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Tetrahedron 60 (2004) 1281–1286
Tetrahedron

Zirconium-catalyzed preparation of aluminacyclopentanes and synthesis of five-membered carbo- and heterocycles

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Received 30 June 2003; revised 29 September 2003; accepted 11 October 2003

Abstract—Novel 'one-pot' catalytic methods for the synthesis of cyclopentanols, tetrahydrothiophenes, silacyclopentanes and phospholanes are based on successive transformations of olefins and organoaluminium compounds (R_2AlR') in the presence of Cp_2ZrCl_2 catalyst. In situ generated aluminacyclopentanes serve as common intermediates in these processes.

1. Introduction

The development of the chemistry of reagents containing active metal–carbon bonds has contributed very significantly to the advancement of organic chemistry. Among the most commonly used reagents, lithium, magnesium, zinc, aluminium and boron organic compounds are also the most useful for carbon–carbon bond formations.

Meanwhile, in the last 10–15 years, new effective methods for construction of carbon–carbon, heteroatom–carbon and metal–carbon bonds based on zirconium organic derivatives have provided interesting carbocyclic and heterocyclic compounds. Negishi E.,[1–6] Takahashi T.,[7–13] Buchwald S.L.,[14–20] Nugent W.A., Fagan P.J.[21–23] and others have contributed to the development of these methods.

Concurrently, the chemistry of cyclic organoaluminium compounds (OAC) and their derivatives, in particular, aluminacyclopentanes and aluminacyclopentenes and their applications toward the synthesis of cyclobutanes,[24,25] cyclopropanes,[26–29] thiophanes and selenophanes[30,31] has been published. Based on these ideas and in order to extend the use of OAC in organic and organometallic synthesis, we focused our attention on 'one-pot' methods for the preparation of substituted cyclopentanols, tetrahydrothiophenes, phospholanes and silacyclopentanes from aluminacyclopentanes,[32–35] which were generated in situ by cycloalumination of olefins in the presence of Zr-containing catalysts.

2. Results and discussion

In accordance with previously reported work,[36] trialkylalanes were found to interact with carboxylic esters at 35–80 °C to give a complicated mixture of alcohols and ketones. We herein report that aluminacyclopentanes **1**, generated in situ from α-olefins and $AlEt_3$ in the presence of Cp_2ZrCl_2 catalyst,[32–35] reacted selectively with carboxylic esters in the presence of 10 mol% CuCl at 20–21 °C for 6–8 h to form cyclopentanols **2a–j** in 60–75% yield (Scheme 1).

This reaction represents a convenient route for the synthesis of cyclopentanols with substitution patterns determined by the structure of the starting olefins. For example, cycloalumination of styrene, allylbenzene, or 4-vinylcyclohex-1-ene with $AlEt_3$ catalyzed by Cp_2ZrCl_2 was found to generate aluminacyclopentanes **1e–j**. Further transformations of these metallocycles under the action of alkyl formiate and catalytic amounts of CuCl led to the formation of two additional C–C bonds as shown for cyclopentanols **2e–j**.

In an analogous fashion, the interaction between *trans*-3,4-dialkylsubstituted aluminacyclopentanes **3**, generated in situ,[37] and methyl formiate in the presence of CuCl catalyst (10 mol%) led to cyclopentanoles **4** with retention of the relative configuration of the alkyl substituents (Scheme 2).

Earlier[30,31] we have demonstrated a method for the selective synthesis of tetrahydrothiophenes from aluminacyclopentanes and S_8 in benzene at 80 °C. In the course of

