Calculated total energy[a] of alkadienes, corresponding radical anions, silylated radicals and silylated anions at the B3LYP/6-311++G(d,p) level of theory, with zero-point energy (ZPE) correction[b]

Entry	Compound	Total energy with ZPE corr. (hartree)	*cis–trans* energy difference (kcal/mol)
1	*s-cis* 1,3-Butadiene	−155.951 024	
2	*s-trans* 1,3-Butadiene	−155.957 050	−3.78
3	***3cis***	−155.942 042	
4	***3trans***	−155.942 256	−0.13
5	***4cis***	−155.804 066	
6	***4trans***	−155.811 388	−4.60
7	***5cis***	−565.173 080	
8	***5trans***	−565.174 212	−0.71
9	***6cis***	−565.193 782	
10	***6trans***	−565.190 450	2.09
11	*s-cis* Isoprene	−195.251 812	
12	*s-trans* Isoprene	−195.257 151	−3.35
13	***12cis***	−195.242 132	
14	***12trans***	−195.246 357	−2.65
15	***13cis***	−195.112 933	
16	***13trans***	−195.119 245	−3.96
17	***14cis***	−604.471 731	
18	***14trans***	−604.471 858	−0.08
19	***15cis***	−604.473 320	
20	***15trans***	−604.473 283	0.02
21	***16cis***	−604.493 264	
22	***16trans***	−604.486 452	4.27
23	***17cis***	−604.491 595	
24	***17trans***	−604.490 348	0.79
25	***21cis***	−234.548 140	
26	***21trans***	−234.555 083	−4.36
27	***24cis***	−234.537 103	
28	***24trans***	−234.543 756	−4.17
29	***25cis***	−234.421 655	
30	***25trans***	−234.423 283	−1.02
31	***26cis***	−643.768 473	
32	***26trans***	−643.768 513	−0.02
33	***27cis***	−643.786 478	
34	***27trans***	−643.785 359	0.70
35	1,3,5-Cycloheptatriene	−271.458 573	
36	**32**	−271.458 151	
37	**33**	−680.673 774	
38	**34**	−680.705 128	
39	**35**	−271.326 088	
40	1,3-Cyclohexadiene	−233.363 520	
41	**39**	−233.344 607	
42	**40**	−642.576 710	
45	**41**	−642.590 642	
45	**42**	−233.229 543	

[a] Hartrees.

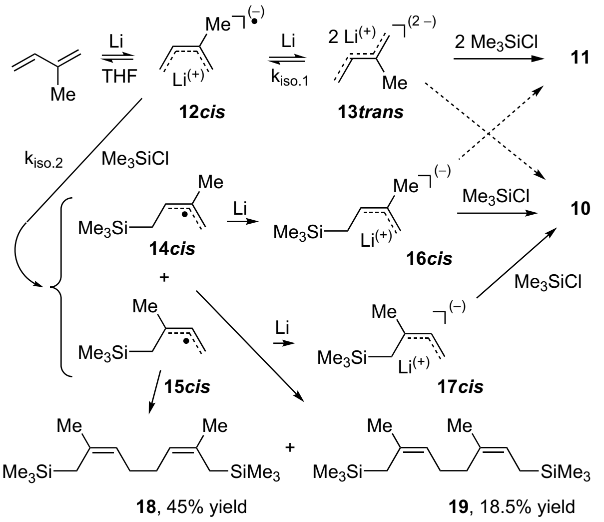
[b] ZPEs are scaled by a factor of 0.989, as recommended for calculation at the Becke3LYP/6-311++G(3df,2p) level of theory.[34]

As shown by Nelson,[6] the disilylation reaction of isoprene in the presence of dispersed lithium metal leads mainly to the *trans*-isomer **11** (Scheme 4).



Scheme 4.

By using pieces of lithium, isoprene reacts to yield **10** (9%), **11** (14%) and the disilyloctadienes, which are isolated as an inseparable mixture (63%, 2.4:1) of (*Z*,*Z*)-isomer **18** (2,7-dimethyl) and of **19** (2,6-dimethyl) (Scheme 5).[16] In 1984, Sakurai showed that the palladium complex-catalyzed reaction of hexamethyldisilane with isoprene gave the symmetrical (*E*,*E*)-3,6-dimethyl-1,8-bis-(trimethylsilyl)-2,6-octadiene.[17] Titanium tetrachloride-mediated reactions of **18** and **19** with various electrophiles gave rise to products confirming to these structures.[18]

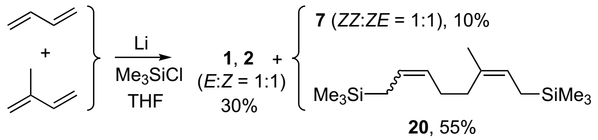


Scheme 5.

Thus, the use of lithium wire induces a modification of the ratio of *cis*–*trans* isomers for the disilylbutenes **10**–**11** to the detriment of the *trans*-isomer **11**. Decreasing the surface of the lithium metal ($k_{\text{iso.2}}>k_{\text{iso.1}}$) would favour the route via the silylated anions **16*cis*** or **17*cis*** to give a more large proportion of **10**.

