Activation of the Ge–H bond of Et₃GeH in photochemical reaction with molybdenum(0) carbonyl complexes and hydrogermylation of norbornadiene

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ABSTRACT

The germane intermediate σ-complexes, characterized by high-field resonances in the region from −6 to −8 ppm, have been detected during the ^{1}H NMR spectroscopy monitoring of the photochemical reaction of Et$_3$GeH with Mo(CO)$_6$, [Mo(CO)$_4$(η^4-cod)], and [Mo(CO)$_4$(η^4-nbd)] in the NMR tube. The activation of the Ge–H bond of germane in photochemical reaction of the norbornadiene (nbd) complex [Mo(CO)$_4$(η^4-nbd)] has been applied in the hydrogermylation of norbornadiene, which leads to the formation of triethylgermylnorbornene.

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1. Introduction

Interest in the process of activation of the germanium–hydrogen bond of germanes by transition metals has been growing over the last two decades due to its significance for the basic science concerning the activation of σ-bonds (H–H, H–C, H–Si, and H–Ge) [1–7] and also because of its relevance to the catalytic process known as hydrogermylation [8–13]. The electron-rich Group 6 metal carbonyl complexes are particularly interesting because of their potential to react with a variety of σ-bonds to give σ-complexes and/or oxidative addition products [1–7,14]. For example, the coordinatively unsaturated 16e complex [Mo(CO)(diphosphine)$_2$] coordinates the H–H, H–Si, and H–Ge bonds in η^2-fashion [6], while [MoH$_4$(diphosphine)$_2$] activates the H–Si, H–Ge, and H–C bonds by oxidative addition [7]. Our previous studies have demonstrated that photochemically activated molybdenum and tungsten carbonyl complexes react via oxidative addition at the Sn–Cl and Ge–Cl σ-bonds to yield seven-coordinate heterobimetallic complexes [14]. In recent years, the focus of our research has involved the activation of H–Si bonds by W(0) and Mo(0) centers [3–5,15–17]. Recently, the activation of the H–Si bond by a photochemically generated coordinatively unsaturated molybdenum(0) complex has been applied in the hydrosilylation of norbornadiene (nbd) [16]. In comparison to H–Si bonds, the reactivity of H–Ge bonds towards W(0) and Mo(0) complexes is less well studied [6,7]. The activation of the H–Ge bond of germanes by platinum and palladium complexes is better investigated [18–20]. In this paper, we present studies of the activation of the H–Ge bond of triethylgermane using photochemically generated coordinatively unsaturated molybdenum(0) carbonyl complexes. We also report hydrogermylation reaction of norbornadiene by the tertiary germane Et$_3$GeH in the presence of photochemically activated molybdenum(0) carbonyls.

2. Results and discussion

2.1. Photochemical reaction of Mo(CO)$_6$ with Et$_3$GeH. Identification of the complex [Mo(CO)$_5$(η^2-HGeEt$_3$)] (1)

When the photochemical reaction of Mo(CO)$_6$ with Et$_3$GeH in methylcyclohexane-d_{14} was monitored by ^{1}H NMR spectroscopy at 253 K, the formation of a Mo–H bond was observed due to the appearance of a high-field resonance at δ −7.95 (Fig. S1 in Appendix A). The latter signal is observed as a septet with the proton–proton coupling constant substantially smaller ($^3J_{H–H(Et)}$ = 1.4 Hz) than that detected in the free triethylgermane spectrum ($^3J_{H–H(Et)}$ = 2.8 Hz). These NMR data support the existence of a three-centre, two-electron Mo–H···Ge bond characteristic of σ-bond complexes (Scheme 1) [1]. Similar complexes have recently been identified in reactions of Group 6 metal hexacarbonyls and triethylsilane [4,5]. In the latter complexes the value of $^3J_{H–H(Et)}$ = 3.2 Hz for free silane was reduced to ca. 1.9 Hz for chromium and molybdenum complexes and ca. 1.5 Hz for a tungsten complex.

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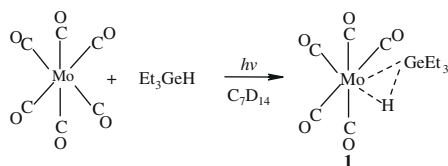
Scheme 1. Formation of the germane complex [Mo(CO)$_5$(η^2-H–GeEt$_3$)] (**1**).

