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Cyclomagnesation of Olefins with Ethylmagnesium Bromide in the Presence of Titanium Complexes

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Abstract—Cyclomagnesation of terminal and cyclic olefins and 1,2-dienes with RMgHlg and R_2Mg in the presence of dichloro(dicyclopentadienyl)titanium(IV) gives non-Grignard cyclic and acyclic organomagnesium compounds. The reaction direction depends on the structure of unsaturated initial compound. The most probable reaction mechanism is discussed.

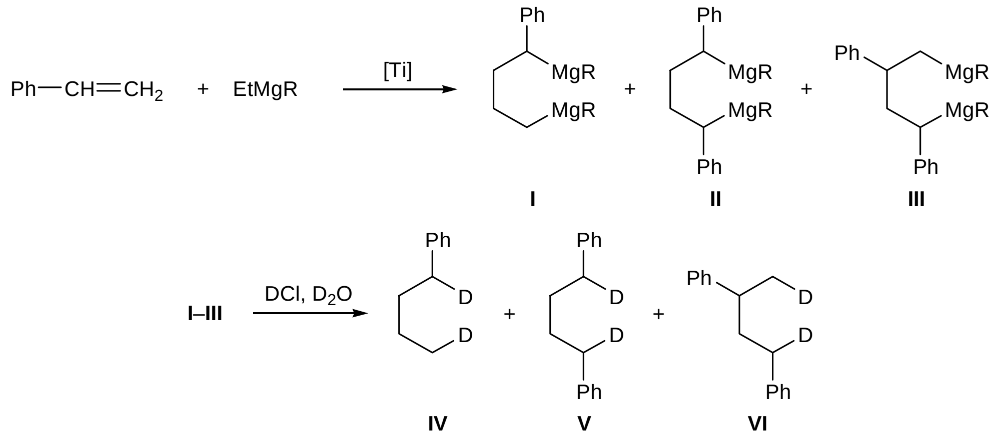
In 1989, we reported [1] on the cyclomagnesation of olefins with RMgR' (R' = Alk, Hlg) in the presence of Cp_2ZrCl_2 as catalyst, which afforded 1,4-dimagnesium compounds and/or magnesacyclopentanes. These studies were subsequently developed in [2–9]. According to the data of [3, 6, 8], depending on the conditions, the cyclomagnesation process can be accompanied by carbomagnesation [10–14] which involves formation of zirconacyclopentane intermediates. The yields and ratio of cyclo- and carbomagnesation products depends on the solvent nature, temperature, and initial reactant ratio [3, 8]. As a rule, the reaction is catalyzed by zirconium complexes [1–14]. We have found no published data on the use of coordination compounds derived from other transition metals to catalyze cyclomagnesation.

With the goal of extending the scope of application of catalytic cyclomagnesation of unsaturated compounds with organomagnesium reagents and searching for new catalysts capable of promoting such reactions, we examined reactions of ethylmagnesium bromide and diethylmagnesium (EtMgR; R = Br, Et) with olefins (1-octene, allylbenzene, styrene, and *endo*-dicyclopentadiene) in the presence of catalytic systems on the basis of Ti, Hf, Fe, Co, Ni, Pd, and Rh, i.e., transition metals whose coordination compounds are widely used to catalyze various transformations of olefins, dienes, and acetylenes. Preliminary experiments showed that the maximal yields of the cyclomagnesation products are attained in the presence of titanium complexes, in particular Cp_2TiCl_2. Therefore, all subsequent experiments on cyclomagnesation of the above listed olefins were performed with the use of Cp_2TiCl_2 as catalyst.

Depending on the substrate nature, the reactions with EtMgBr and Et_2Mg in the presence of Cp_2TiCl_2 gave cyclo-, carbo-, and hydromagnesation products. Styrene reacted with EtMgBr in the presence of Cp_2TiCl_2 (20°C, 20 h, THF, $PhCH=CH_2$–EtMgBr–[Ti] ratio 1 : 2 : 0.05) to afford a mixture of mono- and diphenyl-substituted magnesacyclopentanes and/or (in keeping with the Schlenk equilibrium) 1,4-dimagnesium derivatives **I**–**III** [3, 8]. Deuterolysis of the latter led to formation of 1,4-dideuterobutanes **IV**–**VI** at a ratio of ~3 : 2 : 1 in an overall yield of ~75% (Scheme 1). In each experiment, unidentifiable high-molecular compounds were formed (~15%) in addition to the above products. When the reaction of styrene was performed with Et_2Mg instead of EtMgBr, other conditions being equal, the products were magnesacyclopentanes and/or 1,4-dimagnesium derivatives **I**–**III** (ratio ~5 : 1 : 2) in an overall yield of ~60%; in this case, no high-molecular products were formed.