As regards isoprene, the overall mechanism is more complex than the butadiene one since two isomeric silylated radicals **14** and **15** can be formed from the radical anion **12** and chlorosilane.

Structure determination of various intermediates by calculations at the B3LYP/6-311++G(d,p) level of theory reveals that the relative stabilities of the *cis*–*trans* isomers are variable: **12*trans***>**12*cis***; **13*trans***≫**13*cis***; **14*trans***~**14*cis***; **15*cis***~**15*trans***; **16*cis***≫**16*trans***; **17*cis***~**17*trans*** (Table 1, entries 13–24). Interesting result is the great stability of the silylated anion **16*cis*** against **16*trans*** (ΔE=4.27 kcal/mol), **17*cis*** (ΔE=1.05 kcal/mol), or **17*trans*** (ΔE=1.83 kcal/mol) and the relative stability of the silylated radical **15** in comparison with **14** (**15*cis***–**14*cis***: ΔE=1.0 kcal/mol; **15*trans***–**14*trans***: ΔE=0.89 kcal/mol). The dimerization of **15*cis*** in the head to head manner[19] giving **18** as major product is in accordance with the steric hindrance and the Mulliken atomic spin density (C(1)=0.685; C(3)=0.650) (see Supplementary data). However, theoretical results do not explain the formation of the (*Z*,*Z*)-isomer. **15*cis*** and **15*trans*** have similar energies, consequently, the importance of the counter-ion lithium will be confirmed. As envisaged by Nelson,[6] the *cis* configuration of **12*cis*** would allow a better neutralization of the charge than the *trans* one, **12*trans***. As regards 3-neopentylallyllithium, a dimeric form has been envisioned by Glaze and co-workers to explain the lithium exchange between the α and γ positions.[9]



Scheme 6.

It was very interesting to study the reductive dimerization of an equimolar mixture of 1,3-butadiene and isoprene in the presence of lithium and chlorotrimethylsilane (Scheme 6). The distillation of reaction mixture followed by GC analysis revealed that the first fraction contained only 1,4-bis(trimethylsilyl)-2-butene *cis* **1** and *trans* **2** (30%) in equal proportions. In the second fraction, we found **7** (10%) and **20** as a mixture of inseparable isomers (55%).

The disilyloctadienes **18** and **19** resulting from the reductive dimerization of isoprene are not formed during this reaction.

The (*Z*)-configuration of the trisubstituted double bound of **20** was established by NOE experiment that showed cross-peaks between the signal of allylic protons and the vinylic one. The structure of **20** has been confirmed after its $TiCl_4$-mediated addition reaction to the benzoyl chloride.[20]

From this experience, we can conclude that the butadiene is faster reduced than the isoprene. This relative fast reduction is confirmed by theoretical calculations (vide infra and Table 2, entries 1 and 3).

The disilylation of 2,3-dimethyl-1,3-butadiene **21** is a practical reaction as only few products have been obtained after distillation, an inseparable mixture of **22** (19%) and **23** (28%), and then a mixture of **28** (36%) and **29** (7.5%) (Fig. 1). The latter mixture was stored at −20 °C and **28** slowly crystallized. Its *trans*–*trans* structure was confirmed by X-ray crystallographic analysis (Fig. 2). We have recently described titanium tetrachloride-mediated stereoselective reactions of **28** with aldehydes, anhydrides and acyl chlorides.[21] As for isoprene, when lithium sand is used, the *trans*-isomer **23** is obtained in larger proportion (96%) comparatively to the *cis*-isomer **22** (4%).[6] By addition of metal-free trimethylsilyl anion to **21**, Hiyama and his co-workers have obtained only **23**.[22]

Then, we studied the disilylation of the cycloheptatriene. This is an interesting case because an unusual base-promoted [π6s+π8s] cyclodimerization can occur by treatment with potassium amide in liquid ammonia. In addition ditropyl was subjected to lithium–ammonia reduction to give the same cyclodimers.[23] Likewise, the oxidative dimerization of heptafulvenes yields bicycloheptatrienyl derivatives according to a single electron transfer reactions.[24] Treatment of a THF solution of cycloheptatriene with lithium wire in the presence of chlorotrimethylsilane gave mainly a monocyclic

Table 2
Total energy differences between alkadienes and corresponding radical anions at the B3LYP/6-311++G(d,p) level of theory, with zero-point energy (ZPE) correction

Entry	1,3-Diene (or 1,3,5-heptatriene)+e→radical anion	ΔE (kcal/mol)
1	(*s-cis*)-1,3-Butadiene→**3*cis***	5.63
2	(*s-trans*)-1,3-Butadiene→**3*trans***	9.28
3	(*s-cis*)-Isoprene→**12*cis***	6.07
4	(*s-trans*)-Isoprene→**12*trans***	6.77
5	(*s-cis*)-**21**→**24*cis***	6.93
6	(*s-trans*)-**21**→**24*trans***	7.11
7	1,3,5-Cycloheptatriene→**32**	0.26
8	1,3-Cyclohexadiene→**39**	11.87

