Organometallic Chemistry

Synthesis of [μ-methylenebis(η^5-3-*tert*-butyl-2-methylinden-1-yl)]dichlorozirconium(IV)

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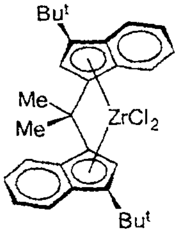
An efficient synthetic approach to 3-alkyl(aryl)-2-bromoindenes was developed. The reaction of 2-bromo-3-*tert*-butylindene with MeMgI catalyzed by Ni(dppp)Cl_2 afforded 3-*tert*-butyl-2-methylindene from which bis(3-*tert*-butyl-2-methylinden-1-yl)methane and the corresponding *ansa*-zirconocene were synthesized.

Key words: indenes, zirconocenes, synthesis.

Bis(indenyl) *ansa*-zirconocenes are efficient catalysts of polymerization of α-olefins. Recently, *ansa*-metallocene **1** was prepared. This compound exhibited high activity in isotactic polymerization of propylene. The resulting polymer was characterized by a substantial degree of isotacticity; however, its molecular weight was low.[1]

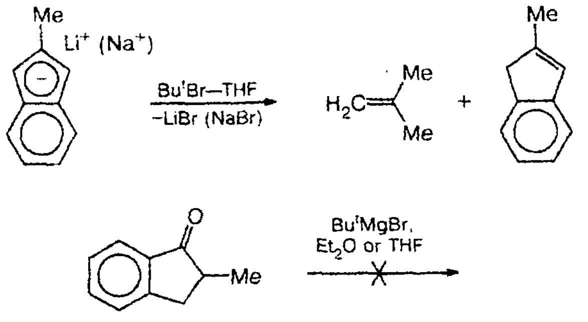
Previously,[2] it has been demonstrated that the introduction of the methyl group at position 2 of the indenyl fragment of *ansa*-zirconocene containing a short bridge (>SiMe_2 or —CH_2CH_2—) led to an increase in the molecular weight of the resulting polypropylene. In this connection, we performed the synthesis of the bis-3-*tert*-butyl-2-methylindenyl complex of Zr^{IV} containing the one-membered carbon bridge. This complex is the simplest analog of metallocene **1** containing the methyl group at position 2 of the indenyl ring.



1

The best studied approaches to substituted indenes involve either reactions of the corresponding indenides of alkali or alkaline-earth metals with alkyl halides or reactions of indanones with organomagnesium or organolithium compounds followed by dehydration of the resulting alcohols. However, we failed to synthesize 3-*tert*-butyl-2-methylindene according to these procedures (starting from either 2-methylindenide or 2-methylindan-1-one) (Scheme 1). In the first case, we observed only elimination of LiBr. In the second case, the product of addition of Bu^{t}MgBr was not detected either (according to the ^{1}H NMR spectral data, the reaction mixture contained only the starting 2-methylindan-1-one).

Scheme 1



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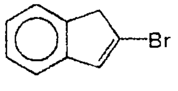
Previously, an alternative approach to the synthesis of 2-alkylindenes, which involves cross-coupling of 2-bromoindene with Grignard reagents catalyzed by [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride, Ni(dppp)Cl_2, was proposed, and 2-methyl-, 2-ethyl-, 2-*n*-propyl-, and 2-*n*-butylindenes were prepared according to this procedure.[3] Based on this approach, we attempted to synthesize 3-*tert*-butyl-2-methylindene by the reaction of 2-bromo-3-*tert*-butylindene with MeMgI.