2.2. Photochemical reaction of [Mo(CO)$_4$(η^4-cod)] with Et$_3$GeH. Identification of the complex [Mo(CO)$_3$(η^4-cod)(η^2-H–GeEt$_3$)] (2)

When the photochemical reaction of the cyclooctadiene (cod) complex with Et$_3$GeH in methylcyclohexane-d_{14} was monitored by ^{1}H NMR spectroscopy at 253 K, the formation of a Mo–H bond was observed due to the appearance and growth in intensity of a high-field resonance at δ −6.46. This reaction is accompanied by the decay of signals at δ 4.44, 2.50, and 2.20 ppm due to the η^4-cod ligand in [Mo(CO)$_4$(η^4-cod)] and the appearance of six well-separated groups of signals of the η^4-cod ligand in the new molybdenum hydride complex (**2**) at δ 4.66, 3.59, 2.56, 2.38, 2.31, and 2.06 ppm (all of equal intensity), integrated for 12 protons versus the hydride signal. The absorption at δ 4.66 is due to two protons attached to one of the two double bonds, while the peak at δ 3.59 is due to two protons attached to the other double bond of the η^4-cod ligand. The resonance of olefin protons is at a higher and a lower-field than that of the η^4-cod ligand in the starting molybdenum(0) complex by 0.85 and 0.22 ppm, respectively. This indicates asymmetrical, stronger and weaker interactions of the olefin bonds with the molybdenum atom in the new complex **2**, than in the starting one. Similar conclusions can be drawn from the ^{13}C NMR spectra of **2**, which show two olefin carbon signals of the η^4-cod ligand at 95.3 and 74.6 ppm, which in the 2D ^{13}C–^{1}H HMQC spectra correlate with olefin proton signals at δ 4.66 and 3.59 ppm, respectively. The lower-field olefin carbon signal of **2** could be assigned to the carbons of the C=C unit trans to the CO ligand, a better π-acceptor than the olefin, and the signal at higher field to the carbons of the double bond trans to a ligand with a weaker π-accepting ability than the CO ligand, i.e. a H–Ge bond of the germane ligand. This results in the stabilization of the η^2-H–Ge interaction and prevents oxidative addition, because the C=C olefin bond is a better π-acceptor than the H–Ge σ-bond of the germane ligand. The ^{13}C NMR spectra of **2** showed two carbonyl resonances, at δ 222.3 and 221.1 ppm, in an intensity ratio of 1:2. The resonance at δ 221.1 can be assigned to the two carbonyls that are mutually trans. This resonance is slightly high-field shifted compared with the signal of the CO group that is approximately trans to the olefin unit of the η^4-cod ligand. However, both of the carbon signals of the CO ligands of **2** are lower-field shifted compared with the signals of the CO groups of the starting molybdenum(0) compound, observed at δ 217.9 and 216.1 ppm, in an intensity ratio of 1:1. On the basis of the NMR data, a molecular structure has been proposed for compound **2** (Scheme 2). It must be noted that compound **2** is very unstable and decays within a few days, even at a low temperature.
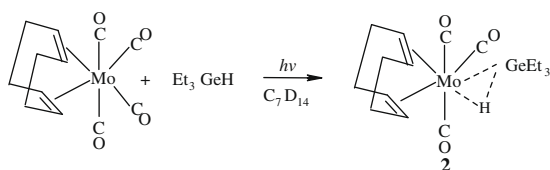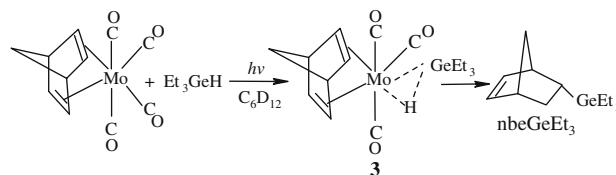
2.3. Photochemical reaction of [Mo(CO)$_4$(η^4-nbd)] with Et$_3$GeH