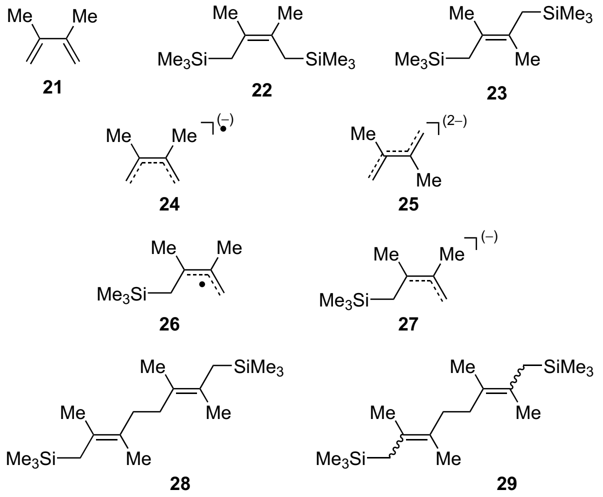


Figure 1.

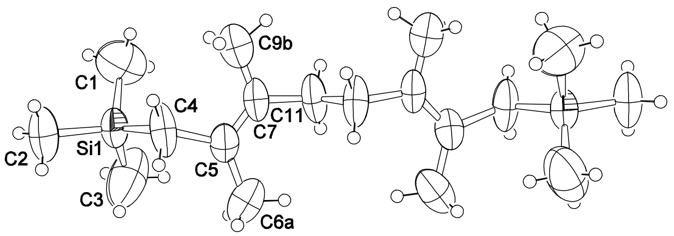
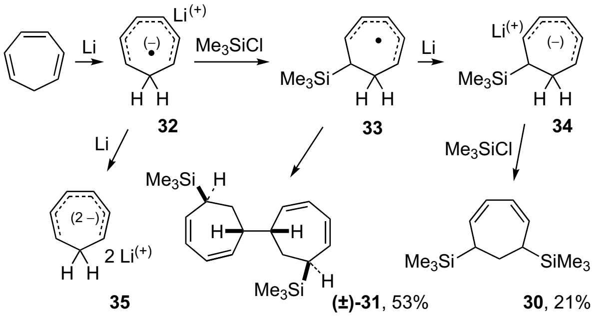


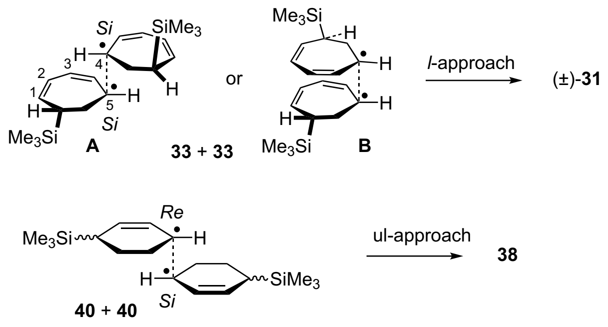
Figure 2. ORTEP drawing for **28**. Non-hydrogen atoms are drawn with 50% probability thermal ellipsoids.

disilane **30** (21%) and the 1,1′-bi[(S*,S*)-6-trimethylsilylcyclohepta-2,4-dien-1-yl] (±)-**31** (53%) (Scheme 7).[25]

Compound **31**, which appeared as one isomer with a C_2 axis should be the result of a C–C bond formation exclusively from the less hindered face of the rings of **33** and with a *like* relative topicity.[26] Consequently, transition state corresponding to an *unlike* relative approach with a possibility of a large molecular orbitals overlap did not occur (Scheme 8). In contrast, the dimerization of the methyl 2,4,6-cycloheptatriencarboxylate radical cation yields to the *unlike* (*meso*) dimer.[24] This stereoselectivity is remarkable since the dimerization of two organic radicals is known to take place non-stereoselectively[27] (dimerization of secondary and tertiary benzyl radicals gave a 1:1 ratio of diastereoisomeric products).[28] The relative high yield of dimeric product **31** confirms the stability of the radical **33**. The hyperconjugation of the C–Si bond with the pentatrienyl radical moiety is confirmed by calculations: the C–Si bond is nearly perpendicular to the medium plane of the pentadienyl radical moiety (see Supplementary data). The stereo- and regioselectivity of coupling of **33** is controlled only by steric effects (Scheme 8, **A**). The largest coefficient of the singly occupied MO (SOMO) is at the C(1) of the pentadienyl radical [SOMO, 46th MO, Σatom. coef. (2s, 2p): C(1), 0.231; C(2), 0.032; C(3), −0.255; C(4), 0.017; C(5), 0.224] and, thus, steric effects might well dominate over frontier molecular orbital control.[29] Interestingly, the steric approach **A** induces a minimization of the dipole moment along the reaction coordinate.[30]



Scheme 7.



