

# Synthesis and Characterization of *as*- and *s*-Indacene Bridging Ligands and Their Trimethyltin and Manganese Tricarbonyl Derivatives

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1,6-Dihydro-2,7-dimethyl-*as*-indacene and dihydro-*s*-indacene have been prepared on a large scale. The synthesis of the methyl-substituted *as* isomer also yields 1,7-dihydro-2,6-dimethyl-*s*-indacene as a minor product. These ligand precursors have been selectively deprotonated to give both mono- and dianions, which were characterized by NMR spectroscopy and by reaction with chlorotrimethyltin to yield the corresponding trimethyltin derivatives. All of these tin derivatives are stereochemically nonrigid on the NMR time scale. The mono- and bis(trimethyltin) derivatives of *s*-indacene undergo transmetalation reactions with manganese pentacarbonyl bromide to yield (5-hydro-*s*-indacene)manganese tricarbonyl and (*s*-indacene)bis(manganese tricarbonyl), respectively. Both of these manganese complexes have been characterized by X-ray crystallography; the manganese atoms in the dinuclear complex are disposed trans with respect to the near-planar bridging ligand.

## Introduction

The geometry, electronic structure, and reactivity of polynuclear transition-metal compounds with bridging carbocyclic ligands are areas of general interest.<sup>2</sup> In previous studies, a series of dinuclear metal complexes of the bridging fulvalene dianion, **1**, has been prepared, which includes bis(fulvalene)dimetal derivatives, (C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>M<sub>2</sub>, of V,<sup>3a</sup> Cr,<sup>3b</sup> Mo,<sup>3c</sup> Fe,<sup>3d</sup> Co,<sup>3e</sup> Rh,<sup>3f</sup> and Ni,<sup>3g</sup> as well as (fulvalene)metal carbonyl complexes of Cr,<sup>3h</sup> Mo,<sup>3hi</sup> W,<sup>3h</sup> Mn,<sup>3j</sup> Co,<sup>3h</sup> and Ru<sup>3h</sup> and also several early-transition-metal complexes with one bridging fulvalene ligand.<sup>3h-p</sup> These complexes exhibit a variety of structural features including metal-metal bonding in the range of 3.3-4.2 Å that contributes to geometric distortion of the fulvalene ligand.

Structural studies of the neutral (η<sup>4</sup>:η<sup>4</sup>-C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Ni<sub>2</sub><sup>3b</sup> indicate that the oxidized "antiaromatic" 14-π-electron polyolefin form of the ligand (i.e., fulvalene) is coordinated to two nickel atoms. Recently Vollhardt and co-workers<sup>3n,o</sup> have characterized related fulvalene complexes (η<sup>4</sup>-

C<sub>10</sub>H<sub>8</sub>)Mo(CO)<sub>2</sub>L<sub>2</sub> and (η<sup>4</sup>-C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Ru(CO)<sub>2</sub>L<sub>2</sub>, with a metal carbonyl group coordinated to one five-membered ring. The interrelationship of metal oxidation state and oxidation level of the ligand in these complexes and their mixed-valence derivatives is of fundamental importance to an understanding of their novel electronic structures relative to those of the analogous metallocene and cyclopentadienylmetal carbonyl complexes.

In an effort to extend this chemistry to more annulated bridging ligands, we have developed efficient synthetic routes to the isomeric *as*- and *s*-indacene ligands shown in Figure 1. We utilized the aromatic *as*- and *s*-indacene mono- and dianions that were obtained by selective deprotonation of the corresponding dihydroindacenes **2** (as the 2,7-dimethyl derivative) and **4**. These ligands have the potential to bridge two metal moieties in both their reduced aromatic dianion forms **3** and **5** or as oxidized "antiaromatic" neutral polyolefins (i.e., *as*- and *s*-indacene). In addition, the anionic ligands have the potential to allow metal bonding to the five-membered ring to slip from an η<sup>5</sup>- to an η<sup>3</sup>-allyl mode (i.e., **3a-b** and **5a-c**), as exhibited in structural and reaction studies of indenyl metal complexes,<sup>4</sup> or to an η<sup>4</sup>-butadiene bonding mode in the neutral ligands. Unlike fulvalene dianion, the rigid indacene ligands also allow two metal moieties to bond in either cis or trans dispositions with respect to the plane of the tricyclic hydrocarbons.

Structural studies indicate that the distance from the centers of the five-membered rings in *as*-indacene, like that of a relatively planar fulvalene ligand, is approximately 4.0 Å as compared to approximately 4.8 Å for *s*-indacene.

The preparation of dihydro-*as*-indacene (**2**) has been previously reported.<sup>5,6</sup> Katz and co-workers have isolated