The reaction of *endo*-dicyclopentadiene (tricyclo-[5.2.1.0^{2,6}]deca-3,8-diene) with EtMgBr (20°C, 50 h, THF, substrate–EtMgBr–[Ti] ratio 1 : 2 : 0.05) involved the double bond in the norbornene moiety and afforded a ~1 : 1 mixture of regioisomeric carbomagnesation products **VIIIa** and **VIIIb** in ~70% yield. As shown in [15], addition of chemically activated magnesium changes the chemoselectivity of the process, and the reaction gives a mixture of cyclo-, carbo-, and hydromagnesation products **VII**–**IX** (~5 : 2 : 2) in an overall yield of ~75%, the *endo*-configuration of the cyclo-

Scheme 1.



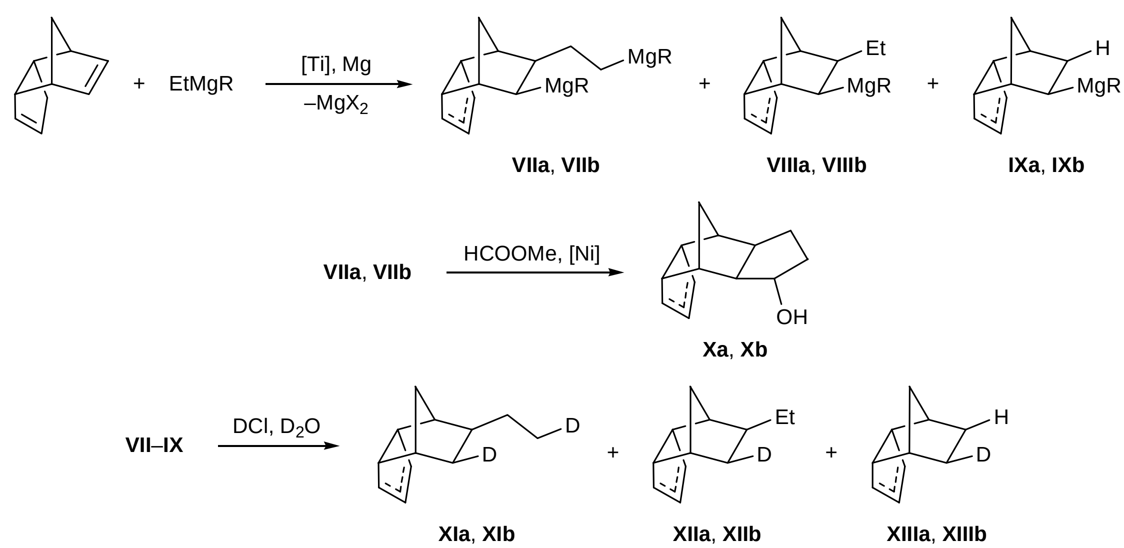
R = Br, Et.

pentene fragment being retained. Presumably, activated magnesium reduces Cp_2TiCl_2 to $[Cp_2Ti]$ which is responsible for formation of titanacyclopentane intermediates [16, 17]. The structure of organomagnesium compounds **VII**–**IX** was established by analysis of the corresponding deuterolysis products **XI**–**XIII**. Treatment of compounds **VIIa** and **VIIb** with methyl formate gave cyclopentanols **Xa** and **Xb** [18], providing an additional support to the assumed structure of magnesacyclopentanes (Scheme 2).

Terminal olefins, namely 1-octene and allylbenzene, reacted with EtMgBr in the presence of Cp_2TiCl_2 (~20°C, 20 h, THF, olefin–EtMgBr–[Ti] molar ratio 1 : 4 : 0.05) to give a mixture of cyclo-, carbo-, and hydromagnesation products **XIV**–**XVI** at a ratio of 2 : 5 : 6 (Scheme 3). In the reaction with Et_2Mg, the ratio of deuterolysis products **XVIIa–XVIIIa**–**XIXa** was 4 : 7 : 1. In experiments with allylbenzene, the substrate underwent partial isomerization to 2-propenylbenzene (~30%) [19]. We failed to effect cyclomagnesation of internal olefins with inactivated doubly or triply substituted double bonds (such as cyclohexene, 1,5,9-trimethyl-1,5,9-cyclododecatriene, and 5-ethyl-5-decene).

