

Synthesis of 2-methylbenz[*f*]indene and (η^5 -2-methylbenz[*f*]indenyl)rhodium dicarbonyl¹

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Abstract

The compound 2-methylbenz[*f*]indene (**8**) was synthesized by modification of the procedure used to synthesize benz[*f*]indene (**1**). Attempts to form Group 4 metal complexes of **8** were unsuccessful giving similar results to those obtained when attempting to metallate **1**. The complex (η^5 -2-methylbenz[*f*]indenyl)rhodium dicarbonyl was synthesized by the reaction of **8** with butyllithium and subsequent reaction with [RhCl(CO)₂]₂ in a 41% yield. © 1998 Elsevier Science S.A. All rights reserved.

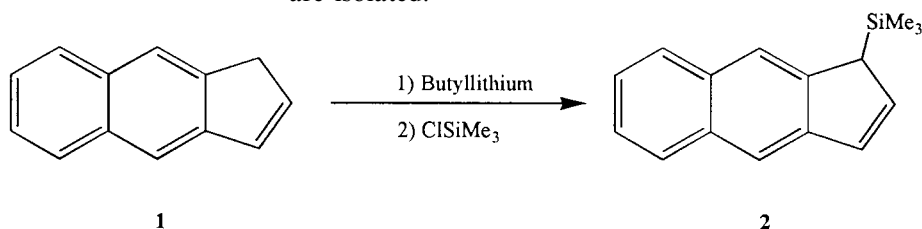
Keywords: Benz[*f*]indene; Dicarbonyl; Butyllithium; Rhodium

1. Introduction

Since the discovery that bridged metallocenes were effective catalysts for the stereoregular polymerization of propylene when activated by methylaluminoxane (MAO) [1,2], an enormous amount of research has been performed in order to synthesize new pentahapto ligands which can improve the catalytic properties of the corresponding ansa-metallocene [3,4]. There appears to be two important components to incorporate when synthesizing a new indenyl pentahapto ligand. First, a methyl substituent at the C-2 position of the indenyl ligand is important for controlling the molecular weight

of the resulting polymer [5]. Secondly, an annulated benzo ring has been found to increase both the stereoselectivity and productivity of the catalytic system [3,4].

Recently, we have reported the attempted synthesis of metal complexes of benz[*f*]indene (**1**) [6]. In our hands, we were unable to form Group 4 metal derivatives of **1** using conventional metallation routes. Deprotonation of **1** using butyllithium followed by addition of chlorotrimethylsilane produced the desired trimethylsilyl derivative **2**. The success of this reaction shows that **1** is readily deprotonated using a strong base, however, when attempts are made to react this anion with Group 4 metal halides no desired products are isolated.



In this work, we report the synthesis of an alkyl derivative of **1** which incorporates the alkyl group at the desired C-2 position of the ligand. In addition to attempts at making Group 4 metal complexes, a late transition complex was synthesized.