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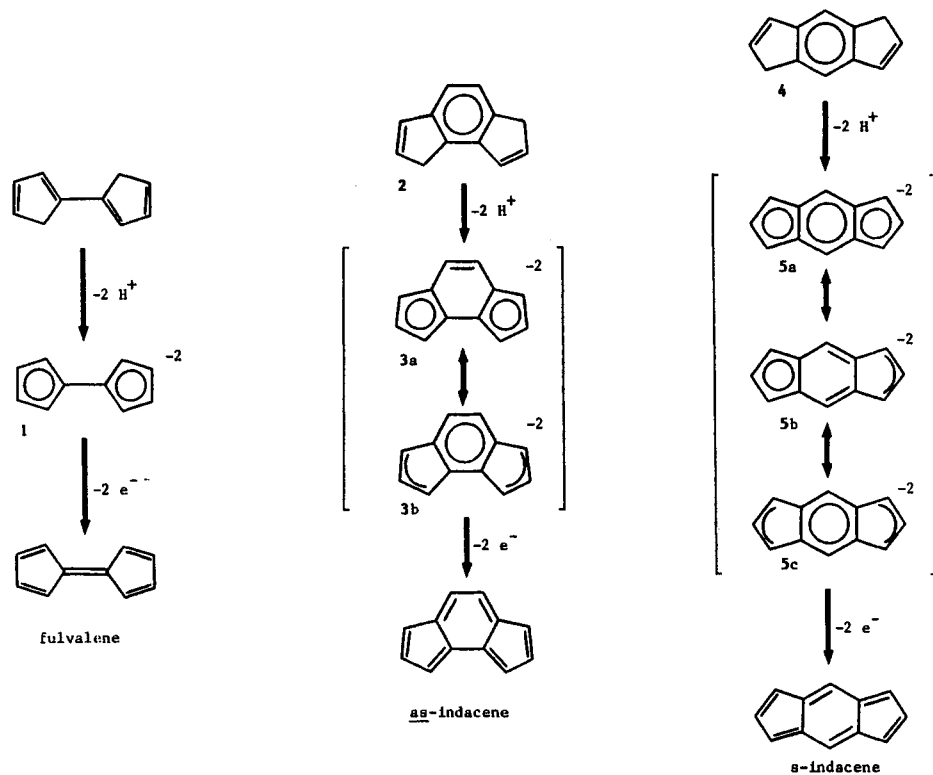


Figure 1. Valence-bond representations of fulvalene and indacene ligands.

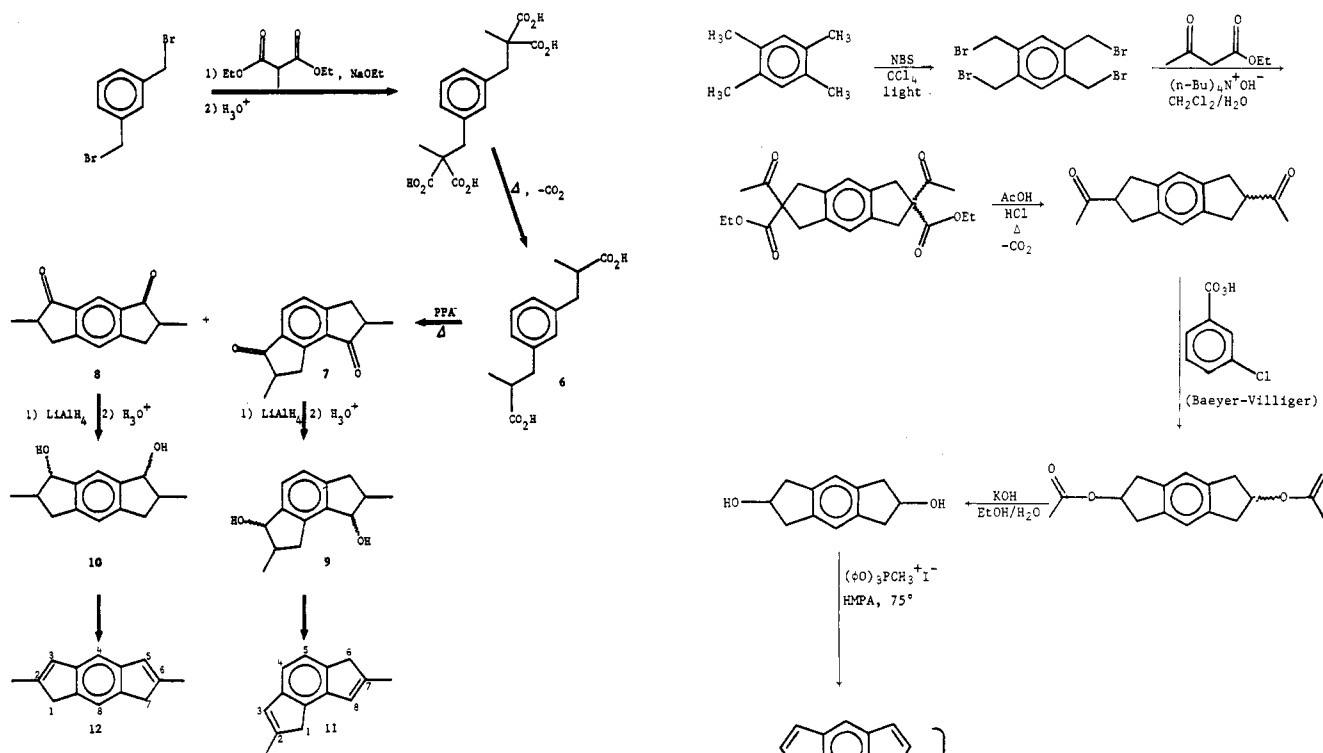


Figure 2. Synthesis of dihydromethyl-*s*- and dihydrodimethyl-*as*-indacenes.

and characterized the *as*-indacene dianion **3**,<sup>5a</sup> the preparation of the doubly bridged bis(*as*-indacene)diiron has been described<sup>5b</sup> and an X-ray structure reported.<sup>7</sup> Singly bridged (*as*-indacene)bis(cyclopentadienyliron) has been prepared by the reaction of **3** with cyclopentadienyl anion and iron(II) chloride,<sup>8</sup> and its *trans* configuration was