Keywords: Catalysis; Zr Complexes; Organoaluminium compounds; Olefins; Cycloalumination; Cyclopentanols; Tetrahydrothiophenes; Phospholanes; Silacyclopentanes.
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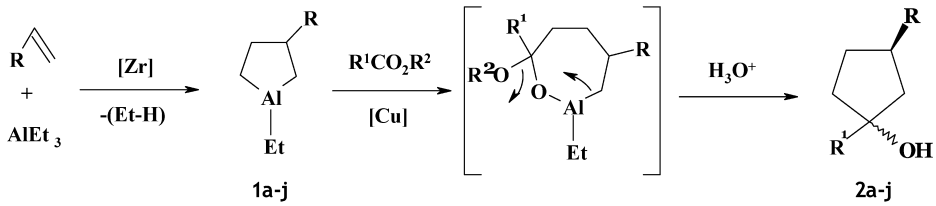
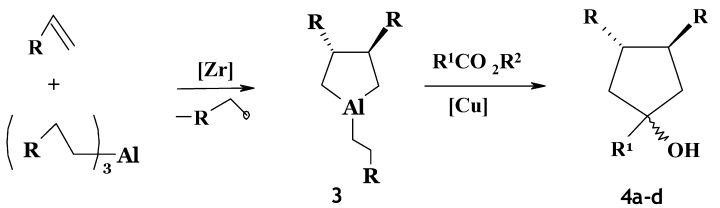
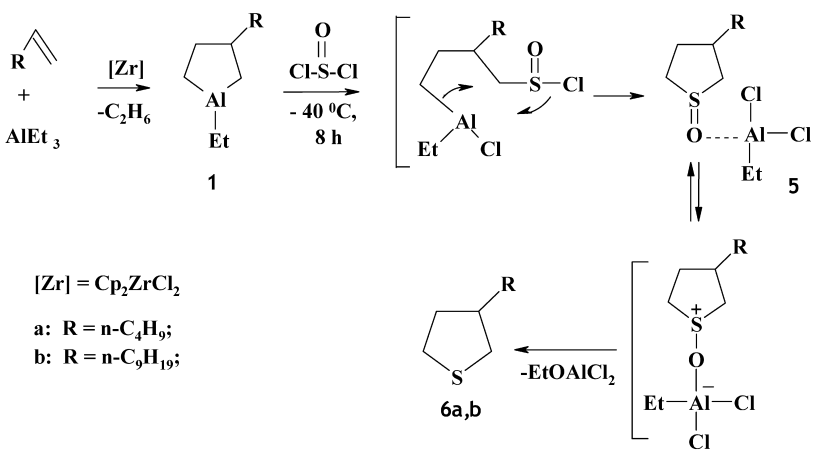
doi:10.1016/j.tet.2003.10.082



Scheme 1. [Zr]=Cp_2ZrCl_2; [Cu]=CuCl; a: R=*n*-C_4H_9, R^1=H; b: R=*n*-C_6H_{13}, R^1=H; c: R=*n*-C_6H_{13}, R^1=CH_3; d: R=*n*-C_6H_{13}, R^1=C_2H_5; e: R=3-cyclohexenyl, R^1=H; f: R=Ph, R^1=H; j: R=CH_2Ph, R^1=H; R^2=alkyl.



Scheme 2. [Zr]=Cp_2ZrCl_2; a: R=*n*-C_4H_9, R^1=H; b: R=*n*-C_6H_{13}, R^1=H; c: R=*n*-C_4H_9, R^1=CH_3; d: R=*n*-C_4H_9, R^1=C_2H_5, R^2=alkyl.



Scheme 3.

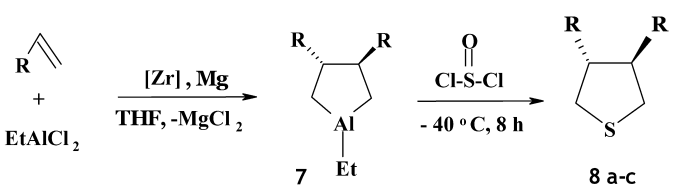
further investigations on transformations of cyclic OAC to give five-membered heterocycles—1-ethyl-3-alkylalumina-cyclopentanes **1**, obtained in situ from α-olefins, $AlEt_3$ and catalytic amounts of Cp_2ZrCl_2,[32–35] were found to interact with thionyl chloride in hexane at −40 °C to give 3-alkyltetrahydrothiophenes **6** in 85% yield. The probable formation of sulfoxide intermediate[38] **5** followed by its further conversion into the isolated product represent the key steps in this reaction (Scheme 3).

