

Synthesis and reactivity of tricarbonyl(indan-2-one)chromium(0)

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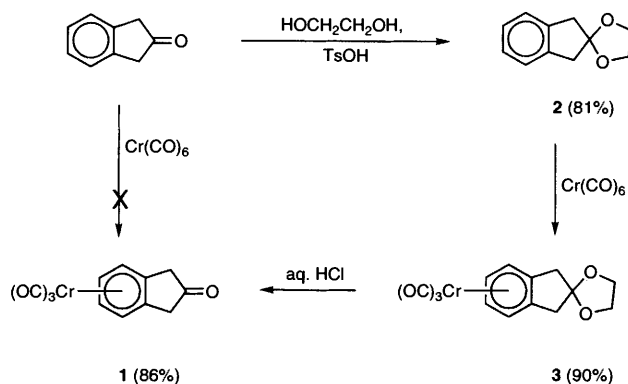
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Stable crystalline tricarbonyl(indan-2-one)chromium(0) **1** has been synthesised from relatively unstable indan-2-one by ketone protection, chromium complexation and ketone deprotection; addition of non-basic nucleophiles to the ketone of **1** and deprotonation/alkylation procedures proceed efficiently and stereoselectively to give good yields of diastereoisomerically pure products.

As part of an ongoing project concerned with the desymmetrisation of organometallic complexes, we recently required a sample of tricarbonyl(indan-2-one)chromium(0) **1**. Since tricarbonyl(indan-1-one)chromium(0) has been known for over 30 years and its chemistry explored in some depth,[†] we were somewhat surprised to find that the corresponding indan-2-one complex had not been synthesised earlier. In view of the instability of indan-2-one⁶ and the high levels of stereocontrol normally observed in the reactions of (arene)tricarbonylchromium(0) complexes,⁷⁻⁹ we envisage that tricarbonyl(indan-2-one)chromium(0) **1** will prove to be a very useful synthetic building block. Herein we communicate a straightforward multigram synthesis of complex **1** together with a preliminary survey of its fundamental reactivity.

Attempted syntheses of compound **1** by direct complexation reactions between indan-2-one and hexacarbonylchromium(0) under several sets of reaction conditions were unsuccessful. These failures offered a possible explanation for the absence of complex **1** from the literature and prompted us to take an indirect route to it. Thus indan-2-one was initially converted into its ketal **2** [(CH₂OH)₂, TsOH, C₆H₆, 78 °C, 6 h]. (The known instability of indan-2-one⁶ is worthy of comment at this point. Crystallisation of commercial samples of indan-2-one from different sources which varied in colour from brown to green gave white needles, which when exposed to air at room temperature for 2 days became a brown oil. Although formation of the ketal **2** was carried out under nitrogen in order to minimise side reactions, the product mixture still became very dark green and the optimised yield of 81% for this transformation is lower than normally expected for ketal formation.) The ketal **2** reacted smoothly with hexacarbonylchromium(0) [Cr(CO)₆, Bu₂O-THF (10:1), 145 °C, 30 h] to give the novel‡ tricarbonylchromium(0) complex **3** (90%), the ketone of which was deprotected with hydrochloric acid [6 mol dm⁻³ aq. HCl-acetone (1:2), 50 °C, 2 h] to afford complex **1** (86%) as a yellow crystalline solid. In contrast to indan-2-one, this showed no visible signs of decomposition when exposed to air at room temperature for 7 days, and is stable indefinitely