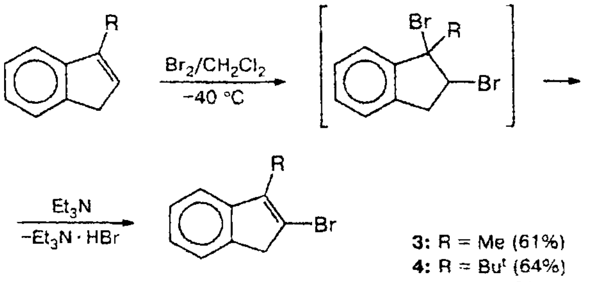
3-Alkyl-2-bromoindenes were previously unknown. When we started this investigation, only 2-bromoindene (**2**), which can be prepared by two routes, was described.[4,5] Bromination of indene in boiling tetralin, which was accompanied by elimination of HBr,[4] afforded product **2** in 13% yield. An alternative two-step procedure for the synthesis of compound **2** involves the reaction of indene with bromine water followed by dehydration of carbinol that formed. In this case, the total yield of 2-bromoindene was also low (55%).[5]



2

We performed bromination of 3-methyl-, 3-*tert*-butyl-, and 3-phenylindenes and found that the presence of a substituent at position 3 of indene leads to a substantial acceleration of dehydrobromination of the corresponding dibromo derivative. Thus in all three cases, spontaneous liberation of HBr was observed at –20 °C. In order to achieve the completeness of the reaction and to increase the yield of the target 2-bromoindenes, an equimolar amount of Et_3N was added to the reaction mixture at the stage of dehydrobromination. As a result, 2-bromoindenes **3—5** were obtained in satisfactory yields (Scheme 2).

Scheme 2



3—5

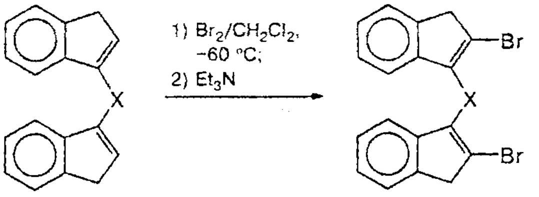
3: R = Me (61%)
4: R = Bu^t (64%)
5: R = Ph (72%)

Bromination/dehydrobromination of 3-substituted indenes proceeded so selectively that we succeeded in preparing also 2,2'-dibromo derivatives of bis(indenyl) compounds **6** and **7** under the same conditions (Scheme 3).

Compounds **3—7** are stable over several days and usually turn dark upon prolonged storage.

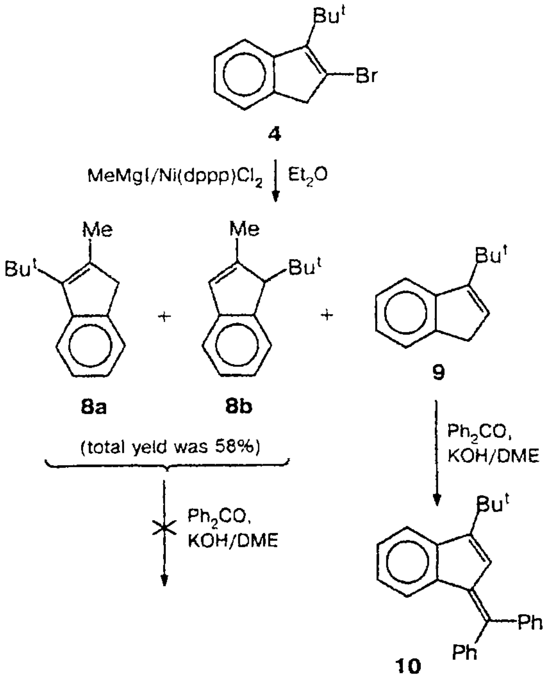
We found that compound **4** entered into the cross-coupling reaction with MeMgI under conditions reported previously.[3] However, compound **4**, unlike 2-bromoindene, reacted much more slowly to give a mixture consisting of two isomers (with respect to the position of the double bond) of the disubstituted indene (**8a** and **8b**) and 3-*tert*-butylindene (**9**) (Scheme 4), which is a debromination product of bromoindene **4**, in the ratio (**8a** + **8b**) : **9** = 2 : 1 (the ^1H NMR spectral data).