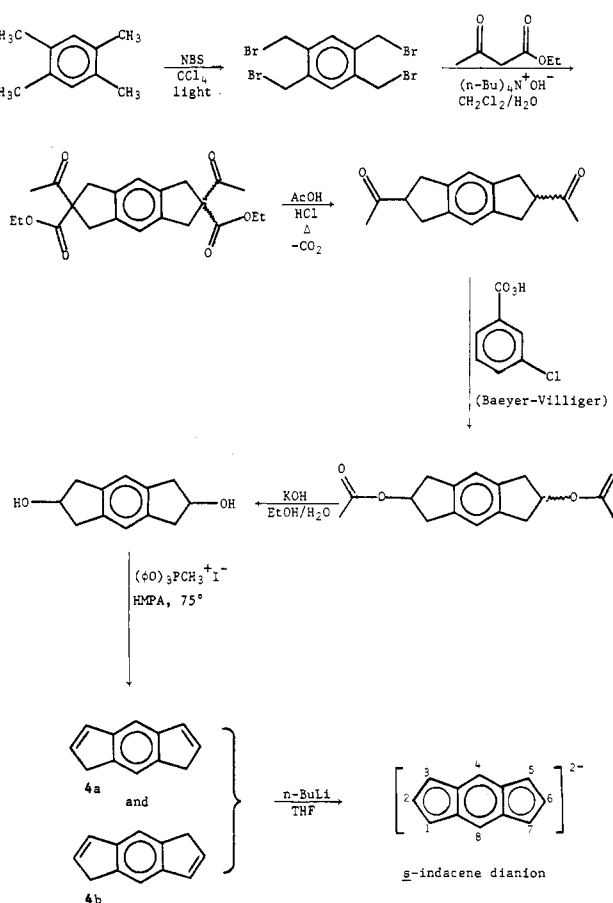


Figure 3. Synthesis of dihydro-*s*-indacene.

confirmed by X-ray crystallography.

Our alternative synthesis of methyl-substituted dihydroindacenes shown in Figure 2 provides an efficient route to 1,6-dihydro-2,7-dimethyl-*as*-indacene (**11**) and also yields 1,7-dihydro-2,6-dimethyl-*s*-indacene (**12**) as a minor

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product by prior separation of the precursor diketones 7 and 8.

The *s*-indacene hydrocarbon system was first developed by Hafner and co-workers.<sup>9a,b</sup> This was followed by an alternative synthesis of dihydro-*s*-indacene by Trogen and Edlund<sup>10</sup> shown in Figure 3, together with our modifications described in this work. The alternative routes to the *s*-indacene ligands shown in Figures 2 and 3 are relatively efficient and allow the synthesis of symmetrical 2,6-disubstituted derivatives. Yet another synthesis of 2,6-disubstituted dihydro-*s*-indacenes has been developed by Hafner and co-workers.<sup>9d</sup> Alkylation reactions of the *s*-indacene dianions offer the potential of 1,3,5,7-substitution, analogous to alkylation of the indenyl anion. Hafner has also demonstrated<sup>9</sup> the addition of alkyllithium to the six-membered ring of neutral *s*-indacene to yield 4,8-disubstituted *s*-indacene dianions. This potential for systematic and symmetrical variations in ring substituents of derived metal complexes would allow relatively small variations of geometry and electronic structure to be probed. Substituted ligands are also expected to impart greater solubility to bis(indacene)dimetal complexes than was found for the unsubstituted bis(fulvalene)dimetal complexes.

Hafner and co-workers<sup>11</sup> have reported two interesting (*s*-indacene)rhodium complexes: [(C<sub>5</sub>Me<sub>5</sub>)Rh(1,5-dihydro-*s*-indacene)]<sup>2+</sup> in which (C<sub>5</sub>Me<sub>5</sub>)Rh is η<sup>6</sup>-coordinated to the six-membered ring and [(C<sub>5</sub>Me<sub>5</sub>)Rh(1-hydro-*s*-indacene)]<sup>+</sup> in which (C<sub>5</sub>Me<sub>5</sub>)Rh is η<sup>5</sup>-coordinated to the five-membered ring.

### Experimental Section

**General Data.** NMR spectra were obtained on a JEOL FX-90Q instrument at 89.55 MHz for <sup>1</sup>H and 22.50 MHz for <sup>13</sup>C; chemical shifts are reported in parts per million downfield from internal tetramethylsilane unless otherwise noted. IR spectra were obtained on a Perkin-Elmer 599B and were calibrated against the 1601 cm<sup>-1</sup> band of polystyrene. Mass spectra were obtained on a Hewlett-Packard 5985 instrument, using the direct insertion probe. Melting points were determined on a Thomas-Hoover apparatus, using sealed capillary tubes for air-sensitive compounds, and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Hydrocarbon and ether solvents were distilled under nitrogen from sodium benzophenone ketyl. Hexamethylphosphoramide was distilled from calcium hydride onto molecular sieve 4A and stored under nitrogen. THF-*d*<sub>8</sub> was dried over sodium, toluene-*d*<sub>8</sub> was dried over CaH<sub>2</sub>, and both were purified by vacuum transfer.

Reactions involving organolithium and organotin reagents were performed in oven-dried glassware under a nitrogen atmosphere; modified Schlenk techniques were used for transfer and filtration processes. Stock solutions of *n*-butyllithium were standardized by titration against diphenylacetic acid.<sup>12</sup> Sample preparation and other operations on air-sensitive compounds were performed in a Vacuum Atmospheres glovebox under a helium atmosphere.