In the presence of $EtAlCl_2$, Zr catalyst and Mg-metal, 1-alkyl-*trans*-3,4-dialkylaluminacyclopentanes[39,40] **7** were formed and found to react with thionyl chloride at −40 °C to give *trans*-3,4-dialkyltetrahydrothiophenes **8** in 80% yield (Scheme 4).

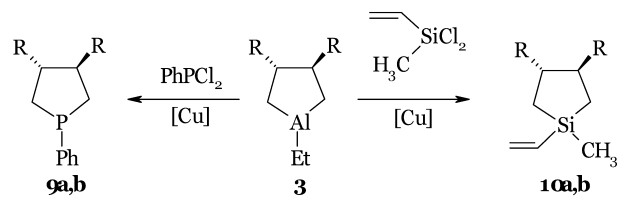
The preparation of phospholes[21,23] or silols[41] from stoichiometric amounts of zirconacyclopentadienes and phosphorus and silicon dihalogenides is well known. To investigate the possibilities of preparing analogous P- or Si-containing heterocycles from aluminacyclopentanes[39,40] in the presence of catalytic amounts of Zr complex, solutions of aluminacyclopentanes **3** in THF were exposed at rt (ca. 20 °C) to copper halides (CuCl, CuBr, CuI, 10–15 mol%) and dichlorophenylphosphine, as well as dichloromethyl-vinylsilane. Gratifyingly, the expected phospholanes **9** or silacyclopentanes 10 were obtained in total yields of 50–65% (Scheme 5).

3. Conclusions

The synthetic strategies presented in this paper allow the straightforward conversion of α-olefins into cyclopentanols, tetrahydrothiophenes, phospholanes or silacyclopentanes



Scheme 4. [Zr]=Cp_2ZrCl_2; a: R=$(CH_3)_2CH(CH_2)_2$; b: R=$PhCH_2$; c: R=3-cyclohexenyl.



Scheme 5. a: R=*n*-C_4H_9; b: R=*n*-C_6H_{13}.

via intermediate in situ prepared aluminacyclopentanes in the presence of Cp_2ZrCl_2 catalyst.

Several carbon–carbon and carbon–heteroatom bonds can be formed in a single reaction setup, and this efficiency combined with catalytic use of the more precious transition metals contributes to the promise of this methodology for the large-scale preparation of organic building blocks. Aluminacyclopentanes were found to react selectively with carboxylic esters, thionyl chloride, dichlorophosphines and dichlorosilanes.

4. Experimental

4.1. General

All solvents were dried (hexane over $LiAlH_4$, Et_2O and THF over Na) and freshly distilled before use. All reactions were carried out under a dry argon atmosphere. The reaction products were analyzed using chromatography on a 'Chrom-5' instrument (1200×3 mm^2 column packed with 5% of SE-30 and 15% PEG-6000 on Chromaton N-AW, carrier gas—He). Infrared spectra (IR) were recorded on a IR-75 instrument (thin film). Mass spectral measurements were performed on a MX-1306 spectrometer at 70 eV and working temperature 200 °C. The ^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on 'Bruker AM-300' spectrometer (75.46 MHz for ^{13}C and 300 MHz for ^1H). The chemical shifts are reported as δ values in ppm relative to internal standard Me_4Si. ^{13}C NMR spectra were edited by *J*-modulation (JMOD) on CH constants.