Scheme 3



6, 7

6: X = CMe_2 (82%)
7: X = CH_2CH_2 (59%)

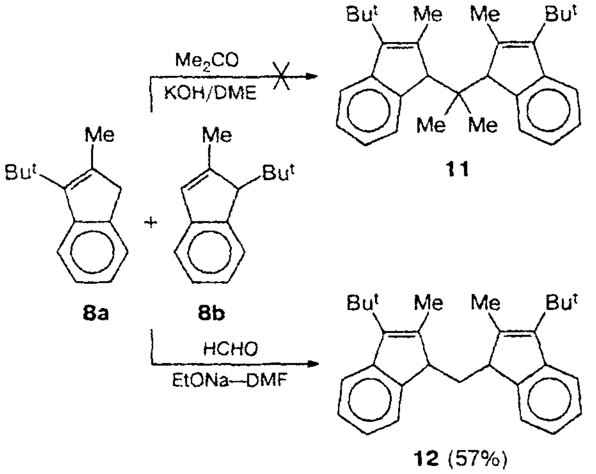


Scheme 4

Since the *physical* properties of compounds **8a,b** and **9** are similar, we attempted to separate these compounds based on the difference in their *chemical* properties. Taking into account the fact that the reactions of salts of 2-alkyl-substituted indenes with ketones proceed very slowly, we carried out the reaction of a mixture of compounds **8a,b** and **9** with benzophenone in the presence of a suspension of KOH in DME. As expected, the reaction of 3-*tert*-butylindene with Ph_2CO proceeded to completion yielding the corresponding fulvene **10**. Under the above-mentioned conditions, compounds **8a,b** did not react with benzophenone and were separated from fulvene **10** by distillation. Subsequently, we separated trace amounts of benzophenone, whose boiling point is close to those of compounds **8a,b**, by chromatography.

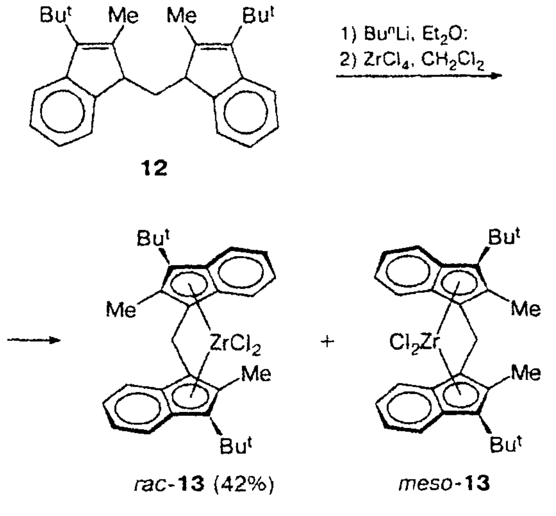
With the aim of linking molecules of 2,3-disubstituted indenes **8a,b** through the one-membered carbon bridge, we examined two approaches, *viz.*, the introduction of the 1-methylethylidene bridge (compound **11**) by the reaction of acetone with compounds **8a,b** in the presence of a suspension of KOH in DME[1,6] as well as the introduction of the methylene bridge (compound **12**) by the reaction of indenes **8a,b** with formaldehyde in the EtONa—DMF system[7] (Scheme 5). We found that bis(indenyl) compound **11** did not form even in trace amounts, whereas bis(indenyl) derivative **12** containing the methylene bridge was obtained in 57% yield.

Scheme 5



Treatment of compound **12** with *n*-butyllithium afforded the dilithium derivative. The reaction of the latter with $ZrCl_4$ in CH_2Cl_2 yielded the corresponding *ansa*-zirconocene **13** (Scheme 6).

Scheme 6



It should be noted that the diastereomeric forms of complex **13** can be readily separated. The pure racemic form of zirconocene **13** was isolated in 42% yield by single recrystallization from Et_2O.

To summarize, a series of 2-bromo-substituted indenes **3—5** as well as two bis-2,2′-dibromoindenyl compounds **6** and **7** were synthesized. Starting from 2-bromoindene **4**, a mixture of dialkyl-substituted indenes **8a,b** was prepared. Based on the latter, *ansa*-zirconocene **13** containing the methylene bridge was synthesized in high yield.

