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LETTERS

Indenyl esters as potential electronically modified cyclopentadienyl ligands for transition metal complexes

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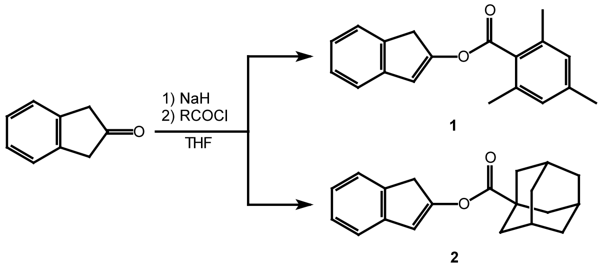
Abstract—The preparation of two new indenyl esters 2-(2,4,6-trimethylbenzoyloxy)indene (**1**) and 2-(adamantanoyloxy)indene (**2**) is reported. Both compounds can be deprotonated with alkyllithiums such as *n*-BuLi and the resulting anions trapped by addition of TMSCl or iodomethane, rendering them as potential electronically modified cyclopentadienyl ligand analogues for complexation with transition metals. © 2002 Elsevier Science Ltd. All rights reserved.

Substituted indenes function as versatile ligand precursors for a variety of transition metal complexes.[1] In particular, bridged and unbridged group 4 bis(indenyl) metallocenes have gained attention as stoichiometric reagents or catalyst precursors for enantioselective organic transformations[2] and catalytic olefin polymerization.[3] The catalytic performance of these complexes is determined by steric and electronic effects induced by the ancillary ligand substituents. Although synthetic methods for preparing 1- (or 3-) and 2-alkyl/aryl substituted indenyl ligand precursors are well established,[4,5] the preparation of heteroatom functionalized indenes has remained relatively unexplored.[6–9] We were interested in studying the applicability of indenyl esters as potential electronically modified cyclopentadienyl ligands for transition metal complexes. Herein we report the simple preparation and spectroscopic characterization of two new -OCOR ester substituted indenes, 2-(2,4,6-trimethylbenzoyloxy)indene (**1**) and 2-(adamantanoyloxy)indene (**2**). Both compounds can be successfully deprotonated with alkyllithiums to generate the corresponding indenyl anions.

Only a few examples of 2-indenyl esters have been described in the literature. 2-(Benzoyloxy)indene has been prepared by reaction of 2-indanone with iodobenzene in the presence of CO (40–45 atm), Et_3N and $Cl_2Pd(PPh_3)_2$ in DMF.[10] 2-(Acetoxy)indene has been obtained by reaction of 2-indanone with isopropenyl acetate[11] and as a low yield byproduct of manganese(III) mediated γ-lactone annulation of indene.[12] In addition, Gibson et al. have reported the preparation of the arenetricarbonylchromium(0) complex of 2-(acetoxy)indene by deprotonation of tricarbonyl(indan-2-one) with LDA followed by quenching with acetic anhydride.[13] Based on the available reactivity data,[14] we did not expect these esters to be stable under standard deprotonation conditions. Thus, sterically more hindered indenyl esters were chosen as targets for the present study.

Synthesis of the mesitoyl and adamantanoyl esters **1** and **2** are presented in Scheme 1. Reaction of 2-indanone with an equimolar amount of NaH in THF generated the corresponding enolate ion[15] that was cooled to −80°C and reacted with 2,4,6-trimethylbenzoic acid chloride (obtained by chlorination of 2,4,6-trimethylbenzoic acid with $SOCl_2$) and adamantane-1-carboxylic acid chloride (Aldrich), respectively. The reaction mixture was slowly warmed up to room temperature, quenched by addition of saturated aqueous ammonium chloride, washed with water and dried over sodium sulphate. Evaporation of the solvent and subsequent crystallization from Et_2O



Scheme 1. Synthesis of the indenyl esters **1** and **2**.