4.2. Reaction of 1-ethyl-3-alkyl-substituted aluminacyclopentanes with carboxylic esters catalyzed by CuCl

A 50 mL glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol) in dry hexane (3 mL), olefin (10 mmol), and $AlEt_3$ (12 mmol) under a dried argon atmosphere at 0 °C. The resulting solution was raised to ambient temperature and stirred for 12 h, then cooled to −15 °C and after addition of CuCl (1 mmol) the corresponding ester (30 mmol) was added dropwise. The reaction mixture was allowed to warm to ~20 °C and stirred for 8 h. The reaction was quenched with 8–10% (aq.) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The combined organic extracts were washed with water, saturated aqueous $NaHCO_3$, dried ($CaCl_2$), filtered and concentrated in vacuo. The products were isolated by column chromatography on silica gel (40–100 mesh grade) with hexane/Et_2O=10:1 for elution.

4.2.1. *cis/trans*-3-Butylcyclopentanol ~(2:1) (2a). IR (thin film) 3355, 2985, 2950, 2840, 1730, 1450, 1385, 1230, 1030, 925, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.0 Hz, 3H, CH_3), 1.15–1.52 (m, 6H, CH_2), 1.78–2.35 (m, 7H, CH and CH_2 ring), 4.29 (m, C*H*–OH); ^{13}C NMR ($CDCl_3$) δ 14.50, 22.74, 30.28, 30.78(30.86), 32.08(32.79), 35.97(36.05), 37.98(37.84), 39.95, 76.82(76.47); MS *m/z*: 124 [M^+-H_2O]. Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.76; Found: C, 75.82; H, 12.63. Yield 76%.

4.2.2. *cis/trans*-3-Hexylcyclopentanol ~(2:1) (2b). IR (thin film) 3380, 2990, 2950, 2840, 1720, 1460, 1380, 1185, 1030, 950, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, *J*=6.0 Hz, 3H, CH_3), 1.18–1.51 (m, 10H, CH_2), 1.78–2.35 (m, 7H, CH and CH_2 ring), 4.30 (m, C*H*–OH); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.62, 29.46; 28.49, 30.57(30.66), 31.87, 32.20(32.96), 35.77(35.86), 37.90(36.52), 39.62, 76.95(76.55); MS (*m/z*, %): 152 (5, [M^+-H_2O]), 112(1.5), 85(2.5), 71(2.6), 67(100), 57(16), 43(31), 29(27.5). Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02; Found: C, 77.39; H, 12.87. Yield 75%.

4.2.3. *cis/trans*-1-Methyl-3-(*n*-hexyl)cyclopentanol ~(2:1) (2c). IR (thin film) 3350, 2990, 2950, 2840, 1720, 1460, 1380, 1235, 1100, 1030, 1000, 925, 900, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J*=6.0 Hz, 3H, CH_3), 1.20–1.58 (m, 10H, CH_2), 1.33 (s, 3H, CH_3), 1.61–2.51 (m, 7H, CH, CH_2 ring); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.67, 28.52(28.78), 29.50, 29.56, 31.19 (31.45), 31.90, 36.52 (36.98), 38.41 (39.06), 40.75 (41.59), 48.62 (48.23), 79.96 (79.74); MS *m/z*: 184 M^+. Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13; Found: C, 78.02; H, 13.01. Yield 68%.

4.2.4. *cis/trans*-1-Ethyl-3-(*n*-hexyl)cyclopentanol ~(2:1) (2d). IR (thin film) 3350, 2990, 2950, 2840, 1720, 1450, 1380, 1230, 1030, 920, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83–1.02 (m, 6H, CH_3), 1.20–1.57 (m, 12H, CH_2), 1.61–2.51 (m, 7H, CH and CH_2 ring); ^{13}C NMR ($CDCl_3$) δ 8.72(8.49), 14.00, 22.68, 28.48, 29.49, 30.86(31.38), 31.87, 34.41(34.47), 36.33(36.37), 36.95 (37.14), 38.02(38.57), 46.45 (46.00), 82.80(82.31); MS *m/z*: 198 (M^+). Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21; Found: C, 78.58; H, 13.04. Yield 60%.