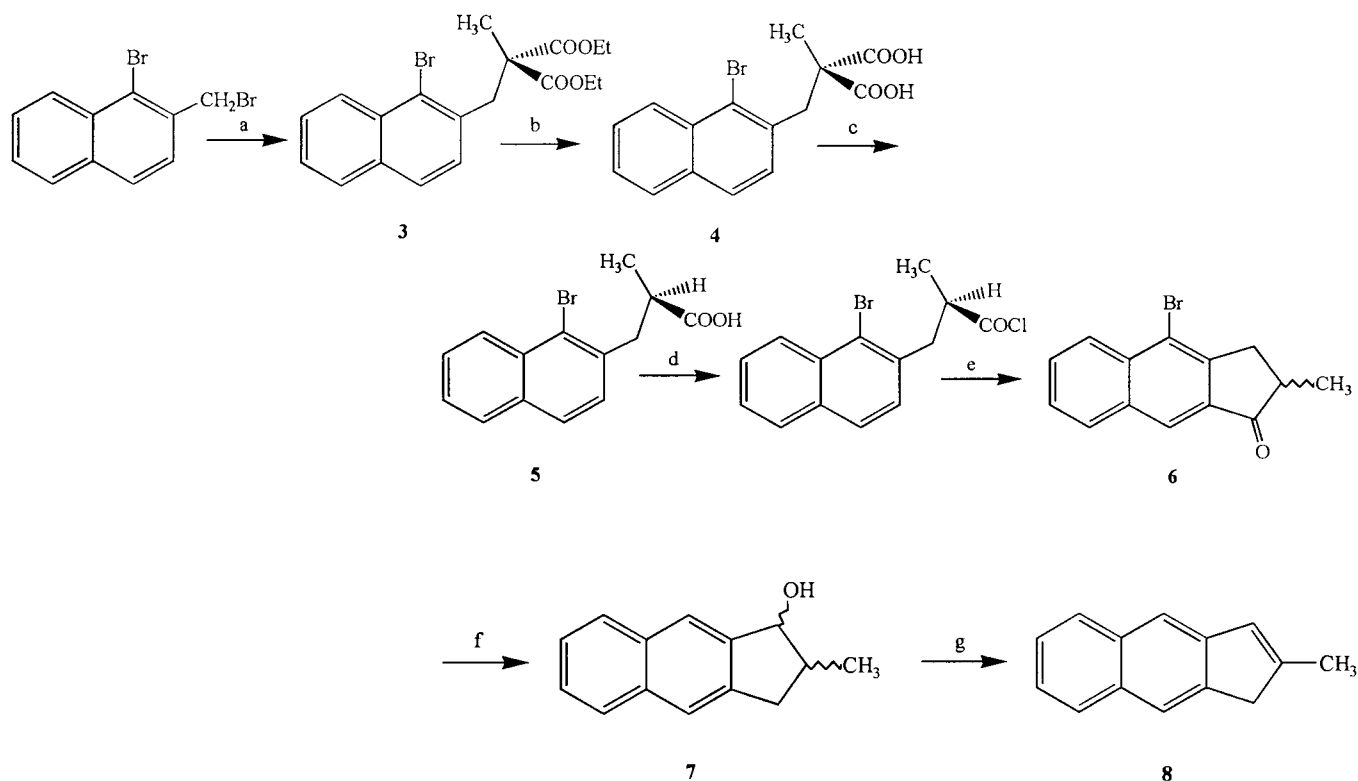
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¹ Dedicated to Professor Nakamura, on the occasion of his retirement from Osaka University and in recognition of his many outstanding contributions to organometallic chemistry.

2. Results and discussion

2.1. Synthesis of 2-methylbenz[*f*]indene

In order to synthesize the desired 2-alkyl derivative of **1**, a modified procedure to that used for **1** was employed. The starting material 1-bromo-2-bromomethylnaphthalene was prepared using the procedure of Carpino et al. [7], and reacted with a diethyl methylmalonate anion to give diethyl 2-[(1-bromo-2-naphthyl)methyl] methylmalonate (**3**) in a 65% yield. Compound **3** was saponified with NaOH in methanol which gave 2-[(1-bromo-2-naphthyl)methyl]methylmalonic acid (**4**) in a 51% yield. The diacid **4** was then decarboxylated by heating to its melting point to give 2-methyl-3-(1-bromo-2-naphthyl)propionic acid (**5**) in a 76% yield. Subsequent reaction of compound **5** with SOCl₂ followed by reaction with AlCl₃ gave 2-methyl-4-bromobenz[*f*]indan-1-one (**6**) in a 65% yield.

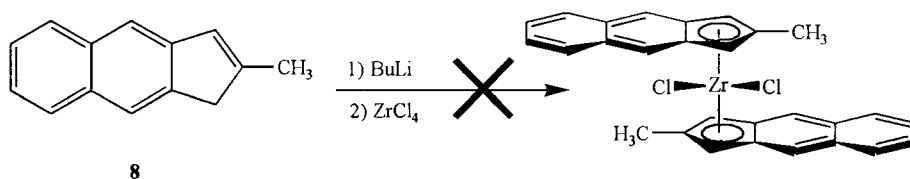


Legend: (a) NaOEt, diethyl methylmalonate, EtOH, 65%. (b) NaOH, MeOH, 51%. (c) heat to melting point, 76%. (d) SOCl₂, CH₂Cl₂. (e) AlCl₃, CH₂Cl₂, 65%. (f) LAH, CeCl₃, THF, 82%. (g) oxalic acid, toluene, 87%.