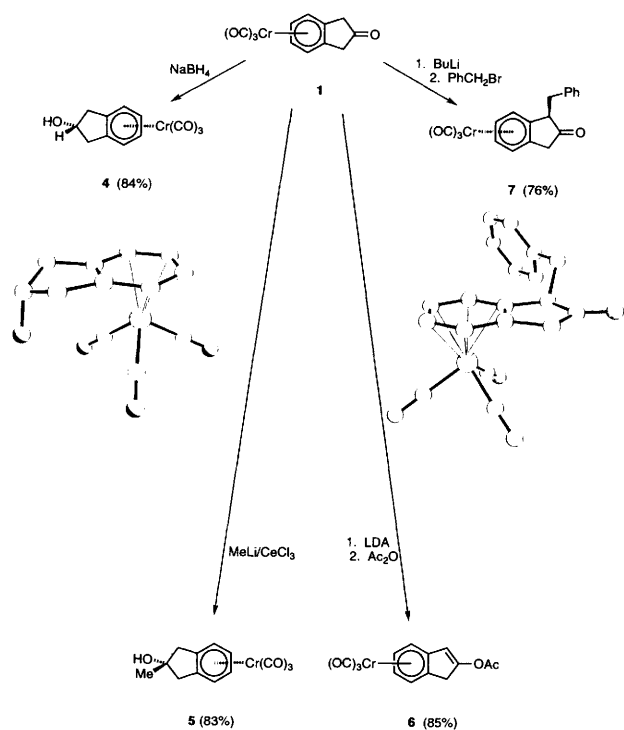
when stored under nitrogen; the route described is amenable to multi-gram syntheses of **1**.

A preliminary survey of the reactivity of complex **1** has been performed. The viability and stereoselectivity of nucleophilic addition to the ketone of **1** was probed first. Although hydride and Grignard additions to tricarbonyl(indan-1-one)chromium(0) have been shown to occur exclusively on the *exo* face of the complex,^{1,2} such high levels of stereoselectivity for addition to the ketone of complex **1**, more remote from the steric effects of the tricarbonylchromium(0) rotor, could not be assumed. It was thus pleasing to find that addition of sodium borohydride to complex **1** (NaBH₄, MeOH, 0 °C, 1 h) gave only one diastereoisomer in the crude product mixture ($\geq 98\%$ de by 270 MHz ¹H NMR spectroscopy). The known alcohol complex **4**¹⁰ was isolated diastereoisomerically pure in 84% yield and nucleophilic addition from the *exo* face was confirmed by an X-ray crystallographic analysis of **4**.§ In contrast, addition of Grignard and alkyllithium reagents to **1** were less than smooth, giving alcohol complexes in very low conversions and yields. The problems encountered with these additions were ascribed to the high acidity of the aliphatic hydrogens in **1** which are rendered acidic not only by the ketone but also by the tricarbonylchromium(0) moiety.⁷ Thus, organocerium reagents, known for their low basicity and high oxophilicity,¹¹ were enlisted. Reaction of complex **1** with the organocerium reagent derived from methyl lithium and anhydrous cerium chloride [MeLi:CeCl₃ (1.5:1.4), THF, -78 °C, 0.5 h] proceeded smoothly to give a good yield (83%) of the novel diastereoisomerically pure alcohol complex **5**. The crude product

† Reactivity studies on the tricarbonylchromium(0) complex of indan-1-one include examination of hydride and Grignard addition to the ketone,^{1,2} C-2 deprotonation/alkylation,² classical annulations using methyl vinyl ketone,³ hyperiodination to give an α -hydroxymethyl ketal⁴ and reduction of the ketone with baker's yeast.⁵ Both enantiomers of the indan-1-one complex have been prepared in optically pure form.²

‡ All novel complexes (**1**, **3** and **5-7**) gave satisfactory spectroscopic (IR, ¹H NMR, ¹³C NMR and low-resolution MS) and microanalytical or high resolution MS data.

§ Details of this analysis will be reported in the full account of this work.



mixture from this reaction contained essentially only one diastereoisomer of **5** (98:2 by ^1H NMR spectroscopy) and this was assigned as the *endo* alcohol by comparison with the stereochemical outcome of the sodium boranuide reaction.

The viability of deprotonation followed by an electrophilic quench was probed next. Reaction of complex **1** with lithium diisopropylamide (1 equiv.; THF, -78°C , 0.25 h) followed by quenching with acetic anhydride led to reaction of the lithium enolate through oxygen and the generation of the novel enol acetate **6** (85%). In contrast, carbon-carbon bond formation is observed on deprotonation with butyllithium (2.1 equiv.; THF, -100°C , 0.66 h) followed by an alkyl halide quench. Thus, using benzyl bromide as the quench gave a good yield (76%) of the novel essentially diastereoisomerically pure (98:2) ketone complex **7**. The crude product mixture contained the two diastereoisomers of **7** (98:2 by ^1H NMR spectroscopy) and the major one was found to have the relative stereochemistry indicated by an X-ray crystallographic analysis. §

