446 *Organometallics* **2005,** *24,* 446−454

# Radical Hydrometalation of Functional Ethylenic Compounds: Radical Autoinhibition Changes the Regioselectivity

Abdelkrim El Kadib,[†,‡] Amal Feddouli,[§] Pierre Rivière,[*,†] Fabien Delpech,[†]
Monique Rivière-Baudet,[†] Annie Castel,[†] Mohamed Ahra,[‡] Aissa Hasnaoui,[§]
Francisco Burgos,[‖] Juan M. Manriquez,[‖] and Ivone Chavez[‖]

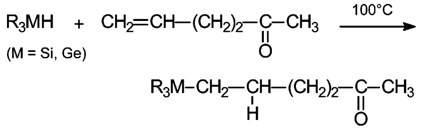
*Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France, Laboratoire de Chimie Organique et Organométallique, Faculté des Sciences, Université Ibn Zohr, BP 6S, Agadir, Maroc, Laboratoire des Substances Naturelles et des Hétérocycles, Faculté des Sciences Semlalia, BP 2390, Marrakech 40000, Maroc, and Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Casilla 306, Chile*

*Received June 30, 2004*

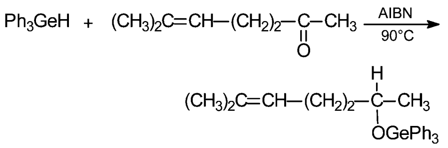
Hydrometalation of carbon−carbon double bonds by group 14 hydrides is inhibited by carbonyl compounds—mainly by α,*β*-unsaturated carbonyl groups—as efficiently as by classical radical trapping compounds, such as galvinoxyl and hydroquinone. This phenomenon, in the case of polyfunctional C═C- and C═O-containing compounds, such as carvone, leads to an autoinhibition of the exocyclic alkenylic hydrometalation under normal reaction conditions, while under drastic conditions, the O-metalation of the α,*β*-unsaturated carbonyl group occurs.

## Introduction

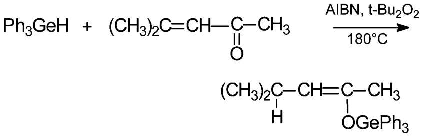
In the particular field of group 14 chemistry and especially in the case of silicon and germanium chemistry, hydrometalations of alkenes, of carbonyl compounds, and of α,*β*-unsaturated carbonyl compounds have been extensively studied.[1−6] From these studies emerged the catalytic effect of transition-metal complexes (Pt, Ru, Rh, etc.),[9,10] as well as an alternative and useful radical-initiated reaction.[6−8] In polyfunctional compounds containing both CH═CH$_2$ and C═O unsaturation, the vinyl group is more reactive than the carbonyl (eq 1),[11,12] but a steric effect at the carbon−carbon double bond can reverse the regioselectivity, leading to 1,2-addition to the carbonyl group (eq 2)[12] or 1,4-addition in a conjugated system (eq 3).[12]



$$\underset{(M = Si, Ge)}{R_3MH} + CH_2{=}CH{-}(CH_2)_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{100°C} R_3M{-}CH_2{-}\underset{H}{\underset{|}{C}}H{-}(CH_2)_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \tag{1}$$

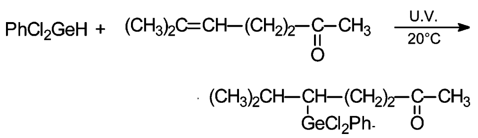


$$Ph_3GeH + (CH_3)_2C{=}CH{-}(CH_2)_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow[90°C]{AIBN} (CH_3)_2C{=}CH{-}(CH_2)_2{-}\overset{\overset{H}{|}}{\underset{\underset{OGePh_3}{|}}{C}}{-}CH_3 \tag{2}$$



$$Ph_3GeH + (CH_3)_2C{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow[180°C]{AIBN,\ t\text{-}Bu_2O_2} (CH_3)_2\underset{\underset{H}{|}}{C}{-}CH{=}\underset{\underset{OGePh_3}{|}}{C}{-}CH_3 \tag{3}$$

In these hydrometalations initiated by radical species, halosilanes and halogermanes are more reactive than their aryl or alkyl analogues (eq 4),[12] and this sometimes leads to a change in regioselectivity.



$$PhCl_2GeH + (CH_3)_2C{=}CH{-}(CH_2)_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow[20°C]{U.V.} (CH_3)_2CH{-}\underset{\underset{GeCl_2Ph}{|}}{CH}{-}(CH_2)_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \tag{4}$$

In the case of conjugated carbonyl compounds, such as benzaldehyde, benzophenone, mesityl oxide, *o*-nitro-

---

[*] To whom correspondence should be addressed. E-mail: riviere@chimie.ups-tlse.fr.

[†] Université Paul Sabatier.

[‡] Université Ibn Zohr.

[§] Faculté des Sciences Semlalia.

[‖] Universidad Católica de Chile.

(1) Armitage, D. A. Organosilanes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 2, pp 83−108.

(2) Armitage, D. A. Organosilanes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1995; Vol. 2, pp 1−39.

(3) Birkofer, L.; Stuhl, O. General synthetic pathways to organosilicon compounds. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 661−663.

(4) Kendrick, T. C.; Parbhoo. C.; White J. W. Siloxane polymers and copolymers. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989, pp 1342−1344.

(5) Ojima, I. The hydrosilylation reaction. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; pp 1480−1525.

(6) Rivière, P.; Rivière-Baudet, M.; Satgé, J. Germanium. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1982; Vol. 2, pp 399−518 (COMC I). Rivière, P.; Rivière-Baudet, M.; Satgé, J. Germanium. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, U.K., 1995; Vol. 2, pp 137−216 (COMC II),

(7) Chatgilialoglu, C. *Organosilanes In Radical Chemistry: Principles, Methods and Applications*; Wiley: Chichester, U.K., 2004.

(8) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95,* 1229.

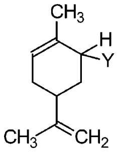
(9) Speier, J. L. Homogeneous catalysis of hydrosilylation by transition metals. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1979; Vol. 17, pp 407−447.

(10) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1989**, *366*, 275.

(11) Komarov, N. V.; Roman, V. K. *Zh. Obshch. Khim.* **1965**, *35*, 2017; *Chem. Abstr.* **1966**, *64*, 6675g.

10.1021/om049525g CCC: $30.25

**Table 1. Hydrometalation of Limonene and Carveol as a Function of Experimental Conditions**



| M−H | Y | *T* (°C) | time (h) | initiator or catalyst[a] | inhibitor[a] | reacn (%) | adduct |
|---|---|---|---|---|---|---|---|
| $Ph_3GeH$ | H | 100 | 24 | none | none | 0 | **1** |
| | | 130 | 24 | none | none | 70 | |
| | | 100 | 24 | AIBN | none | 72 | |
| | | 130 | 24 | RIS | none | ∼100 | |
| | | 20 | 7 | UV | none | 65 | |
| | | 130 | 24 | none | galvinoxyl | 0 | |
| | | 130 | 24 | none | benzophenone | 0 | |
| | | 130 | 24 | none | nitrocinnamaldehyde | 0 | |
| | | 130 | 24 | none | carvone | 5 | |
| | | 20 | 7 | UV | nitrocinnamaldehyde | 0 | |
| $Ph_3GeH$ | OH | 100 | 24 | none | none | 70 | **2** |
| | | 100 | 24 | AIBN | none | 95 | |
| | | 100 | 24 | none | nitrocinnamaldehyde | 0 | |
| | | 100 | 24 | none | carvone | 0 | |
| $Ph_2ClGeH$ | H | 100 | 24 | none | none | 69 | **3** |
| | | 100 | 24 | AIBN | none | 97 | |
| | | 100 | 24 | none | galvinoxyl | 0 | |
| | | 100 | 24 | none | nitrocinnamaldehyde | 6 | |
| $Ph_3SiH$ | H | 150 | 36 | none | none | 0 | **3** |
| | | 80−120[c] | 36 | AIBN | none | 0 | |
| | | 150 | 36 | RIS | none | 0 | |
| $Cl_3SiH$ | H | 120 | 36 | none | none | 0 | **4**[b] |
| | | 150 | 36 | none | none | 25 | |
| | | 80−120[c] | 36 | AIBN | none | 85 | |
| | | 150 | 36 | none | galvinoxyl | 0 | |
| | | 150 | 36 | none | nitrocinnamaldehyde | 2 | |
| | | 150 | 36 | none | dihydrocarvone | 3 | |
| | | 150 | 36 | none | carvone | 0 | |
| | | 100 | 24 | $Pt^0$ | none | ∼100 | |

