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Synthesis and structures of organometallic derivatives of 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene

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A new fused-ring compound 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene (H_2L^1) has been synthesized from *p*-xylene. Three transition-metal derivatives [$Mn(\eta^5$-$HL^1)(CO)_3$], [$Rh(\eta^5$-$HL^1)(\eta$-$C_5Me_5)]^+[SbF_6]^-$ and [$Cr(\eta^6$-$H_2L^1)(CO)_3$] have been characterised: spectroscopic and crystallographic data for these compounds show the ligand system is strongly electron donating. Although H_2L^1 is readily deprotonated to the monoanion by potassium metal or potassium hydride, surprisingly we have been unable to form $(L^1)^{2-}$. The crystal structure of $[K]^+[HL^1]^-\cdot$18-crown-6 reveals the potassium ion to be sandwiched between the crown ether (1,4,7,10,13,16-hexaoxacyclooctadecane) and the $(HL^1)^-$ anion.

Oligomers and polymers comprising strongly interacting metallocene units are expected to exhibit interesting delocalisation properties. One way to realise such materials may be a polymer in which metal atoms alternate with ligands such as pentalene and *s*-indacene (Fig. 1); these ligands can be regarded as two cyclopentadienyl units fused to one another, either directly or through a benzene ring respectively.[1] The bimetallic species $[\{M(\eta$-$C_5Me_5)\}_2L]^{n+}$ (L = pentalene or *s*-indacene; M = Fe, Co or Ni; *n* = 0, 1 or 2) have been studied by Manríquez and co-workers.[2–5] Electron spin resonance, Mössbauer, electrochemical and magnetic measurements showed the coupling between metal centres to be extremely strong compared to many other linked metallocene systems.[6] This is not surprising when one examines the bonding in these molecules; an extended-Hückel molecular orbital scheme published for the pentalene species is related to those for $(\eta$-$C_5H_5)_3M_2$ triple-decker complexes.[2] Systems based on related ligands, such as *as*-indacene, for which relatively localised structures can be drawn, show significantly weaker interactions. Strategies for the rational stepwise construction of fused-ring oligomers and polymers have been outlined by Manríquez and Román.[1] However, synthetic progress towards such a goal has been hampered by escalating insolubility with increasing oligomerisation; trimetallic iron species based on pentalene have been reported[7] but the molecule shown in Fig. 2, which could, in principle, function as a building block for higher oligomers, has a solubility in boiling toluene of only *ca.* 400 mg l^{-1}.[7] Clearly, further progress will require a readily available fused-ring ligand with solubilising substituents. To this end we have recently begun investigating the organometallic chemistry of substituted *s*-indacene ligand systems. Our first strategy was to investigate the effect of permethylation on the *s*-indacene system, since many differences, including solubility, have been reported between C_5H_5 and C_5Me_5 chemistry.[8–16] We also hoped that permethylation would afford kinetic and/or thermodynamic stability to $\{M(\eta$-$C_5Me_5)\}_2L$ type complexes for metals other than Fe, Co and Ni. Thus, here we described the synthesis and some chemistry of 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene. Part of this work has appeared as a preliminary communication.[17]

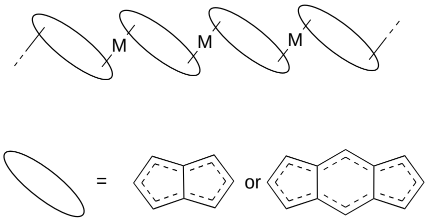

Fig. 1 Schematic view of an organometallic polymer based on pentalene or *s*-indacene

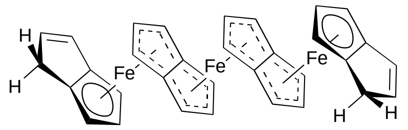

Fig. 2 A poorly soluble pentalene-based oligomer

Experimental

Instrumental methods

Elemental analyses were performed by the analytical department of the Inorganic Chemistry Laboratory, Oxford. Solution NMR spectra were recorded using a Bruker AM 300 or a Varian Unity Plus 500 spectrometer, referenced *via* the residual protio-solvent; chemical shifts (δ) are quoted in ppm relative to $SiMe_4$ at 0 ppm. Low-resolution electron impact (EI) mass spectra were recorded using an AEI MS 9802 instrument calibrated with perfluorokerosene. Fourier-transform infrared spectra were recorded using a Perkin-Elmer FT 1710 spectrometer, employing neat liquids or strong solutions between KBr plates.

General considerations

Operations involving oxygen- or water-sensitive materials were carried out under nitrogen or *in vacuo* using standard Schlenk techniques or a Vacuum Atmospheres glove-box. Where necessary solvents were dried by reflux over either sodium–potassium alloy [pentane, light petroleum (b.p. 40–60 °C), diethyl ether], potassium (tetrahydrofuran, thf), sodium [toluene, light petroleum (b.p. 100–120 °C)] or P_2O_5 (dichloromethane). These solvents were distilled under nitrogen and stored under nitrogen over activated type 4 Å molecular sieves. They, and others when appropriate, were deoxygenated prior to use by passage of a stream of nitrogen through the solvent. The compounds $CDCl_3$, CD_2Cl_2 and $(CD_3)_2CO$ were used as received; C_6D_6 was dried by reflux over potassium and purified by trap to trap distillation. The following materials were used as supplied commercially without further purification: methyllithium, *tert*-butyllithium and *n*-butyllithium solutions, *p*-xylene (99%),

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methyl iodide (99.5%), and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (99%) from Aldrich; silver(I) hexafluoroantimonate from Fluorochem. Potassium hydride was obtained from Aldrich as a dispersion in mineral oil; it was washed repeatedly with dry light petroleum (b.p. 40–60 °C) under nitrogen, dried *in vacuo* and stored in an inert atmosphere. Potassium was obtained from Aldrich under mineral oil. It was washed with light petroleum (b.p. 40–60 °C) and cut and weighed out under light petroleum before transferring to the reaction vessel against a counter flow of nitrogen. Literature procedures were followed for the synthesis of $[Cr(CO)_3(NH_3)_3]$[18,19] and $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$[20] (from C_5Me_5H[21] and $RhCl_3\cdot xH_2O$). The compound $FeCl_2\cdot 1.5thf$ was obtained by Soxhlet extraction of anhydrous $FeCl_2$, obtained by heating commercial $FeCl_2\cdot 4H_2O$ to 200 °C *in vacuo* for 15 h. The compound $[Mn(CO)_3(py)_2Br]$ (py = pyridine) was prepared following the general method given by Abel and Wilkinson.[22] Specifically, $[Mn(CO)_5Br]$[23] (3.40 g, 12.3 mmol) and pyridine (15 cm^3) were loaded in a Schlenk tube and deoxygenated before heating slowly to 120 °C under nitrogen (with free access to an oil bubbler to allow CO to escape). After 30 min at 120 °C the pyridine was removed *in vacuo*. The solids were transferred to a sintered-glass Buchner funnel, washed with pentane (3 × 20 cm^3) and then dried on the Buchner funnel and *in vacuo*. The resulting orange-yellow powder gave satisfactory elemental analysis and showed strong carbonyl stretches in the infrared spectrum at 1911, 1950 and 2033 cm^{-1}.

Syntheses

2,3,4,7-Tetramethylindan-1-one I. Aluminium chloride (260 g, 1.95 mol) and carbon disulfide (1 l), pre-dried on activated molecular sieves, were placed in a round-bottomed flask (3 l) fitted with a mechanical stirrer and a nitrogen inlet. The mixture was cooled in ice–salt and vigorously stirred under nitrogen. To this mixture was added a mixture of tiglyl (2-methylbut-2-enoyl) chloride (169 g, 1.42 mol) and *p*-xylene (175 cm^3, 1.43 mol) over a period of 1 h. After 2 h of stirring at *ca.* −10 °C the orange reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The flask was then fitted with a reflux condenser; the red-brown mixture was then refluxed under nitrogen for 3 h. After cooling to room temperature, the reaction mixture was poured carefully, in air, onto a mixture of concentrated HCl (1.25 l) and ice (2 kg). When the reaction had subsided the mixture was transferred to a separating funnel; the green lower (CS_2) layer was run off and the aqueous layer extracted with diethyl ether (3 × 500 cm^3). The combined CS_2 and ether layers were dried over $MgSO_4$ and filtered prior to solvent removal on a rotary evaporator. The brown residue was distilled at *ca.* 0.1 mmHg (*ca.* 13.3 Pa) using a 60 cm Vigreux column; the major fraction was a colourless liquid boiling at *ca.* 97 °C (147 g, 0.78 mol, 55%) and partially crystallising in the condenser; the liquid was found to be a mixture of the two isomers of 2,3,4,7-tetramethylindan-1-one **I** (*ca.* 3 : 1 **Ia** to **Ib**). ^1H NMR ($CDCl_3$) **Ia**, δ 1.26 (d, 3 H, $J = 7.5$, $CHCH_3$), 1.35 (d, 3 H, $J = 7.0$, $CHCH_3$), 2.25 (q of d, 1 H, $J =$ *ca.* 2.3, 7.5, aliphatic CH), 2.37 (s, 3 H, benzylic CH_3), 2.60 (s, 3 H, benzylic CH_3), 2.96 (q of d, 1 H, $J =$ *ca.* 2.3, 7.5, aliphatic CH), 7.03 (d, 1 H, $J = 7.5$, aromatic CH, 7.24 (d, 1 H, $J = 7.5$, aromatic CH); **Ib**, δ 1.09 (d, 3 H, $J = 7.1$ Hz, $CHCH_3$), 1.24 (d, 3 H, $J = 7.3$ Hz, $CHCH_3$), 2.37 (s, 3 H, benzylic CH_3), 2.60 (s, 3 H, benzylic CH_3), 2.77 (pseudo-quintet, 1 H, $J =$ *ca.* 7, aliphatic CH), 3.48 (pseudo-quintet, 1 H, $J =$ *ca.* 7 Hz, aliphatic CH), 7.03 (d, 1 H, $J = 7.5$, aromatic CH) and 7.24 (d, 1 H, $J = 7.5$ Hz, aromatic CH). EI mass spectrum: *m/z* 188 (M^+), 173 (M^+ − Me), 158 (M^+ − 2Me) and 143 (M^+ − 3Me). IR (selected data, liquid): 1699 cm^{-1}.