α,α'-Dibromo-*m*-xylene was obtained from Aldrich Chemical Co. Tetrabromodurene was purchased from Aldrich or prepared by the procedure of Stapler and Bornstein.<sup>13</sup> Methyltriphenoxyphosphonium iodide (MTPI) was purchased from Aldrich or prepared by the literature procedure.<sup>14</sup>

Flash chromatography was carried out as described by Still et al.,<sup>15</sup> using silica gel (Baker, 40-μm average particle size) and the

indicated solvent. Trimethyltin chloride was obtained from Alfa Products. Manganese pentacarbonyl bromide was obtained from Strem Chemicals.

**Preparation of Dicarboxylic Acid 6** Intermediate 6 was prepared according to the reported procedure.<sup>16</sup> The tetracarboxylic acid precursor was purified by recrystallization from water; the dicarboxylic acid 6, obtained as a mixture of diastereoisomers by decarboxylation, was used without further purification in subsequent reactions.

**Preparation of Diketones 7 and 8** Polyphosphoric acid (PPA) (1 kg) was poured into a 3-L three-neck flask equipped with a mechanical stirrer and an internal thermometer. The PPA was heat in an oil bath until the internal temperature was stable at 95 °C. Dicarboxylic acid 6 (91 g, 0.36 mol), heated to 120 °C in an oven to facilitate transfer of the viscous liquid, was added to the hot PPA with stirring. The reaction mixture turned red, and the temperature increased to 110 °C. After 20 min the reaction mixture was poured onto crushed ice (ca. 1 kg). The resulting mixture was stirred by hand and water added to bring the total volume to ca. 4 L. The mixture was extracted with 4 × 400 mL of CHCl<sub>3</sub>, and the combined extracts were washed with 2 × 500 mL of 2 M NaOH, followed by 200 mL of H<sub>2</sub>O, and finally 200 mL of saturated NaCl. After drying over MgSO<sub>4</sub>, solvent was removed under reduced pressure to give 71 g of a red oil.

The oil was treated with 300 mL diethyl ether, giving a red solution and a light yellow solid. Evaporation of solvent from the solution and recrystallization from ether gave the *as*-diketone 7 (25 g, 32%). The solid was stirred in 350 mL of hot acetone and filtered, removing traces of insoluble material; the filtrate was concentrated to 125 mL and cooled to yield *s*-diketone 8 (5.9 g, 7.5%).

7: mp 105–112 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.93 (d, 1, *J* = 8 Hz, H-5), 7.45 (d, 1, *J* = 8 Hz, H-4), 4.1–2.5 (m, 6, H-2,3,7,8), 1.37 and 1.29 (d, 6, *J* = 1.5 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 208.8, 208.1 (C-1,6), 160.8, 152.9, 136.4, 133.5 (quaternary), 129.5, 125.9 (C-4,5), 42.3, 42.0 (C-2,7), 35.8, 33.7 (C-3,8), 16.3 (CH<sub>3</sub>); IR (CHCl<sub>3</sub>) 1710, 1611 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 215 (14.5), 214 (M<sup>+</sup>, 100), 200 (9.1), 199 (48.0), 197 (2.3), 187 (3.3), 186 (18.0), 185 (19.5), 172 (13.9), 171 (96.6). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>: C, 78.48; H, 6.59. Found: C, 78.33; H, 6.50.

8: mp 180–181 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.10 (s, 1, H-8), 7.50 (s, 1, H-4), 3.6–3.3 (m, 2, H-2,6), 2.9–2.7 (m, 4, H-3,5), 1.32 (d, 6, *J* = 7.2 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 207.8 (C-1,7), 159.4 (C-1a,7a), 136.3 (C-3a,5a), 124.4 (C-8), 119.9 (C-4), 42.5 (C-2,6), 35.2 (C-3,5), 16.2 (CH<sub>3</sub>); IR (CHCl<sub>3</sub>) 1721, 1613 cm<sup>-1</sup>; MS, *m/e* (relative intensity) 215(9.4), 214 (M<sup>+</sup>, 50.4), 200 (16.9), 199 (100), 186 (4.4), 185 (3.2), 172 (5.2), 171 (19.6). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>: C, 78.48; H, 6.59. Found: C, 78.30; H, 6.50.

**Reduction of Diketones 7 and 8.** In a typical reaction 12.82 g (0.06 mol) of 7 in 400 mL of THF was added to 2.3 g (0.06 mol) of LiAlH<sub>4</sub> in 800 mL of THF with mechanical stirring; the rate of addition was controlled to maintain gentle reflux. When addition was complete, the reaction mixture was heated to reflux for 2.5 h. After being cooled to 0 °C, the reaction mixture was carefully quenched first with ethyl acetate and then 5% water in THF followed by water. The mixture was extracted with 3 × 600 mL of CHCl<sub>3</sub>, and the combined organic layers were then extracted with 2 × 150 mL of saturated NaCl solution and dried over MgSO<sub>4</sub>. Removal of solvent on a rotary evaporator, followed by 6 h at <0.1 mmHg, gave a mixture of diastereoisomers of diol 9 as a colorless, oily solid in essentially quantitative yield. Diol 10 was prepared in an analogous manner in essentially quantitative yield as a colorless solid.

9: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.4–7.0 (m, 2, H-4,5), 5.0–4.6 (br m, 2 H-1,6), 3.4–2.1 (m, 6, H-2,3,7,8), 1.2 (m, 6, CH<sub>3</sub>).

10: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.36, 7.03 (br s, 2, H-4,8), 5.0–4.6 (br m, 2, H-1,7), 3.2–2.2 (m, 6, H-2,3,5,6), 1.2 (m, 6, CH<sub>3</sub>).