[a] Cf. General Comments in the Experimental Section. [b] References 17, 18, and 21. [c] Range of temperature and time explored to have a convenient comparison with the other experiments.

cinnamaldehyde, etc., hydrometalation (M = Ge) becomes difficult and is observed only with radical initiation at high temperature (180−200 °C).[12] Thus, a low radical activity was ascribed to a high polarization of the conjugated system. A more recent study of radical hydrosilylation of unsaturated fatty acid methyl esters[13] showed a "poisoning" of the radical chain reaction by the esters, which could be avoided by a radical initiation sequence (RIS)[13] using a catalytic mixture of AIBN, $PhCO_2O$-*t*-Bu, and *t*-$Bu_2O_2$ and increasing the temperature slowly from 20 °C up to 150 °C. At the same time, studies of the hydrometalation of carvone (M = Si) showed an unexpected and complete deactivation of the exocyclic carbon−carbon double bond.[14−16]

Therefore, in this work our purpose is to contribute to the answers to the following questions.

(1) Why, in radical hydrometalation reactions, are halosilanes or halogermanes more reactive than triorganosilanes or triorganogermanes, which follows the same scale of reactivity found in electrophilic hydrometalations?

(2) Why, in the case of nonconjugated unsaturated carbonyl compounds, is specific radical-induced hydrometalation of the C═C bond usually observed?

(3) Why can a conjugated carbonyl group inhibit the hydrometalation by group 14 hydrides of a nearby but not conjugated C═C function?

With these purposes in mind, we developed a comparative study of the hydrometalation (Si, Ge) of limonene, carveol, dihydrocarvone, and carvone.

## Results and Discussion

**Limonene and Carveol.** Thermally induced hydrometalation of limonene (Ge, Si) or carveol (Ge) is highly favored by radical initiation but is inhibited by well-known inhibitors, such as galvinoxyl.[6,17−20] We observed similar inhibition using various conjugated carbonyl compounds (cf. Table 1). The regioselectivity in these reactions corresponds to an anti-Markovnikov C═C addition[6−8] (Scheme 1). We observed differences in reactivity of the organometallic compounds in accord with the literature.[1−9] Germanes are more reactive than

---

(12) Satgé, J.; Rivière, P. *J. Organomet. Chem.* **1969**, *16*, 71.

(13) Delpech, F.; Asgatay, S.; Castel, A.; Rivière, P.; Rivière-Baudet, M.; Amine-Alami, A.; Manriquez, J. M. *Appl. Organomet. Chem.* **2001**, *15*, 626.

(14) Kogure, T.; Ojima, I. *J. Organomet. Chem.* **1982**, *234*, 249.

(15) Keinan, E.; Greenspoon, N. *J. Am. Chem. Soc.* **1986**, *108*, 7314.

(16) Schmidt, T. *Tetrahedron Lett.* **1994**, *35*, 3513.

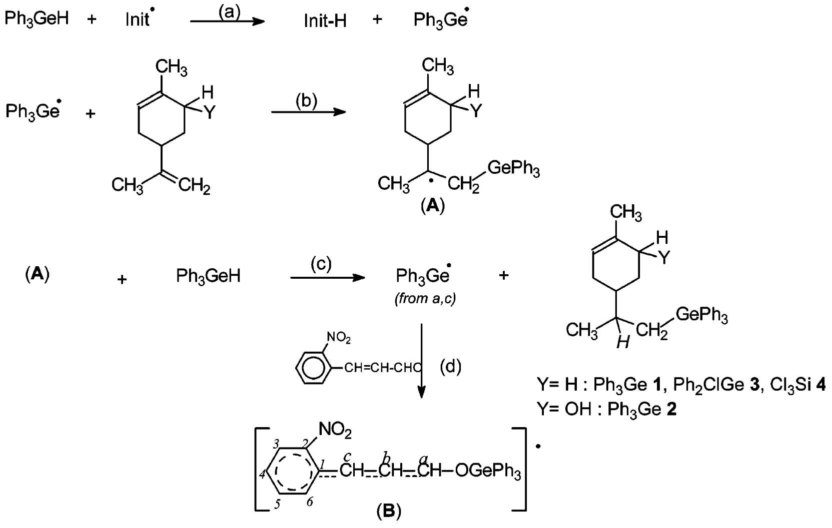
(17) Valade, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1958**, 473.

(18) Skoda-Foldes, R.; Kollar, L.; Heil, B. *J. Organomet. Chem.* **1991**, *408*, 297.

(19) Vorenkov, M. V.; Yarosh, O. G.; Shchukina, L. V.; Alanov, A. I.; Rudakov, G. A. *Zh. Obshch. Khim.* **1996**, *66*, 1941.

(20) Tanaka, R.; Iyoda, J.; Shiihara, I. *Kogyo Kagaku Zasshi* **1968**, *71*, 923 (CODEN, KGKZA7; ISSN, 0368-5462).

**Scheme 1**



the corresponding silanes (cf. $Ph_3GeH/Ph_3SiH$), depending on the M−H bond dissociation energy (BDE) ($E_{Si-H} = 397$ kJ mol$^{-1}$/$E_{Ge-H} = 341$ kJ mol$^{-1}$ for $Me_3MH$).[9,22-27] Within an organometallic series (Si or Ge), halo derivatives $R_nCl_{3-n}$ MH are more reactive than triorganometal hydrides $R_3MH$. However, as ΔBDE apparently is very low in this case (<4 kJ mol$^{-1}$),[23,26] this result may be interpreted in terms of the spin localization characterizing the radical intermediates $M^\bullet$ [8] (and also **A**) (Scheme 1). According to Bent's rule[28] and within the $R_nCl_{3-n}M^\bullet$ series, halogen substituents (compared to organic substituents) induce an increase in the p character contribution of the metal in the metal−halogen bonds and consequently an increase of the s character for the single electron. This was established in $(H_nX)_3Si^\bullet$ (X = H, $CH_3$, Cl) by theoretical studies,[29] which were confirmed by ESR.[8] We obtained similar results within our studied $Ph_nCl_{3-n}Si^\bullet$ series by Hyperchem PM3 computation (Figure 1), confirmed more accurately by theoretical density functional theory (DFT) calculations (Table 2). Within this series, $Cl_3Si^\bullet$ has the highest molecular electronegativity ($\chi_M = 0.1480$) and also the highest molecular hardness ($\eta_M = 0.1178$) (Table 2) and will, therefore, provide the greatest initial electron transfer for reaction and the largest lowering of the activation energy.[30] This results in the highest reactivity, the metal charge being almost the same along the $R_nCl_{3-n}Si^\bullet$ series (Table 2). Then, the electronic structure of the intermediate radical can influence its addition to the substrate (b, Scheme 1), and also the abstraction of hydrogen (c, Scheme 1).[31,32]

**Table 2. DFT Parameters for $Cl_3Si^\bullet$ and $Ph_3Si^\bullet$ [a]**

| | | theor | | exptl | | | | |
|---|---|---|---|---|---|---|---|---|
| | | eV | hartree | eV[b] | hartree[b] | TSD | MC | EC |
| $Cl_3Si^\bullet$ | $I$ | 7.24 | 0.2659 | 7.92 | 0.2910 | 0.736 | 0.728 | %s: 56.94 |
| | $A$ | 0.82 | 0.0302 | 2.50 | 0.0919 | | | %p: 39.75 |
| | $\chi$ | 4.03 | 0.1480 | 5.21 | 0.1911 | | | %d: 3.31 |
| | $\eta$ | 3.21 | 0.1178 | 2.70 | 0.0992 | | | |
| $Ph_3Si^\bullet$ | $I$ | 4.70 | 0.1726 | | | 0.842 | 0.760 | % s: 44.49 |
| | $A$ | 0.73 | 0.0270 | | | | | % p: 53.15 |
| | $\chi$ | 2.72 | 0.0998 | | | | | % d: 2.36 |
| | $\eta$ | 1.98 | 0.0728 | | | | | |

[a] Legend: theor, theoretical; exptl, experimental; TSD, total spin density; MC, metal charge; EC, electronic character; $I = -\epsilon_{HOMO}$; $A = -\epsilon_{LUMO}$. [b] Values taken from ref 30.