4.2.5. *cis/trans*-3-Cyclohexenylcyclopentanol ~(2:1) (2e). ^1H NMR ($CDCl_3$) δ 1.60–2.21 (m, 14H, CH, CH_2), 4.28 (m, H, C*H*–OH), 5.15–5.75 (m, 2H, CH=CH); ^{13}C NMR ($CDCl_3$) δ 25.26, 27.60(27.82), 28.52, 30.73, 35.32(35.68), 37.32(37.68), 39.16(39.39), 43.50(43.07), 76.18(75.81), 126.50, 127.18; MS (*m/z*, %): 166 (0.7, M^+), 148(18), 134(0.6), 122(1), 108(2), 94(8.5), 81(40), 80(100), 58(1), 44(2), 30(1), 29(18). Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91; Found: C, 79.28; H, 10.74. Yield 65%.

4.2.6. *cis/trans*-3-Phenylcyclopentanol ~(2:1) (2f). IR (thin film) 3380, 3015, 2990, 2950, 2840, 1710, 1490, 1450, 1395, 1180, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45–2.25 (m, 6H, CH_2), 3.10–3.25 (m, H, C*H*–Ph), 4.40 (m, H, C*H*–OH), 7.00–7.50 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 28.91(29.20), 32.65(33.49), 35.65(36.01), 44.25(43.95), 73.75(73.51), 126.04, 127.08, 127.53, 128.48, 141.62; MS (*m/z*, %): 162(32, M^+), 145(9),

144(100), 143(53), 118(26), 104(54), 90(2), 77(30), 29(18). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70; Found: C, 81.23; H, 8.52. Yield 64%.

4.2.7. *cis/trans*-3-Benzylcyclopentanol ~(2:1) (2j). IR (thin film) 3380, 2990, 3015, 2995, 2950, 1715, 1600, 1490, 1450, 1400, 1180, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58–2.25 (m, 7H, CH, CH_2), 2.62 (d, J=5.6 Hz, 2H, CH_2–Ph), 4.28 (m, H, CH–OH), 7.00–7.48 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 30.34(30.54), 32.09(32.39), 38.78(39.36), 39.72(40.33), 42.06(41.60), 76.38(76.57), 126.00, 128.24, 128.42, 141.38; MS (*m*/*z*, %): 176(19, M^+), 158(7), 132(2), 118(7), 104(5), 91(100), 77(7), 29(27). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15; Found: C, 81.59; H, 9.01. Yield 69%.

4.3. Reaction of *trans*-3,4-dialkylaluminacyclopentanes with carboxylic esters catalyzed by CuCl

To the solution of tri(*n*-hexyl)aluminium (10 mmol), prepared in situ according to the literature method[37] at −15 °C under a dried argon atmosphere was added CuCl (1 mmol) and dropwise the corresponding ester (30 mmol). The reaction temperature was raised to rt (ca. 20 °C), and the mixture was stirred for 8 h. The reaction was quenched with 8–10% (aq.) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The combined organic extracts were washed with water, saturated aqueous $NaHCO_3$, dried ($CaCl_2$), filtered and concentrated in vacuo. The products were isolated by column chromatography on silica gel (40–100 mesh grade) with hexane/Et_2O=10:1 for elution.

4.3.1. *trans*-3,4-Di(*n*-butyl)cyclopentanol (4a). ^1H NMR ($CDCl_3$) δ 0.86–0.90 (m, 6H, CH_3), 1.15–1.30 (m, 12H, CH_2), 1.65–2.35 (m, 6H, CH and CH_2 ring), 5.30 (m, H, CH–OH); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.66, 29.85, 34.35, 39.10, 42.02, 73.25. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21; Found: C, 76.68; H, 13.01. Yield 75%.

4.3.2. *trans*-3,4-Di(*n*-hexyl)cyclopentanol (4b). ^1H NMR ($CDCl_3$) δ 0.88–0.91 (m, 6H, CH_3), 1.15–1.30 (m, 20H, CH_2), 1.65–2.35 (m, 6H, CH and CH_2 ring), 5.30 (m, H, CH–OH); ^{13}C NMR ($CDCl_3$) δ 14.15, 22.54, 26.15, 29.42, 31.72, 34.31, 39.02, 41.45, 72.18. Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47; Found: C, 80.03; H, 13.29. Yield 74%.