**Dehydration of Either Diol 9 or Diol 10.** Under an inert atmosphere to exclude water, a 1-L flask was charged with 13 g (0.06 mol) diol 9 and 76 g (.17 mol) MTPI. HMPA (350 mL) was added and the mixture stirred under an inert atmosphere at 75–80 °C for 4 h; during this time all of the MTPI went into solution.

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The reaction mixture was then poured into 600 mL of 2 M KOH, washing the flask with an additional 400 mL. This was extracted with 3 × 300 mL hexanes, and the combined organic layers were extracted with 200-mL portions of water, followed by saturated NaCl solution, and dried over MgSO<sub>4</sub>. Removal of solvent gave 11 as a pale yellow solid that was purified by recrystallization from hexanes, yield 9.66 g (88%). The product could also be purified by sublimation (50 °C, 2 × 10<sup>-5</sup> torr). Diol 10 was dehydrated in an analogous manner to give 12 in essentially quantitative yield.

**1,6-Dihydro-2,7-dimethyl-*as*-indacene (11):** mp 42–50 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.10 (q, 2, H-4,5), 6.49 (m, 2, H-3,8), 3.30 (br s, 4, H-1,6), 2.15 (s, 6, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 146.50, 144.45, 144.23, 140.60 (quaternary), 138.87, 133.83 (C-2,7), 127.49, 120.99, 115.08 (C-3,4,5,8), 42.54, 40.87 (C-1,6), 16.76, 16.60 (CH<sub>3</sub>). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.79.

**1,7-Dihydro-2,6-dimethyl-*s*-indacene (12):** mp 107–114 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.33 (s, 1, H-4 or 8), 7.11 (s, 1, H-8 or 4), 6.47 (br s, 2, H-3,5), 3.25 (br s, 4, H-1,7), 2.12 (s, 6, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 144.88, 144.34 (quaternary), 139.30 (C-2,6), 127.38 (C-3,5), 118.82 (C-8), 111.35 (C-4), 42.38 (C-1,7), 16.76 (CH<sub>3</sub>); IR (CH<sub>2</sub>Cl<sub>2</sub>) 2900, 1610, 1330, 1190, 1020, 918, 871, 573, 448, 415 cm<sup>-1</sup>. MS, *m/e* (relative intensity) 183(13.5), 182 (M<sup>+</sup>, 97.0), 181 (21.0), 168 (13.8), 167 (100), 166 (29.7), 165 (50.7). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.72.

**Preparation of Dihydro-*s*-indacene.** The procedure of Trogen and Edlund<sup>10</sup> was followed as outlined in Figure 2. Diketone 13 was purified by recrystallization from ethyl acetate or by flash chromatography (CHCl<sub>3</sub>). Dihydro-*s*-indacene was purified by sublimation (40 °C, 2 × 10<sup>-5</sup> torr). The product was obtained and used as an isomeric mixture of 1,5- and 1,7-dihydro-*s*-indacene (4a and 4b).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.4 (m, 2, H-4,8), 6.8 (m, 2, H-2,6), 6.4 [m, 2, H-3,5 (in 4a), H-3,7 (in 4b)], 3.3 (br s, 4, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 133.48, 133.27, 132.18 (vinyl), 119.44, 116.50, 113.46 (aryl), 38.70 (CH<sub>2</sub>). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>: C, 93.46; H, 6.54. Found: C, 93.30; H, 6.55.

**Preparation of Indacenyllithium Reagents.** Dihydro-*s*-indacene (4) and 1,6-dihydro-2,7-dimethyl-*as*-indacene (11) were converted to the mono- and dilithio species by using 1 or 2 equiv of alkylolithium, respectively. In each case the alkylolithium reagent was added to 1.0 mmol of indacene hydrocarbon in 25 mL of THF at -78 °C and the reaction mixture allowed to warm slowly to 25 °C and stirred at that temperature for 1–2 h. For both of the monolithio compounds *n*-butyllithium was used with hexane as solvent; the resulting indacenyllithium compounds precipitated and were isolated by Schlenk filtration. The dilithio compounds were prepared in THF solution by using *n*-butyllithium to deprotonate 4 and *tert*-butyllithium to deprotonate 11. The dilithio compounds were then isolated by removal of solvent under vacuum. NMR spectra were recorded in THF-*d*<sub>6</sub>; chemical shifts were assigned with reference to the downfield THF signal, assumed to be 3.58 ppm downfield from Me<sub>4</sub>Si in the <sup>1</sup>H spectrum and 67.4 ppm in the <sup>13</sup>C spectrum.

14: <sup>1</sup>H NMR δ 7.40 (s, 1, H-4 or 8), 7.32 (s, 1, H-8 or 4), 6.8 (m, 1, H-2), 6.49 (t, 1, H-6), 5.8–6.1 (m, 3, H-3,5,7), 3.3 (br s, 2, CH<sub>2</sub>); <sup>13</sup>C NMR δ 134.9 (C-2), 133.9, 133.0, 130.2, 128.6 (quaternary), 126.6 (C-3), 115.3, 114.6, 111.6 (C-4,6,8), 92.3, 91.4 (C-5,7), 38.2 (C-1).

15: <sup>1</sup>H NMR δ 7.40 (s, 2, H-4,8), 6.48 (t, 2, H-2,6; *J* = 3.4 Hz), 5.64 (d, 4, H-1,3,5,7, *J* = 3.2 Hz); <sup>13</sup>C NMR δ 128.1 (quaternary), 116.8 (C-4,8), 105.2 (C-2,6), 83.6 (C-1,3,5,7).