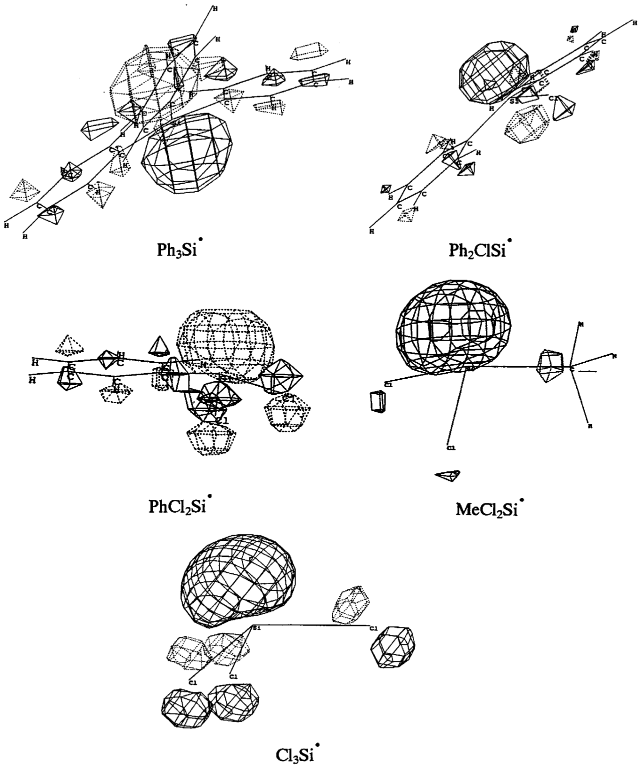


**Figure 1.** Spin localization density in $R_nCl_{3-n}$ $Si^\bullet$ (Hyperchem PM3 calculations).

**Dihydrocarvone.** Dihydrocarvone was almost as reactive as limonene toward hydrogermylation. The reaction led to similar regioselectivity (Scheme 2, Table 3).

---

(21) Dindi, H.; Gregorovich, B.; Hazan, I.; Milligan, S.; U.S. Patent 5 527 936, 1996.

(22) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: London, 1977.

(23) McKean, D. C.; Torto, I.; Morrisson, A. R. *J. Phys. Chem.* **1982**, *86*, 307.

(24) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

(25) Wu, Y.-D.; Wong, C.-L. *J. Org. Chem.* **1995**, *60*, 821.

(26) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746.

(27) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67.

(28) Bent, H. A. *Chem. Rev.* **1961**, *61*, 290.

(29) Guerra, M. *J. Am. Chem. Soc.* **1993**, *115*, 11926.

(30) Pearson, R. G. In *Chemical Hardness*; Wiley-VCH: Weinheim, Germany, 1997.

(31) Drozdova, T. I.; Denisov, E. T. *Kinet. Catal.* **2002**, *43*, 10.

**Scheme 2**

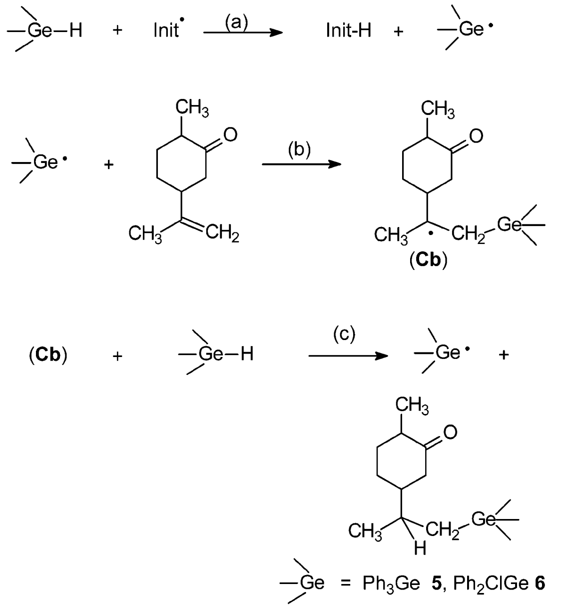
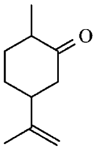


**Table 3. Hydrometalation of Dihydrocarvone According to Experimental Conditions**



| M–H | $T$ (°C) | time (h) | initiator or catalyst | inhibitor | reacn (%) | adduct |
|---|---|---|---|---|---|---|
| $Ph_3GeH$ | 100 | 24 | none | none | 0 | **5** |
| | 120 | 24 | none | none | 12 | |
| | 100 | 24 | AIBN | none | ~100 | |
| | 120 | 24 | none | galvinoxyl | 0 | |
| | 120 | 24 | none | nitrocinnamaldehyde | 0 | |
| $Ph_2ClGeH$ | 100 | 24 | none | none | 8 | **6** |
| | 120 | 48 | none | none | 48 | |
| | 100 | 24 | AIBN | none | ~100 | |
| | 120 | 24 | none | galvinoxyl | 7 | |
| | 120 | 24 | none | nitrocinnamaldehyde | 5 | |
| $Ph_3SiH$ | 150 | 24 | none | none | 0 | **6** |
| | 80–120[a] | 24 | AIBN | none | 0 | |
| | 150 | 24 | RIS | none | 0 | |
| $Cl_3SiH$ | 150 | 36 | none | none | 0 | **7** |
| | 100 | 36 | $Pt^0$ | none | ~100 | |
| $Cl_3SiH$ | 100 | 24 | AIBN | none | 54 | **8** |
| | 150 | 36 | RIS | none | 61 | |

[a] Range of temperature explored.

The regiospecific radical hydrometalation of the exocyclic C=C bond can be explained by the relative accessibility of the HOMO electrons in dihydrocarvone (HOMO, $E_{C=C} = -10.09$ eV > $E_{C=O} = -13.38$ eV) to the metal-centered radical ($E_{Ph_3Ge\bullet}$: HOMO, $-8.66$ eV; LUMO, $-2.27$ eV) and by the relative stabilities of the two possible radical intermediates (**Ca** and **Cb**) which could be implicated in the reaction (Figure 2) (DFT computations).

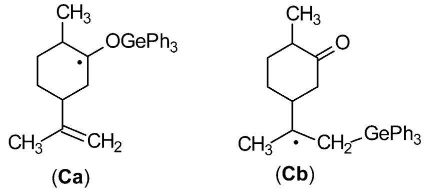
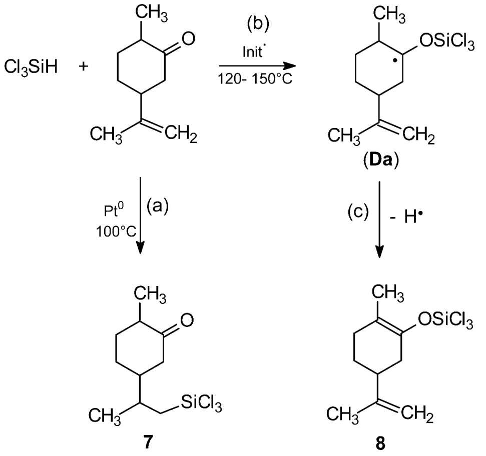


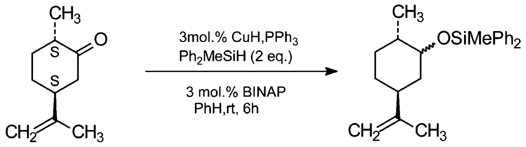
**Figure 2.** Two possible radical intermediates in the addition of $Ph_3GeH$ to dihydrocarvone. $E_{Ca} > E_{Cb}$; $\Delta E = 38.22$ kJ mol$^{-1}$ for the 2*S*,5*R* isomer as an example.