4.3.3. 1-Methyl-*trans*-3,4-di(*n*-butyl)cyclopentanol (4c). ^1H NMR ($CDCl_3$) δ 0.83–0.95 (m, 6H, CH_3), 1.14–1.29 (m, 12H, CH_2), 1.32 (s, 3H, CH_3), 1.65–2.35 (m, 6H, CH and CH_2 ring); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.69, 26.92, 31.93, 34.53, 38.15, 41.94, 72.83. Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29; Found: C, 78.98; H, 13.11. Yield 73%.

4.3.4. 1-Ethyl-*trans*-3,4-di-(*n*-butyl)cyclopentanol (4d). ^1H NMR ($CDCl_3$) δ 0.86–0.92 (m, 9H, CH_3), 1.24–1.62 (m, 14H, CH_2), 1.67–2.54 (m, 6H, CH and CH_2 ring); ^{13}C NMR ($CDCl_3$) δ 8.80, 14.11, 22.69, 29.95, 33.90, 32.42, 37.41, 38.44, 76.65. Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36; Found: C, 79.41; H, 13.20. Yield 69%.

4.4. Reaction of *trans*-3-alkylaluminacyclopentanes with thionyl chloride

A 50 mL glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol) in dry hexane (3 mL), olefin (10 mmol), and $AlEt_3$ (12 mmol) under a dried argon atmosphere at 0 °C. The resulting solution was raised to ambient temperature and stirred for 12 h, then cooled to −40 °C, and thionyl chloride (30 mmol) was added dropwise, stirred for 8 h and treated with 8–10% (aq.) solution of HCl. The crude products were extracted with diethyl ether or hexane and purified by distillation in vacuo.

4.4.1. 3-(*n*-Butyl)tetrahydrothiophene (6a). IR (thin film) 2970, 2940, 2870, 1470, 1385, 1265, 1220, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87–0.95 (m, 3H, CH_3), 1.35 (m, 6H, CH_2), 1.87–2.48 (m, 3H, CH and CH_2 ring), 2.65–3.01 (m, 4H, CH_2–S); ^{13}C NMR ($CDCl_3$) δ 14.10, 22.90, 30.80, 31.00, 33.30, 36.81, 44.80; MS *m*/*z*: 144 M^+. Yield 85%.

4.4.2. 3-(*n*-Nonyl)tetrahydrothiophene (6b). IR (thin film) 2960, 2925, 2855, 1460, 1375, 1260, 1210, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83–0.92 (m, 3H, CH_3), 1.21 (m, 16H, CH_2), 1.93–2.47 (m, 3H, CH, CH_2 ring), 2.58–2.83 (m, 4H, CH_2–S); ^{13}C NMR ($CDCl_3$) δ 14.10, 22.70, 28.80, 29.40, 29.70, 29.90, 30.80, 31.90, 33.60, 36.80, 44.80; MS *m*/*z*: 214 M^+. Yield 83%.

4.5. Reaction of *trans*-3,4-dialkylaluminacyclopentanes with thionyl chloride

A 50 mL glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol), Mg (powder) (12 mmol), dry THF (10 mL), olefin (20 mmol), and $EtAlCl_2$ (12 mmol) under a dried argon atmosphere at 0 °C. The resulting solution was allowed to warm to ambient temperature and stirred for 12 h, then cooled up to −40 °C and thionyl chloride (30 mmol) was added dropwise, stirred for 8 h and treated with 8–10% (aq.) solution of HCl. The crude products were extracted with diethyl ether or hexane and purified by distillation in vacuo. Compounds **8a–c** were identified by comparison with the known samples [31].