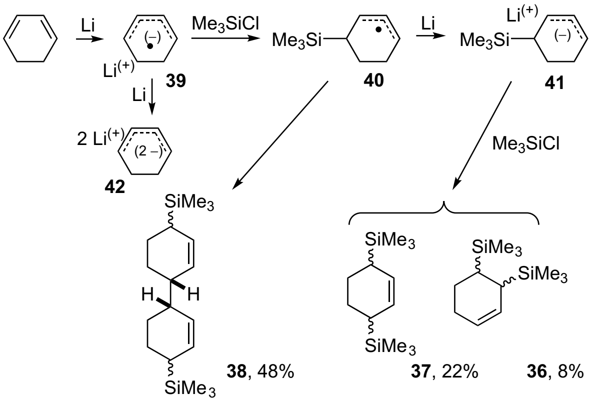
Scheme 8.

We also investigated the reductive dimerization of 1,3-cyclohexadiene.[31] Three disilanes were obtained and mainly the 4,4′-bis(trimethylsilyl)-bicyclohexyl-2,2′-diene **38** (48% yield), an interesting intermediate in organic synthesis (Scheme 9). This compound appeared as a mixture of three isomers (1.5:1:1) but its TiCl$_4$-mediated reaction with 2-naphthaldehyde gave rise to one crystallized tricyclic hydrocarbon (62% yield) corresponding to a double alkylation. Its structure has been achieved by an X-ray diffraction analysis. This structure determination confirms the *meso* configuration of the two stereogenic centres of the bond linkage.[32]

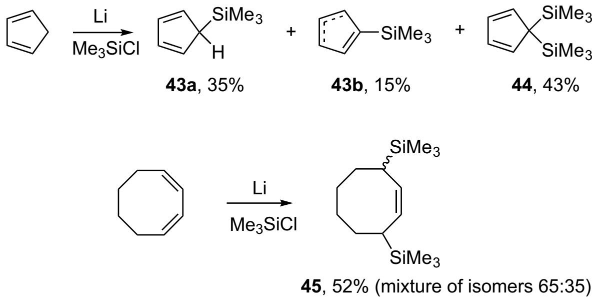
Contrary to the **31** formation, the stereoselectivity of the dimerization of **40** comes from a transition state corresponding to an *unlike* relative approach with an *anti* geometry indifferent to the uncontrolled centres bearing trimethylsilyl groups (Scheme 8). Interestingly, in both cases, formation of **31** or **38**, a transition state involving a large molecular orbitals overlap did not occur. The dimerization of **33** to give **31** is weakly exothermic (28.72 kcal/mol) at the B3LYP/6-311++G(d,p) level of theory in contrast to the dimerization of **40** (66.29 kcal/mol). This comparison underlines the stability of the silylated radical **31**.

Finally, we are interested in the cyclopentadiene reductive dimerization. The major product is 1,1-bis(trimethylsilyl)cyclo-2,4-diene **44** coming from the disilylation of the cyclopentadienyl anion (Scheme 10). Dimerization product was not observed.

It is the same for 1,3-cyclooctadiene, which gave rise only to a mixture of *meso* and DL (±)-1,4-bis(trimethylsilyl)cyclooct-2-ene **45** (Scheme 10).



Scheme 9.



Scheme 10.

3. Conclusion

Major steps of the reductive dimerization of alkadienes correspond to the capture of one electron coming from lithium metal. These reactions are moderately endothermic for the formation of radical anion ($\Delta E=5.63$–11.87 kcal/mol; 1,3,5-heptatriene, $\Delta E=0.26$ kcal/mol) (Table 2). As regards butadiene and isoprene, the reaction is less endothermic for the *Z*-isomers than the *E*-one (Table 2, entries 1, 2 and 3, 4), justifying the easy formation of the *cis*-derivatives and particularly **3*cis***. In contrast, the obtaining of corresponding dianions is highly unlikely even in the presence of lithium counter-ion ($\Delta E=72.20$–86.58 kcal/mol) (Table 3).

Interestingly, the reduction of silylated unsaturated radical is an exothermic reaction ($\Delta E=-8.74$ to -19.67 kcal/mol) (Table 4). To establish the importance of the trimethylsilyl group for the stabilization of the negative charge, we have calculated the energy of reduction of allylic radical **46** to the corresponding allylic anion **47** (Scheme 11) and we have compared it to the reaction energy **14*cis*→16*cis*** (one hydrogen atom is substituted by the trimethylsilyl group). The reaction is not as exothermic ($\Delta E=-11.64$ kcal/mol) as the **14*cis*→16*cis*** one ($\Delta E=-13.51$ kcal/mol). So, the presence of the trimethylsilyl group stabilizes the negative charge by 1.87 kcal/mol at this level of computation. We also note that the 1,3,5-cycloheptatriene is very easily reduced (Table 2, entry 7) as its silylated radical **33** (Table 4, entry 9).

Strangely, excepting butadiene derivatives, the silylation reaction of radical anions is more exothermic for the *cis*-isomers than for the *trans* one (Table 5, entries 4, 7, and 10) (see Supplementary data).