The ketone **6** was then reduced with a mixture of CeCl₃ and LAH which reduced both the ketone group and the aromatic halide giving 2-methylbenz[*f*]indan-1-ol (**7**) in an 82% yield. Finally, reaction of compound **7** with oxalic acid gave the desired product, 2-methylbenz[*f*]indene (**8**), in an 87% yield. The overall yield of compound **8** from the starting material was 12%.

2.2. Attempted synthesis of Group 4 metal complexes

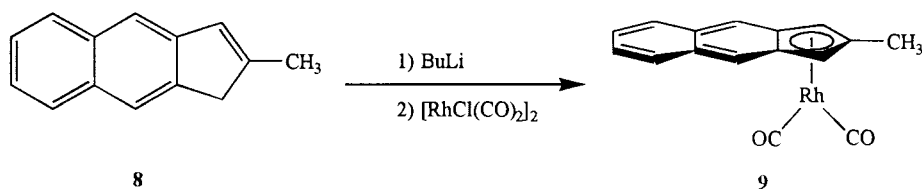
Since attempts to prepare titanium complexes of the unsubstituted benz[*f*]indene (**1**) were unsuccessful, zirconium, a metal with a larger atomic radius, was used in an attempt to produce a more stable organometallic species with 2-methylbenz[*f*]indene (**8**). However, several synthetic attempts to prepare the zirconocene dichloride complex of compound **8** did not yield the desired product. Deprotonation of compound **8** with butyllithium proceeded as expected, giving a deep red solution



indicative of the corresponding anion. However, reaction of the anionic solution with ZrCl₄ at low temperature in either diethyl ether or toluene gave an orange solution which decomposed rapidly at room temperature (r.t.), resulting in a pale yellow solution and a white precipitate.

2.3. Synthesis of rhodium complex

Since attempts to prepare Group 4 organometallic complexes of **8** were unsuccessful, a rhodium dicarbonyl complex was prepared. Reaction of compound **8** with butyllithium followed by reaction with $[\text{RhCl}(\text{CO})_2]_2$ gave (η^5 -2-methylbenz[*f*]indenyl)-rhodium dicarbonyl (**9**) as red–orange crystals in a 41% yield. The symmetric structure of the ligand system was observed in the $^1\text{H-NMR}$ spectrum of **9**, which exhibited a methyl resonance at 2.33 ppm, a singlet at 5.88 ppm for the two equivalent C_5 protons, and an AA' and BB' set of multiplets at 7.85–7.70 and at 7.33–7.28 ppm for the aromatic benzo ring protons.



mixture was refluxed overnight, the ethanol was removed until 200 ml of ethanol was collected. The remaining mixture was dissolved in 400 ml of CH_2Cl_2 and washed with 350 ml of H_2O . The aqueous layer was extracted with CH_2Cl_2 (2×100 ml) and the combined organic layers were washed with H_2O (3×100 ml). The organic layer was dried with MgSO_4 , filtered, and the solvent removed. Vacuum distillation (165 – $170^\circ\text{C}/0.01$ mmHg) of the residue gave **3** (108.0 g, 65%) as a yellow liquid. $^1\text{H-NMR}$ (CDCl_3): δ 8.49–8.25 (m, 1H, arom H); 7.64–7.25 (m, 5H, arom H); 4.28 (q, 4H, OCH_2); 3.79 (s, 2H, Ar-CH_2); 1.41 (s, 3H, CH_3); 1.25 (t, 6H, $\text{OCH}_2\text{-CH}_3$).

Anal. Found: C, 57.91; H, 5.36. $\text{C}_{19}\text{H}_{21}\text{BrO}_4$. Calc.: C, 58.03; H, 5.38%.

3. Experimental section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. The argon was purified by deoxygenating with a BTS catalyst and drying with molecular sieves, calcium chloride, and P_2O_5 . THF was predried over sodium wire, distilled from sodium under argon, and finally distilled from a Na/K alloy under argon. Diethyl ether was predried over sodium wire and distilled from a Na/K alloy under argon. Toluene, hexane, and pentane were distilled from a Na/K alloy under argon. Methylene chloride was distilled under argon from calcium hydride.