1,2,3,4,7-Pentamethylindene II. A solution of methyl iodide (45 cm^3, 103 g, 0.73 mol) in dry diethyl ether (250 cm^3) was added under nitrogen to a round-bottomed flask (2 l) containing a stirred suspension of magnesium turnings (16.2 g, 0.67 mol) in dry diethyl ether (120 cm^3). The rate of addition was controlled so the exothermic reaction maintained the contents of the flask at a gentle reflux. After the addition was complete the resulting grey solution was stirred for 45 min before addition of dry light petroleum (b.p. 100–120 °C) (80 cm^3). The ether was then removed under reduced pressure to yield a grey suspension, to which dry light petroleum (b.p. 40–60 °C) (160 cm^3) was added. The resulting slurry of methylmagnesium iodide was cooled in ice; a solution of compound **I** (102 g, 0.54 mol) in dry light petroleum (b.p. 40–60 °C) (100 cm^3) was then added under nitrogen over a period of 1 h. When the addition was complete the mixture was refluxed for 3 h. When the reaction mixture had cooled a mixture of concentrated HCl (100 cm^3) and water (300 cm^3) was added slowly. The resulting mixture was transferred in air to a separating funnel and extracted with diethyl ether (3 × 250 cm^3). During this time the organic layers rapidly darkened, presumably due to the aerial oxidation of iodide to iodine. The combined organic layers were therefore washed with 0.25 M aqueous sodium thiosulfate (3 × 200 cm^3). The organic layers were filtered into a round-bottomed flask and stirred for 15 h with concentrated HCl (50 cm^3). After this time a saturated aqueous solution of Na_2CO_3 was carefully added until the mixture was neutral. The layers were separated; the organic layer was washed with water (2 × 250 cm^3). After drying over anhydrous Na_2CO_3 and filtering, the solvent was removed *in vacuo*. The resulting white crystalline solid (97 g, 0.52 mol, 96%) was found to be essentially pure 1,2,3,4,7-pentamethylindene **II** by ^1H NMR spectroscopy ($CDCl_3$): δ 1.27 (d, 3 H, $J = 7.3$, $CHCH_3$), 1.98 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 3.19 (q, 1 H, $J = 7.3$, aliphatic CH), 6.83 (d, 1 H, $J = 7.6$, aromatic CH) and 6.93 (d, 1 H, $J = 7.6$ Hz, aromatic CH). EI mass spectrum: *m/z* 186 (M^+), 171 (M^+ − Me), 156 (M^+ − 2Me) and 141 (M^+ − 3Me).

Ketone III. A mixture of aluminium chloride (95 g, 0.71 mol) and carbon disulfide (300 cm^3), pre-dried on activated molecular sieves, was mechanically stirred in a flask (1 l) and cooled in ice–salt; a solution of tiglyl chloride (65 g, 0.56 mol) and compound **II** (97 g, 0.52 mol) in carbon disulfide (70 cm^3) was added under nitrogen over a period of 90 min. After 2 h stirring at *ca.* −10 °C the orange reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The flask was then fitted with a reflux condenser; the red-brown mixture was refluxed under nitrogen for 3 h. After cooling to room temperature the reaction mixture was carefully poured onto a mixture of concentrated HCl (500 cm^3) and ice (1 kg). Diethyl ether (400 cm^3) were added and the mixture was transferred to a separating funnel. The brown lower (aqueous) layer and green organic layer were separated; the aqueous layer was further extracted with diethyl ether (2 × 400 cm^3). After drying over $MgSO_4$ the combined organic layers were filtered and the solvent removed *in vacuo* to yield a thick green oil. Proton NMR spectroscopy showed this oil was a complex mixture of products including two isomers of the ketone, **IIIa** and **IIIb**, in a ratio of *ca.* 2 : 1. Cooling a solution of the oil in dichloromethane–light petroleum (b.p. 40–60 °C), to −80 °C yielded a white powder (22.5 g) which was collected on a sintered-glass Buchner funnel, washed with cold light petroleum (b.p. 40–60 °C) and characterised as **III**, principally the isomer denoted **IIIa**. Recrystallisation from hexane at −30 °C gave pure **IIIa** (Found: C, 85.45; H, 8.75. Calc. for $C_{19}H_{24}O$: C, 85.03; H, 9.01%). ^1H NMR ($CDCl_3$): δ 1.25 (d, 3 H, $J = 7.3$, H^h), 1.28 (d, 3 H, $J = 7.8$, H^a), 1.32 (d, 3 H, $J = 6.9$, H^d), 1.99 (s, 3 H, H^g), 2.25 (s, 3 H, H^f), 2.26 (q of d, 1 H, $J =$ *ca.* 1.5, 7.8, H^b), 2.55 (s, 3 H, H^e), 2.67 (s, 3 H, H^j), 2.98 (q of d, 1 H, $J =$ *ca.* 1.5, 6.9, H^c) and 3.22 (q, 1 H, $J = 7.3$ Hz, H^i) (assignments refer to Scheme 1). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 12.7 (CH_3), 14.4 (2 × CH_3), 15.1 (CH_3), 15.4 (CH_3), 17.7 (CH_3), 21.7 (CH_3), 40.4 (CH), 45.6 (CH), 52.4 (CH), 124.4

(quaternary), 128.6 (quaternary), 130.0 (quaternary), 132.5 (quaternary), 147.3 (quaternary), 149.6 (quaternary), 150.5 (quaternary), 158.8 (quaternary) and 210.8 (C=O quaternary). EI mass spectrum: *m/z* 268 (M^+, 100), 253 ($M^+ - \text{Me}$, 35), 238 ($M^+ - 2\text{Me}$, 3), 223 ($M^+ - 3\text{Me}$, 5) and 212 ($M^+ - \text{CHMe=CHMe}$, 48%) and many lower mass fragments. IR (strong CH_2Cl_2 solution, selected data): 1586 and 1685 cm^{-1}.

Concentration of the dichloromethane–light petroleum supernatant, followed by cooling, produced a pale green powder (3.9 g) identified as principally compound **IIIb**. Recrystallisation from hexane at −30 °C afforded pure **IIIb** (Found: C, 86.11; H, 9.31. Calc. for $C_{19}H_{24}O$: C, 85.03; H, 9.01%.) ^{1}H NMR ($CDCl_3$): δ 1.09 (d, 3 H, *J* = 7.1, H^d), 1.23 (d, 3 H, *J* = 7.3, H^a), 1.26 (d, 3 H, *J* = 7.3, H^h), 2.00 (s, 3 H, H^g), 2.27 (s, 3 H, H^f), 2.58 (s, 3 H, H^e), 2.67 (s, 3 H, H^j), 2.80 (pseudo-quintet, 1 H, *J* = *ca.* 7.3, H^b), 3.24 (q, 1 H, *J* = 7.3, H^i) and 3.50 (pseudo-quintet, 1 H, *J* = *ca.* 7.1 Hz, H^c). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 10.2 (CH_3), 12.6 (CH_3), 14.2 (CH_3), 14.4 (CH_3), 14.6 (CH_3), 15.4 (CH_3), 17.8 (CH_3), 35.8 (CH), 45.6 (CH), 48.1 (CH), 123.8 (quaternary), 128.8 (quaternary), 129.7 (quaternary), 132.5 (quaternary), 146.9 (quaternary), 149.3 (quaternary), 149.9 (quaternary), 159.3 (quaternary) and 209.9 (C=O quaternary). EI mass spectrum: *m/z* 268 (M^+, 100), 253 ($M^+ - \text{Me}$, 35), 238 ($M^+ - 2\text{Me}$, 3), 223 ($M^+ - 3\text{Me}$, 5) and 212 ($M^+ - \text{CHMe= CHMe}$, 48%) and many lower mass fragments. IR (strong CH_2Cl_2 solution, selected data): 1587 and 1689 cm^{-1}.

The remaining supernatant from the powders was chromatographed on silica (Fluka 60739). The column was eluted with hexane containing increasing proportions of diethyl ether, producing a number of bands. Neat ether eluted a yellow band; solvent removal afforded a yellow solid (47 g) shown to be a mixture of isomers of **III**, sufficiently pure for use in further reactions. The total yield was, therefore, 72 g (53%).

1,2,3,4,5,6,7,8-Octamethyl-1,5-dihydro-*s*-indacene IV (H_2L^1). Methylmagnesium iodide (22 cm^3, 50 g, 0.35 mol) was prepared as for compound **II**. A solution of **III** (72 g, 0.27 mol) in dry light petroleum (b.p. 40–60 °C) (50 cm^3) was then added to a suspension of MgMeI in light petroleum (b.p. 40–60 °C) under nitrogen over a period of 90 min. When the addition was complete the mixture was refluxed for 5 h. When the reaction mixture had cooled a mixture of concentrated HCl (50 cm^3) and water (150 cm^3) was added slowly. The resulting mixture was transferred in air to a separating funnel together with diethyl ether (200 cm^3). The aqueous layer and solids were extracted with diethyl ether (4 × 500 cm^3). White solids suspended in the organic layer (22 g) were filtered off and dried by washing with methanol and diethyl ether on a Buchner funnel. Proton NMR spectroscopy showed this solid to be essentially pure 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene **IV**. The diethyl ether solution was stirred for 15 h with concentrated HCl (100 cm^3). After neutralisation with saturated aqueous Na_2CO_3, separation, and drying over $MgSO_4$ the solution was concentrated and cooled to −80 °C to yield additional (*ca.* 8 g) **IV**. The total yield was, therefore, *ca.* 30 g (0.11 mol, 42%). An analytical sample was obtained after two recrystallisations from hot toluene (Found: C, 90.79; H, 10.04. Calc. for $C_{20}H_{26}$: C, 90.16; H, 9.84%). ^{1}H NMR ($CDCl_3$): δ 1.25 (d, 6 H, *J* = 7.5, $CHCH_3$), 1.95 (s, 6 H, CH_3), 2.23 (s, 6 H, CH_3), 2.56 (s, 6 H, CH_3) and 3.18 (q, 2 H, *J* = 7.5 Hz, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 12.2 (CH_3), 14.5 (CH_3), 15.9 (CH_3), 16.0 (CH_3), 46.1 (CH), 122.9 (quaternary), 132.1 (quaternary), 140.1 (quaternary), 142.6 (quaternary) and 147.3 (quaternary). EI mass spectrum: *m/z* 266 (M^+, 100), 252 ($M^+ - \text{Me}$, 98), 236 ($M^+ - 2\text{Me}$, 33), 222 ($M^+ - 3\text{Me}$, 29), 206 ($M^+ - 4\text{Me}$, 21) and 192 ($M^+ - 5\text{Me}$, 5%).

$[K]^+[HL^1]^-\cdot$0.1thf Va and $[K]^+[HL^1]^-\cdot$18-crown-6 Vb. $[K]^+[HL^1]^-\cdot$0.1thf **Va**, *method A.* Potassium hydride (450 mg, 11.2 mmol) and dry thf (50 cm^3) were stirred in a Rotaflo ampoule. A slurry of compound **IV** (1.00 g, 3.75 mmol) in dry thf (80 cm^3) was added to this suspension; the ampoule was evacuated until the solvent began to boil, then closed and placed in an oil-bath at 85 °C for $5\frac{1}{2}$ h to yield a red solution. The excess of KH was filtered off; the solvent was then removed *in vacuo* to afford an orange-yellow oily solid. Prolonged drying *in vacuo* resulted in an essentially quantitative yield of a golden solid, shown by NMR spectroscopy to be $[K]^+[HL^1]^-\cdot$0.1thf, **Va**.

$[K]^+[HL^1]^-\cdot$0.1thf **Va**, *method B.* Potassium sand was made in a Rotaflo ampoule from potassium metal (421 mg, 10.8 mmol) in dry thf (40 cm^3). A slurry of compound **IV** (1.00 g, 3.75 mmol) in dry thf (35 cm^3) was added. After stirring for 2 h the indacene had mostly disappeared and the solution was reddish. The ampoule was then evacuated until the solvent began to boil, then closed and placed in an oil-bath at 85 °C for 14 h. The excess of potassium was filtered off; the solvent was then removed *in vacuo* to afford an orange-yellow oily solid. Prolonged drying *in vacuo* resulted in an essentially quantitative yield of a golden solid, shown by NMR spectroscopy to be $[K]^+[HL^1]^-\cdot$0.1thf **Va**. ^{1}H NMR (C_6D_6): δ 1.14 (d, 3 H, *J* = 6.5, $CHCH_3$), 1.37 (m, 0.5 H, CH_2, thf), 1.88 (s, 3 H, CH_3), 1.92 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3), 3.08 (q, 1 H, *J* = 6.4 Hz, CH) and 3.39 (m, 0.5 H, CH_2, thf). ^{13}C-{^{1}H} NMR (C_6D_6): δ 10.9 (CH_3), 12.5 (CH_3), 13.2 (CH_3), 14.0 (CH_3), 15.9 (CH_3), 16.8 (CH_3), 17.3 (CH_3), 18.4 (CH_3), 25.7 (CH_2, thf), 45.1 (CH), 67.5 (CH_2, thf), 98.2 (quaternary), 99.1 (quaternary), 116.8 (quaternary), 118.7 (quaternary), 122.0 (quaternary), 123.9 (quaternary), 124.2 (quaternary), 131.2 (quaternary), 133.0 (quaternary), 134.1 (quaternary) and 137.7 (quaternary).