16: <sup>1</sup>H NMR δ 7.0 (m, 2, aryl), 6.5 (m, 1, vinyl), 5.7 (m, 2, H-6,8), 3.16 (br s, 2, CH<sub>2</sub>), 2.35, 2.33, 2.12, 2.09 (singlets, 6, CH<sub>3</sub>).

17: <sup>1</sup>H NMR δ 6.56 (s, 2, H-4,5), 5.53 (br s, 4, H-1,3,6,8), 2.27 (s, 6, CH<sub>3</sub>). <sup>13</sup>C: δ 111.8 (C-4,5), 93.9, 90.1 (C-1,3,6,8), 16.3 (CH<sub>3</sub>).

**Synthesis of 1-(Trimethylstannyl)-1,5-dihydro-*s*-indacene (18).** Dihydro-*s*-indacene (417 mg, 2.71 mmol) was dissolved in 40 mL of THF and cooled to -78 °C. *n*-Butyllithium (1.7 mL of 1.6 M solution in hexanes, 2.72 mmol) was added and the resulting solution allowed to warm slowly to 5–10 °C. This yellow solution was added by cannula to a magnetically stirred solution of trimethyltin chloride (0.60 g, 3.0 mmol) in 60 mL of hexanes. The color was discharged immediately on addition, and a fine white precipitate of LiCl formed. Solvent was removed under reduced pressure and 20 mL of hexanes added. The resulting slurry was filtered by cannula (paper over glass fiber pad); the

resulting light yellow solution deposited more finely divided LiCl on standing for 1 h. This was removed by using the same procedure to yield a stable solution. Removal of solvent under reduced pressure yielded a light yellow oil which crystallized on standing (859 mg, 100%); mp 45–52 °C.

<sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 35 °C): δ 7.45 (br s, 2, H-4,8), 6.8–6.9 (m, 2, H-3,7), 6.57 (t, 1, H-2), 6.3 (d of t, 1, H-6), 3.87 (br s, 1, SnCH), 3.21 (br s, 2, H-5), -0.11 (s, 9, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 35 °C): δ 141.8, 140.2, 134.9 (quaternary carbons), 134.1, 133.0, 132.5 (vinyl C), 116.9, 113.9 (aryl C), 43.4 (SnCH), 38.7 (CH<sub>2</sub>), -9.7 (Sn(CH<sub>3</sub>)<sub>3</sub>). IR (liquid film): 3045 (m), 2985 (m), 2900 (s), 1498 (w), 1450 (m), 1438 (s), 1390 (m), 1350 (m), 1296 (w), 1268 (w), 1210 (w), 1182 (m), 1128 (w), 978 (w), 930 (s) 860 (s), 758 (s), 728 (m), 700 (s), 654 (m), 644 (m), 530 (s), 508 (s) cm<sup>-1</sup>. MS (normalized to <sup>120</sup>Sn): *m/e* (relative intensity) 318 (46, M<sup>+</sup>), 273 (12), 169 (11), 167 (20), 165 (Sn(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 23), 163 (20), 162 (4), 161 (16), 154 (13), 153 (C<sub>12</sub>H<sub>9</sub><sup>+</sup>, 100), 151 (69). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>Sn: C, 56.84; H, 5.72; Sn, 37.44. Found: C, 56.85; H, 5.66; Sn, 37.71.

**Synthesis of 1,5-Bis(trimethylstannyl)-1,5-dihydro-*s*-indacene (19).** Dihydro-*s*-indacene (718 mg, 4.66 mmol) was dissolved in 150 mL of THF and the solution was cooled to -78 °C. *n*-Butyllithium (5.8 mL of 1.6 M solution, 9.28 mmol) was added to give a yellow-orange solution. The solution was allowed to warm slowly to room temperature, and solvent was removed under vacuum to give an orange-red solid; 50 mL of hexanes was added. To the magnetically stirred slurry was added trimethyltin chloride (1.85 g, 9.30 mmol) in 50 mL of hexanes. The mixture was stirred for 1/2 h; the color was discharged and a fine white precipitate (LiCl) appeared. This suspension was filtered by cannula (paper over glass fiber mat) and solvent removed from the filtrate to give an off-white solid (2.08 g, 93%), mp 123–129 °C.

<sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 35 °C): δ 7.6 (br s, 2, H-4,8), 6.9 (m, 2, H-3,7), 6.6 (m, 2, H-2,6), 3.9 (br s, 2, SnCH), -0.9 (s, 18, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 35 °C): δ 143.0 and 139.9 (quaternary), 133.8 (C-2,6), 125.8 (C-3,7), 113.8 (C-4,8), 43.3 (C-1,7), -9.8 (Sn(CH<sub>3</sub>)<sub>3</sub>). IR (Nujol mull): 1530 (w), 1430 (s), 1190 (m), 1170 (m), 1120 (m), 980 (w), 925 (s), 860 (s), 760 (s), 710 (m), 670 (s), 570 (m) cm<sup>-1</sup>. MS (normalized to <sup>120</sup>Sn): *m/e* (relative intensity) 482 (M<sup>+</sup>, 0.3), 317 (0.5), 302 (2.3), 272 (2.3), 183 (1.3), 165 (Sn(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 13.8), 43 (100). Anal. Calcd for C<sub>18</sub>H<sub>26</sub>Sn<sub>2</sub>: C, 45.06; H, 5.46; Sn, 49.48. Found: C, 46.00; H, 5.61; Sn, 48.03.