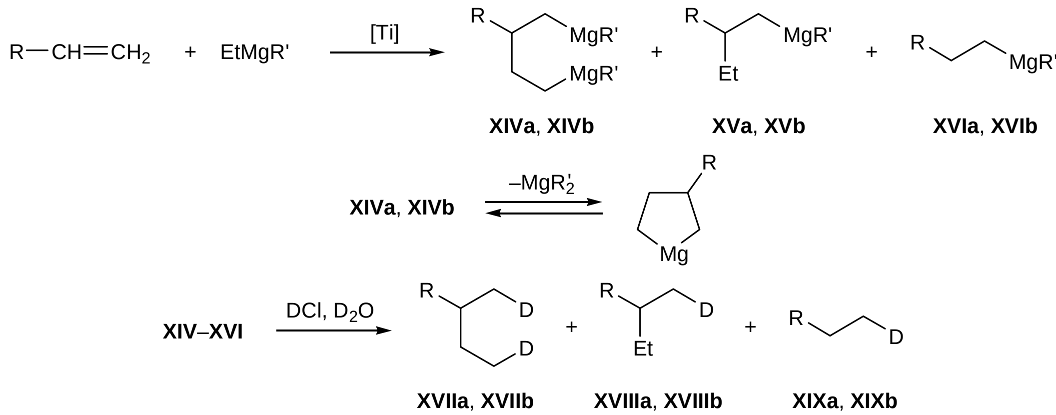
Cyclomagnesation of 1,2-dienes with 2 equiv of EtMgBr in the presence of chemically activated magnesium and a catalytic amount (5 mol %) of Cp_2TiCl_2 (THF, 20°C, 8 h) gave 2,5-dialkylidenemagnesacyclopentanes **XXa**–**XXd** and dimagnesium derivatives **XXIa**–**XXId**, the ratio **XXa**–**XXIa** being equal to

Scheme 2.



$[Ti] = Cp_2TiCl_2$; $[Ni] = Ni(acac)_2 + 2Ph_3P$; X = Cl, Br; R = Br, Et.

Scheme 3.



[Ti] = Cp_2TiCl_2; R = C_6H_{13} (**a**), Ph CH_2 (**b**); R' = Br, Et.

~1 : 1 (according to the ^{13}C NMR spectrum) [20]. Treatment of compounds **XXI** with D^+/D_2O furnished more than 90% of 1,6-dialkyl-2,5-dideutero-1,5-hexadienes **XXIIa**–**XXIId** (Scheme 4).

The selectivity of cyclomagnesation of allenes with EtMgBr in the presence of Cp_2TiCl_2 as catalyst depends on the initial 1,2-diene structure. For example, the reaction of phenylallene under optimal conditions resulted in formation of a complex mixture of unsaturated organomagnesium compounds. The reactions performed in diethyl ether were characterized by poor selectivity and poor yield.

Taking into account published data [19, 21, 22] and the results of our experiments, the formation of cyclic and acyclic organomagnesium compounds can be rationalized as shown in Scheme 5. According to this scheme, the reaction of EtMgBr with olefins in the presence of Cp_2TiCl_2 involves formation of such key intermediates as titanacyclopropanes [16], titanacyclopentanes [17], and alkyl and hydride titanium compounds [19]; these intermediates undergo transmetalation with EtMgX to give the final products.