All reagents were purchased from Aldrich and were used without further purification. Celite was purchased from Fisher Scientific and used without pretreatment.

$^1\text{H-NMR}$ spectra were recorded on a Varian XL-200 spectrometer with TMS as an internal standard. $^{13}\text{C-NMR}$ spectra were recorded on a Bruker MSL-300 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

3.1. Diethyl

2-[(1-bromo-2-naphthyl)methyl]methylmalonate (**3**)

To a solution of NaOEt, prepared from sodium metal (9.66 g, 0.42 mol) and 210 ml of 100% ethanol, was added diethyl methylmalonate (73.16 g, 0.42 mol) and the solution was refluxed for 2 h. The heating was removed, and 1-bromo-2-bromomethylnaphthalene (126 g, 0.42 mol), prepared using the procedure of Carpino et al. [7], was added slowly. After the reaction

3.2. 2-[(1-Bromo-2-naphthyl)methyl]methylmalonic acid (**4**)

To a solution of **3** (165.96 g, 0.42 mol) in 250 ml of methanol was added 500 ml of 5 M NaOH. The mixture was refluxed for 2 h, after which the methanol was removed by distillation. The aqueous solution was acidified to pH = 1 and the precipitate was filtered and dried in vacuo. The crude diacid was recrystallized from H_2O to give **4** (72.3 g, 51%) as a white solid. $^1\text{H-NMR}$ (acetone- d_6): δ 8.34 (d, 1H, arom H); 7.94–7.47 (m, 5H, arom H); 3.77 (s, 2H, Ar-CH_2); 1.39 (s, 3H, CH_3).

3.3. 2-Methyl-3-(1-bromo-2-naphthyl)propionic acid (**5**)

Complex **4** (60.0 g, 0.18 mol) was placed in a 500 ml round bottom flask and heated until the solid melted and the evolution of CO_2 was evident. Heating was continued until no further gas evolution was noticeable. The flask was cooled to r.t. and the residue was dissolved in 500 ml of CH_2Cl_2 . The organic layer was washed with water (2×100 ml) and dried with MgSO_4 . Following filtration, the solvent was removed and the crude acid was recrystallized from ethanol to give **5** (40.1 g, 76%) as a white solid, m.p. 129 – 130°C . $^1\text{H-NMR}$ (CDCl_3): δ 8.33 (d, 1H, arom H); 7.81–7.69 (m, 2H, arom H); 7.62–7.48 (m, 2H, arom H); 7.36 (d, 1H, arom H); 3.45–3.30 (m, 1H, CH); 3.14–3.01 (m, 2H, CH_2); 1.25 (d, 3H, CH_3). Anal. Found: C, 57.26; H, 4.26. $\text{C}_{14}\text{H}_{13}\text{BrO}_2$. Calc.: C, 57.36; H, 4.47%.

3.4. 2-Methyl-4-bromobenz[*f*]indan-1-one (**6**)

To a solution of **5** (31.62 g, 0.11 mol) in 500 ml of

CH_2Cl_2 was slowly added SOCl_2 (25.66 g, 0.22 mol) and the mixture was refluxed for 5 h. The solvent was removed using a rotary evaporator, and the residue was washed with CH_2Cl_2 and dried in vacuo. The crude acid chloride was used without further purification.

The crude acid chloride was dissolved in 600 ml of CH_2Cl_2 and the solution was cooled to 0°C . A sample of AlCl_3 (21.60 g, 0.16 mol) was added in small portions and the mixture was refluxed for 3 h. After cooling to r.t., the reaction mixture was stirred overnight. The mixture was cooled to 0°C , and a mixture of 500 ml of H_2O and 60 ml of HCl was slowly added. The suspension was filtered and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×100 ml) and the combined organic layers were washed with H_2O (2×100 ml). The organic layer was dried with MgSO_4 , filtered, and the solvent removed. Recrystallization of the residue from ethanol gave **6** (19.73 g, 65%) as yellow needles, m.p. 125 – 126°C . $^1\text{H-NMR}$ (CDCl_3): δ 8.32–8.27 (m, 1H, arom H); 8.01–7.75 (m, 2H, arom H); 7.71–7.56 (m, 2H, arom H); 3.64–3.49 (m, 1H, CH); 2.91–2.80 (m, 2H, CH_2); 1.41 (d, 3H, CH_3). Anal. Found: C, 61.62; H, 4.00. $\text{C}_{14}\text{H}_{11}\text{BrO}$. Calc.: C, 61.11; H, 4.03%.