**Scheme 3**



Although $\Delta E$ is not very large, it is larger than the thermodynamic parameters which account for differences between the reactivities of primary, secondary, or tertiary carbon-centered radicals in the propagation step of the radical chain mechanism, whose energies of activation for hydrogen abstraction are about 15 kJ mol$^{-1}$. The differences in stabilization energies of Et/*i*-Pr/*t*-Bu, for example, are in the range 2–7 kJ mol$^{-1}$.[32–34]

In the case of silanes, hydrosilylation of alkenes was more difficult and was achieved only by means of $Pt^0$ catalysis (cf. general comments) for the most reactive $Cl_3SiH$ (leading to **7**) (Scheme 3, path a) (Table 3). In the case of an alkylarylsilane ($Ph_2MeSiH$), silylation of the carbonyl group was obtained selectively using $CuH\cdot PPh_3$ as catalyst (eq 5).[35]



(5)

In the case of $Cl_3SiH$ under radical initiation, we also observed a regioselective silylation of the carbonyl group in accord with the relative stabilities of the two possible radical intermediates **Da** and **Db**, which could be implicated in the reaction (Scheme 3, path b) (Figure 3), the former undergoing a well-known hydrogen elimination (Scheme 3, path c).[36,37]

Thus, in the case of dihydrocarvone one can speak of radical-initiated autoinhibition, since the carbonyl group of the molecule acts as an inhibitor for the hydrosilylation of the exocyclic carbon–carbon double bond in the same molecule. This result is confirmed by the fact that hydrosilylation of limonene, observed under mild ther-

---

(32) Carey, F. A.; Sundberg, R. J. In *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: London, 1990; Chapter 12, p 651.

(33) Huyser, E. S. In *Free Radical Chain Reactions*; Wiley-Interscience: London, 1970; p 91.

(34) Leroy, G.; Peeters, D.; Wilante, C. *THEOCHEM* **1982**, *5*, 217.

(35) Lipshutz, B. H.; Chrisman, W.; Noson, K. *J. Organomet. Chem.* **2001**, *624*, 367.

(36) Brook, A. G. Acylsilane Photochemistry. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; p 984.

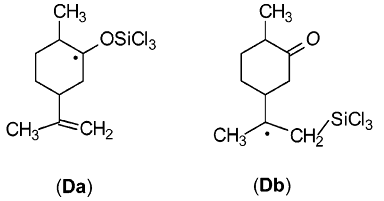
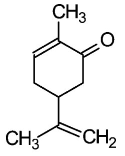


**Figure 3.** Two possible radical intermediates **Da** and **Db** in the radical addition of $Cl_3SiH$ to dihydrocarvone. $E_{\mathbf{Da}} < E_{\mathbf{Db}}$; $\Delta E = 45.33$ kJ mol$^{-1}$ for (2*S*,5*R*)-dihydrocarvone as an example.

**Table 4. Hydrometalation of Carvone**

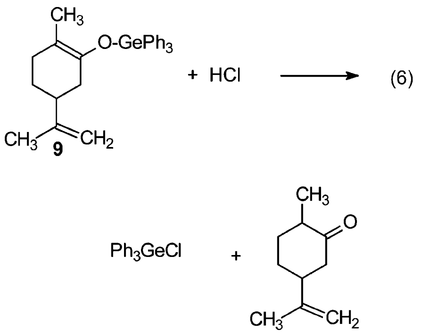


| M−H | *T* (°C) | time (h) | initiator or catalyst | reacn (%) | adduct |
|---|---|---|---|---|---|
| $Ph_3GeH$ | 130 | 24 | none | 0 | **9** |
| | 120 | 24 | AIBN | 26 | |
| | 150 | 36 | RIS | 85 | |
| $Ph_2ClGeH$ | 130 | 24 | none | 17 | **10** |
| | 120 | 36 | AIBN | 55 | |
| | 150 | 36 | RIS | ~100 | |
| $Cl_3SiH$ | 150 | 24 | none | 0 | **8** |
| | 120 | 24 | AIBN | 16 | |
| | 150 | 36 | RIS | 41 | |
| $Cl_3SiH$ | 100 | 24 | $Pt^0$ | ~100 | **12** |

mal conditions, is completely inhibited by catalytic amounts of dihydrocarvone (Table 1).

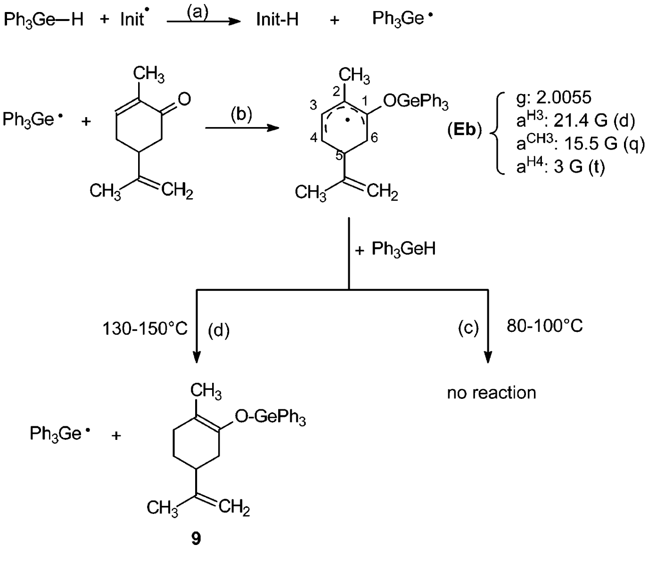
**Hydrometalation of Carvone.** By comparison with hydrocarvone, limonene, and carveol, carvone was less reactive toward hydrometalation. In the case of triphenylgermane, no thermally induced reaction was observed in the range 80−150 °C. Radical initiation (by AIBN, 80−100 °C) was ineffective. Initiation by radicals at 130 °C (using $PhCO_2Ot$-Bu) led to hydrogermylation (**9**, 41%), which was completed only under RIS conditions (see Table 4). The reaction was regiospecific and corresponded to 1,4-addition to the conjugated α,β-unsaturated carbonyl function (Scheme 4).

The 1,4-adduct **9** was isolated, characterized, and chemically identified through the derivatives formed in its acid hydrolysis (eq 6).



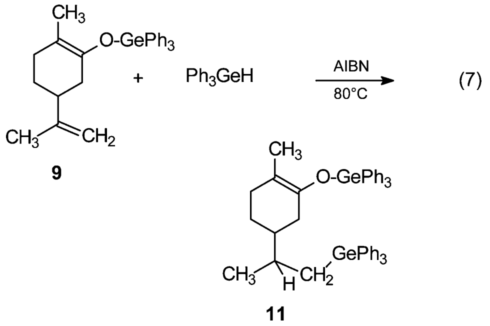
(6)

Scheme 4



This comparative study of hydrometalation of limonene, carveol, hydrocarvone and carvone shows that the reactivity of the conjugated carbonyl function is greater than that of the exocyclic C=$CH_2$ group, which usually is the more reactive. This fact could be the result of an easier trapping of metal-centered radicals by the conjugated carbonyl group. In the case of carvone, the relative scale of HOMO energy levels explains the easier trapping of the metal-centered radical by the conjugated carbonyl group (carvone, HOMO $E_{C=CC=O} = -9.7$ eV $> E_{C=C}$(exo) $= -10.17$ eV; $Ph_3Ge^{\bullet}$, HOMO −8.66 eV, LUMO −2.27 eV, PM3 computations). Therefore, the reaction goes through the most delocalized and stabilized[32] intermediate **Eb** (Figure 4), whose formation was detected by ESR[38] (Scheme 4).