The high endothermic character of the reduction of radical anions in contrast with the exothermic formation of the silylated anions allows to consider that the most likely way for the reductive dimerization of alkadienes is the following: diene→radical anion→silylated radical→bis(silyl)-diene and concerning the formation of monomers: silylated radical→silylated anion→bis(silyl)-alkene.

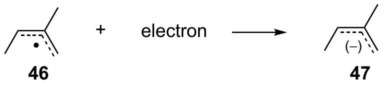
Even in the case of moderate yields, the very easy and cheap reductive dimerization of dienes or trienes is of considerable interest because of the synthetic potential of the resulting diallysilane.

Table 3
Total energy differences between radical anions and corresponding dianions at the B3LYP/6-311++G(d,p) level of theory with zero-point energy (ZPE) correction

Entry	Radical anion+e→dianion	ΔE (kcal/mol)
1	**3*cis*→4*cis***	86.58
2	**3*trans*→4*trans***	82.12
3	**12*cis*→13*cis***	81.07
4	**12*trans*→13*trans***	79.76
5	**24*cis*→25*cis***	72.44
6	**24*trans*→25*trans***	75.60
7	**32→35**	82.87
8	**39→42**	72.20

Table 4
Total energy differences between silylated radicals and corresponding silylated anions and comparison with isoprenyl derivatives **46** and **47** at the B3LYP/6-311++G(d,p) level of theory with zero-point energy (ZPE) correction

Entry	Silylated radical+e→silylated anion	ΔE (kcal/mol)
1	**5*cis*→6*cis***	−12.99
2	**5*trans*→6*trans***	−10.19
3	**14*cis*→16*cis***	−13.51
4	**14*trans*→16*trans***	−9.16
5	**15*cis*→17*cis***	−11.47
6	**15*trans*→17*trans***	−10.71
7	**26*cis*→27*cis***	−11.30
8	**26*trans*→27*trans***	−10.57
9	**33→34**	−19.67
10	**40→41**	−8.74
11	**46→47**	−11.64



Scheme 11.

3.1. X-ray crystallography

CCDC-629277 (for **28**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].

Crystallographic data: $C_{18}H_{38}Si_2$, $M_w=310.66$, monoclinic, colourless crystal ($0.5\times0.5\times0.1$ mm^3), $a=13.484(1)$ Å, $b=11.9711(8)$ Å, $c=7.1118(6)$ Å, $\beta=104.434(5)^\circ$, $V=1111.74(15)$ Å^3, space group *C*2, $Z=2$, $\rho=0.928$ g cm^{-3}, μ(Mo Kα)$=1.53$ cm^{-1}, 1118 unique reflections, 118 parameters refined on F^2 [Shelxl] to final indices $R[F^2>4\sigma F^2]=0.0492$ (951 reflections), $wR[w=1/[\sigma^2(F_o^2)]=0.138$ (all reflections). The last residual Fourier positive and negative peaks were equal to 0.115 and −0.131, respectively (Table 6).

3.2. Computational methods

Calculations by using Gaussian 03, revision D.02.[33] For the open-shell species (radicals and radical anions), the ⟨*S*2⟩ values of calculations were less than 0.7862 (see, Table S8 in Supplementary data).

Table 5
Calculations of relative energy of silylation of radical anions to give corresponding silylated radicals at the DFT/6-311++G(d,p) level of theory with correction of the zero-point energy

Entry	Radical anion	Corresponding silylated radical	Relative energy reaction (kcal/mol)
1	**3*cis***	**5*cis***	0.67
2	**3*trans***	**5*trans***	0.09
3	**12*cis***	**14*cis***	1.57
4	**12*cis***	**15*cis***	0.57
5	**12*trans***	**14*trans***	4.14
6	**12*trans***	**15*trans***	3.25
7	**24*cis***	**26*cis***	0.46
8	**24*trans***	**26*trans***	4.61
9	**32**	**33**	10.34
10	**39**	**40**	0.00

Table 6
Crystal data and structure refinement for **28**

Crystallographic data: $C_{18}H_{38}Si_2$, M_w=310.66, monoclinic, colourless crystal (0.5×0.5×0.1 mm^3), a=13.484(1) Å, b=11.9711(8) Å, c=7.1118(6) Å, β=104.434(5)°, V=1111.74(15) Å^3, space group $C2$, Z=2, ρ=0.928 g cm^{-3}, μ(MoKα)=1.53 cm^{-1}, 1118 unique reflections, 118 parameters refined on F^2 [Shelxl] to final indices $R[F^2>4\sigma F^2]$=0.0492 (951 reflections), $wR[w=1/[\sigma^2(F_o^2)]$=0.138 (all reflections). The last residual Fourier positive and negative peaks were equal to 0.115 and −0.131, respectively

4. Experimental section

4.1. General

All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F254. Flash chromatography was performed on silica gel (230–400 mesh) obtained from Macherey-Nagel & Co. CH_2Cl_2 was distilled before use from calcium hydride and THF was distilled from sodium-benzophenone. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions at 300, and 75 MHz, respectively, using a Bruker AC300 spectrometer. Chemical shift is reported in parts per million relative to $CDCl_3$ (signals for residual $CDCl_3$ in the $CDCl_3$: 7.24 for ^{1}H NMR and 77.16 (central) for ^{13}C NMR). Carbon–proton couplings were determined by DEPT sequence experiments. High resolution ESI-MS analyses were performed using a Qstar Elite (Applied Biosystems SCIEX) mass spectrometer.