**Synthesis of 1-(Trimethylstannyl)-1,6-dihydro-2,7-dimethyl-*as*-indacene (20).** 1,6-Dihydro-2,7-dimethyl-*as*-indacene (410 mg, 2.25 mmol) was dissolved in 50 mL of THF and the solution cooled to -78 °C. *tert*-Butyllithium (1.4 mL, 2 M solution in pentane, 2.8 mmol) was added and the reaction mixture warmed to ca. 10 °C. The red-orange solution was transferred by cannula into a magnetically stirred solution of trimethyltin chloride (0.60 g, 3.0 mmol) in 100 mL of hexanes. The color of the indacene monoanion solution was immediately discharged, and LiCl precipitated from the pale yellow solution. Solvent was removed under reduced pressure, 50 mL of hexanes added, and the mixture filtered by cannula (paper over glass fiber mat). The resulting clear solution deposited a fine white solid on standing for 1 h; when this mixture was filtered by using the same procedure, the resulting solution was stable. Solvent was removed under reduced pressure; excess trimethyltin chloride sublimed out under vacuum and mild heating. The product was a light yellow oil (0.75 g, 96%) and pure by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

<sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 35 °C): δ 7.4–7.1 (m, 2, ArH), 6.8–6.4 (m, 2, vinyl H), 3.6 (br s, 1, SnCH), 3.1 (br s, 2, CH<sub>2</sub>), 2.03 and 1.91 (br s, 6, RCH<sub>3</sub>), -0.10 (s, 9, Sn(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 35 °C): δ 147.34, 144.41, 142.79 (quaternary), 123.07, 120.25, 119.49, 118.08, 116.95, 115.10 (vinyl, aryl), 47.55, 46.73 (SnCH), 43.00, 41.43 (CH<sub>2</sub>), 16.67 (RCH<sub>3</sub>), -8.36, -8.69, -9.66 (Sn(CH<sub>3</sub>)<sub>3</sub>). MS (normalized to <sup>120</sup>Sn), *m/e* (relative intensity) 346 (M<sup>+</sup>, 13), 181 (30), 180 (27), 179 (12), 178 (14), 165 (Sn(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, 100). IR (liquid film): 3040 (m), 2945 (m), 2900 (s), 2840 (w), 1608 (w), 1420 (s), 1390 (w), 1296 (w), 1218 (s), 1180 (m), 1020 (w), 936 (s), 898 (s), 830 (s), 762 (s), 526 (s), 508 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>22</sub>Sn: C, 59.18; H, 6.43; Sn, 34.40. Found: C, 59.22; H, 6.54; Sn, 34.67.

**Synthesis of 1,6-Bis(trimethylstannyl)-1,6-dihydro-2,7-dimethyl-*as*-indacene (21).** 1,6-Dihydro-2,7-dimethyl-*as*-

indacene (1.033 g, 5.67 mmol) was dissolved in 125 mL of THF and the solution cooled to  $-78^{\circ}\text{C}$ . *tert*-Butyllithium (5.7 mL of 2 M solution in pentane, 11.4 mmol) was added by syringe to give a red solution. This was allowed to warm slowly to room temperature; on warming the color changed from red to yellow. The solvent was removed under vacuum, and 100 mL of hexanes was added. Trimethyltin chloride (2.30 g, 11.6 mmol) in 60 mL of hexanes was added by cannula to the stirred slurry. The slurry was stirred for 1.5 h at room temperature; the yellow solid dianion was consumed and a fine white precipitate (LiCl) appeared. This suspension was filtered by cannula (paper over glass fiber mat) to give a clear solution which deposited a white precipitate on standing for several hours. When this material was filtered in the same manner as above, a clear, stable solution resulted. Removal of hexanes gave the product as a pale yellow oil, which crystallized on standing; yield 2.72 g (94%).

$^1\text{H}$  NMR (toluene- $d_6$ ,  $35^{\circ}\text{C}$ ):  $\delta$  6.3–7.1 (m, 4 H, H-3,4,5,8), 3.4–3.6 (m, 2 H, SnCH), 1.87 (s, 6 H,  $\text{RCH}_3$ ),  $-0.30$  (s, 18 H,  $\text{Sn}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_7\text{D}_8$ ,  $35^{\circ}\text{C}$ ):  $\delta$  123.2, 121.8, 121.1, 117.8, 116.2, 115.9, 115.5 (vinyl, aryl C), 47.7 and 46.8 (SnCH), 16.9 ( $\text{RCH}_3$ ),  $-8.8$ ,  $-9.7$  ( $\text{Sn}(\text{CH}_3)_3$ ). IR (liquid film): 3040 (m), 2965 (m), 2900 (s), 2850 (m), 1575 (w), 1415 (s), 1370 (w), 1300 (m), 1230 (m), 1218 (s), 1180 (m), 1165 (w), 1025 (w), 935 (s), 900 (s), 830 (s), 760 (s)  $\text{cm}^{-1}$ . MS:  $m/e$  (relative intensity) 510 ( $\text{M}^+$ , 1.0), 345 (5.4), 330 (5.1), 180 (37.6), 165 ( $\text{Sn}(\text{CH}_3)_3^+$ , 100.0). Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{Sn}_2$ : C, 47.30; H, 5.95; Sn, 46.67. Found: C, 47.22; H, 6.10; Sn, 46.58.