Experimental

All operations associated with the preparation of the lithium derivatives and zirconium complexes were carried out in sealed glass systems of the Schlenk vessel type. The ether solvents were kept and distilled successively over KOH and sodium benzophenone ketyl; CH_2Cl_2 was successively washed with water, concentrated H_2SO_4, and water until the reaction solution became neutral, dried over $CaCl_2$, and distilled over P_2O_5. Commercial DMF (Merck) was used without additional purification. The ^1H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Varian VXR-300 instruments. Elemental analysis of the organic compounds was carried out on an automated Carlo-Erba C,H-analyzer. We failed to obtain reliable data of elemental analysis for zirconocene, because the sample obtained after combustion contained impurities of zirconium carbide.

2-Bromo-3-methyl-1*H*-indene (3). Bromine (2.1 mL, 0.041 mol) was added dropwise with stirring to a solution of 3-methyl-1*H*-indene[8] (5.36 g, 0.041 mol) in CH_2Cl_2 (100 mL) cooled to −40 °C until decoloration of the reaction mixture ceased. Then cooling was discontinued and a solution of Et_3N (6 mL, 0.041 mol) in CH_2Cl_2 (10 mL) was added. The reaction mixture was allowed to warm to ~20 °C. Then the mixture was refluxed with stirring for 15 min and allowed to cool to ~20 °C with stirring for 15—20 min. The cooled reaction mixture was poured into a 10% H_3PO_4 solution (100 mL) and the organic phase was extracted with CH_2Cl_2 (2×80 mL). The combined organic phases were successively washed with water (3×100 mL), 10% H_3PO_4 (1×100 mL), and water (1×100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was distilled at the b.p. 165—168 °C (45 Torr). Compound **3** was obtained in a yield of 5.23 g (61%). ^1H NMR (30 °C, $CDCl_3$), δ: 2.13 (t, 3 H, CH_3, $J = 2.14$ Hz); 3.57 (q, 2 H, CH_2, $J = 2.1$ Hz); 7.16—7.38 (m, 4 H, H(Ar)).

2-Bromo-3-(*tert*-butyl)-1*H*-indene (4). By analogy with the procedure described for the synthesis of compound **3**, compound **4** was prepared from 3-(*tert*-butyl)-1*H*-indene[9] (15.15 g, 0.088 mol), Br_2 (4.48 mL, 0.088 mol), and Et_3N (12.2 mL, 0.088 mol) as a yellow labile liquid (b.p. 140—147 °C (10—12 Torr)) in a yield of 14.14 g (64%). ^1H NMR (25 °C, $CDCl_3$), δ: 1.54 (s, 9 H, $C(CH_3)_3$); 3.58 (s, 2 H, CH_2); 7.13 and 7.22 (both td, 1 H each, H(Ar), $J = 5.25$ Hz, $J' = 1.2$ Hz); 7.32 and 7.65 (both br.d, 1 H each, H(Ar), $J = 6$ Hz). Found (%): C, 62.20; H, 5.98. $C_{13}H_{15}Br$. Calculated (%): C, 62.17; H, 6.02.

2-Bromo-3-phenyl-1*H*-indene (5). By analogy with the procedure described for the synthesis of compound **3**, compound **5** was prepared from 3-phenyl-1*H*-indene[10] (2.1 g, 0.01 mol), Br_2 (0.5 mL, 0.01 mol), and Et_3N (2 mL, 0.01 mol). After column chromatography (silica gel 60, hexane as the eluent), compound **5** was obtained in a yield of 1.95 g (72%). ^1H NMR (25 °C, $CDCl_3$), δ: 3.75 (s, 2 H, CH_2); 7.01—7.48

(m. 9 H. H(Ar), H(Ph)). Found (%): C, 66.48; H, 4.11. $C_{15}H_{11}Br$. Calculated (%): C, 66.44; H, 4.09.