3.5. 2-Methylbenzyljindan-1-ol (**7**)

A solution of CeCl_3 (11.8 g, 48 mmol) in 100 ml of dry THF was stirred for 1 h. A solution of **6** (8.7 g, 32 mmol) in 50 ml of dry THF was added, followed by the slow addition of LiAlH_4 (8.0 g, 0.21 mol) in 50 ml of dry THF. The mixture was refluxed for 18 h. The reaction mixture was cooled in an ice bath and quenched by the slow addition of 10 ml of H_2O , 10 ml of 15% aqueous NaOH , and finally an additional 30 ml of H_2O . The resulting suspension was filtered, and the solution was dried with MgSO_4 . After filtration, the solvent was evaporated to give **7** (5.2 g, 82%) as a light yellow solid. The crude alcohol was dehydrated without further purification.

3.6. 2-Methylbenzyljindene (**8**)

To a solution of **7** (5.0 g, 25 mmol) in 300 ml of toluene was added 10 g of oxalic acid and the mixture was refluxed for 3 h while the water produced was separated using a Dean–Stark trap. The reaction mixture was cooled to r.t., and the excess oxalic acid was neutralized by the slow addition of 200 ml of saturated aqueous NaHCO_3 . The organic layer was separated and the aqueous layer was extracted with an additional 100

ml of toluene. The combined organic layers were dried with MgSO_4 , filtered, and the solvent was removed. The residue was chromatographed over silica gel (elution with pentane) to give **8** as a white solid. The solid was then vacuum sublimed ($97^\circ\text{C}/0.01$ mmHg) to give **8** (3.91 g, 87%) as white crystals, m.p. 137 – 139°C . $^1\text{H-NMR}$ (CDCl_3): δ 7.84–7.77 (br m, 3H, arom H); 7.61 (s, 1H, arom H); 7.42–7.37 (m, 2H, arom H); 6.60 (br s, 1H, $\text{C}_5\text{-sp}^2$); 3.44 (s, 2H, $\text{C}_5\text{-sp}^3$); 2.21 (s, 3H, CH_3). Anal. Found: C, 93.28; H, 6.83. $\text{C}_{14}\text{H}_{12}$. Calc.: C, 93.29; H, 6.71%.

3.7. (η^5 -2-Methylbenzyljindenyl)rhodium dicarbonyl (**9**)

A solution of **8** (1.0 g, 5.6 mmol) in 35 ml of THF was cooled to 0°C and 1.6 M butyllithium in hexane (3.50 ml, 5.6 mmol) was slowly added. The reaction mixture was warmed to r.t. and stirred for 4 h. The solution was cooled to 0°C and $[\text{RhCl}(\text{CO})_2]_2$ (0.80 g, 2.8 mmol) was added. The solution was warmed to r.t. and stirred overnight. The solvent was removed and the residue was extracted with 30 ml of pentane. Following filtration, the solution was concentrated to half its original volume. Cooling to -20°C gave **9** (0.78 g, 41%) as red–orange crystals. $^1\text{H-NMR}$ (CDCl_3): δ 7.75–7.70 (m, 2H, arom H); 7.47 (s, 2H, arom H); 7.33–7.28 (m, 2H, arom H); 5.88 (s, 2H, $\text{C}_5\text{-H}$); 2.33 (s, 3H, CH_3). IR (CH_2Cl_2), $\nu(\text{CO})$: 2040 (s), 1970 (s) cm^{-1} . Anal. Found: C, 57.20; H, 3.59. $\text{C}_{16}\text{H}_{11}\text{O}_2\text{Rh}$. Calc.: C, 56.83; H, 3.28%.

Acknowledgements

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