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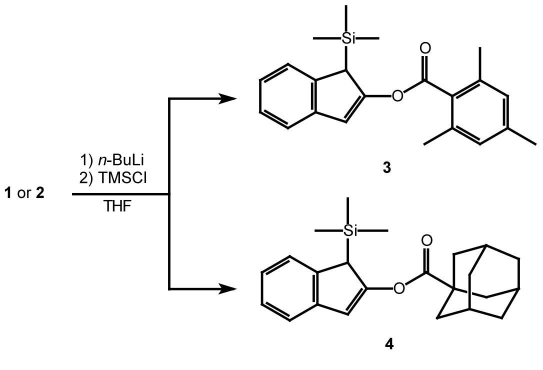
provided **1** and **2** in 57% and 50% isolated yields, respectively.[16,17]

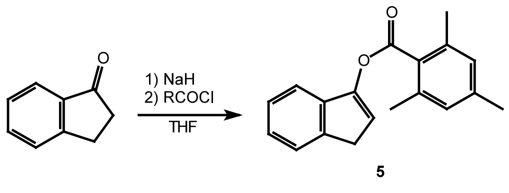
Various conditions were examined for the deprotonation of the new indenyl esters. In a typical experiment, **1** (1.04 g, 3.75 mmol) or **2** (1.10 g, 3.75 mmol) was dissolved in THF and reacted with an equimolar amount of *n*-BuLi (2.5 M solution in hexanes) at −80°C to generate the corresponding indenyllithium salts. Stirring for 5 minutes and subsequent quenching with TMSCl gave after work-up and crystallization from pentane the trimethylsilyl derivatives **3** and **4** in isolated yields of 69% and 44%, respectively (Scheme 2).[18,19] ^{1}H NMR analyses of the crude products were in both cases consistent with 85–90% conversions of **1** and **2** to the trimethylsilyl adducts. Alternatively, the indenyl anions could be trapped by addition of iodomethane and the corresponding 1- (3-) methyl derivatives identified by GC/MS analysis.

The analogous method can be applied to the synthesis of 3-indenyl esters as well.[20] Thus, reaction of 1-indanone with NaH in THF followed by subsequent addition of 2,4,6-trimethylbenzoic acid chloride at −80°C gave, after work-up and distillation, 3-(2,4,6-trimethylbenzoyloxy)indene (**5**) in 53% yield (Scheme 3).[21] Compound **5** was likewise successfully deprotonated in THF solution at −80°C using *n*-BuLi or *tert*-BuLi. Quenching with TMSCl gave the trimethylsilyl derivative as identified by GC/MS analysis. Other promising deprotonation conditions for the 2-substituted esters include NaH/THF/ambient temperature and *n*-BuLi/DMF/−80°C.

In summary, we have demonstrated the compatibility of sterically congested ester substituents with indenyl derived anions. These new ligand precursors are available in good yields from commercial starting materials.



Scheme 2. Synthesis of the trimethylsilyl derivatives **3** and **4**.



Scheme 3. Synthesis of the indenyl ester **5**.

As shown in previous reports, electronic modifications of bis(cyclopentadienyl)[22] and bis(indenyl) metallocenes may significantly influence their catalytic performance in various applications, including olefin polymerization.[8d,23] Compounds **1**–**5** may thus prove to be interesting ligand candidates for structural tailoring of transition metal as well as alkali metal[20] cyclopentadienyl complexes.