When the photochemical reaction of the norbornadiene (nbd) complex [Mo(CO)$_4$(η^4-nbd)] with Et$_3$GeH in cyclohexane-d_{12} at 283 K or methylcyclohexane-d_{14} at 253 K was monitored by ^{1}H NMR spectroscopy, the formation of a Mo–H bond was observed due to the appearance of a high-field resonance at δ −7.25. This reaction is accompanied by the decay of signals at δ 4.73, 3.70 and 1.29 ppm due to the η^4-nbd ligand in [Mo(CO)$_4$(η^4-nbd)] and the appearance of signals due to the η^4-nbd ligand in the new molybdenum hydride complex (**3**) at δ 4.91 and 4.55 ppm in an intensity ratio of 1:1, integrated for four protons versus the hydride signal (other signals of the nbd moiety are not detected). However, compound **3** is very unstable and decays within a few minutes. The proton signals which appear and increase in intensity were assigned to the hydrogermylation product of norbornadiene, triethylgermylnorbornene (nbeGeEt$_3$) (Scheme 3). The compound nbeGeEt$_3$ was detected by ^{1}H NMR due to the characteristic olefinic proton signals at ca. 6 ppm and the methine proton signals at ca. 3 ppm in an intensity ratio of 1:1 (Fig. S2 in Appendix A). However, the hydrogenation of the olefin bond of nbeGeEt$_3$ gives triethylgermylnorbornane (nbaGeEt$_3$). The latter compound was detected by ^{1}H NMR due to the characteristic two methine (HC^{1,4}) and one of the two methylene (H$_2$C^3) proton signals at δ 2.37, 2.27, and 1.87, all three of equal intensity. The very low yield of nbaGeEt$_3$ at the beginning of the reaction increased with longer time of photolysis, particularly in the presence of an excess of Et$_3$GeH. It was not surprising to detect by ^{1}H NMR spectroscopy (δ 5.00, 4.96, 3.00, and 2.89 ppm, other signals obscured) a new molybdenum compound containing the η^2-nbeGeEt$_3$ ligand. The ^{1}H NMR data of the latter compound are very similar to those of the previously identified norbornene (nbe) complex [Mo(CO)$_5$-(η^2-nbe)] and its silane analog [Mo(CO)$_5$(η^2-nbeSiEt$_3$)] [16].

2.4. Hydrogermylation of norbornadiene by Et$_3$GeH

The hydrogermylation of nbd by Et$_3$GeH in the presence of a small amount (ca. 2 mol%) of the photochemically activated molybdenum carbonyl complex [Mo(CO)$_4$(η^4-nbd)] or Mo(CO)$_6$ gave triethylgermylnorbornene (nbeGeEt$_3$), which was identified by NMR spectroscopy and GC–MS as a 76:24 mixture of two isomers (Scheme 3). The *endo*-stereoselectivity of nbeGeEt$_3$ formation was identified by NMR methods (^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HMQC). The ^{13}C{^{1}H} NMR spectrum of the major isomer of nbeGeEt$_3$ shows seven carbon signals due to the norbornyl moiety at δ 135.5, 134.3, 50.7, 45.0, 41.9, 27.5, and 22.9 ppm. Analysis of the two-dimensional ^{1}H–^{13}C HMQC NMR spectrum reveals a correlation between the singlet proton resonances at δ 2.96 and 2.84 and the ^{13}C resonances at δ 45.0 and 41.9 ppm, respectively. These resonances can thus be assigned to two bridgehead carbons (HC^{1,4}). The correlation between the resonance at δ 50.7 and the proton signals at δ 1.39 and 1.10 ppm indicates a bridge carbon (H$_2$C^7) resonance. The methylene carbon (H$_2$C^6) resonance was detected at δ 27.5 due to correlation with two proton signals at δ 1.87 and 1.00 ppm, whose chemical shifts and magnitudes of splitting indicated *exo* and *endo* proton positions, respectively [21–24]. A corre-

Scheme 2. Formation of the germane complex [Mo(CO)$_3$(η^4-cod)(η^2-H–GeEt$_3$)] (**2**).

Scheme 3. Transformation of the norbornadiene complex [Mo(CO)$_4$(η^4-nbd)] in photochemical reaction with Et$_3$GeH.

lation can also be seen between the ^{13}C resonance at δ 22.9 (GeHC^5) and the proton resonance at δ ca. 1.38. Analysis of the two-dimensional ^{1}H–^{1}H COSY NMR spectrum reveals a correlation between resonances at δ 1.87, 1.00, and ca. 1.38 ppm. The multiplicity of proton signals at δ 1.87 (ddd, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 9.6, $^4J_{H-H}$ = 3.7 Hz) and the relatively large value of proton–proton coupling constants suggested the *endo* position of the germyl substituent and the *exo* position of the proton at the adjacent carbon atom (HC^{5}Ge). A similar analysis of the NMR data of the minor isomer revealed that a bridge carbon (H$_2$C^7) resonance (δ 47.1) is at higher field than for the major isomer (δ 50.7), which is in agreement with the description of the minor isomer as *exo*-nbeGeEt$_3$ and the major isomer as *endo*-nbeGeEt$_3$. This is a very similar result to that obtained in reaction of photochemically activated molybdenum carbonyl complexes with triethylsilane; however, the hydrosilylation reaction is more stereoselective, giving 99% of the *endo* isomer of triethylsilylnorbornene [16]. A similar high *endo*-stereoselectivity of hydrosilylation and hydrogermylation reaction of norbornadiene was detected in reaction catalyzed by chloroplatinic acid [25].