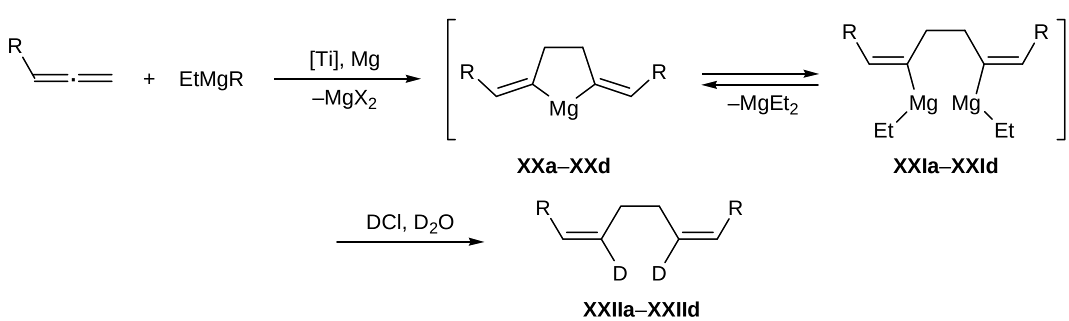
Thus our results showed that titanium complexes successfully catalyze cyclomagnesation of olefins and 1,2-dienes with RMgHlg and R_2Mg, which results in formation of cyclic and acyclic organomagnesium compounds in fairly high yields.

EXPERIMENTAL

The deuterolysis products were analyzed by GLC on a Chrom-5 chromatograph equipped with a 3-m× 3-mm column; stationary phase 5% SE-30); carrier gas helium. The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films. The mass spectra (70 eV) were obtained on an MKh-1306 mass spectrometer; ion source temperature 200°C. The ^1H and ^{13}C NMR spectra were measured on Jeol FX-90Q (89.55 MHz for ^1H and 22.5 MHz for ^{13}C) and Bruker AM-300 instruments (75.46 MHz for ^{13}C and 300 MHz for ^1H) using $CDCl_3$ as solvent.

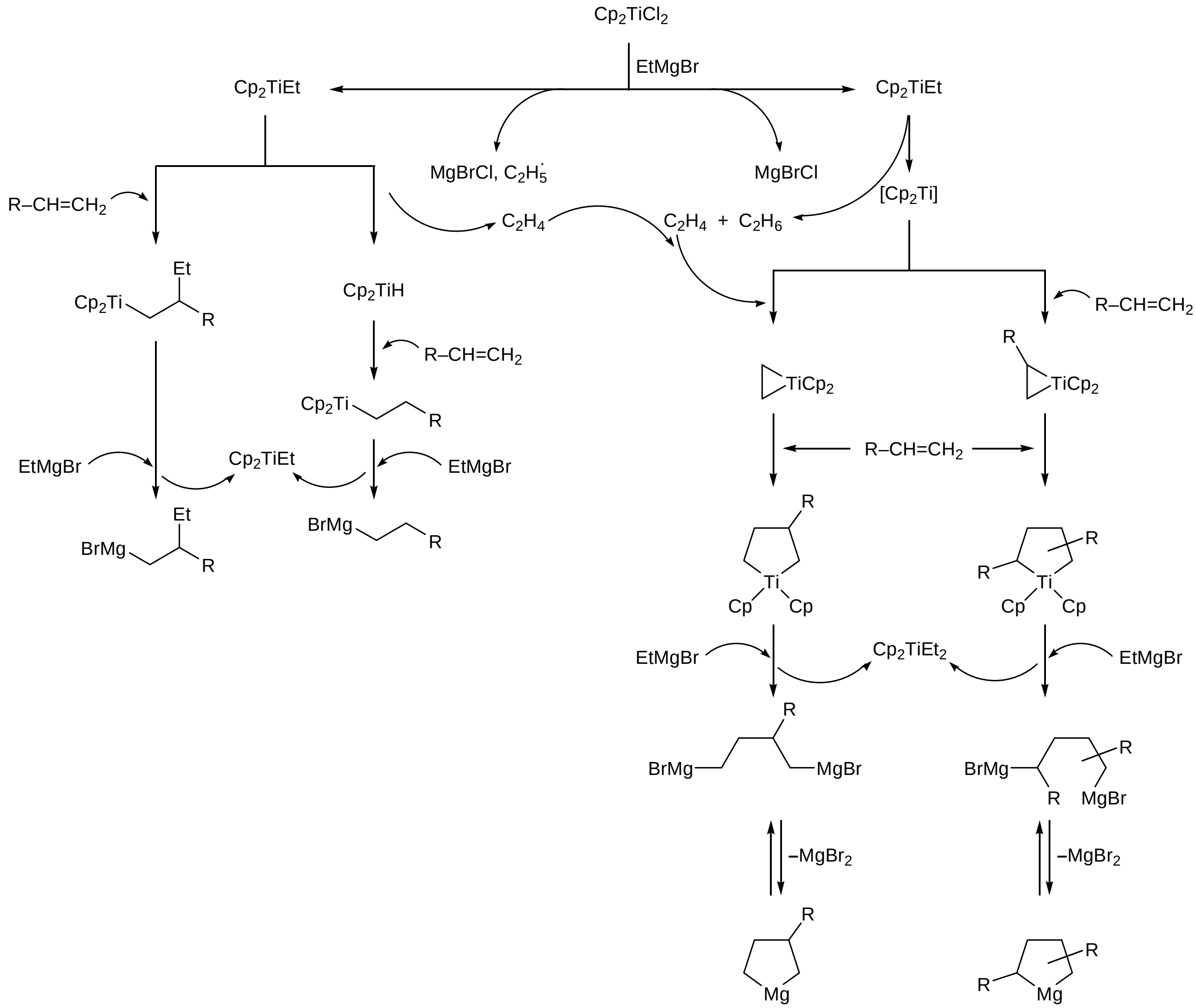
Tetrahydrofuran was dried over metallic sodium and was distilled just before use. Solutions of EtMgBr and Et_2Mg in THF were prepared as described in [23].