2,2-Bis(2-bromo-1*H*-inden-3-yl)propane (6). By analogy with the procedure described for the synthesis of compound **3**, compound **6** was prepared from 2,2-bis(1*H*-inden-3-yl)propane[6] (5 g, 0.0116 mol), Br_2 (1.2 mL, 0.023 mol), and Et_3N (5 mL, 0.023 mol). After recrystallization from toluene, compound **6** was obtained in a yield of 4.1 g (82%), m.p. 97 °C. ^1H NMR (25 °C, $CDCl_3$), δ: 2.10 (s, 6 H, CH_3); 3.52 (s, 4 H, CH_2); 7.11—7.42 (m, 8 H, H(Ar)). Found (%): C, 58.57; H, 4.26. $C_{21}H_{18}Br_2$. Calculated (%): C, 58.63; H, 4.22.

1,2-Bis(2-bromo-1*H*-inden-3-yl)ethane (7). By analogy with the procedure described for the synthesis of compound **6**, compound **7** was prepared from 1,2-bis(1*H*-inden-3-yl)ethane[11] (2.35 g, 0.0091 mol), Br_2 (0.93 mL, 0.018 mol), and Et_3N (3 mL, 0.018 mol) in a yield of 2.23 g (59%). ^1H NMR (25 °C, $CDCl_3$), δ: 2.83 (br.s, 4 H, CH_2CH_2); 3.52 (br.s, 4 H, CH_2 of the indenyl ring); 7.12—7.37 (m, 8 H, H(Ar)). Found (%): C, 57.69; H, 3.86. $C_{20}H_{16}Br_2$. Calculated (%): C, 57.72; H, 3.88.

3-(*tert*-Butyl)-2-methyl-1*H*-indene (8a) and 1-(*tert*-butyl)-2-methyl-1*H*-indene (8b). Ni(dppp)Cl_2 (Merck) (0.75 g) was added to a solution of MeMgI, which was prepared from Mg (3.74 g, 0.154 mol) and MeI (9.45 g, 0.15 mol) in Et_2O (100 mL), at ~20 °C. Then a solution of compound **4** (15.47 g, 0.062 mol) in Et_2O (50 mL) was added and the reaction mixture was refluxed for 5 h after which Ni(dppp)Cl_2 (0.5 g) was added with heating and the mixture was refluxed for 4 h. Then the reaction mixture was poured into 10% HCl (200 mL) and extracted with Et_2O (3×50 mL). The combined organic phases were washed with water (3×100 mL), dried over $MgSO_4$, and concentrated. The residue was distilled *in vacuo* with the use of a water-aspirator pump at the b.p. 100—125 °C (10—12 Torr). A mixture of compounds **8a,b** and 3-(*tert*-butyl)-1*H*-indene (**9**) (as a thick oil) was obtained in a yield of 9.8 g in a ratio (**8a** + **8b**) : **9** ≈ 2 : 1 (the ^1H NMR spectral data). The resulting mixture of indenes was added to a suspension of KOH (3.46 g, 0.062 mol) in DME (50 mL). The mixture was stirred at ~20 °C for 20 min and heated to boiling. Then Ph_2CO (11.2 g, 0.062 mol) was added and the reaction mixture was refluxed for 1 h, cooled to ~20 °C, and poured into an aqueous solution of NH_4Cl (150 mL). The resulting mixture was extracted with Et_2O (4×50 mL) and the combined organic phases were washed with water (2×80 mL), dried over $MgSO_4$, concentrated, and distilled *in vacuo*, the fraction with the b.p. 100—130 °C (10 Torr) being collected. A mixture of isomers (with respect to the position of the double bond) **8a** and **8b** was isolated from the residue by chromatography (silica gel 60, hexane as the eluent) as a light-yellow oil in a yield of 6.7 g (58%). ^1H NMR of the **8a** + **8b** mixture (~1 : 1) (25 °C, $CDCl_3$), δ: 1.10 and 1.51 (both s, 9 H each, $C(CH_3)_3$, **8a** + **8b**); 2.20 and 2.30 (both s, 3 H each, CH_3, **8a** + **8b**); 3.10 (br.s, 1 H, $-CH<$, **8b**); 3.30 (s, 2 H, CH_2, **8a**); 6.50 (br.s, 1 H, $=CH-$, **8b**); 7.04—7.65 (m, 8 H, H(Ar), **8a** + **8b**). Found (%): C, 90.21; H, 9.79. $C_{14}H_{18}$. Calculated (%): C, 90.26; H, 9.74.