2.5. Summary and conclusions

We have shown that photolysis of Mo(CO)$_6$, [Mo(CO)$_4$(η^4-cod)], or [Mo(CO)$_4$(η^4-nbd)] in alkane solution creates a species which can interact with the Ge–H bonds of Et$_3$GeH in η^2-fashion. The η^2-germane complexes [Mo(CO)$_5$(η^2-H–GeEt$_3$)] (**1**), [Mo(CO)$_3$-(η^4-cod)(η^2-H–GeEt$_3$)] (**2**), and [Mo(CO)$_3$(η^4-nbd)(η^2-H–GeEt$_3$)] (**3**) have been detected by NMR spectroscopy in the photochemical reaction of Et$_3$GeH with Mo(CO)$_6$, [Mo(CO)$_4$(η^4-cod)], and [Mo(CO)$_4$(η^4-nbd)]. The η^4-nbd ligand of the [Mo(CO)$_4$(η^4-nbd)] complex in photochemical reaction with Et$_3$GeH transforms to triethylgermylnorbornene. The activation of the Ge–H bond of germane by a molybdenum complex [Mo(CO)$_4$(η^4-nbd)] has been applied in the hydrogermylation of norbornadiene.

3. Experimental

3.1. General considerations

The synthesis and all operations were conducted using standard Schlenk techniques under an atmosphere of nitrogen. Solvents and liquid reagents were dried with CaH$_2$ and vacuum transferred into small storage flasks prior to use. IR spectra were measured with a Nicolet-400 FT-IR instrument in solution, as Nujol mulls or KBr pellets. Analyses of the reaction products were performed on a Hewlett-Packard GC–MS system. ^{1}H NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. ^{13}C and two-dimensional ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC NMR spectra were recorded with a Bruker AMX 500 MHz instrument at 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C. All proton and carbon chemical shifts were referenced to the residual proton signal for ^{1}H NMR (δ 7.24 CDCl$_3$, and 1.40 C$_6$D$_{12}$). ^{1}H chemical shifts measured in methylcyclohexane-d_{14} as the solvent were referenced relative to SiMe$_4$ used as an internal standard. The photolysis source was an HBO 200 W high-pressure Hg lamp. Mo(CO)$_6$ and Et$_3$GeH (Aldrich) were used as received. The cyclooctadiene (cod) and norbornadiene (nbd) compounds, [Mo(CO)$_4$(η^4-cod)] [26] and [Mo(CO)$_4$(η^4-nbd)] [27–29], were obtained from a reaction of [Mo(CO)$_4$(NCMe)$_2$] and diene in *n*-heptane solution and purified by sublimation.

3.2. NMR tube reactions

3.2.1. Identification of complex [Mo(CO)$_5$(η^2-HGeEt$_3$)] (**1**)

A solution of Mo(CO)$_6$ (0.01 g, 0.04 mmol) and one drop of Et$_3$GeH in methylcyclohexane-d_{14} (0.7 cm^3) at 263 K was periodically

irradiated and then analyzed by ^{1}H NMR spectroscopy over a period of two hours. ^{1}H NMR spectra (300 MHz, methylcyclohexane-d_{14}, 253 K) revealed a signal at δ −7.95 (septet, $^3J_{H-H}$ = 1.4 Hz) which decays in the dark.