Scheme 4.



[Ti] = Cp_2TiCl_2; X = Cl, Br; R = C_5H_{11} (**a**), C_7H_{15} (**b**), 2-(3-cyclohexenyl)ethyl (**c**), $PhCH_2$ (**d**).

Scheme 5.



R = Alk, Ph.

Dicloro(dicyclopentadienyl)titanium(IV) was synthesized by the procedure described in [24].

The yields of organomagnesium compounds were determined by GLC analysis of the corresponding deuterium derivatives. Compounds **IV–VI** [25], **Xa**, **Xb**, **XIa**, **XIb** [26], **XIIIa**, **XIIIb** [27], **XVIIa** [28], **XVIIb** [29], **XIXa**, **XIXb**, [30], and **XXIIa–XXIId** [20] were identified by comparing their physical properties and spectral parameters with those of authentic samples.

Reaction of terminal olefins with EtMgBr and Et_2Mg in the presence of Cp_2TiCl_2. A glass reactor was charged at 0°C under dry argon with 20 mmol of EtMgBr or Et_2Mg (a solution in THF), 10 mmol of styrene, 1-octene, or allylbenzene, and 0.5 mmol of Cp_2TiCl_2. The mixture was allowed to warm up to room temperature, stirred for 20 h using a magnetic stirrer, treated with a 10–12% solution of DCl in D_2O, and extracted with diethyl ether or hexane. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to fractional distillation under reduced pressure.

3-Deuteromethylnonane (XVIIIa). bp 55–56°C (10 mm). ^1H NMR spectrum, δ, ppm: 0.85 m (8H, CH_3, CH_2D), 1.15–1.50 m (13H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 11.40 (C^1), 14.11 (C^9), 18.91 t (J_{CD} = 19.5 Hz), 22.72 (C^8), 27.10 (C^5), 29.51 (C^2), 29.71 (C^6), 31.99 (C^7), 34.36 (C^4), 37.11 (C^3). Found,

%: C 83.54; H+D 15.79. $C_{10}H_{21}D$. Calculated, %: C 83.83; H 14.78; D 1.39.

1-[2-(Deuteromethyl)butyl]benzene (XVIIIb). bp 82–83°C (20 mm). ^{1}H NMR spectrum, δ, ppm: 0.82 m (5H, CH_3, CH_2D), 1.10–1.58 m (1H, CH), 2.45 d (2H, C**H**$_2C_6H_5$, J = 6.0 Hz), 7.05–7.50 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 11.50 (C^4); 18.70 t (J_{CD} = 19.5 Hz); 29.91 (C^3); 36.72 (C^2); 43.53 (C^1); 125.60, 128.15, 129.22, 141.61 (C_{arom}). Found, %: C 88.34; H+D 11.27. $C_{11}H_{21}D$. Calculated, %: C 88.53; H 10.13; D 1.34.