$[K]^+[HL^1]^-\cdot$18-crown-6 **Vb**. The addition of thf (30 cm^3) to a flask containing potassium chunks (127 mg, 3.25 mmol), 18-crown-6 (860 mg, 3.25 mmol), and compound **IV** (433 mg, 1.63 mmol) gave a yellow heterogeneous mixture that slowly grew homogeneous and turned red-yellow within 2 h. After 3 h the mixture was filtered through filter aid on a frit. Pentane was layered onto the solution and allowed slowly to diffuse, resulting in the formation of thin orange plates of $[K(18\text{-crown-}6)]^+[HL^1]^-$ suitable for X-ray crystallography. The same results were obtained using toluene as the solvent at reflux, followed by filtration and cooling to −45 °C (675 mg, 73%). ^{1}H NMR (C_6D_6): δ 1.58 (d, 3 H, *J* = 7.0, $CHCH_3$), 2.11 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.66 (s, 3 H, CH_3), 3.03 (s, 3 H, CH_3), 3.11 (s, 24 H, CH_2), 3.16 (s, 3 H, CH_3), 3.25 (s, 3 H, CH_3) and 3.35 (q, 1 H, CH). ^{13}C-{^{1}H} NMR (C_6D_6): δ 70.1 (CH_2, 18-crown-6); the remaining resonances could not be satisfactorily resolved due to low solubility of the compound.

$[Mn(\eta^5\text{-}HL^1)(CO)_3]$ 1. A solution of compound **Va** (536 mg, 1.76 mmol) in dry thf (30 cm^3) was cooled to −78 °C; a slurry of $[Mn(CO)_3(py)_2Br]$ (665 mg, 1.76 mmol) in thf (40 cm^3) was added dropwise. After the addition was complete the mixture was allowed to warm to room temperature; it soon became orange. After 20 h the solvent was removed *in vacuo* and the solids were extracted with light petroleum (b.p. 40–60 °C). The extracts were filtered through a bed of Celite, reduced in volume and cooled to −80 °C. The solvent was decanted from the resulting solids which were washed with cold light petroleum (b.p. 40–60 °C) and dried *in vacuo* to yield orange-yellow microcrystals (351 mg, 0.87 mmol, 49%), shown by NMR spectroscopy to be an approximately 1 : 1 mixture of the two isomers of $[Mn(\eta^5\text{-}HL^1(CO)_3]$ **1** (Found: C, 68.97; H, 6.37. Calc. for $C_{23}H_{25}MnO_3$: C, 68.31; H, 6.23%). ^{1}H NMR (C_6D_6): **1a**, δ 1.02 (d, 3 H, *J* = 7.0, $CHCH_3$), 1.60 (s, 3 H, CH_3), 1.66 (s, 6 H, CH_3), 1.98 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3) and 2.97 (q, 1 H, *J* = 7.0, CH); **1b**, δ 1.04 (d, 3 H, *J* = 7.0, $CHCH_3$), 1.60 (s, 3 H, CH_3), 1.63 (s, 6 H, CH_3), 1.98 (s, 3 H, CH_3), 2.07 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.32 (s, 3 H, CH$_3$), 2.65 (s, 3 H, CH$_3$) and 2.78 (q, 1 H, J = 7.0 Hz, CH). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): **1a**, δ 10.5 (CH$_3$), 12.3 (CH$_3$), 13.3 (CH$_3$), 13.7 (CH$_3$), 15.2 (CH$_3$), 16.2 (CH$_3$), 16.3 (CH$_3$), 17.0 (CH$_3$), 45.3 (CH), 85.3 (quaternary), 87.5 (quaternary), 101.7 (quaternary), 104.1 (quaternary), 122.0 (quaternary), 123.5 (quaternary), 132.4 (quaternary), 142.0 (quaternary), 145.2 (quaternary), 145.8 (quaternary) and 227.3 (MnCO) (remaining quaternary obscured by solvent); **1b**, δ 10.6 (CH$_3$), 12.2 (CH$_3$), 12.5 (CH$_3$), 12.8 (CH$_3$), 13.6 (CH$_3$), 15.2 (CH$_3$), 16.2 (CH$_3$), 16.9 (CH$_3$), 44.9 (CH), 86.3 (quaternary), 86.6 (quaternary), 100.2 (quaternary), 103.8 (quaternary), 122.1 (quaternary), 123.5 (quaternary), 132.4 (quaternary), 142.5 (quaternary), 145.5 (quaternary), 145.6 (quaternary) and 227.3 (MnCO) (remaining quaternary obscured by solvent). EI mass spectrum: m/z 404 (M^+, 17), 348 ($M^+ - 2$CO, 8), 320 ($M^+ - 3$CO, 88), 265 [(HL^1)$^+$, 50], 250 [(HL^1)$^+$ − Me, 30] and 235 [(HL^1)$^+$ − 2Me, 11%] and many lower mass fragments. IR (strong CH$_2$Cl$_2$ solution, selected data): 1914s (br) and 2001s cm^{-1}. Single crystals of the *endo* isomer, **1a**, were obtained by slow cooling of a pentane solution of the isomeric mixture to −80 °C.

[Rh(η^5-HL^1)(η-C$_5$Me$_5$)]$^+$[SbF$_6$]$^-$ 2. Silver(I) hexafluoroantimonate, weighed out under nitrogen owing to its hygroscopic behaviour (684 mg, 1.99 mmol), was added, against a counterflow of nitrogen, to a deoxygenated solution of [{Rh(η-C$_5$Me$_5$)-Cl$_2$}$_2$] (684 mg, 0.498 mmol) in acetone (4 cm^3). White silver(I) chloride instantly precipitated. After 10 min the precipitate was filtered off, in air, using a Buchner funnel with a bed of Celite. The precipitate and Celite was washed with acetone (14 cm^3); the combined acetone solutions were stirred with compound **IV** (200 mg, 0.75 mmol) for 24 h. The mixture was then filtered and diethyl ether (*ca.* 20 cm^3) added; the yellow solution was slowly cooled to −80 °C to yield yellow microcrystals. The solvent was decanted off and the solids were washed with diethyl ether (2 × 20 cm^3) before drying *in vacuo* to give the *endo* isomer of [Rh(η^5-HL^1)(η-C$_5$Me$_5$)]$^+$[SbF$_6$]$^-$ **2a** (105 mg, 0.14 mmol, 19%). Attempts to isolate more solids by addition of diethyl ether to the combined supernatant and washings resulted in deposition of a brown oil which was not investigated. The analytical sample of **2a** was obtained by recrystallisation from dichloromethane–diethyl ether. The crystals of **2a** used for structure determination were grown by layering a dichloromethane solution (*ca.* 5 mg in 1 cm^3) with diethyl ether (*ca.* 6 cm^3) (Found: C, 48.74; H, 6.03. Calc. for C$_{30}$H$_{40}$F$_6$RhSb: C, 48.74; H, 5.45%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.24 (d, 3 H, J_{HH} = 7.3, CHCH_3), 1.57 (s, 15 H, C$_5$Me$_5$ CH$_3$), 1.82 (s, 3 H, HL^1 CH$_3$), 1.96 (s, 3 H, HL^1 CH$_3$), 2.21 (s, 3 H, HL^1 CH$_3$), 2.26 (s, 3 H, HL^1 CH$_3$), 2.27 (s, 3 H, HL^1 CH$_3$), 2.43 (s, 3 H, HL^1 CH$_3$), 2.60 (s, 3 H, HL^1 CH$_3$) and 3.26 (q, 1 H, J_{HH} = 7.3 Hz, CH). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 8.2 (s, C$_5$Me$_5$ CH$_3$), 8.8 (s, HL^1 CH$_3$), 12.0 (s, HL^1 CH$_3$), 12.4 (s, HL^1 CH$_3$), 12.9 (s, HL^1 CH$_3$), 15.3 (s, HL^1 CH$_3$), 16.1 (s, HL^1 CH$_3$), 17.3 (s, HL^1 CH$_3$), 17.6 (s, HL^1 CH$_3$), 45.7 (s, CH), 91.8 (d, J_{RhC} = 6.5, HL^1 RhC), 91.9 (d, J_{RhC} = 7.5, HL^1 RhC), 98.0 (d, J_{RhC} = 7.0, C$_5$Me$_5$ RhC), 100.8 (d, J_{RhC} = *ca.* 5, HL^1 RhC), 102.9 (d, J_{RhC} = *ca.* 9, HL^1 RhC), 103.9 (d, J_{RhC} = *ca.* 6 Hz, HL^1 RhC), 117.9 (s, HL^1, quaternary), 122.1 (s, HL^1, quaternary), 132.3 (s, HL^1, quaternary), 146.2 (s, HL^1, quaternary) and 149.8 (s, HL^1, quaternary).