*4.1.1. 1,4-Bis(trimethylsilyl)but-2-ene (**1** and **2**) and 1,8-bis(trimethylsilyl)octa-2,6-diene (**7**)*

A 3-L three-necked flask equipped with a thermometer, a dropping funnel, a reflux condenser connected with a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with 600 mL of anhydrous tetrahydrofuran. The solution was cooled to 0 °C with an ice bath and lithium metal (3 mm wires cut as pieces of 1.5 cm long, 28 g, 4 atoms) was added. The stopper of the addition funnel is removed under a slight positive flow of argon and 434 g (507 mL, 4 mol) of chlorotrimethylsilane is poured into the addition funnel. The stopper is put in place and chlorotrimethylsilane is added neat over 20 min. The U-shaped double-tipped needle connected to the flask containing neat cold liquid 1,3-butadiene is introduced through the rubber septum of the dropping funnel and butadiene (450 mL, ca. 280 g, ca. 5.18 mol) is transferred. The reactants are vigorously stirred and butadiene is slowly added over approximately a 1.5 h period. The reaction mixture is stirred at 0 °C for 6 h and overnight at room temperature. Then pentane (or light petroleum) is added to fill in the flask, and the possibly small remaining pieces of lithium are removed with tweezers. The milked solution is poured onto 1 kg of crushed ice in a 6-L Erlenmeyer, after stirring, the layers are separated. The organic one is washed with chilled water (6×500 mL) and then dried over anhydrous $MgSO_4$. After filtration and concentration in vacuo, the colourless residue was distilled through 12-cm Vigreux column.

*4.1.2. (Z)-1,4-Bis(trimethylsilyl)but-2-ene (**1**) and (E)-1,4-bis(trimethylsilyl)but-2-ene (**2**)*

Colourless oil, bp 40 °C, 0.2 Torr, 36 g, 0.18 mol, 18% overall yield (1:1). **1**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.00 (s, 9H), 1.40 (br s, 2H), 5.27–5.31 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.5 (q), 18.0 (t), 123.3 (d). **2**, ^{1}H NMR (300 MHz, $CDCl_3$): δ=−0.01 (s, 9H), 1.37 (br s, 2H), 5.18–5.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.8 (q), 23.0 (t), 124.5.

*4.1.3. 1,8-Bis(trimethylsilyl)octa-2,6-diene (**7**)*

Colourless oil, bp 87–95 °C, 0.2 Torr, 355.6 g, 1.4 mol, 70% yield. Compound **7** is a mixture of (*Z,Z*)-isomer (50%), (*Z,E*)-isomer (40%) and (*E,E*)-isomer (4%) contaminated with 4% of (2*Z*)-1,6-bis(trimethylsilyl)-2,7-octadiene and 2% of (2*E*)-1,6-bis(trimethylsilyl)-2,7-octadiene. IR ν_{max}/cm^{-1} 3015, 2962, 1255, 1159, 852, (*Z*)-isomers ν_{max}/cm^{-1} 695, (*E*)-isomers, ν/cm^{-1} 964; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.07 (s, 9H), 0.09 (s, 9H), 1.47–1.57 (m, 4H), 2.12 (br d, J=7.9 Hz, 4H), 5.30–5.50 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) (*Z,Z*)-isomer: δ=−1.6 (q), 18.6 (t), 21.5 (t), 125.7 (d), 127.4 (d); (*Z,E*)-isomer, −1.8 (q), −1.6 (q), 18.6 (t), 22.8 (t), 29.1 (t), 33.2 (t), 125.5 (d), 125.7 (d), 127.4 (d), 128.7 (d). ^{29}Si NMR δ/TMS: (*Z,Z*)-isomer, 1.20, (*Z,E*)-isomer, 0.44, 1.25.

*4.1.4. 1,12-Bis(trimethylsilyl)dodeca-2,6,10-triene (**8**)*

Colourless oil, mixture of isomers, bp 130–140 °C, 0.2 Torr, 61.6 g, 0.2 mol, 10% yield. The major isomer ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.04 (s, 9H), −0.03 (s, 9H), 1.37–1.47 (m, 4H), 2.01 (br s, 8H), 5.24–5.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−1.8 (q), −1.6 (q), 18.6 (t), 22.8 (t), 27.4 (t), 32.6 (t), 34.3 (t), 38.6 (t), 126.7 (d), 127.1 (d), 127.7 (d), 128.5 (d), 129.7 (d), 129.9 (d).