Reaction of *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene with EtMgBr in the presence of activated magnesium and Cp_2TiCl_2. Metallic magnesium, 20 mmol, was activated with EtBr in THF under dry argon [15] in a glass reactor. The mixture was cooled at 0°C, and a solution of 20 mmol of EtMgBr in THF, 10 mmol of *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, and 0.5 mmol of Cp_2TiCl_2 were added. The mixture was allowed to warm up to room temperature, stirred for 50 h using a magnetic stirrer, treated with a 10–12% solution of DCl in D_2O, and extracted with diethyl ether or hexane. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to fractional distillation.

***exo*-9-Deutero-8-ethyl-*endo*-tricyclo[5.2.1.0^{2,6}]-dec-3-ene (XIIa) and *exo*-9-deutero-8-ethyl-*endo*-tricyclo[5.2.1.0^{2,6}]dec-4-ene (XIIb) (**mixture of isomers**).** bp 76–78°C (5 mm). ^{1}H NMR spectrum, δ, ppm: 0.82 m (3H, CH_3), 1.0–1.70 m (5H, CH_2, CH, CHD), 1.82–2.70 m (6H, CH, C**H**$_2$CH=), 2.95 m (1H, C**H**CH=), 5.48–5.66 m (2H, CH=CH). ^{13}C NMR spectrum, δ, ppm: **XIIa**: 12.23, 29.11, 28.72 (C^{10}), 37.10 t (C^9, J_{CD} = 19.5 Hz), 40.91 (C^5), 43.00 (C^1), 43.51 (C^8), 44.52 (C^6), 47.82 (C^7), 55.33 (C^2), 131.90 (C^3), 132.34 (C^4); **XIIb**: 12.23, 28.82 (C^{10}), 29.31, 36.80 t (C^9, J_{CD} = 19.5 Hz), 40.91 (C^3), 43.42 (C^8), 43.80 (C^2), 44.31 (C^1), 44.93 (C^7), 56.61 (C^6), 131.90 (C^5), 132.61 (C^4). Found, %: C 88.16; H+D 11.39. $C_{12}H_{17}D$. Calculated, %: C 88.28; H 10.49; D 1.23.

Reaction of organomagnesium compounds VIIa and VIIb with methyl formate in the presence of phosphine nickel complex. A 1:2 mixture of nickel(II) acetate and triphenylphosphine (0.5 mmol of the catalyst) was added at –15°C to the reaction mixture containing compound **VIIa** or **VIIb**, and 3 equiv (with respect to EtMgBr) of methyl formate was slowly added dropwise. The mixture was allowed to warm up to room temperature, stirred for 8 h, treated with 8–10% hydrochloric acid, and extracted with diethyl ether or hexane. The extract was dried over $CaCl_2$ and evaporated, and the residue was subjected to column chromatography on silica gel (L 40/100 μm) using hexane–diethyl ether 10:1) as eluent.

Reaction of 1,2-dienes with EtMgBr in the presence of activated magnesium and Cp_2TiCl_2. Metallic magnesium, 20 mmol, was activated with EtBr in THF under dry argon [15] in a glass reactor. The mixture was cooled to 0°C, and a solution of 20 mmol of EtMgBr in THF, 10 mmol of the corresponding 1,2-diene, and 0.5 mmol of Cp_2TiCl_2 were added. The mixture was allowed to warm up to room temperature, stirred for 10 h using a magnetic stirrer, treated with a 10–12% solution of DCl in D_2O, and extracted with diethyl ether or hexane. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to fractional distillation under reduced pressure.

2,5-Dihexylidenemagnesacyclopentane (XXa). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 14.18 (C^{11}, C^{17}), 22.72 (C^{10}, C^{16}), 28.67 (C^3, C^4), 28.71 (C^7, C^{13}), 29.50 (C^8, C^{14}), 32.00 (C^9, C^{15}), 142.84 (C^6, C^{12}), 188.30 (C^2, C^5).

(6*Z*,10*Z*)-7,10-Bis(ethylmagnesio)hexadeca-6,10-diene (XXIa). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: –1.13 ($MgCH_2$), 12.27 ($MgCH_2$**C**H_3), 14.18 (C^1, C^{16}), 19.89 (C^8, C^9), 22.72 (C^2, C^{15}), 28.71 (C^5, C^{12}), 29.50 (C^4, C^{13}), 32.00 (C^3, C^{14}), 142.84 (C^6, C^{11}), 166.36 (C^7, C^{10}).

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