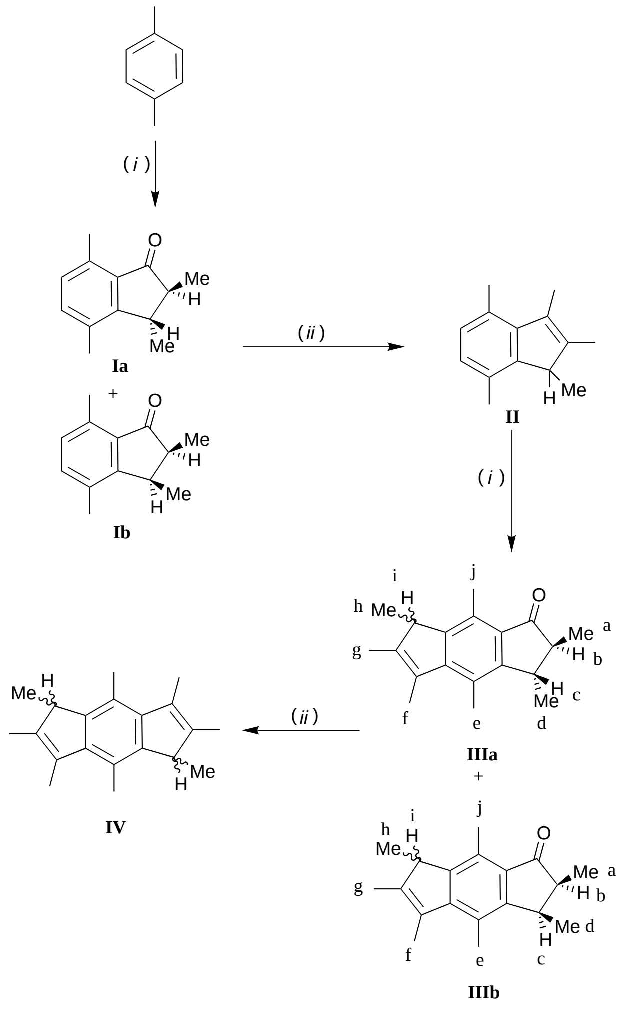
[Cr(η^6-H$_2$L^1)(CO)$_3$] 3. The compound [Cr(NH$_3$)$_3$(CO)$_3$] (1.304 g, 6.97 mmol) and **IV** (H$_2$L^1) (1.305 g, 4.90 mmol) were refluxed in sieve-dried *p*-dioxane (50 cm^3) under N$_2$ for 7 h. After solvent removal the olive-green residue was extracted with dichloromethane. The extracts were filtered through Celite, the solvent volume was reduced *in vacuo* and the solution was cooled to −80 °C. The resulting yellow microcrystals were filtered off, washed with cold dichloromethane and dried *in vacuo*. A second crop was obtained by adding light petroleum (b.p. 40–60 °C) to the supernatant, reducing the solvent volume and cooling to −80 °C. The total yield was 1.660 g (4.12 mmol, 84%). The NMR spectra showed the product to be an approximately 1 : 1 : 2 *endo*/*endo* (**3a**) : *exo*/*exo* (**3b**) : *endo*/*exo* (**3c**) isomer mixture. Single crystals of the *endo*/*exo* isomer, **3c**, were obtained by slow cooling of a dichloromethane solution of the isomeric mixture (Found: C, 67.79; H, 6.03. Calc. for C$_{23}$H$_{26}$CrO$_3$: C, 68.64; H, 6.51%). ^{1}H NMR (C$_6$D$_6$): isomeric mixture, δ 0.89 (d, J = 7.5, *exo* CHCH_3), 0.96 (d, J = 7.5, *exo* CHCH_3), 1.26 (d, J = 7.5, *endo* CHCH_3), 1.31 (d, J = 7.5, *endo* CHCH_3), 1.51 (s, 2 × CH$_3$), 1.58 (s, CH$_3$), 1.59 (s, CH$_3$), 1.87 (s, CH$_3$), 1.90 (s, CH$_3$), 1.92 (s, CH$_3$), 2.00 (s, CH$_3$), 2.22 (s, CH$_3$), 2.23 (s, CH$_3$), 2.27 (s, CH$_3$), 2.39 (s, CH$_3$), 2.60 (q, J = 7.5, CH), 2.62 (q, J = 7.5, CH), 2.93 (q, J = 7.5, CH) and 3.30 (q, J = 7.5 Hz, CH). ^{13}C-{^{1}H} NMR (C$_6$D$_6$): isomeric mixture, δ 12.0 (CH$_3$), 12.3 (2 × CH$_3$), 12.4 (CH$_3$), 13.8 (2 × CH$_3$), 14.7 (CH$_3$), 14.8 (CH$_3$), 14.9 (CH$_3$), 15.1 (CH$_3$), 15.4 (CH$_3$), 16.3 (2 × CH$_3$), 16.4 (CH$_3$), 19.7 (CH$_3$), 20.2 (CH$_3$), 45.5 (CH), 45.8 (CH), 45.9 (CH), 46.6 (CH), 93.3 (quaternary), 94.6 (quaternary), 104.2 (quaternary), 104.9 (quaternary), 108.6 (quaternary), 113.3 (quaternary), 115.0 (quaternary), 117.4 (quaternary), 117.7 (quaternary), 118.5 (quaternary), 120.8 (quaternary), 122.6 (quaternary), 130.2 (quaternary), 130.3 (quaternary), 130.4 (quaternary), 131.0 (quaternary), 144.1 (quaternary), 147.1 (quaternary), 147.2 (quaternary), 147.9 (quaternary) and 236.7 (CO). EI mass spectrum: m/z 402 (M^+, 2), 346 ($M^+ - 2$CO, 1), 318 ($M^+ - 3$CO, 12) and 300 (2%) and many lower mass fragments. IR: (strong CH$_2$Cl$_2$ solution, selected data) 1844s and 1934s; (strong thf solution, selected data 1863s and 1941s cm^{-1}.

Crystallography

Experimental details of the crystal structure determinations are summarised in Table 4. All crystallographic data were acquired with Mo-Kα radiation (λ = 0.710 73 Å). In the case of compounds **Vb** and **3c** the crystal was mounted on a fibre under oil and then cooled on the diffractometer. In the case of **1a** and **2a** crystals were mounted in Lindemann tubes under nitrogen which were then sealed with a small flame. For all structures the positions of the heavier atoms were determined by direct methods using SIR 92.[24] Subsequent Fourier-difference syntheses revealed the positions of the other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures on F. Hydrogen atoms were fixed in geometrically idealised positions and allowed to ride on their attached carbon atoms with isotropic thermal parameters according to the atom to which they were attached (these were not refined). Absorption corrections were applied using DIFABS.[25] Chebyshev weighting schemes[26] were applied in the refinement of all the structures; in all cases the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall extinction parameter)[27] in the final stages of refinement. All crystallographic calculations were performed using the Oxford CRYSTALS system[28] running on a Silicon Graphics Indigo R4000 computer. Neutral atom scattering factors were taken from the usual sources.[29] The figures were produced using CAMERON.[30]

For compound **Vb** systematic absences clearly indicated $P2_1/n$. Inspection of the residual electron density after the final refinement showed peaks primarily around the crown ether, as well as one peak suggesting disorder of the methyl group attached to C(1); the latter disorder methyl was modelled successfully using two sites and refining their occupancies whilst constraining the total occupancy to be 1. However, attempts to model disorder of the crown ether did not give chemically realistic bond lengths nor did it improve the overall fit of the model; the disorder is, therefore, simply reflected by the large thermal ellipsoids of some of the crown ether atoms. Presumably the unresolved disorder is responsible for the high R values.

In the case of compound **2a** systematic absences could not



Scheme 1 (*i*) MeCH=CMeCOCl, $AlCl_3$, CS_2, then concentrated HCl; (*ii*) MgMeI, light petroleum (b.p. 40–60 °C), then concentrated HCl

unambiguously identify the space group; solution and refinement were therefore carried out in both $P2_1$ and $P2_1/m$. Refinement in the former space group gave chemically unreasonable lengths and angles. A much more satisfactory refinement was achieved in the latter space group. However, in $P2_1/m$ the $[SbF_6]^-$ ion lies on an inversion centre whilst the cation is bisected by a crystallographic mirror plane. This requires disorder of the indacene ring system about the mirror plane; the 5 and 7 positions are superimposed. Fourier maps showed this disorder could not be satisfactorily resolved. Thus, the out-of-plane 5- and in-plane 7-methyl groups were represented by a single carbon at an intermediate position.

CCDC reference number 186/683.

Results and Discussion

Ligand synthesis

We wanted our synthesis for 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene to be cheap and straightforward compared to pre-existing routes to various dihydro-*as*-[31–35] and *s*-indacene systems[35–40] and to dihydropentalene,[41] hoping it would lead to an expansion of the field of fused-ring chemistry. The route we adopted is shown in Scheme 1; it is based on a modification of previously described preparations of 1,3-dimethylindene,[42] 1,2,3-trimethylindene[42,43] and 1,2,3,4,5,6,7-heptamethylindene.[44–46]

The aluminium chloride-catalyzed reaction of tiglyl chloride[45] and *p*-xylene in carbon disulfide produced moderate yields of 2,3,4,7-tetramethylindan-1-one **I** as a colourless liquid. Proton NMR spectroscopy revealed the presence of two isomers in an approximate ratio of 3:1. Examination of the coupling constants suggests that the major isomer is **Ia**. Similar isomerism is observed in 2,3,4,5,6,7-hexamethylindan-1-one, prepared by the analogous reaction of tiglyl chloride and 1,2,3,4-tetramethylbenzene with aluminium chloride in dichloromethane.[47] We have found sieve-dried dichloromethane gives similar results in place of carbon disulfide in this type of Friedel–Crafts acylation reaction.[48]

1,2,3,4,7-Pentamethylindene **II** is a waxy solid and was obtained in excellent yield through the methylation of 2,3,4,7-tetramethylindan-1-one **I** with a light petroleum suspension of methylmagnesium iodide. This reaction was carried out in an analogous fashion to the procedure described for the methylation of 2,3,4,5,6,7-hexamethylindan-1-one.[46] The methylation of 2,3,4,5,6,7-hexamethylindan-1-one has also been achieved by the use of methyllithium in either diethyl ether[45] or light petroleum.[46] However, use of methyllithium often leads to greatly varying yields due to competitive enolisation of the ketone, which is then recovered after the aqueous work-up.[46] The same problems occur with methyllithium in the present reaction.[49]

The reaction of tiglyl chloride and 1,2,3,4,7-pentamethylindene **II** was carried out in an analogous fashion to that with and *p*-xylene; moderate yields of the ketone **III** were obtained. Four readily distinguishable isomers may be envisaged, differing in the relative disposition of the functionalities in the two five-membered rings and in the configurations of the chiral centres in the ketone ring. Additional isomers arising from different configurations of the chiral centre in the indene ring relative to those in the ketone ring would not be expected to be distinguishable by spectroscopic techniques. Proton and ^{13}C NMR spectroscopy show two isomers are present in the reaction product in an approximate ratio of 2:1; these were separated and purified by fractional recrystallisation. The relative disposition of the functionalities in the two five-membered rings was shown, by nuclear Overhauser effect spectroscopy (NOESY) experiments, to be the same for both isomers. In both isomers the C=C group of the indene ring was shown to be bonded to the benzene ring *para* to the C=O of the ketone group, *i.e.* the two isomers are **IIIa** and **IIIb** in Scheme 1. The difference between the NMR spectra of the two isomers is reminiscent of that found between the isomers of 2,3,4,7-tetramethylindan-1-one and between those of 2,3,4,5,6,7-hexamethylindanone, both with respect to the difference in chemical shifts and the different coupling patterns of the ketone ring CH protons in the two isomers. This is consistent with both isomers having the same relative dispositions of indene and ketone rings, as shown by the NOESY experiments, but differing in the relative configurations of the chiral centres in the ketone ring. Again, the coupling patterns suggest the major isomer is that with the two methyl groups in the ketone ring *trans* to one another (**IIIa**). This assumption is confirmed by the NOESY experiments.

Compound **IV** (H_2L^1) was obtained in moderate yield by the methylation of its ketone precursor, **III**; in analogy with the methylation of 2,3,4,7-tetramethylindan-1-one, a light petroleum slurry of methylmagnesium iodide was used. The number of resonances observed in the ^1H and ^{13}C NMR spectra indicates the isomer is that with a C_2 axis perpendicular to the plane of the molecule, *i.e.* 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene, rather than that with a plane of symmetry perpendicular to the plane of the molecule, *i.e.* 1,2,3,4,5,6,7,8-octamethyl-1,7-dihydro-*s*-indacene. Further isomerism can arise from different relative configurations of the chiral centres in the two five-membered rings; however, it is unlikely these isomers could readily be distinguished by NMR spectroscopy since the two centres are so distant as to have little effect on one another.

1,2,3,4,5,6,7,8-Octamethyl-1,5-dihydro-*s*-indacene shows surprisingly low solubility in common organic solvents; it is most soluble in aromatic and halogenated solvents but, even so, the solubility in boiling toluene is only *ca.* 40 g l^{-1}.