3.2.2. Identification of complex [Mo(CO)$_3$(η^4-cod)(η^2-H–GeEt$_3$)] (**2**)

A solution of [Mo(CO)$_4$(η^4-cod)] (0.01 g, 0.03 mmol) and one drop of Et$_3$GeH in methylcyclohexane-d_{14} (0.7 cm^3) at 253 K was periodically irradiated and then analyzed by ^{1}H NMR spectroscopy over a period of 2 h. ^{1}H NMR spectra revealed the decay of signals at δ 4.44, 2.50, and 2.20 ppm due to the η^4-cod ligand of complex [Mo(CO)$_4$(η^4-cod)] and the appearance of six signals of the η^4-cod ligand and a hydride signal at δ −6.46. The sample was next analyzed by ^{13}C and 2D ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HMQC NMR spectroscopic methods, making it possible to identify a new complex **2**. It must be noted that compound **2** is very unstable and decays within a few days, even at a low temperature. **2**: ^{1}H NMR (δ, 300 MHz, methylcyclohexane-d_{14}, 253 K): 4.66 (2H, CH), 3.59 (2H, CH), 2.56 (2H, CH$_2$), 2.38 (2H, CH$_2$), 2.31 (2H, CH$_2$), 2.06 (2H, CH$_2$), −6.46 (s, 1H, Mo-H). ^{13}C{^{1}H} NMR (δ, 125.76 MHz, methylcyclohexane-d_{14}, 253 K): 222.3 (1CO), 221.1 (2CO), 95.3 (2C, CH), 74.6 (2C, CH), 32.8 (2C, CH$_2$), 31.1 (2C, CH$_2$).

3.2.3. Photochemical reaction of [Mo(CO)$_4$(η^4-nbd)] and Et$_3$GeH in cyclohexane-d_{12}

A solution of [Mo(CO)$_4$(η^4-nbd)] (0.01 g, 0.03 mmol) and one drop (ca. 0.03 mL) of Et$_3$GeH in cyclohexane-d_{12} (0.7 cm^3) at 263 K was periodically irradiated and then analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR spectra revealed the decay of signals at δ 4.73, 3.70 and 1.29 ppm due to the η^4-nbd ligand in complex [Mo(CO)$_4$(η^4-nbd)] and the appearance of a hydride signal at δ −7.25 and new signals of the η^4-nbd ligand at δ 4.91 and 4.55 ppm due to complex **3**. Signals at δ 4.91 and 4.55 ppm are in an intensity ratio of 1:1, integrated for four protons versus the hydride signal. Other signals of new η^4-nbd ligand are not detected; they are overlapped by signals of triethylgermylnorbornene (nbeGeEt$_3$), which was fully characterized in a separate experiment (see below). The coordination of nbeGeEt$_3$ to the molybdenum atom is indicated by signals at δ = 5.00 (m, 1H, CH), 4.96 (m, 1H, CH), 3.00 (s, 1H), and 2.89 (s, 1H). The hydrogenation of nbeGeEt$_3$ leads to the formation of triethylgermylnorbornane (nbaGeEt$_3$), which was identified by NMR methods.

nbaGeEt$_3$: ^{1}H NMR (δ, C$_6$D$_{12}$, 500.13 MHz, 283 K): 2.37 (s, 1H, HC^1), 2.27 (s, 1H, HC^4), 1.87 (ddd, $^2J_{H-H}$ = 12.0 Hz, $^3J_{H-H}$ = 12.0 Hz, $^4J_{H-H}$ = 4.0 Hz, 1H, H$_2$C^3), 1.56 (ddd, $^2J_{H-H}$ = 12.1 Hz, $^3J_{H-H}$ = 9.8 Hz, $^4J_{H-H}$ = 2.3 Hz, 1H, H$_2$C^6), 1.51 (ddd, $^2J_{H-H}$ = 12.3 Hz, $^3J_{H-H}$ = 9.8 Hz, $^4J_{H-H}$ = 2.3 Hz,1H, H$_2$C^5), 1.38 (m, 2H, H$_2$C^{5,6}), 1.32 (dd, $^2J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.3 Hz, 1H, H$_2$C^7), 1.26 (dd, $^2J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.3 Hz, 1H, H$_2$C^7), 1.21 (ddd, $^2J_{H-H}$ = 12.0 Hz, $^3J_{H-H}$ = 9.4 Hz, $^4J_{H-H}$ = 1.6 Hz, 1H, H$_2$C^3), 1.03 (t, $^3J_{H-H}$ = 8.0, 9H, CH$_3$-Et), 0.98 (m, 1H, H$_2$C^2), 0.76 (q, $^3J_{H-H}$ = 8.0, 6H, CH$_2$-Et). ^{13}C{^{1}H} NMR (δ, C$_6$D$_{12}$, 125.76 MHz, 283 °C): 41.6 (1C, H$_2$C^7), 41.3 (1C, HC^1), 40.2 (1C, HC^4), 37.5 (1C, H$_2$C^3), 33.3, 1C, HC^5), 29.4, 1C, HC^6), 28.8 (1C, HC^2), 10.3 (3C, CH$_3$-Et), 4.0 (3C, CH$_2$-Et).