This highly delocalized radical (**Eb**) is too “soft” and requires too high an activation energy to be able to initiate, under mild conditions, an abstraction of hydrogen from M−H bonds[31]—as observed with radical **Cb** in Scheme 2, path c—and, therefore, undergoes a break in the chain process. This can explain why 1,4-addition was observed only under drastic conditions (Scheme 4, path d). This hypothesis is supported by the result of the second hydrogermylation of carvone, which was observed under the same mild experimental conditionsused for the hydrogermylation of limonene or carveol (eq 7).



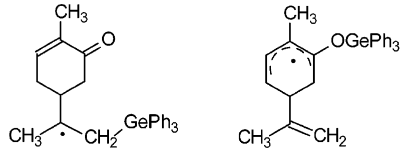
(7)

Thus, in carvone, a radical autoinhibition process occurs, the intramolecular conjugated carbonyl impeding the hydrogermylation of the exocyclic C=C bond. The observed inhibition is similar to the intermolecular

---

(37) Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 352.

(38) Feddouli, A.; El Kadib, A.; Rivière, P.; Delpech, F.; Rivière-Baudet, M.; Castel, A.; Manriquez, J. M.; Chavez, I.; Ait Itto, M. Y.; Ahbala, M. *Appl. Organomet. Chem.* **2004**, *18*, 233.



(**Ea**) (**Eb**)

**Figure 4.** Possible radical intermediates in the reaction of $Ph_3GeH$ with carvone. $E_{\mathbf{Ea}} > E_{\mathbf{Eb}}$; $\Delta E = 10.93$ kJ mol$^{-1}$ calculated for (*R*)-(−)-carvone.

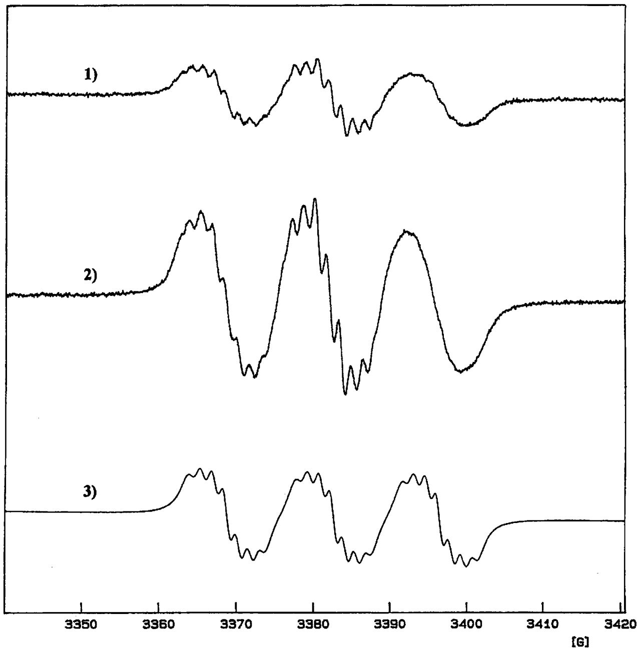
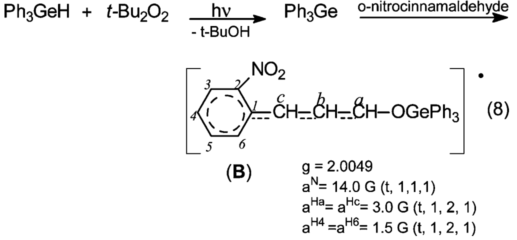


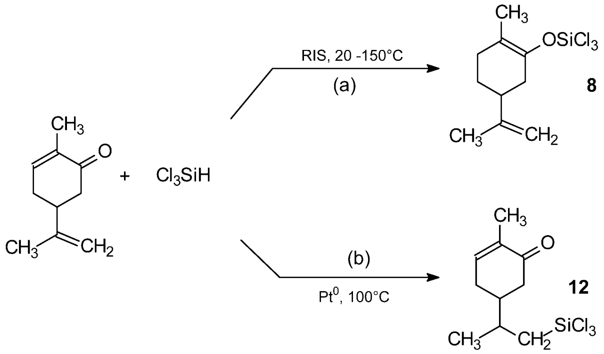
**Figure 5.** ESR study of reactions: (1) $Ph_3GeH$ + limonene (toluene, *hν*) + *o*-$NO_2C_6H_4CH{=}CHCHO$; (2) $Ph_3GeH$ + *t*-$Bu_2O_2$ (toluene, *hν*) + *o*-$NO_2C_6H_4CH{=}CHCHO$; (3) simulation using pure Gaussian functions of 1.6 G width.

radical inhibition reaction in the hydrometalation of limonene, carveol, and hydrocarvone by carbonyl compounds (Table 1). It can be explained by the trapping of the metal-centered radicals having conjugated carbonyl groups undergoing a "poisoning" of the radical chain (Scheme 1, path d). This hypothesis is supported by the fact that α,*β*-unsaturated carbonyl compounds, such as *o*-nitrocinnamaldehyde and carvone, are as good inhibitors as galvinoxyl itself in these hydrometalation reactions (Table 1). They act as a spin trap for group 14 element centered radicals. This was verified by an ESR study of the reaction of $Ph_3GeH$ with limonene, in the presence of *o*-nitrocinnamaldehyde, which showed the formation of radical **B** (Scheme 1, Figure 5). This radical was reproduced independently (eq 8) and analyzed by following data of the corresponding radical anion.[39] The complex pattern of the spectra was very satisfactorily simulated (Figure 5). This radical-induced autoinhibition affects both alkenylic hydrogermylations ($Ph_3GeH$, $PhCl_2GeH$) and hydrosilylations ($Ph_3SiH$, $Cl_3SiH$). Silanes showed a very low activity toward carvone, $Ph_3SiH$ was inactive, and $Cl_3SiH$ gave under radical initiation only a small percentage of 1,4-addition (Scheme 5, path a), while the alkenylic addition was obtained quantitatively on $Pt^0$ (Scheme 5, path b). In this case a change from transition-metal catalysis to radical initiation drastically changes the regioselectivity (Scheme 5).



g = 2.0049
$a^N$= 14.0 G (t, 1,1,1)
$a^{Ha}$= $a^{Hc}$= 3.0 G (t, 1, 2, 1)
$a^{H4}$ =$a^{H6}$= 1.5 G (t, 1, 2, 1)

**Scheme 5**



In conclusion, the answers to the initial questions are as follows.

(1) Halosilanes and halogermanes are the most reactive in radical hydrometalation reactions, because the halogen substituents on the metal enhance the molecular electronegativity and the molecular hardness of the metal-centered radical, favoring the initial electron transfer.

(2) In the case of nonconjugated carbonyl containing olefinic compounds, specific radical hydrometalation of the C=C function (or of the carbonyl) is mainly dependent on the energy parameters characterizing the different possible intermediate radicals.

(3) α,*β*-unsaturated carbonyl functions act as very efficient radical inhibitors for the radical-initiated hydrometalation of C=C bonds. In this last case, metal catalysis (Pt, Pd, etc.) is recommended to obtain the hydrometalation of the carbon−carbon double bond. For the metalation of the carbonyl bond, recourse to RIS is essential.

By a change in the initiation step of the reaction (radical initiation or transition-metal catalysis) it is possible to obtain a dramatic change in the orientation of these hydrometalation reactions and to perform especially difficult hydrometalation of industrial interest.

## Experimental Section

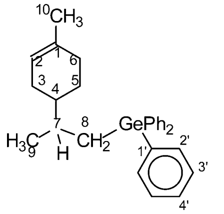
**General Comments.** All reactions were performed under nitrogen using standard Schlenk tube techniques, Carius tubes, and dry solvents. NMR spectra were recorded on Bruker AC 80 ($^1H$, 80 MHz) and AC 200 ($^{13}C$ in the sequence Jmod, 50.3 MHz) spectrometers and with a Bruker 300 MHz instrument ($^{29}Si$). Gas chromatography (GC) was undertaken on a Hewlett-Packard HP 6890 instrument, and mass spectra were recorded with a Hewlett-Packard HP5989 instrument in the electron impact mode (EI, 70 eV) or with a Rybermag R10-10

---

[39] Rivière, P.; Castel, A.; Rivière-Baudet, M. *Main Group Met. Chem.* **1994**, *17*, 679.