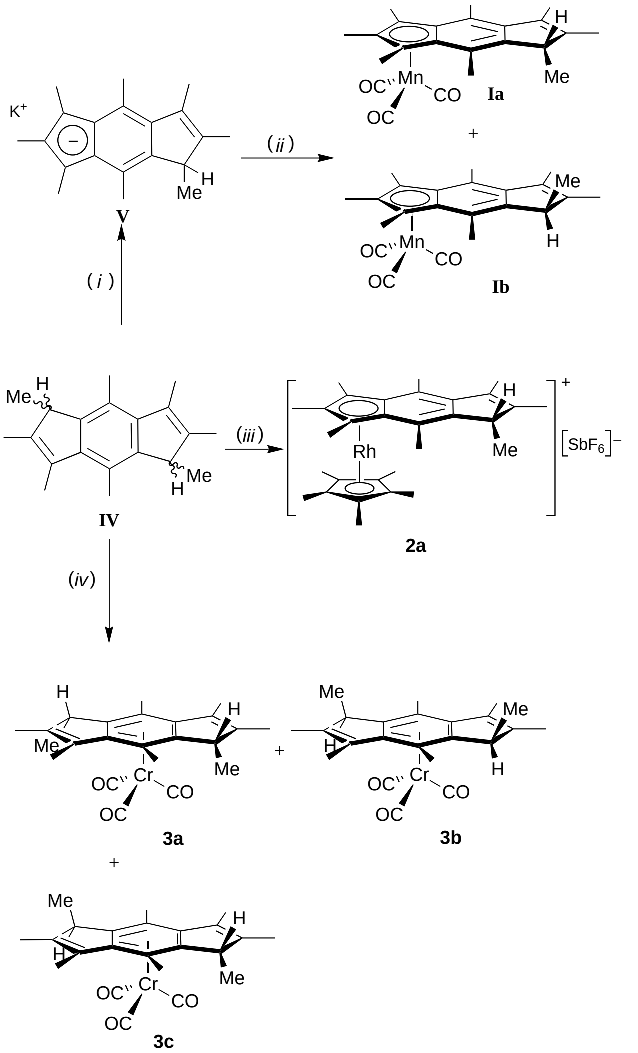
Synthesis and characterisation of organometallic derivatives

Deprotonation of compound IV. Most organometallic indacene chemistry has involved the reaction of *as*- or *s*-indacene dianions or the hydro-*s*-indacene anion.[5,32,35,50–52] In general these anions are derived from deprotonation of the corresponding dihydroindacene, although the dianion of *s*-indacene has also been obtained by the reduction of *s*-indacene with sodium in liquid ammonia.[37] For example, Manríquez's compounds were made from dilithio-*s*-indacene and [M^{II}(η-C$_5$Me$_5$)(acac)] (M = Fe, Co or Ni; acac = acetylacetonate).[3–5,53] (We have recently discovered another route to such compounds: the reaction of neutral 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (H$_2$L^2) with [Co^I(η-C$_5$H$_5$)(C$_2$H$_4$)$_2$] yields [{Co(η-C$_5$H$_5$)}$_2$(H$_2$L^2)], remarkably as a mixture of *cis* (major) and *trans* (minor) isomers.[54,55])

Hence, attempts were made to prepare mono- and di-lithium salts of compound **IV** by reaction with appropriate quantities of *n*-butyllithium or *tert*-butyllithium in thf. The use of LiBu^n, with or without added *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen), gave only the monoanion while LiBu^t gave no reaction at all. Unlike potassium, which reacts with **IV** at room temperature, freshly cut lithium metal does not react in refluxing 1,2-dimethoxyethane (dme) or thf. Reaction of solutions of the monolithiated material with compounds such as FeCl$_2$·1.5thf and [Mn(CO)$_3$(py)$_2$Br] gave no tractable products. It was suspected that this chemistry was unsuccessful partly because any lithiated materials formed were strongly reducing. Therefore, it was decided to synthesize a potassium salt of **IV**, which might be expected to be less reducing.

Refluxing a thf slurry of compound **IV** with either an excess of potassium hydride or of molten potassium metal led to disappearance of **IV** and formation of red solutions. Filtration and solvent removal afforded golden solids, **Va**. Surprisingly, given the relatively harsh conditions employed for the deprotonations, ^{1}H and ^{13}C NMR spectra (C$_6$H$_6$) were entirely consistent with the formation of [K]$^+$[HL^1]$^-$·*x*thf (*x* = *ca.* 0.1) in both potassium hydride and potassium metal reactions, with no evidence for formation of [L^1]$^{2-}$. The use of toluene instead of thf did not enable isolation of the dipotassium salt. The use of 18-crown-6 did not aid formation of the dianion. However, we were able successfully to isolate crystals of [K]$^+$[HL^1]$^-$·18-crown-6 **Vb** and determine its crystal structure (see below). Reaction with LiBu^n–KOBu^t, Schlosser's base, in light petroleum gave unselective deprotonation of the methyl groups without abstraction of both ring protons. The compound [K]$^+$[HL^1]$^-$·0.1thf is much more soluble in solvents such as thf and benzene than is **IV** itself. Attempts to crystallise **Va** from these solvents by cooling or by precipitation with pentane gave oils which solidified upon complete solvent removal. It is possible that the increased solubility of **Va** relative to **IV** is related to favourable π-stacking interactions between the molecules of **IV**, which are disrupted by metallation, allowing the solubilising effect of the methyl groups to dominate.

[Mn(η^5-HL^1)(CO)$_3$]. The reaction of compound **V** with [Mn(CO)$_3$(py)$_2$Br] gave moderate yields of orange [Mn(η^5-HL^1)(CO)$_3$] **1** (Scheme 2) which we could then compare with other Mn(CO)$_3$ species to assess the effect of methylation on the indacene ligand system. We chose [Mn(CO)$_3$(py)$_2$Br][22] as a '[Mn(CO)$_3$]$^+$' synthon as it has previously been found to be less easily reduced than [Mn(CO)$_5$Br]. The reaction of [Mn(CO)$_3$(py)$_2$Br] with lithium or potassium reagents has previously been used to obtain Mn(CO)$_3$ complexes of *as*-indacene,[52] trindene (2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopent-*as*-indacene)[56] and truxene (10,15-dihydro-5*H*-diindeno-[1,2-*a*:1′,2′-*c*]fluorene).[57]



Scheme 2 (*i*) K or KH, thf, reflux; (*ii*) [MnCO$_3$(py)$_2$Br], thf; (*iii*) [Rh(η-C$_5$Me$_5$)(Me$_2$CO)$_3$]$^{2+}$2[SbF$_6$]$^-$, acetone; (*iv*) [Cr(CO)$_3$(NH$_3$)$_3$], *p*-dioxane, reflux

Two isomers of compound **1** are possible depending whether the methyl group of the CHCH$_3$ unit is on the same (*endo*) or opposite (*exo*) face of the indacene ring system as the manganese moiety. Cooling the saturated light petroleum extracts of the crude reaction product to −80 °C gave an approximately 1 : 1 **1a** to **1b** isomer mixture (according to ^{1}H NMR spectroscopy). Subsequent recrystallisations revealed **1a** to be the less soluble isomer, indicating **1b** is probably the major product, with more remaining in solution in the initial crystallisation. As X-ray crystallography (see below) identifies **1a** to be the *endo* isomer, it is not surprising that **1b** is formed as the major isomer, as it would be expected to be both kinetically and thermodynamically favoured. Interestingly the manganese complex is much more soluble in common organic solvents than is the parent hydrocarbon; the solubility of **1** in light petroleum (b.p. 40–60 °C) at 20 °C is approximately the same as that of **IV** in boiling toluene. Again this may reflect disruption of π-stacking interactions by complexation of the metal fragment. The ^{13}C NMR spectrum of **1a** shows a single carbonyl resonance (at δ 227.3 in C$_6$D$_6$); this is usual for Mn(CO)$_3$ complexes and reflects the rapid reorientation of the Mn(CO)$_3$ unit relative to the indacene ring. The ^{13}C NMR CO resonance of **1b** occurs at a very similar shift to that of **1a**.

The infrared spectrum of compound **1** in dichloromethane shows two intense carbonyl stretching bands at 1914 and 2001 cm^{-1}, the former of which is rather broad. Two bands are generally seen for [Mn(η-C$_5$H$_5$)(CO)$_3$] complexes, but, in principle, three should be observed for indenyl-type com-

Table 1 Infrared C≡O stretching frequencies for selected $Mn(CO)_3$ derivatives

L	Medium	$\tilde{\nu}_{CO}/cm^{-1}$	Ref.
(*a*) In $[MnL(CO)_3]$			
C_5H_5	Cyclohexane	1953, 2018	58
C_5Me_5	Hexane	1928, 2017	59
Indenyl	Cyclohexane	1940, 1949, 2030	60
Fluorenyl	Cyclohexane	1944, 2027	60
5-Hydro-*s*-indacene	CH_2Cl_2	1930, 2004	35
HL^1 (Isomer mixture of **1**)	CH_2Cl_2	1914, 2001	This work
(*b*) In $[\{Mn(CO)_3\}_2L]$			
trans-*s*-Indacene	CH_2Cl_2	1945, 2004	35
trans-2,7-Dimethyl-*as*-indacene	CH_2Cl_2	1942, 2012	52
cis-2,7-Dimethyl-*as*-indacene	CH_2Cl_2	1926, 1958, 2008, 2028	52

plexes owing to raising of the degeneracy of the antisymmetric pair of vibrations. However, as shown in Table 1, this splitting is not necessarily observed in practice. The complexes tricarbonyl(5-hydro-*s*-indacene)manganese, (*s*-indacene)-bis(tricarbonylmanganese)[35] and (2,7-dimethyl-*as*-indacene)-bis(tricarbonylmanganese)[52] have been reported by Smart's group. The last compound is unusual among bimetallic indacene compounds in that it is formed as a mixture of *cis* (minor) and *trans* (major) isomers; the crystal structure of the *cis* isomer features an indacene ring system significantly distorted from planarity due to steric repulsion between the two $Mn(CO)_3$ moieties. Table 1 compares the stretching frequencies for **1** with those of Smart's compounds, including the close analogue tricarbonyl(5-hydro-*s*-indacene)manganese, and also with other $Mn(CO)_3$ species. The lower values seen for **1** reflect the weakening of the C–O bonds through more back-bonding, owing to the more electron-donating HL^1 ligand. The difference between the hydro-*s*-indacene and HL^1 are similar to those between the C_5H_5 and C_5Me_5 species.

$[Rh(\eta^5\text{-}HL^1)(\eta\text{-}C_5Me_5)]^+[SbF_6]^-$. This compound was synthesized by following a procedure adapted by Bickert and Hafner[61] from one originally described by Maitlis and co-workers.[62] They showed that solutions of $[\{M(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) react with silver salts to give species, formulated as $[M(\eta\text{-}C_5Me_5)(solv)_3]^{2+}$ (solv = solvent), which react with arenes to give $[M(\eta\text{-}C_5Me_5)(\eta^6\text{-arene})]^{2+}$ salts.[62] When the arene is an indene derivative the product may be $[M(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_9H_8)]^{2+}$; alternatively, loss of H^+ and migration of the $(\eta\text{-}C_5Me_5)M$ can lead to $[M(\eta\text{-}C_5Me_5)(\eta^5\text{-}C_9H_7)]^+$ salts. In some cases the loss of H^+ may be reversed by addition of strong acid. The balance between η^6-indene and η^5-indenyl co-ordination depends on the substitution pattern of the indene and whether the metal is rhodium or iridium. Bickert and Hafner[61] extended the reaction to three dihydro-*s*-indacenes: although (η^5-hydro-*s*-indacene)(η-pentamethylcyclopentadienyl)rhodocenium hexafluoroantimonate was obtained [with no evidence for any formation of (η^6-dihydro-*s*-indacene)(η-pentamethylcyclopentadienyl)rhodocenium bis(hexafluoroantimonate)], two 2,6-disubstituted *s*-indacenes gave the η^6 products. In general it appears that electron-donating substituents on the five-membered ring of an indene or indacene impedes the formation of η^5 complexes. Thus, the reaction of **IV** with $[Rh(\eta\text{-}C_5Me_5)(Me_2CO)_3]^{2+}$ was carried out to see whether methylation of *both* five- and six-membered rings would lead to η^5 or η^6 products. The poor solubility of **IV** in acetone is presumably responsible for the rather slow rate of reaction, as judged by the rate of disappearance of the indacene ligand, and consequently, owing to competing side reactions of the rhodium species, the low isolated yield. The product was isolated as an air-stable yellow microcrystalline powder by crystallisation from the reaction mixture: elemental analysis and NMR spectroscopy showed it to be $[Rh(\eta^5\text{-}HL^1)(\eta\text{-}C_5Me_5)]^+[SbF_6]^-$, **2**.