4.1.5. General procedure for the preparation of the other bis-silylated products

The previous procedure was employed with 250 mL of THF, 9 g (1.28 g atom) of pieces of lithium, 156 mL (1.22 mol) of chlorotrimethylsilane and 1.22 mol of diene.

*4.1.6. 2-Methyl-1,4-bis(trimethylsilyl)but-2-ene (**10** and **11**), (Z,Z)-2,7-dimethyl-1,8-bis(trimethylsilyl)octa-2,6-diene (**18**), 2,6-dimethyl-1,8-bis(trimethylsilyl)octa-2,6-diene (**19**)*

From isoprene, **10** and **11**, colourless oil, bp 32–35 °C, 0.2 Torr, 30 g, 0.14 mol, 23% overall yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.03 (s, 18H), 1.35 (dd, J=8.7, 8.9 Hz, 2H), 1.48 (d, J=4.4 Hz, 2H), 1.53 (s, 3H), 4.99 (dd, J=8.7, 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz). (*Z*)-isomer (**10**) (40%), δ=−1.0 (q), 18.7 (q), 18.8 (t), 22.9 (t), 117.3 (d), 131.0 (s). (*E*)-isomer (**11**) (60%), δ=−1.5 (q), 18.9 (t), 26.4 (q), 30.2 (t), 118.0 (d), 130.1 (s). **18** and **19** (2.4:1), colourless oil, bp 85–90 °C, 0.2 Torr, 73.3 g, 0.26 mol, 63% overall yield. **18**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.02 (s, 18H), 1.50 (s, 4H), 1.65 (s, 6H), 1.91–1.93 (m, 2H), 1.97 (br d, J=7.0 Hz, 2H), 5.00 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−0.85 (q), 23.4 (t), 26.4 (q), 29.1 (t), 122.4 (d), 133.1 (s). **19**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.02 (s, 18H), 1.41 (d, J=8.3 Hz, 2H), 5.13 (t, J=8.5 Hz, 1H), 5.16 (t, J=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−0.85 (q), 18.5 (t), 23.6 (q), 27.1 (t), 120.4 (d), 133.1 (s).

*4.1.7. 3-Methyl-1,8-bis(trimethylsilyl)octa-2,6-diene (**20**)*

From 1,3-butadiene–isoprene (1:1), colourless oil, mixture of isomers, bp 95–98 °C, 0.2 Torr, 107.2 g, 0.4 mol, 65% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.01 (s, 18H), 1.37–1.53 (m, 4H), 1.66 (s, 3H), 1.92–2.02 (m, 4H), 5.34–5.36 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−1.6 (q), −1.0 (q), 18.6 (t), 22.8 (t), 23.4 (t), 26.4 (d), 27.5 (t), 125.6 (d), 127.3 (d), 128.7 (d), 133.3 (s).

*4.1.8. 1,6-Bis(trimethylsilyl)cyclohepta-2,4-diene (**30**)*

From 1,3,5-cycloheptatriene, yellow oil, one isomer, bp 55–60 °C, 0.2 Torr, 31 g, 0.13 mol, 21% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.00 (s, 9H), 0.05 (s, 9H), 2.10–2.19 (m, 2H), 2.25 (t, J=6.1 Hz, 1H), 2.50–2.65 (m, 1H), 5.29 (dd, J=4.3, 11.9 Hz, 1H), 5.51–5.57 (m, 1H), 5.64–5.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−1.91 (q), −1.66 (q), 29.9 (d), 31.6 (d), 39.1 (t), 124.1 (d), 127.3 (d), 129.6 (d), 131.8 (d).

4.1.9. 1,1-Bi[(S,S*)-6-(trimethylsilyl)cyclohepta-2,4-diene-1-yl] (**31**)*

Yellow oil, bp 120–122 °C, 0.2 Torr, 105.6 g, 0.32 mol, 53% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.05 (s, 18H), 1.24–1.53 (m, 2H), 2.27–2.30 (m, 4H), 2.53–2.57 (m, 2H), 5.43 (br s, 4H), 5.64–5.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−1.5 (q), 31.0 (t), 39.0 (d), 44.8 (d), 128.0 (d), 128.1 (d), 131.7 (d), 132.6 (d). $C_{20}H_{34}Si_2$, MS: m/z (%)=330 (M^+, 12%), 91 (52), 73 (100), 45 (25).

4.1.10. 3,4-Bis(trimethylsilyl)cyclohexene (*36*) and 3,6-bis(trimethylsilyl)cyclohexene (*37*)

From 1,3-cyclohexadiene. Colourless oil, bp 50 °C, 0.2 Torr, 40.7 g, 0.18 mol, 30% overall yield. **37**, (70%), ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.02 (s, 9H), 1.33–1.82 (m, 3H), 5.60 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−2.5 (−3.2) (q), 23.5 (24.6) (t), 26.6 (26.1) (d), 126.0 (126.5) (d). $C_{12}H_{26}Si_2$, MS: *m*/*z* 226 (M^+ 80%), 211 (50), 152 (40), 138 (38), 78 (41), 73 (100), 45 (30). **36**, (30%), ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.01 (s, 18H), 1.33–1.82 (m, 6H), 5.60 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−2.1 (q), 20.7 (d), 22.1 (t), 23.8 (t), 26.9 (d), 124.3 (d), 128.2 (d). $C_{12}H_{26}Si_2$, MS: *m*/*z* 226 (M^+ 28%), 211 (20), 152 (35), 137 (18), 78 (45), 73 (100), 45 (30).