3.2.4. Photochemical reaction of Mo(CO)$_6$ with norbornadiene and Et$_3$GeH

A solution of Mo(CO)$_6$ (0.005 g, 0.019 mmol), nbd (0.1 cm^3, 0.95 mmol), and Et$_3$GeH (0.15 cm^3, 1.9 mmol) in *n*-heptane solution (20 cm^3) was stirred and irradiated at room temperature for 3 h. All volatile materials were then evaporated under reduced pressure at room temperature and the residue was analyzed by GC–MS and by NMR spectroscopy, which revealed the formation of triethylgermylnorbornene (nbeGeEt$_3$) as a mixture of *endo* and *exo* isomers (76/24% ratio by ^{1}H NMR method).

3.2.5. Identification by GC–MS and spectroscopic characteristic of hydrogermylation product

Endo-nbeGeEt$_3$: C$_{13}$H$_{24}$Ge, M_r = 252.9, GC–MS, m/z (relative intensity): 39 (8), 66 (10), 77 (22), 91 (16), 103 (47), 131 (61), 159 (100), 225 (29), 253 (M^+, 0.3). ^{1}H NMR (δ, CDCl$_3$, 500.13 MHz): 5.95 (dd, $^3J_{H-H}$ = 5.5 Hz, $^4J_{H-H}$ = 2.8 Hz, 1H, HC^2), 5.89 (dd, $^3J_{H-H}$ = 5.5 Hz, $^4J_{H-H}$ = 3.0 Hz, 1H, HC^3), 2.95 (s, 1H, HC^4), 2.83 (s, 1H, HC^1), 1.87 (ddd, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 9.6 Hz, $^4J_{H-H}$ = 3.7 Hz, 1H, H$_2$C^6), 1.39 (d, $^2J_{H-H}$ = 8.0 Hz, 1H, H$_2$C^7), 1.38 (ddd, $^3J_{H-H}$ = 13.0, $^3J_{H-H}$ = 9.6, $^4J_{H-H}$ = 3.0, 1H, HC^5), 1.10 (d, $^2J_{H-H}$ = 8.0 Hz, 1H, H$_2$C^7) 1.03 (dd, $^2J_{H-H}$ = 11.1, $^3J_{H-H}$ = 13.0, 1H, H$_2$C^6), 0.99 (t, $^3J_{H-H}$ = 8.0 Hz, 9H, CH$_3$-Et), 0.64 (q, $^3J_{H-H}$ = 8.0, 6H, CH$_2$-Et). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 125.76 MHz): 135.5 (1C, HC^2), 134.3 (C, HC^3), 50.7 (1C, H$_2$C^7), 45.0 (1C, HC^4), 41.9 (1C, HC^1), 27.5 (1C, H$_2$C^6), 22.9 (1C, HC^5), 9.2 (3C, CH$_3$-Et), 3.9 (3C, CH$_2$-Et).

Exo-nbeGeEt$_3$: GC–MS, m/z (relative intensity): 39 (9), 66 (11), 77 (27), 91 (19), 103 (47), 131 (70), 159 (100), 225 (24), 253 (M^+, 1). ^{1}H NMR (δ, CDCl$_3$, 500.13 MHz) 6.10 (dd, $^3J_{H-H}$ = 5.6, $^4J_{H-H}$ = 2.9 Hz, 1H, HC^2), 5.88 (m, 1H, HC^3), 2.90 (s, 1H, HC^4), 2.76 (s, 1H, HC^1), 1.61 (m, 1H, H$_2$C^6), 1.20 (dd, $^2J_{H-H}$ = 8.0 Hz, $^4J_{H-H}$ = 2.0 Hz, 1H, H$_2$C^7), 1.15 (m, 1H), other signals are overlapped by signals of the major isomer. ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 125.76 MHz): 137.5 (1C, HC^2), 133.0 (C, HC^3), 47.2 (1C, H$_2$C^7), 43.5 (1C, HC^1), 42.3 (1C, HC^4), 27.5 (1C, H$_2$C^6), 22.3 (1C, HC^5), other signals unresolved.

Acknowledgments

Appendix A. Supplementary material

Supplementary data involve NMR spectra of complex [Mo(CO)$_5$(η^2-H–GeEt$_3$)] and triethylgermylnorbornene. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.013.

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