Table 2 Proton NMR chemical shifts in $(CD_3)_2CO$ for the C_5Me_5 resonances of selected complexes $[RhL(\eta\text{-}C_5Me_5)]^+X^-$

L	X^-	δ	Ref.
η^5-Indenyl	$[PF_6]^-$	1.86	62
η^5-4,6-Dimethylindenyl	$[PF_6]^-$	1.82	62
η^5-2-Methylindenyl	$[SbF_6]^-$	1.82	61
η^5-5-Hydro-*s*-indacene	$[SbF_6]^-$	1.83	61
η^5-HL^1	$[SbF_6]^-$ (**2a**)	1.70	This work

Proton and ^{13}C NMR spectroscopy show compound **2** is formed as a single isomer (shown to be the *endo* isomer, **2a**, by X-ray diffraction, see below). A possible explanation of why the major isomer is the (5-*endo*-CH_3) assumes that **IV** occurs as a statistical (1 : 1) mixture of two isomers, differing in whether the 1- and 5-methyl groups are on the same or opposite sides of the ring system. It may also be assumed, following from previous work on the reaction of indenes and dihydroindacenes with '$(\eta\text{-}C_5Me_5)Rh^{2+}$',[61,62] that co-ordination of the $(\eta\text{-}C_5Me_5)Rh$ initially occurs in η^6 fashion to the central ring. By analogy with the synthesis of $[Cr(\eta^6\text{-}H_2L^1)(CO)_3]$ (see below), a 1 : 1 : 2 mixture of *endo*/*endo*, *exo*/*exo* and *endo*/*exo* isomers of $[Rh(\eta^6\text{-}H_2L^1)(\eta\text{-}C_5Me_5)]^{2+}$ would be expected. Subsequent migration of the rhodium fragment might be expected to occur towards the less-hindered five-membered ring. In the *endo*/*exo* isomer, where there is a choice, the *endo* isomer of $[Rh(\eta^5\text{-}HL^1)(\eta\text{-}C_5Me_5)]^+$ would be expected to be formed. The net result would be a 1 : 3 *exo* to *endo* ratio, from which it is not surprising that the pure *endo* isomer is isolated by crystallisation from the reaction mixture. An interesting feature of the ^{13}C NMR spectrum of **2** is the coupling to ^{103}Rh (100%, $I = \frac{1}{2}$) of the C_5Me_5 ring carbon resonance and of the resonances corresponding to the indacene ring carbon atoms bound to rhodium. Unfortunately, no ^{13}C NMR data for (η^5-5-hydro-*s*-indacene)(η-pentamethylcyclopentadienyl)rhodium are available for comparison; however, the Rh–C coupling constants are similar in magnitude to those reported for $[Rh(\eta^5\text{-}C_9H_7)(\eta\text{-}C_5Me_5)]^+[PF_6]^-$ and for $[Rh(\eta^5\text{-}C_9H_5Me_2\text{-}4,6)(\eta\text{-}C_5Me_5)]^+[PF_6{}^-]$.[61] Table 2 compares the ^1H NMR shift of the C_5Me_5 methyl groups of **2** in $(CD_3)_2CO$ with those of other indenyl and hydroindacene ligands; the upfield shift of the resonance of **2** again demonstrates the electron richness of the HL^1 ligand.

$[Cr(\eta^6\text{-}H_2L^1)(CO)_3]$. The preparation of the yellow $Cr(CO)_3$ complex of H_2L^1, **3**, was carried out in an analogous fashion to that of $[Cr(\eta^6\text{-}C_9HMe_7)(CO)_3]$.[63] Compound **3** is only the third reported η^6 derivative of an indacene system (the other two complexes are Bickert and Hafner's rhodium compounds)[61] and the first to be structurally characterised (see below). This complex could be a useful precursor for the construction of trimetallic indacene complexes and of *cis*-bimetallic indacene complexes. Doubly deprotonating **3** and treating with a '$[(\eta\text{-}(C_5H_5)M]^{+}$' synthon, one could envisage both $(\eta\text{-}C_5H_5)M$ units complexing to the opposite face of the ligand from the chromium moiety, which might be removable at a later stage. In a preliminary investigation we carried out the reaction of **3** with 2 equivalents of $LiBu^n$ in thf at 0 °C, quenching with $SiMe_3Cl$. The ^1H NMR spectrum of the crude product showed no resonances corresponding to Me_3Si-containing products. However, Ceccon and co-workers[63–65] have found haptotropic shifts of the chromium tricarbonyl moiety to be a complication in the deprotonation reactions of $[Cr(\eta^6\text{-}C_9H_8)(CO)_3]$ and various substituted derivatives; careful choices of base and temperature were necessary to circumvent their problems.

Proton and ^{13}C NMR spectra of compound **3** show all three possible isomers to be present; the spectra are consistent with

Table 3 Infrared C≡O stretching frequencies for selected [Cr(η^6-arene)(CO)$_3$] derivatives

η^6-Arene	Medium	$\tilde{\nu}_{CO}$/cm^{-1}	Ref.
η^6-C_6H_6	Cyclohexane	1917, 1987	66
η^6-C_6Me_6	Cyclohexane	1888, 1962	66
η^6-Naphthalene	Cyclohexane	1905, 1918, 1977	66
η^6-Styrene	Cyclohexane	1913, 1980	19
η^6-Indene	thf	1898, 1975	67
η^6-Fluorene	thf	1892, 1966	67
(1-*endo*)η^6-1,2,3,4,5,6,7-Heptamethylindene	thf	1862, 1943	63
(1-*exo*)	thf	1866, 1945	63
*	thf	1851, 1861, 1937	63
η^6-H_2L^1 (isomeric mixture of **3**)	thf	1863, 1941	This work
	CH_2Cl_2	1844, 1934	This work

* *trans*-[(η^4-cod)Rh(μ-η^5:η^6-C_9Me_7)Cr(CO)$_3$], where cod = cycloocta-1,5-diene.

an approximate 1 : 1 : 2 mixture of *endo*/*endo*, *exo*/*exo* and *endo*/*exo* isomers, which is the situation that would occur if **IV** exists as an approximately 1 : 1 mixture of the two diastereomers possible and if complexation to chromium is unselective. This is, however, somewhat different from the situation reported for heptamethylindene, the chromium complex of which is formed in a 19 : 3 *exo* to *endo* ratio.[63] The ^{13}C NMR spectrum of an isomeric mixture shows a single carbonyl resonance, a single peak at δ 236.4 in $CDCl_3$ (δ 236.7 in C_6D_6), presumably because of the very similar shifts for the three isomers. This is almost identical to the CO shift of the heptamethylindene analogue, where the two isomers are observed at δ 235.7 and 236.0 in $CDCl_3$. The IR spectrum of a thf solution shows strong C≡O bands at 1863 and 1941 cm^{-1}. In Table 3 these data are compared with carbonyl stretching frequencies for a number of other [Cr(η^6-arene)(CO)$_3$] complexes. Two C≡O stretching modes are expected for such species; a symmetric and a two-fold degenerate antisymmetric combination.[68] In principle, significant distortion of the complex from pseudo-axial symmetry should lead to lifting of the degeneracy of the antisymmetric pair of vibrations. However, three bands are only observed in practice for severely distorted species, generally where another aromatic ring is fused to the arene, *e.g.* the rhodium–chromium bimetallic in Table 3. A notable trend among the data in Table 3 is the decrease in ν_{CO} with increasing electron richness of the ligand (*e.g.* compare the benzene and hexamethylbenzene complexes); this may be attributed to increased electron density at the metal and consequently stronger Cr–CO back bonding weakening the C≡O bonds. The frequencies for **3** are very similar to those for [Cr(η^6-C_9HMe_7)(CO)$_3$], as are the ^{13}C NMR shifts of the carbonyl groups, indicating the two ligands have very similar electron-donating abilities in this situation.

Crystal structures of organometallic H_2L^1 derivatives

We have determined the single-crystal structures of the alkali- and transition-metal derivatives of compound **IV** (**Vb**, **1a**, **2a** and **3c**) discussed above. Crystallographic details are given in the Experimental section. Views of the structures of are shown in Figs. 3 (**Vb**), 4 and 5 (**1a**), 6 (**2a**) and 7 (**3c**); whilst selected bond lengths and angles are given in Tables 5–9.

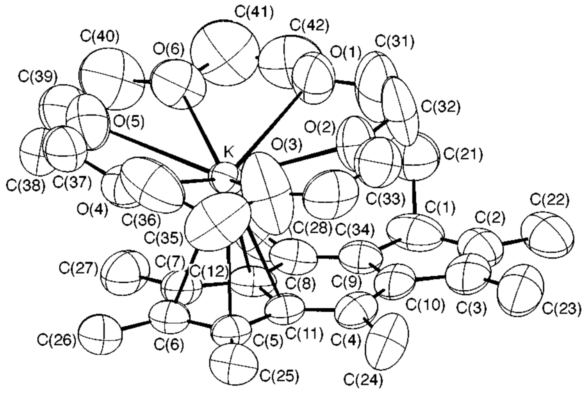


Fig. 3 View of the molecular structure of compound **Vb** in the crystal, showing 50% thermal ellipsoids

The molecular structure of compound **Vb** is shown in Fig. 3. The potassium ion is sandwiched between the crown ether and the deprotonated five-membered ring of the [HL^1]$^-$ anion; this is similar to the arrangement in [Li]$^+$[C_5H_5]$^-$·12-crown-4 (12-crown-4 = 1,4,7,10-tetraoxacyclododecane).[69] The unresolved disorder associated with the crown ether means that the details of its co-ordination to the potassium ion cannot be meaningfully discussed. The co-ordination of the potassium ion to the hydrooctamethylindacene anion, which can be regarded as an elaborate indenide ion, is somewhat distorted from ideal η^5 geometry with two relatively long and three relatively short bonds. However the pattern of long and short bonds is different to the slippage towards a η^3-allyl/benzene type structure which has been observed in many transition-metal indenyl complexes (see below) and in [Li]$^+$[C_9H_7]·tmen;[70] in **Vb** the slippage appears to be towards a structure where the potassium is bound to one of the ring junction carbons and to two non-junction carbons. Since the potassium–anion interaction is presumably largely ionic and hence not strongly directional, it is possible that the packing constraints of the other portions of the molecule, rather than any electronic factor, are responsible for this distortion. The K–C distances 3.007(5)–3.363(6) (average 3.194 Å) (Table 5) may be compared to those in [K]$^+$-[C_5Me_5]$^-$·2py [polymer with μ-η^5:η^5-C_5Me_5 units; K–C 2.962(2)–3.104(2), average 3.034 Å],[71] [K]$^+$[$C_5H_4SiMe_3$]$^-$ [polymer with μ-η^5:η^5-$C_5H_4SiMe_3$ units; K–C 2.988(10)–3.079(10), average 3.03 Å][72] and [K]$^+$[$C_5(CH_2Ph)_5$]$^-$·3thf [monomeric 'piano stool' structure; K–C 2.968(5)–3.095(5), average 3.035 Å].[73] The longer K–C distances in **Vb** may be at least partly due to the separation of the ion pair induced by the crown ether; comparison of the structures of [Li]$^+$[C_5H_5]$^-$·12-crown-4 (average Li–C 2.380 Å)[69] and [Li]$^+$[C_5H_4Me]$^-$·tmen (average Li–C 2.26 Å)[74] reveals an analogous effect.