Experimental

Tricarboxyl{spiro[indane-2,2'-dioxolane]}chromium(0) **3**

A 250 cm³ round-bottom flask fitted with an air condenser below a water condenser connected in series was charged with compound **2**¹² (4.00 g, 22.7 mmol), hexacarbonylchromium(0) (7.00 g, 31.8 mmol), dibutyl ether (120 cm³) and THF (12 cm³). The mixture was heated at reflux under nitrogen in the dark for 30 h (bath temp. 145°C) after which it was cooled, filtered

through a short pad of silica, and evaporated under reduced pressure. Purification of the resulting yellow solid by flash column chromatography [SiO_2 ; CH_2Cl_2 -light petroleum (bp 40 – 60°C), 5:3] gave the *title complex* **3** as a yellow crystalline solid (6.37 g, 90%); mp 120 – 121.5°C (Found: C, 53.6; H, 3.8. $\text{C}_{14}\text{H}_{12}\text{CrO}_5$ requires C, 53.85; H, 3.87%); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2/\text{cm}^{-1})$ 1971s and 1894br s ($\text{C}=\text{O}$); $\delta_{\text{H}}(300\text{ MHz}; \text{CDCl}_3)$ 3.00 and 3.13 (4 H, ABd, J 16, CH_2CCH_2), 3.92–3.97 and 4.03–4.09 (4 H, 2 \times m, $\text{OCH}_2\text{CH}_2\text{O}$) and 5.23–5.42 (4 H, m, ArH); $\delta_{\text{C}}(75\text{ MHz}, \text{CDCl}_3)$ 42.1 (CH_2CCH_2), 64.2, 64.4 ($\text{OCH}_2\text{CH}_2\text{O}$), 89.1, 91.0 ($C_{\text{ortho/meta}}$), 109.5 (C_{ipso}), 114.7 (OCO) and 232.8 ($\text{C}=\text{O}$); m/z (CI, NH_3) 313 (MH^+ , 100%) and 177 [$\text{MH}^+ - \text{Cr}(\text{CO})_3$, 49].

Tricarboxyl{indane-2-one}chromium(0) **1**

A solution of complex **3** (6.35 g, 20.3 mmol) in acetone (60 cm³) and aqueous hydrochloric acid (6 mol dm⁻³; 30 cm³) was heated at 50°C under nitrogen in the dark for 2 h after which it was diluted with water (50 cm³) and diethyl ether (50 cm³). The layers were separated and the aqueous layer was extracted with diethyl ether (6 \times 50 cm³). The combined organic layer and extracts were washed with aqueous saturated NaHCO_3 (200 cm³) and brine (200 cm³), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2 ; CH_2Cl_2) to give the *title complex* **1** as a yellow crystalline solid (4.69 g, 86%); mp 82 – 83°C (Found: C, 53.5; H, 3.2. $\text{C}_{12}\text{H}_8\text{CrO}_4$ requires C, 53.74; H, 3.01%); $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2/\text{cm}^{-1})$ 1971s and 1893br s ($\text{C}=\text{O}$); $\delta_{\text{H}}(300\text{ MHz}; \text{CDCl}_3)$ 3.41 and 3.56 [4 H, ABd, J 22, $\text{CH}_2\text{C}(\text{O})\text{CH}_2$] and 5.34–5.57 (4 H, m, ArH); $\delta_{\text{C}}(75\text{ MHz}, \text{CDCl}_3)$ 41.4 ($\text{CH}_2\text{C}(\text{O})\text{CH}_2$), 88.0, 90.1 ($C_{\text{ortho/meta}}$), 106.5 (C_{ipso}), 206.2 [$\text{CH}_2\text{C}(\text{O})\text{CH}_2$] and 230.8 ($\text{C}=\text{O}$); m/z (CI, NH_3) 286 ($\text{M} + \text{NH}_4^+$, 100%), 268 (M , 49), 132 [$\text{M} - \text{Cr}(\text{CO})_3$, 56] and 104 [$\text{M} - \text{Cr}(\text{CO})_3 - \text{CO}$, 81].

Acknowledgements

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§ Details of this analysis will be reported in the full account of this work.