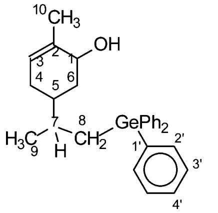
spectrometer operating in the EI mode or by chemical desorption (DCI/CH$_4$). Infrared spectra were recorded on a Perkin-Elmer 1600FT spectrometer. ESR spectra were recorded on a Bruker ER200 instrument with an EIP frequency meter, in toluene solutions at 243 K. Elemental analyses were done by the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. Theoretical calculations were performed at the Hyperchem PM3 level or with the Gaussian 98 package.[40] Density functional theory (DFT) was employed with the three-parameter hybrid exchange functional of Becke[41] and the Lee, Yang, and Parr correlation functional[42] (B3LYP). The basis set was the standard 6-311G included in Gaussian. The geometries were obtained by full-geometry optimization at the B3LYP level and checked by frequency calculations. Graphical pictures were obtained with the MOLEKEL program.[43] Karstedt's catalyst Pt$^0$ (platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, 0.100 M in poly(dimethylsiloxane)), initiators and inhibitors, were used in a 1% concentration relative to organic reagents. All the tests of hydrometalation of limonene, carveol, and carvone with different catalysts or radical initiators (Tables 1, 3, and 4) were performed on similar samples of M−H (1 mmol) and reagent (1.1 mmol). All organic reagents ((*S*)-(−)-limonene, (−)-carveol, (+)-dihydrocarvone, and (*R*)-(−)-carvone) were obtained from Aldrich. The organogermanium compounds were prepared according to the literature procedure.[6] Triphenylsilane was purchased from Aldrich.

**Preparation of 1.**



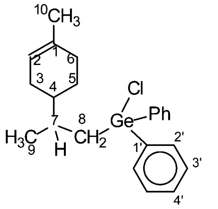
A mixture of (*S*)-(−)-limonene (0.80 g, 5.87 mmol) and Ph$_3$GeH (1.50 g, 4.92 mmol) was heated at 130 °C in a Carius tube under RIS conditions[13] for 24 h. The reaction was almost quantitative ($^1$H NMR analysis). Distillation under reduced pressure gave 1.57 g of **1**. Yield: 72%. Bp: 180 °C/5 × 10$^{-2}$ mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1644 (C═C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.82 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6.5 Hz), 1.55 (m, 6H in 4, 5, 7, 8), 1.62 (broad s, 3H, CH$_3$ on 10), 1.80 (m, 4H, CH$_2$ in 3, 6), 5.35 (m, 1H, CH in 2), 7.40 (m, 15H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 19.33 and 19.61 (C9), 19.69 and 19.87 (C8), 23.87 (C10), 25.35 and 27.07 (C5), 28.04 and 29.24 (C3), 31.30 and 31.06 (C6), 34.22 and 34.53 (C4), 41.03 and 41.55 (C7), 121.25 (C2), 128.45 (C′3), 129.07 and 130.18 (C′4), 134.15 (C1), 135.29 (C′2), 138.10 (C′1). MS (EI): *m/z* (%): [M$^{\bullet+}$] 442 (3%); [M$^{\bullet+}$ − PhH] 364 (33%). Anal. Calcd for C$_{28}$H$_{32}$Ge: C, 76.23; H, 7.31 Found: C, 76.11; H, 7.12.

**Preparation of 2.**



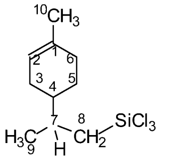
A mixture of (−)-carveol (0.80 g, 5.26 mmol), Ph$_3$GeH (1.50 g, 4.92 mmol), and AIBN was heated at 100 °C in a Carius tube for 24 h. The reaction was almost quantitative (95% by $^1$H NMR analysis). The mixture was then distilled under reduced pressure, giving 1.38 g of **2**. Yield: 46%. Bp: 200 °C/0.1 mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 3602 (OH), 1662 (C═C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.90 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6 Hz), 1.60 (m, 9H in 4, 5, 6, 7, 8, and OH), 1.80 (s, 3H, CH$_3$ on 10), 4.04 (m, 1H, CH in 1), 5.50 (m, 1H, CH in 3), 7.42 (m, 9H, Ph), 7.55 (m, 6H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 18.96 and 19.51 (C9), 19.07, 19.27, 19.31, and 19.82 (C8), 21.02 and 21.05 (C10), 27.59, 28.00, 29.08, and 29.27 (C4), 33.62, 33.95, 34.84, and 34.85 (C5), 37.35, 35.57, and 35.83 (C6), 40.35, 40.83, and 43.09 (C7), 68.84, 68.95, 71.32, and 71.39 (C1), 124.26, 125.68, and 125.73 (C3), 128.28 (C′3), 128.93 (C′4), 134.60 and 134.64 (C′1), 135.06 (C′2), 136.44, 137.30, 137.67 and 137.73 (C2). MS (EI; *m/z* (%)): [M$^{\bullet+}$] 458 (25); [M$^{\bullet+}$ − PhH] 380 (100). Anal. Calcd for C$_{28}$H$_{32}$GeO: C, 73.57; H, 7.06. Found: C, 72.97; H, 6.93

**Preparation of 3.**



A mixture of (*S*)-(−)-limonene (0.48 g, 3.54 mmol), Ph$_2$ClGeH (0.80 g, 3.04 mmol), and AIBN was heated in a Carius tube for 24 h at 100 °C. The reaction was almost quantitative (97% by $^1$H NMR analysis). Distillation under reduced pressure gave 0.92 g of **3**. Yield: 76%. Bp: 164 °C/5 × 10$^{-2}$ mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1646 (C═C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.98 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6.24 Hz), 1.33−1.56 (m, 6H in 4, 5, 7, 8), 1.71 (broad s, 3H, CH$_3$ on 10), 1.82−2.20 (m, 4H, CH$_2$ in 3, 6), 5.43 (m, 1H, CH in 2), 7.49−7.70 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 19.12 (C9), 23.60 (C10), 23.61 and 23.66 (C8), 27.93 and 28.09 (C5), 29.01 (C3), 30.81 and 30.99 (C6), 33.71 and 33.93 (C4), 40.61 and 40.92 (C7), 120.82 (C2), 128.67 (C′3), 130.25 (C′4), 133.55 (C′2), 134.01 (C1), 136.90 (C′1). MS (EI; *m/z* (%)): [M$^{\bullet+}$] 400 (10); [M$^{\bullet+}$ − PhH] 322 (50), [M$^{\bullet+}$ − 2PhH] 322 (8), [Ph$_2$GeCl] (100). Anal. Calcd for C$_{22}$H$_{27}$ClGe: C, 66.14; H, 6.81; Cl, 8.87. Found: C, 66.37; H, 6.72; Cl, 8.74.

**Preparation of 4.**



A mixture of (*S*)-(−)-limonene (1 g, 7.33 mmol), Cl$_3$SiH (1 g, 7.46 mmol), and Pt$^0$ was heated in a Carius tube for 24 h at 100 °C. The reaction was quasi-quantitative ($^1$H NMR analysis). Distillation under reduced pressure gave 1.30 g of **4**. Yield: 65%. Bp: 80 °C/5 × 10$^{-2}$ mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1614(C═C) (conforms to literature[17,19−21]). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 1.06 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6.66 Hz), 1.17−1.37

---

(40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

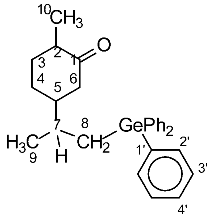
(41) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98,* 1372. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(42) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785.

(43) Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.1*; Swiss Center for Scientific Computing, Manno, Switzerland, 2000−2001.