Acknowledgements

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16. **Compound 1**: 9.20 g (57.5%) of light yellow crystals. Anal. calcd for $C_{19}H_{18}O_2$ (278.4): C, 81.99; H, 6.52. Found: C, 82.24; H, 6.68. EIMS calcd/found: 278.1307/278.1309. ^{1}H NMR ($CDCl_3$, δ): 7.37–7.31(m, 2H, CH); 7.28–7.24 (m, 1H, CH); 7.18–7.14 (m, 1H, CH); 6.90 (s, 2H, CH); 6.78 (m, long range couplings, 1H, CH); 3.67 (m, long range couplings, 2H, CH_2); 2.39 (s, 6H, CH_3); 2.30 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 166.97 (C=O); 155.67 (C-O); 142.87 (C_q); 140.15 (C_q); 137.15 (C_q); 135.81 (2C, C_q); 129.72 (C_q); 128.69 (2C, CH); 126.75 (CH); 124.47 (CH); 123.44 (CH); 121.05 (CH); 115.04 (CH); 37.95 (CH_2); 21.18 (CH_3); 20.03 (2C, CH_3).
17. **Compound 2**: 14.7 g (50%) of white crystals. Anal. calcd for $C_{20}H_{22}O_2$ (294.4): C, 81.60; H, 7.53. Found: C, 82.01; H, 7.52. EIMS calcd/found: 294.1620/294.1616. ^{1}H NMR ($CDCl_3$, δ): 7.34–7.31 (m, 1H, CH); 7.29–7.20 (m, 2H, CH); 7.14–7.10 (m, 1H, CH); 6.58 (m, long range couplings, 1H, CH); 3.55 (m, long range couplings, 2H, CH_2); 2.08–2.06 (m br., 3H, adam.); 2.01–2.00 (m, 6H, adam.); 1.80–1.71 (m br., 6H, adam.). ^{13}C NMR ($CDCl_3$, δ): 174.91 (C=O); 156.20 (C-O); 143.04 (C_q); 137.24 (C_q); 126.57 (CH); 124.14 (CH); 123.32 (CH); 120.79 (CH); 114.53 (CH); 41.21 (C_q, adam.); 38.65 (3C, CH_2, adam.); 37.78 (CH_2); 36.38 (3C, CH_2, adam.); 27.84 (3C, CH_2, adam.).
18. **Compound 3**: 0.91 g (69%) of an off-yellow solid. Anal. calcd for $C_{22}H_{26}O_2Si$ (350.5): C, 75.38; H, 7.48. Found: C, 75.78; H, 7.63. EIMS calcd/found: 350.1702/350.1704. ^{1}H NMR ($CDCl_3$, δ): 7.28–7.26 (m, 1H, CH); 7.22–7.19 (m, 1H, CH); 7.13–7.09 (m, 1H, CH); 7.04–7.00 (m, 1H, CH); 6.79 (overlapping singlets, 3H, CH); 3.55 (m, 1H, CH); 2.28 (s, 6H, CH_3); 2.19 (s, 3H, CH_3); −0.12 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, δ): 167.11 (C=O); 157.61 (C-O); 142.24 (C_q); 139.89 (C_q); 138.72 (C_q); 135.63 (2C, C_q); 130.00 (C_q); 128.67 (2C, CH); 125.25 (CH); 123.34 (CH); 122.65 (CH); 121.00 (CH); 112.41 (CH); 44.19 (CH); 21.18 (CH_3); 20.07 (2C, CH_3); −2.60 (3C, $Si(CH_3)_3$).
19. **Compound 4**: 0.61 g (44%) of an off-yellow solid. Anal. calcd for $C_{23}H_{30}O_2Si$ (366.6): C, 75.36; H, 8.25. Found: C, 75.22; H, 8.27. EIMS calcd/found: 366.2015/366.2013. ^{1}H NMR ($CDCl_3$, δ): 7.32–7.27 (m, 2H, CH); 7.20–7.16 (m, 1H, CH); 7.12–7.08 (m, 1H, CH); 6.63 (d, $^{4}J = 0.7$ Hz, 1H, CH); 3.63 (m, 1H, CH); 2.07–2.05 (m br., 3H, adam.); 2.04–2.00 (m, 6H, adam.); 1.79–1.70 (m br., 6H, adam.); 0.01 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$, δ): 175.00 (C=O); 158.19 (C-O); 142.14 (C_q); 139.07 (C_q); 125.07 (CH); 123.08 (CH); 122.52 (CH); 120.74 (CH); 112.45 (CH); 44.07 (CH); 41.22 (C_q, adam.); 38.77 (3C, CH_2, adam.); 36.39 (3C, CH_2, adam.); 27.87 (3C, CH, adam.); −2.37 (3C, $Si(CH_3)_3$).
20. Preparation of 3-(*N*,*N*-diisopropylcarbamoyloxy)indene from 1-indanone and *N*,*N*-diisopropylcarbamoyl chloride in pyridine has been reported previously, see: Heinl, T.; Retzow, S.; Hoppe, D.; Fraenkel, G.; Chow, A. *Chem. Eur. J.* **1999**, *5*, 3464–3470. This compound was successfully deprotonated with *n*-BuLi in the presence of (−)-sparteine followed by addition of iodomethane or TMSCl to produce the corresponding Me or TMS-substituted derivatives.
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