4.1.11. 4,4′-Bis(trimethylsilyl)bicyclohexyl-2,2′-diene (*38*)

Colourless oil, mixture of isomers, bp 135–145 °C, 0.2 Torr, 91.8 g, 0.3 mol, 48% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=0.01–0.03 (m, 18H), 1.30–1.43 (m, 8H), 1.55–1.80 (m, 2H), 2.06–2.07 (m, 2H), 5.50–5.68 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−3.3 (q), 23.7 (t), 26.4 (d), 26.8 (t), 40.3 (d), 128.1 (d), 128.4 (d). $C_{18}H_{34}Si_2$, MS: *m*/*z* 306 (M^+ 4%), 153 (25), 79 (28), 73 (100), 45 (20).

4.1.12. 1-Trimethylsilylcyclopenta-2,4-diene (*43*)

From cyclopentadiene, yellow oil, two isomers, bp 28–29 °C, 0.2 Torr, 84.2 g, 0.61 mol, 50% overall yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.02 (s, 9H), 0.18 (s, 9H), 3.03–3.39 (m, 3H), 6.50–6.67 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−1.91 (q), −0.61 (d), 130.2 (d) (2C), 133.4 (d) (2C). **43b** (30%): δ=−1.90 (q), 45.2 (t), 132.4 (d), 133.2 (d), 137.9 (d), 141.5 (s).

4.1.13. 1,1-Bis(trimethylsilyl)cyclopenta-2,4-diene (*44*)

Yellow oil, one isomer, bp 50–52 °C, 0.2 Torr, 54.6 g, 0.26 mol, 43% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.06 (s, 18H), 6.50 (d, *J*=5.7 Hz, 2H), 6.70 (d, *J*=5.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−0.65 (q), 57.0 (s), 130.6 (d), 136.2 (d). High resolution ESI-MS calcd for $C_{11}H_{22}Si_2$ $[M+H]^+$ 211.1332; found 211.1328.

4.1.14. 1,4-Bis(trimethylsilyl)cyclooctene (*45*)

From 1,3-cyclooctadiene, colourless oil, mixture of isomers, bp 95 °C, 0.2 Torr, 76.2 g, 0.3 mol, 52% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=−0.04 (s, 9H), 1.47–1.86 (m, 5H), 5.35 (d, *J*=4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=−3.0 (q), 28.3 (t), 28.4 (t), 29.5 (d), 129.0 (d). $C_{14}H_{30}Si_2$, MS: *m*/*z* 254 (M^+ 50%), 239 (50), 180 (51), 165 (100), 151 (40), 73 (40), 45 (10).

4.1.15. Reaction of *8* with succinic anhydride

A 100-mL three-necked flask equipped with a thermometer, septum cap, magnetic stirring bar and an argon outlet was charged with anhydrous CH_2Cl_2 (15 mL) and anhydrous nitromethane (1 mL, 19.5 mmol). The solution was cooled to −60 °C; $TiCl_4$ (0.93 g, 0.5 mL, 4.9 mmol) was added, followed by the slow addition of succinic anhydride (0.5 g, 4.9 mmol). After 1 h, the mixture was cooled to −90 °C and **8** (3 g, 9.7 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred for 2 h at −90 °C and then slowly warmed to −60 °C and stirred for 24 h. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The organic phase was washed with a saturated aqueous solution of $HNaCO_3$, brine and water. The solution was dried with $MgSO_4$, filtered and concentrated in vacuo, and the residue was purified by flash chromatography (petroleum ether–diethyl ether 70:30) on silica gel to give **9**.

4.1.16. 1-Oxa-6,13-divinylspiro [4.8]tridec-9-en-2-one (*9*)

Colourless oil, mixture of isomers, 0.4 g, 1.6 mmol, 33% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=1.15–1.25 (m, 1H), 1.39–1.53 (m, 3H), 1.67–1.77 (m, 3H), 1.78–1.80 (m, 1H), 1.90–2.01 (m, 2H), 2.13–2.22 (m, 1H), 2.43–2.53 (m, 3H), 4.86–4.93 (m, 2H), 5.08–5.16 (m, 4H), 5.63–5.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz), major isomer, δ=25.1 (t), 27.5 (t), 28.7 (t), 28.9 (t), 29.2 (t), 30.5 (t), 43.0 (d), 46.6 (d), 87.7 (s), 114.0 (t), 118.1 (t), 136.0 (d), 137.7 (d), 141.0 (d), 143.3 (d), 177.4 (s). High resolution ESI-MS calcd for $C_{16}H_{22}O_2$ $[M+H]^+$ 247.1692; found 247.1687.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.087.

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