Bis(3-*tert*-butyl-2-methyl-1*H*-inden-1-yl)methane (12). A solution of a mixture of compounds **8a** and **8b** (6 g, 0.032 mol) in DMF (20 mL) was added to a solution of EtONa (1.1 g, 0.016 mol) in DMF (40 mL) under an argon atmosphere at ~20 °C. The resulting mixture was degassed. The vessel was filled with argon, and a formaldehyde solution (1.2 mL of 37% aqueous HCHO solution, 0.016 mol) was rapidly added with slight heating. Then the reaction mixture was stirred upon heating on a water bath (80—85 °C) for 2 h. After completion of the reaction, the mixture was poured into a dilute solution of HCl (5%, 100 mL) and extracted with hexane (3×40 mL). The combined organic phases were washed with water, dried over $MgSO_4$, concentrated, and distilled *in vacuo* at the b.p. 180 °C (0.1 Torr). Bis(indenyl) compound **12** was isolated as a yellow oil in a yield of 3.51 g (57.1%). ^1H NMR (30 °C, $CDCl_3$), δ: 1.00 (s, 18 H, $C(CH_3)_3$); 2.12 (s, 6 H, CH_3); 3.08 (br.s, 2 H, CH_2); 3.62 (br.s, 2 H, CH); 6.98—7.44 (m, 8 H, H(Ar)). Found (%): C, 92.62; H, 7.38. $C_{17}H_{16}$. Calculated (%): C, 92.68; H, 7.32.

[μ-Methylenebis(η^5-3-*tert*-butyl-2-methyl-1*H*-inden-1-yl)]dichlorozirconium (13). A solution of Bu^{n}Li (Merck; 1.6 mol L^{-1}, 9.6 mL, 15.33 mmol, a 10% excess) was carefully added with stirring to a solution of compound **12** (2.68 g, 6.97 mmol) in Et_2O (20 mL) cooled to −40 °C, and the reaction mixture was stirred at 20 °C for 3 h resulting in the formation of a yellow precipitate. Then hexane (50 mL) was added to the reaction mixture. After 30 min, the solution was decanted from the precipitate. The precipitate was washed with Et_2O and dried *in vacuo*. The dilithium salt of compound **12** was obtained in a yield of 1.2 g (43%).

The resulting salt was added to a stirred suspension of $ZrCl_4$ (Merck; 0.7 g, 3.02 mmol) in CH_2Cl_2 (30 mL) cooled to −80 °C. The reaction mixture was stirred with cooling for 5 min and allowed to warm to ~20 °C. Then the mixture was stirred for ~24 h. The solution was decantated from the precipitate of LiCl. The solvent was removed *in vacuo* and the residue was recrystallized from Et_2O. The pure *rac* form of zirconocene **13** was obtained in a yield of 0.69 g (42%). After evaporation of the mother liquor followed by recrystallization from toluene, a mixture of the *rac* and *meso* forms of zirconocene **13** was isolated in a ratio of ~2 : 1 in a yield of 0.23 g (14%). ^1H NMR (30 °C, $CDCl_3$), δ, for *rac*-**13**: 1.45 (s, 18 H, $C(CH_3)_3$); 2.35 (s, 6 H, CH_3); 4.89 (s, 2 H, CH_2); 6.96—7.02, 7.22—7.28, 7.60—7.64, and 7.77—7.82 (all m, 8 H, H(Ar)); *meso*-**13**: 1.55 (s, 18 H, $C(CH_3)_3$); 2.50 (s, 6 H, CH_3); 4.98, 5.15 (AB system, 1 H each, CH_2, J_{AB} = 15 Hz); 6.72—6.78, 6.93—6.97, 7.58—7.68, and 7.72—7.76 (all m, 8 H, H(Ar)).

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