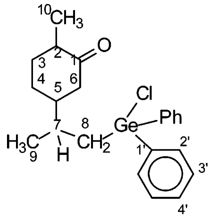
(m, 6H in 4, 5, 7, 8), 1.65 (broad s, 3H, CH$_3$ on 10), 1.92 (m, 4H, CH$_2$ in 3, 6), 5.39 (m, 1H, CH in 2). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 18.44 (C9), 21.68 and 21.81 (C10), 23.08 (C8), 26.66 (C5), 29.27 and 29.56 (C3), 32.57 (C6), 33.57 (C4), 43.75 (C7), 121.39 and 121.70 (C2), 138.06 (C1). $^{29}$Si NMR (CDCl$_3$, ppm): $\delta$ 13.44. MS (EI; *m/z* (%)): [M$^{\bullet+}$] 270 (20); [M$^{\bullet+}$ − Cl] 235 (11); [M$^{\bullet+}$ − SiCl$_3$] 137 (100); [M$^{\bullet+}$ − CH$_3$CHCH$_2$SiCl$_3$] 95 (35).

**Preparation of 5.**



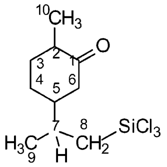
A mixture of (+)-dihydrocarvone (0.70 g, 4.60 mmol) and Ph$_3$GeH (1.22 g, 4 mmol) was heated in the presence of AIBN at 100 °C for 24 h. The reaction was almost quantitative ($^1$H NMR analysis). Distillation led to 1.12 g of pure **5**. Yield: 62%. Bp: 212 °C/0.3 mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1706 (C=O). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.91 (d, 3H, CH$_3$ in 10, $^3J_{\mathrm{CH-CH_3}}$ = 6 Hz), 1.06 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6 Hz), 1.10−2.45 (m, 8H in 3, 4, 5, 7, 8), 2.45−2.60 (m, 3H in 2, 6), 7.52 (m, 15H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 14.57 (C10), 18.92 (C9), 19.36 (C8), 29.19 (C4), 34.49 (C5), 34.95 (C3), 45.02 (C7), 45.68 (C6), 47.68 (C2), 128.37 (C′3), 129.00 (C′4), 134.60 and 137.43 (C′1), 135.02 (C′2), 213.5 (C1). MS (EI; *m/z* (%)): [M$^{\bullet+}$] 458 (15); [M$^{\bullet+}$ −Ph] 381 (30); [M$^{\bullet+}$ − 2Ph] 304 (100); [M$^{\bullet+}$ − 3Ph] 227 (40). Anal. Calcd for C$_{28}$H$_{32}$GeO: C, 73.57; H, 7.06. Found: C, 73.27; H, 7.27.

**Preparation of 6.**



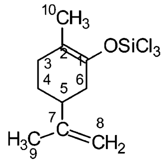
A mixture of (+)-dihydrocarvone (0.60 g, 3.94 mmol) and Ph$_2$ClGeH (0.80 g, 3.04 mmol) was heated in a Carius tube in the presence of AIBN at 100 °C for 24 h. The reaction was almost quantitative ($^1$H NMR analysis). Distillation gave 0.74 g of **6**. Yield: 59%. Bp: 172 °C/6 × 10$^{-2}$ mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1700 (C=O). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.91 (d, 3H, CH$_3$ in 10, $^3J_{\mathrm{CH-CH_3}}$ = 6.6 Hz), 1.00 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6.3 Hz), 1.08−1.92 (m, 8H in 3, 4, 5, 7, 8), 2.03−2.40 (m, 3H in 2, 6), 7.35−7.60 (m, 10H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 14.46 (C10), 18.55 (C9), 24.30 and 24.46 (C8), 29.12 (C4), 33.99 (C5), 34.76 and 34.87 (C3), 44.94 (C2), 45.46 (C6), 46.85 (C7), 128.65 and 128.74 (C′3), 130.39 (C′4), 133.43 and 133.46 (C′2), 136.35 (C′1), 212.98 (C1). MS (EI; *m/z* (%)): [M$^{\bullet+}$] 416 (10); [M$^{\bullet+}$ − Ph] 339 (15); [M$^{\bullet+}$ − 2Ph] 262 (100%); [M$^{\bullet+}$ − 2Ph − Cl] 227 (12); [M$^{\bullet+}$ − Ph$_2$GeCl] 153 (20). Anal. Calcd for C$_{22}$H$_{27}$ClGeO: C, 63.60; H, 6.55; Cl, 8.53. Found: C, 63.28; H, 6.37; Cl, 8.15.

**Preparation of 7.**



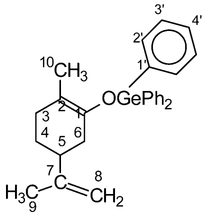
A mixture of (+)-dihydrocarvone (1.52 g, 10 mmol) and Cl$_3$SiH (1.35 g, 10 mmol) was heated in the presence of Pt$^0$ in a Carius tube at 100 °C for 36 h. The reaction was almost quantitative ($^1$H NMR analysis). Distillation led to 1.74 g of **7**. Yield: 61%. Bp: 114 °C/0.1 mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1707 (C=O). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 0.98 (d, 3H, CH$_3$ in 10, $^3J_{\mathrm{CH-CH_3}}$ = 6.4 Hz), 1.06 (d, 3H, CH$_3$ in 9, $^3J_{\mathrm{CH-CH_3}}$ = 6.4 Hz), 1.15−1.94 (m, 8H in 3, 4, 5, 7, 8), 1.96−2.36 (m, 3H in 2, 6). $_{13}$C NMR (CDCl$_3$, ppm): $\delta$ 14.35 (C10), 18.46 (C9), 27.39 (C8), 28.80 (C4), 33.33 (C5), 34.50 (C3), 43.60 (C6), 45.01 (C2), 46.43 and 46.69 (C7), 212.28 (C1). $^{29}$Si NMR (CDCl$_3$, ppm): $\delta$ 12.58. MS (EI; *m/z* (%)): [M$^{\bullet+}$] 286 (10); [M$^{\bullet+}$ − CH$_3$CHCH$_2$SiCl$_3$] 111 (100); [CH$_3$CHCH$_2$SiCl$_3$] 175 (12). Anal. Calcd for C$_{10}$H$_{17}$Cl$_3$SiO: C, 41.75; H, 5.96; Cl, 36.97. Found: C, 41.57; H, 6.17; Cl, 36.42.

**Preparation of 8.**



A mixture of (+)-dihydrocarvone (1.53 g, 10 mmol) and Cl$_3$SiH (1.08 g, 8 mmol) was heated in the presence of AIBN in a Carius tube at 100 °C for 24 h. The mixture was then distilled under reduced pressure, leading to 1.53 g of **8**. Yield: 54%. Bp: 120 °C/0.1 mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1630, 1659 (C=C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 1.62 (b s, 3H, CH$_3$ in 9), 1.72 (broad s, 3H, CH$_3$ in 10), 1.55−2.22 (m, 7H in 3, 4, 5, 6), 4.72 (m, 2H in 8). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 16.24 (C10), 20.80 (C9), 27.46 (C4), 30.60 (C3), 34.31 (C6), 42.14 (C5), 109.25 (C8), 115.92 (C2), 140.95 (C7), 148.26 (C1). MS (CI CH$_4$; *m/z* (%)): [M + 1] 285 (100); [M + 29] 313; [M + 41] 325. Anal. Calcd for C$_{10}$H$_{15}$Cl$_3$SiO: C, 42.04; H, 5.29; Cl, 37.23. Found: C, 42.37; H, 5.12; Cl, 36.95.