4.6. Reaction of *trans*-3,4-di(alkyl)aluminacyclopentanes with dichlorophenylphosphine

A 50 mL glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol), Mg (powder) (12 mmol), dry THF (10 mL), olefin (20 mmol), and $EtAlCl_2$ (12 mmol) under a dried argon atmosphere at 0 °C. The solution was raised to ambient temperature and stirred for 12 h, then cooled to −15 °C and dichlorophenylphosphine (12 mmol) was slowly added dropwise. The reaction mixture was allowed to warm to rt (ca. 20 °C), stirred for 8 h and treated with 8–10% (aq.) solution of HCl. The crude products were extracted with diethyl ether or hexane and purified by distillation in vacuo.

4.6.1. 1-Phenyl-*trans*-3,4-di(*n*-butyl)phospholane (9a). ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 6H, CH_3), 1.26–1.75 (m, 14H, CH_2 and CH), 3.40–3.51 (m, 4H, CH_2P), 7.17–7.87 (m, 5H, Ph). Anal. Calcd for $C_{18}H_{29}P$: C, 78.22; H, 10.58; Found: C, 77.99; H, 10.42. Yield 60%.

4.6.2. 1-Phenyl-*trans*-3,4-di(*n*-hexyl)phospholane (9b). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.5 Hz, 6H, CH_3), 1.23–1.72 (m, 22H, CH_2 and CH), 3.40–3.51 (m, 4H, CH_2P), 7.10–7.64 (m, 5H, Ph). Anal. Calcd for $C_{22}H_{37}P$: C, 79.47; H, 11.22; Found: C, 79.26; H, 11.07. Yield 60%.

4.7. Reaction of *trans*-3,4-di(alkyl)aluminacyclopentanes with dichlorovinylmethylsilane

A 50 mL glass reactor was charged with Cp_2ZrCl_2 (0.5 mmol), Mg (powder) (12 mmol), dry THF (10 mL), olefin (20 mmol), and $EtAlCl_2$ (12 mmol) under a dried argon atmosphere at 0 °C. The solution was raised to ambient temperature and stirred for 12 h, then cooled to −15 °C and dichlorovinylmethylsilane (12 mmol) was slowly added dropwise. The reaction mixture was allowed to warm to r.t. (ca. 20 °C), stirred for 8 h and treated with an 8–10% (aq.) solution of HCl. The crude products were extracted with Et_2O or hexane and purified by distillation in vacuo.

4.7.1. 1-Vinyl-1-methyl-*trans*-3,4-di(*n*-butyl)silacyclopentane (10a). ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 3H, CH_3), 0.75 (d, J=6.5 Hz, 4H, CH_2–Si), 0.96 (t, J=6.5 Hz, 6H, CH_3), 1.38 (m, 14H, CH and CH_2), 5.80–6.15 (m, 3H, CH_2=CH); ^{13}C NMR ($CDCl_3$) δ −0.74, 14.12, 14.66, 23.06, 29.37, 35.42, 36.81, 35.09, 36.72, 133.16, 136.61. Anal. Calcd for $C_{15}H_{30}Si$: C, 75.4; H, 12.68; Found: C, 75.35; H, 12.51. Yield 56%.

4.7.2. 1-Vinyl-1-methyl-*trans*-3,4-di(n-hexyl)silacyclopentane (10b). ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3H, CH_3), 0.81 (d, J=6.5 Hz, 4H, CH_2–Si), 0.96 (t, J=6.3 Hz, 6H, CH_3), 1.38 (m, 22H, CH and CH_2), 5.80–6.13 (m, 3H, CH_2=CH); ^{13}C NMR ($CDCl_3$) δ −0.67, 14.12, 14.54, 22.80, 27.81, 29.82, 32.10, 35.09, 36.72, 133.22, 136.67. Anal. Calcd for $C_{19}H_{38}Si$: C, 77.46; H, 13.00; Found: C, 77.25; H, 12.85. Yield 55%.

Acknowledgements

We thank the Russian Foundation of Basic Research (Project Nos. 03-03-33050 and 02-03-97904) for financial support.

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