Whilst many crystal structures of covalent transition-metal indenyl derivatives have been published, until recently structures of the more ionic indenides of Groups 1A and IIA were limited to those of [M]$^+$[C_9H_7]$^-$·tmen (M = Li[70] or Na[75]) and of [Mg]$^{2+}$2[C_9H_7]$^-$.[76] More recently the structures of [Ca]$^{2+}$-2[C_9H_7]$^-$·2thf, [Sr]$^{2+}$2[C_9H_7]$^-$·thf, [Ca]$^{2+}$2[$C_9H_5Pr^i_2$-1,3]$^-$·thf and [Ba]$^{2+}$2[$C_9H_5Pr^i_2$-1,3]$^-$·thf have been published.[77] The lithium compound is monomeric, with the lithium sandwiched between the tmen and the indenide anion, which is slightly slipped towards an η^3 allyl/benzene structure, whilst the sodium compound is a polymer with Na(tmen) units sandwiched between bridging η^1:η^2 indenide ions. Both polymeric and bis(indenide) sandwich structures are found among the alkaline earths. The pattern of bond lengths in the [HL^1]$^-$ anion in **Vb** is similar to that in the other Group IA and IIA indenides. A notable feature is the greater length of the ring-junction bond [1.471(7) Å] relative to the other C–C bonds of the deprotonated five-membered ring [1.378(8)–1.415(7) Å]. This effect (which is a general feature of the more covalent transition-metal indenyl complexes) is common to the other alkali- and alkaline-earth-metal indenides apart from the magnesium species, but it is most pronounced in **Vb**, perhaps due to the degree of separation of the ion pair effected by the crown ether. The effect can be understood by examining the highest occupied molecular orbital (HOMO) of the indenide anion (illustrated, for example, by Rhine and Stucky)[70] which features an antibonding interaction between the two ring-junction atoms.

The structures of compound **1a** and **2a** both display typical

Table 4 Details of the crystal structure determinations

	Vb	**1a**	**2a**	**3c**
Formula	$C_{32}H_{49}KO_6$	$C_{23}H_{25}MnO_3$	$C_{30}H_{37}F_6RhSb$	$C_{23}H_{26}CrO_3$
M	568.84	404.39	736.27	402.45
Crystal appearance	Orange plate	Orange-yellow block	Yellow plate	Yellow block
Crystal size/mm	0.10 × 0.25 × 0.40	0.54 × 0.60 × 0.81	0.09 × 0.36 × 1.05	0.16 × 0.24 × 0.32
Diffractometer	Enraf-Nonius DIP 2000	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius DIP 2000
T/K	150	298	298	170
Crystal class	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/m$	$P\bar{1}$
a/Å	9.836(1)	13.824(4)	8.961(19)	7.502(4)
b/Å	16.634(1)	15.920(4)	17.535(2)	9.522(4)
c/Å	19.384(1)	18.493(4)	9.530(18)	14.789(6)
α/°				101.125(3)
β/°	97.446(2)		10.611(8)	91.559(3)
γ/°				111.629(3)
U/Å^3	3144.71(1)	40 70(1)	1471.9(3)	963.24(1)
Z	4	8	2	2
D_c/g cm^{-3}	1.20	1.32	1.66	1.39
μ/cm^{-1}	2.0	6.4	15.3	6.0
F(000)	1233	1689	734	424
θ Limits/°	0–26	0–25	0–29	0–26
Total data measured	33 499	4958	4898	17 416
Total unique data	6913	3559	3965	3718
No. least-squares parameters	362	245	185	245
No. observed data*	3920	1752	2752	3236
R	0.087	0.053	0.042	0.051
R'	0.080	0.058	0.049	0.059

* For compound **Vb** reflections with $I > 6\sigma(I)$ were used; for **1a** and **2a** and **3c** those with $I > 3\sigma(I)$.

Table 5 Selected bond lengths (Å) and angles (°) for $[K]^+[HL]^- \cdot$18-crown-6 **Vb**

K1–C(5)	3.007(5)	C(4)–C(11)	1.418(7)
K–C(11)	3.114(5)	C(5)–C(6)	1.395(8)
K–C(6)	3.148(6)	C(5)–C(11)	1.415(7)
K–C(12)	3.338(5)	C(6)–C(7)	1.378(8)
K–C(7)	3.363(6)	C(7)–C(12)	1.406(8)
C(1)–C(2)	1.50(1)	C(8)–C(9)	1.339(8)
C(1)–C(9)	1.536(8)	C(8)–C(12)	1.421(8)
C(2)–C(3)	1.324(9)	C(9)–C(10)	1.420(8)
C(3)–C(10)	1.467(8)	C(11)–C(12)	1.471(7)
C(4)–C(10)	1.437(8)		
C(6)–C(5)–C(11)	108.0(5)	C(5)–C(11)–C(12)	106.0(5)
C(5)–C(6)–C(7)	110.6(5)	C(7)–C(12)–C(11)	107.3(5)
C(6)–C(7)–C(12)	108.1(5)		

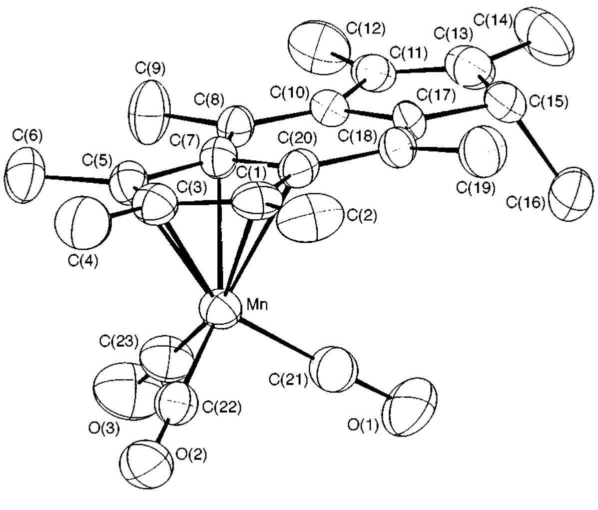


Fig. 4 View of molecule **1a** in the crystal structure, showing 50% thermal ellipsoids

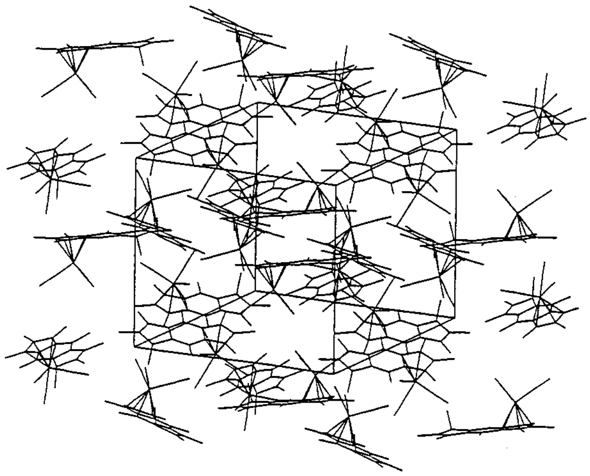


Fig. 5 Packing diagram for compound **1a**

features of covalent η^5-indenyl species: both show two long and three short metal–ring C distances, the long bonds being those to the ring-junction carbons. Representative examples of this phenomenon may be found in the structures of various $Mn(CO)_3$ species compared in Table 7 and in the structures of bis(η^5-1,3-dimethylindenyl)iron hexafluorophosphate [short M–C 2.063(4)–2.079(4) Å; long M–C 2.142(4)–2.156(4) Å],[81] (η^5-indenyl)(η^4-norbornadiene)rhodium [2.224(5)–2.240(5), 2.388(3)–2.401(3) Å],[65] bis(η^5-indenyl)dimethylzirconium [2.502(5)–2.513(5), 2.600(5)–2.622(5) Å][82] and (η^5-heptamethylindenyl)titanium trichloride [2.352(4)–2.360(4), 2.383(4)–2.400(4) Å].[83] The bond-length alternation in the six-membered rings of both **1a** and **2a** is also typical of η^5-indenyl structures. The C–C bonds in the co-ordinated five-membered rings of both compounds are longer than those of **Vb**, paralleling differences seen between alkali- and transition-metal indenyl species.

Several structural parameters for compound **6a** are compared with those for other $Mn(CO)_3$ complexes in Table 7. Interestingly, the asymmetry of the bonding, as measured by the difference of r_a and r_b (defined in Table 7), is significantly lower than in the 1-bromoindenyl and *s*-indacene complexes of $Mn(CO)_3$, although not as low as that of the structurally characterised 2,7-dimethyl-*as*-indacene complex. The Mn–CO bond

Table 6 Selected bond lengths (Å) and angles (°) for compound **1a**

Mn—C(1)	2.125(5)	C(3)–C(5)	1.414(8)
Mn–C(3)	2.137(5)	C(5)–C(7)	1.454(8)
Mn–C(5)	2.128(5)	C(7)–C(8)	1.438(7)
Mn–C(7)	2.185(5)	C(7)–C(20)	1.439(7)
Mn–C(20)	2.197(5)	C(8)–C(10)	1.352(7)
Mn–C(21)	1.763(7)	C(10)–C(11)	1.488(7)
Mn–C(22)	1.743(6)	C(10)–C(17)	1.429(8)
Mn–C(23)	1.766(6)	C(11)–C(13)	1.317(8)
O(1)–C(21)	1.160(7)	C(13)–C(15)	1.515(9)
O(2)–C(22)	1.167(7)	C(15)–C(17)	1.514(8)
O(3)–C(23)	1.164(7)	C(17)–C(18)	1.351(8)
C(1)–C(3)	1.397(8)	C(18)–C(20)	1.437(8)
C(1)–C(20)	1.437(8)		
C(3)–C(1)–C(20)	108.6(5)	C(1)–C(20)–C(7)	107.0(5)
C(1)–C(3)–C(5)	109.7(5)	Mn–C(21)–O(1)	178.0(6)
C(3)–C(5)–C(7)	106.9(5)	Mn–C(22)–O(2)	177.9(5)
C(5)–C(7)–C(20)	107.6(4)	Mn–C(23)–O(3)	178.4(7)

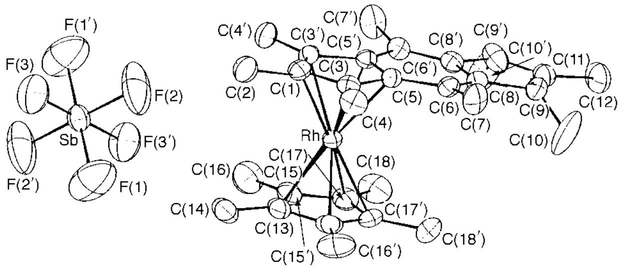


Fig. 6 View of the cation **2a** in the crystal structure, showing 50% thermal ellipsoids, primes denote symmetry-generated atoms. Ring positions 5 and 7 refer to the carbon atoms labelled 9 and 9′