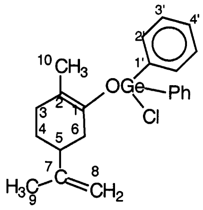
**Preparation of 9.**



A mixture of (*R*)-(−)-carvone (0.80 g, 5.33 mmol) and Ph$_3$GeH (1.50 g, 4.92 mmol) was heated in a Carius tube under RIS conditions for 36 h. $^1$H NMR analysis showed 85% of **9**. The mixture was then distilled under reduced pressure, giving 1.64 g of pure **9**. Yield: 69%. Bp: 175 °C/2 × 10$^{-2}$ mmHg (in conformity with ref 38). IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1645, 1654 (C=C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 1.30−2.50 (m, 7H, in 3, 4, 5, 6), 1.62 (broad s, 6H, CH$_3$ in 9 and 10), 4.62 (m, 2H, CH$_2$ in 8), 7.53 (m, 15H, Ph). $^{13}$C NMR (CDCl$_3$, ppm): $\delta$ 16.55 (C10), 20.70 (C9), 27.94 (C4), 30.50 (C3), 36.71 (C6), 42.55 (C5), 108.49 (C8), 112.05 (C2), 128.45 (C′3), 129.07 (C′4), 134.66 (C′2), 135.01 (C7), 145.66 (C′1), 149.58 (C1). MS (EI; *m/z* (%)): [M$^{\bullet+}$] 456 (25); [M$^{\bullet+}$ − Ph] 379 (35); [M$^{\bullet+}$ −2Ph] 302 (100); [M$^{\bullet+}$ − 3Ph] 225 (75). Anal. Calcd for C$_{28}$H$_{30}$GeO: C, 73.89; H, 6.64. Found: C, 74.32; H, 6.71.

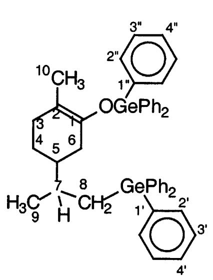
A sample of **9** (0.12 g, 0.26 mmol) in THF solution was treated with an excess of 6 M HCl and analyzed by GC. The formation of Ph$_3$GeCl and dihydrocarvone was almost quantitative.

**Preparation of 10.**
A mixture of (*R*)-(−)carvone (0.51 g, 3.40 mmol) and Ph$_2$ClGeH (0.86 g, 3.26 mmol) was heated in a Carius tube under RIS conditions for 36 h. The reaction was almost quantitative ($^1$H NMR analysis). Distillation under reduced pressure gave 0.94 g of **10.** Yield: 70%. Bp: 163 °C/5 × 10$^{-2}$ mmHg. IR (CDCl$_3$, cm$^{-1}$): $\nu$ 1670 (broad) (C=C). $^1$H NMR (CDCl$_3$, ppm): $\delta$ 1.36



(broad s, 6H, $CH_3$ in 9 and 10), 1.50−2.70 (m, 7H, in 3, 4, 5, 6), 4.75 (m, 2H, $CH_2$ in 8), 7.50 (m, 10H, Ph). $^{13}C$ NMR ($CDCl_3$, ppm): $\delta$ 19.82 (C10), 23.20 (C9), 26.91 (C6), 28.70 (C4), 34.01 (C3), 42.54 (C5), 109.83 (C8), 112.00 (C2), 128.24 (C′3), 128.59 (C′4), 133.23 (C′2), 135.39 (C7), 144.64 (C1), 146.71 (C′1). MS (EI; *m/z* (%)): [$M^{\bullet+}$] 414 (10); [$M^{\bullet+}$ − Cl] 379 (16); [$M^{\bullet+}$ − $Ph_2ClGe$] 151 (46); [$Ph_2ClGe$] 263 (100). Anal. Calcd for $C_{22}H_{25}ClGeO$: C, 63.91; H, 6.09; Cl, 8.57. Found: C, 63.48; H, 5.87; Cl, 8.73.

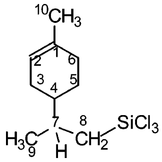
**Preparation of 11.**



**(a) From Carvone and $Ph_3GeH$.** A mixture of (*R*)-(−)-carvone (0.30 g, 2 mmol) and $Ph_3GeH$ (1.20 g, 3.94 mmol) was heated in a Carius tube under RIS conditions for 48 h. The reaction mixture was distilled, leading to 0.91 g of **11**. Yield: 66%. Bp: 255 °C/0.3 mmHg. IR ($CDCl_3$, $cm^{-1}$): $\nu$ 1653 (C=C). $^1H$ NMR ($CDCl_3$, ppm): $\delta$ 0.58−2.21 (m, 10H, $CH_2$ in 3, 4, 6, 8 and CH in 5, 7), 1.07 (d, 3H, $CH_3$ in 9, $^3J_{CH-CH_3} = 6$ Hz), 1.55 (s, 3H, $CH_3$ in 10), 7.50 (m, 30H, Ph). $^{13}C$ NMR ($CDCl_3$, ppm): $\delta$ 16.35 (C10), 18.70 and 19.01 (C9), 19.01 and 19.35 (C8), 27.52 and 29.21 (C4), 30.57 and 30.74 (C3), 32.80 and 34.50 (C5), 36.71 and 35.06 (C6), 43.07 and 45.05 (C7), 111.97 and 112.18 (C2), 128.87 and 129.09 (C′3), 129.71 and 130.18 (C′4), 134.68 and 135.25 (C′2), 137.40 and 137.90 (C′1), 145.96 and 146.07 (C1). MS (EI; *m/z* (%)): [$M^{\bullet+}$] 760 (22); [$M^{\bullet+}$ − Ph] 683 (10); [$M^{\bullet+}$ − 2Ph] 606 (15); [$M^{\bullet+}$ − $Ph_3Ge$] 457 (100). Anal. Calcd for $C_{46}H_{46}Ge_2O$: C, 72.68; H, 6.10. Found: C, 72.42; H, 6.06.

**(b) From 9 and $Ph_3GeH$.** A mixture of **9** (0.23 g, 0.50 mmol) and $Ph_3GeH$ (0.15 g, 0.49 mmol) was heated in a Carius tube for 24 h at 80 °C in the presence of AIBN. NMR analysis showed quantitative formation of **11**.[38]

**Preparation of 12.**



A mixture of (*R*)-(−)-carvone (1.50 g, 10 mmol) and $Cl_3SiH$ (1.35 g, 10 mmol) was heated in a Carius tube in the presence of $Pt^0$ at 100 °C for 36 h. The reaction was quantitative ($^1H$ NMR analysis). Distillation under reduced pressure led to 2.30 g of **12.** Yield: 81%. Bp: 118 °C/0.2 mmHg. IR ($CDCl_3$, $cm^{-1}$): $\nu$ 1711 (C=O), 1660 (C=C). $^1H$ NMR ($CDCl_3$, ppm): $\delta$ 1.05 (d, 3H, $CH_3$ in 9, $^3J_{CH-CH_3} = 6.5$ Hz), 1.20−1.34 (m, 1H) and 1.46−1.55 (m, 1H) (2H in 5,7), 1.57 (s, 3H, $CH_3$ in 10), 1.72−2.48 (m, 6H, $CH_2$ in 4, 6, 8), 6.69 (m, 1H, H in 3). $^{13}C$ NMR ($CDCl_3$, ppm): $\delta$ 15.66 (C10), 18.23 (C9), 28.46 and 29.61 (C8), 32.54 (C5), 40.50 (C4), 41.66 (C6), 44.06 (C7), 135.47 (C2), 144.51 (C3), 199.47 (C1);. $^{29}Si$ NMR ($CDCl_3$, ppm): $\delta$ 12.37. MS (EI; *m/z* (%)): [$M^{\bullet+}$] 284 (20); [$M^{\bullet+}$ − 3Cl] 179 (11); [$M^{\bullet+}$ − $CH_3CHCH_2SiCl_3$] 109 (100). Anal. Calcd for $C_{10}H_{15}Cl_3SiO$: C, 42.04; H, 5.29. Found: C, 41.83; H, 5.12.

The same reaction conducted with AIBN in a Carius tube for 24 h at 120 °C yielded only 16% of **8,** while the reaction under RIS conditions (for 36 h) gave 41% of **8** (Table 4).

**Acknowledgment.** We thank the “Conseil Régional Midi Pyrénées” (AF grant), the Université Paul Sabatier, Action Intégrée France-Maroc (Grant No. 216/SM/00), and the program ECOS CONICYT C01E06 and C04E05 for partial financial support.

OM049525G