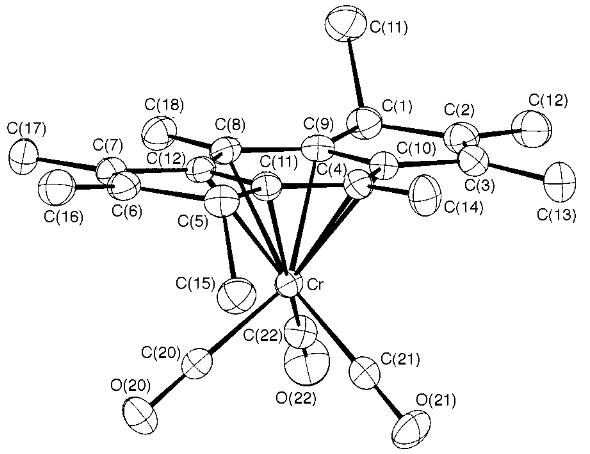


Fig. 7 View of the molecule **8c** in the crystal structure, showing 50% thermal ellipsoids

lengths for **1a** fall in the range 1.743(6)–1.766(6) Å; these are significantly shorter than in most other $Mn(CO)_3$ complexes listed in Table 7. For example, its closest relative, tricarbonyl(5-hydro-*s*-indacene)manganese, has M–CO bond lengths in the range 1.772(6)–1.800(6) Å. The C–O bond lengths are correspondingly longer in **1a** [range 1.160(7)–1.167(7) Å] than in most of the other complexes [range for tricarbonyl(5-hydro-*s*-indacene)manganese 1.143(5)–1.152(5) Å]. The differences in Mn–CO and C–O bond lengths between the hydro-*s*-indacene complex and its octamethylated analogue parallels that between the cyclopentadienyl and pentamethylcyclopentadienyl complexes. In each case the electron-donating effect of the methyl groups is evidently sufficient to lead to appreciably stronger metal d–CO π^* back bonding and consequent shortening of the Mn–CO bonds and lengthening of the C–O bonds.

The isomer **1a** is presumably both thermodynamically and kinetically disfavoured, due to steric considerations, compared to **1b**. It is the least soluble and most easily crystallised of the two isomers. Crystallisation may be facilitated in **1a** as the unencumbered face of the indacene ligand can pack against that of another molecule with favourable π–π interactions; this may be seen in the packing diagram, Fig. 5.

Compound **3a** is only the third rhodocenium species to be structurally characterised. The others are $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\text{-}1,2,3\}_2]^+[C_5(CO_2Me)_5]^-$ [84] and the bimetallic species μ-$\eta^5:\eta^5$-fulvalenebis[(pentamethylcyclopentadienyl)-rhodium].[85] The Rh–C_5Me_5 ring C distances in **2a** range from 2.161(6) to 2.182(4) (average 2.177 Å) and the Rh–HL^1 bonds range from 2.174(5) to 2.217(4) (average 2.194 Å); these are similar to the Rh–C bond lengths for $[Rh\{C_5H_2(CO_2Me)_3\text{-}1,2,3\}_2]^+$ [2.15(2)–2.19(2), average 2.17 Å] and those for the isoelectronic ruthenocenes, *e.g.*, $[Ru(C_5Ph_4H)_2]$[86] has an average Ru–C distance of 2.20 Å. The bimetallic fulvalene species has average Rh–C bond lengths of 2.186 Å to the fulvalene ligand and 2.156 Å to the C_5Me_5.[85] The neutral rhodocene $[Rh(C_5Ph_4H)_2]$ has significantly longer Rh–C distances ranging from 2.220(9) to 2.307(9) (average 2.26 Å) as the nineteenth electron resides in an orbital with some antibonding character.[87] The differences between rhodocene and rhodocenium species parallel those observed between cobaltocenes {*e.g.* $[Co(C_5Ph_4H)_2]$[88] has an average Co–C bond length of 2.152 Å} and cobaltocenium salts $\{2[Co(\eta\text{-}C_5Me_5)_2]^+[tcne]^{2-}$ (tcne = tetracyanoethylene)[89] is a typical example with an average Co–C bond length of 2.052 Å}.

Interestingly, the pentamethylcyclopentadienyl ring and the η^5-indacene ring in compound **2a** completely eclipse one another whereas in both the fulvalene compound[85] and $[Rh\{C_5H_2(CO_2Me)_3\text{-}1,2,3\}_2]^+[C_5(CO_2Me)_5]^-$ [84] the two rings are staggered (presumably staggering is necessary in the last case to prevent steric interference between the rather bulky ester substituents).

In compound **3c** the C–O bond lengths fall in the range 1.158(5)–1.161(4) Å (Table 9) whilst the Cr–CO bond lengths fall in the range 1.830(4)–1.834(4) Å. These are similar values to those reported for other electron-rich $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes; for example, for the hexamethylbenzene complex Cr–CO and C–O bonds are in the ranges 1.832(3)–1.840(3) and 1.155(5) Å respectively.[90] For the benzene species Cr–CO and C–O bonds were found in the range 1.841(1)–1.842(2) and 1.157(2)–1.159(2) Å (according to a 77 K X-ray study; results from 92 K neutron data are very similar).[91] The effect of electron-releasing methyl groups on the bond lengths of the $Cr(CO)_3$ is evidently considerably less pronounced than that seen in $Mn(CO)_3$ complexes (see below). The Cr–HL^1 bond lengths are similar to those seen in other $[Cr(\eta^6\text{-arene})(CO)_3]$ complexes. Bond-length alternation has been observed in the arene rings of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (by diffraction methods in the crystal[91] and by microwave spectroscopy in the gas phase)[92] and $[Cr(\eta^6\text{-}C_6Me_6)(CO)_3]$ (in the crystal).[90] In **3c** the C–C bond lengths in the η^6 ring vary from 1.405(5) to 1.424(5) Å; however, no bond-length alternation is found. This is perhaps unsurprising in view of the conformation of the $Cr(CO)_3$ moiety relative to the ring (see below) and the possible effects of the ring substituents. The torsion angles given in Table 9 show that the $Cr(CO)_3$ unit is *ca.* 21° away from an ideally staggered conformation (*i.e. ca.* 9° away from being perfectly eclipsed) with respect to the six-membered ring of H_2L^1. In this particular conformation one of the CO groups must lie more or less under one of the $CHCH_3$ groups; this is found to be the *exo*-CH_3 group [C(13)] thus avoiding steric interference with the *endo*-CH_3 group. The $Cr(CO)_3$ units of the heptamethylindene analogue of **3c** and two heterobimetallic derivatives are all *ca.* 4–5° from the ideal staggered conformation.[63] Those of the benzene[90,93,94] and hexamethylbenzene[91,95] species are rigorously and essentially perfectly staggered respectively, whilst that of the hexaethylbenzene compound is almost perfectly staggered.[96]

Table 7 Comparison of some average bond lengths (Å) for some $Mn(CO)_3$ derivatives

L	r_a[a]/Å	r_b[b]/Å	r_c[c]/Å	r_d[d]/Å	r_e[e]/Å	Ref.
(*a*) $[MnL(CO)_3]$						
C_5H_5	2.138		1.407	1.793	1.144	78
C_5Me_5	2.129		1.387	1.729	1.175	79
1-Bromoindenyl	2.128	2.213	1.42	1.793	1.14	80
5-Hydro-*s*-indacene	2.119	2.214	1.414	1.788	1.149	35
HL^1 (**1a**)	2.130	2.191	1.428	1.757	1.164	This work
(*b*) $[\{Mn(CO)_3\}_2L]$						
trans-*s*-Indacene	2.127	2.249	1.429	1.797	1.142	35
cis-2,7-Dimethyl-*as*-indacene	2.143	2.181	1.440	1.787	1.140	52

[a] Average manganese–non-ring-junction ring C distance. [b] Average manganese–ring junction ring C distance. [c] Average C–C distance in ring bound to Mn. [d] Average Mn–CO distance. [e] Average C–O distance.

Table 8 Selected bond lengths (Å) and angles (°) for compound **2a**; primes denote atoms generated by symmetry

Rh–C(1)	2.174(5)	C(5)–C(5′)	1.447(7)
Rh–C(3)	2.181(4)	C(5)–C(6)	1.436(5)
Rh–C(5)	2.217(4)	C(6)–C(8)	1.364(6)
Rh–C(13)	2.161(6)	C(8)–C(8′)	1.448(9)
Rh–C(15)	2.180(4)	C(13)–C(15)	1.437(7)
Rh–C(17)	1.282(4)	C(15)–C(17)	1.426(7)
C(1)–C(3)	1.422(6)	C(17)–C(17′)	1.45(1)
C(3)–C(5)	1.453(5)		
C(3)–C(1)–C(3′)	109.7(5)	C(3)–C(5)–C(5′)	107.6(2)
C(1)–C(3)–C(5)	107.5(4)		

Table 9 Selected bond lengths (Å), angles and torsion angles (°) for compound **3c**; CEN is the centroid of the six-membered ring

Cr–C(4)	2.304(3)	C(1)–C(9)	1.515(3)
Cr–C(8)	2.269(2)	C(2)–C(3)	1.345(4)
Cr–C(9)	2.228(2)	C(3)–C(10)	1.489(3)
Cr–C(10)	2.253(2)	C(4)–C(10)	1.423(4)
Cr–C(11)	2.257(2)	C(4)–C(11)	1.410(3)
Cr–C(12)	2.255(2)	C(5)–C(6)	1.518(4)
Cr–C(20)	1.836(3)	C(5)–C(11)	1.510(3)
Cr–C(21)	1.837(3)	C(6)–C(7)	1.344(4)
Cr–C(22)	1.834(3)	C(7)–C(12)	1.496(3)
O(20)–C(20)	1.160(4)	C(8)–C(9)	1.418(5)
O(21)–C(21)	1.151(4)	C(8)–C(12)	1.418(3)
O(22)–C(22)	1.154(4)	C(9)–C(10)	1.420(4)
C(1)–C(2)	1.511(4)		
C(10)–C(4)–C(11)	116.8(2)	C(8)–C(12)–C(11)	121.2(2)
C(9)–C(8)–C(12)	115.7(2)	Cr–C(20)–O(20)	178.4(2)
C(8)–C(9)–C(10)	123.4(2)	Cr–C(21)–O(21)	179.4(2)
C(4)–C(10)–C(9)	120.2(2)	Cr–C(22)–O(22)	179.1(3)
C(4)–C(11)–C(12)	122.6(2)		
C(20)–Cr–CEN–C(4)	9.6(1)	C(22)–Cr–CEN–C(9)	8.7(9)
C(21)–Cr–CEN–C(12)	9.0(9)		

Electronic and intramolecular steric arguments have been used to explain the conformations of $Cr(CO)_3$ complexes in many cases;[97] however, in other cases, such as a series of *p*-disubstituted species studied by Gilbert *et al.*,[98] such arguments were found to be insufficient and intermolecular steric (*i.e.* crystal-packing) arguments had to be invoked.

Conclusion

We have developed a convenient route to a new fused-ring permethylated ligand, 1,2,3,4,5,6,7,8-octamethyl-1,5-dihydro-*s*-indacene (H_2L^1). We have shown that mononucelar organometallic complexes may be formed from it by several different routes. Spectroscopic and crystallographic data indicate both η^5-HL^1 and η^6-H_2L^1 ligands to be strongly electron donating. Unfortunately the synthesis of L^1-based polymetallic species has been hampered by the difficulty of doubly deprotonating H_2L^1.

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