**Preparation of (1-Hydro-*s*-indacene)manganese Tricarbonyl (22).** 1-(Trimethylstannyl)-1,5-dihydro-*s*-indacene (497 mg, 1.57 mmol) was dissolved in 35 mL of toluene; manganese pentacarbonyl bromide 470 mg, 1.71 mmol) was added, and the magnetically stirred suspension was heated to  $60^{\circ}\text{C}$  for 2 h. During this time the mixture became homogeneous. Solvent was removed, and the resulting solid was purified by flash chromatography (silica gel, hexanes). The product is an air-stable yellow solid; yield ca. 300 mg (65%); mp  $250^{\circ}\text{C}$  dec.

$^1\text{H}$  NMR (toluene- $d_6$ ):  $\delta$  6.85 (s, 2, H-4,8), 6.4 (m, 1, H-7), 6.0 (d of t, 1, H-6), m 4.59 (m, 2, H-1,3), 4.35 (t, 1, H-2), 2.82 (s, 2, H-5).  $^{13}\text{C}$  NMR (toluene- $d_6$ ):  $\delta$  136.39 (C-6), 131.89 (C-7), 118.51 (C-4), 114.18 (C-8), 87.25 (C-2), 71.22 (C-1,3), 37.52 (C-5). IR ( $\text{CH}_2\text{Cl}_2$ ): 2004, 1930  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ). MS:  $m/e$  (relative intensity) 293 (4), 292 (22,  $\text{M}^+$ ), 265 (2), 264 (10), 237 (4), 236 (24), 209 (13), 208 (100), 154 (10), 153 (79), 152 (53), 151 (16), 150 (6). Anal. Calcd for  $\text{C}_{15}\text{H}_9\text{MnO}_3$ : C, 61.66; H, 3.10; Mn, 18.80. Found: C, 61.58; H, 3.19; Mn, 18.72.

**Preparation of (*s*-Indacene)bis(manganese tricarbonyl) (23).** Bis(trimethylstannyl)-*s*-indacene (310 mg, 0.65 mmol) and manganese pentacarbonyl bromide (400 mg, 1.46 mmol) were combined in 100 mL of toluene and stirred magnetically. When the mixture was warmed to  $50^{\circ}\text{C}$ , the  $\text{Mn}(\text{CO})_5\text{Br}$  dissolved to give an orange solution. This solution was stirred at  $60$ – $65^{\circ}\text{C}$  for 24 h; at this time the solution was deep red. Solvent was removed under reduced pressure, hexanes were added, and the resulting slurry was filtered (Schlenk apparatus, medium porosity frit). This gave 160 mg (58%) of a red solid. This material was further purified by recrystallization from toluene. The product is not air-sensitive as the crystalline solid; mp (sealed capillary)  $272$ – $275^{\circ}\text{C}$ .

$^1\text{H}$  NMR (toluene- $d_6$ ):  $\delta$  6.89 (s, 2, H-4,8), 4.66 (d, 4, H-1,3,5,7), 4.52 (t, 2, H-2,6). IR ( $\text{CH}_2\text{Cl}_2$ ): 2004, 1945  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_9\text{Mn}_2\text{O}_6$ : C, 50.26; H, 1.87; Mn, 25.55. Found: C, 49.91; H, 2.01; Mn, 25.38.

### X-ray Crystallographic Studies<sup>17</sup>

**(5-Hydro-*s*-indacene)manganese Tricarbonyl (22).** Pale orange needles grown by cooling a hexane/THF solution were

(17) All programs were contained in or derived from the Syntex data reduction routines, MULTAN 78,<sup>18</sup> the Northwestern University Crystallographic Computing Package of Dr. J. A. Ibers, and the SHELX package.<sup>19</sup>

(18) Main, P. MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures, obtained from Dr. Grahame J. B. Williams, Brookhaven National Laboratory, Upton, NY.

(19) Sheldrick, G. M. Programs for Crystal Structure Determination, University of Cambridge, England, 1976.

Table I. Crystal Data

	22	23
formula	$(\text{C}_{12}\text{H}_9)\text{Mn}(\text{CO})_3$	$(\text{C}_{12}\text{H}_9)[\text{Mn}(\text{CO})_3]_2$
mol wt	292.13	430.14
space group	$P2_1/n$	$P\bar{1}$
<i>a</i> , Å	9.288 (3)	6.381 (4)
<i>b</i> , Å	14.307 (4)	7.921 (6)
<i>c</i> , Å	10.131 (3)	9.272 (3)
$\alpha$ , deg	90	72.49 (5)
$\beta$ , deg	113.37 (2)	66.78 (4)
$\gamma$ , deg	90	69.87 (6)
<i>V</i> , Å <sup>3</sup>	1235.8 (7)	396.9 (4)
<i>Z</i>	4	1
$\mu$ , $\text{cm}^{-1}$	10.24	15.60
$\rho_{\text{obsd}}$ , $\text{g}/\text{cm}^3$	1.56	1.78
$\rho_{\text{calcd}}$ , $\text{g}/\text{cm}^3$	1.59	1.80
$n_{\text{obsd}}$	845	1600
$n_{\text{parameters}}$	196	118
<i>R</i> , %	2.69	3.63
<i>R</i> <sub>w</sub> , %	3.05	3.76

Table II. Final Positional and Thermal Parameters for  $(\text{C}_{12}\text{H}_9)\text{Mn}(\text{CO})_3$  (22)

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ , Å <sup>2</sup>
Mn1	0.18285 (7)	0.14214 (4)	0.28558 (7)	3.50 (3)
C3	0.1275 (6)	0.0571 (3)	0.4314 (5)	4.32 (18)
C2	0.2824 (6)	0.0885 (4)	0.4964 (5)	4.68 (19)
C1	0.2851 (5)	0.1855 (3)	0.5038 (5)	4.22 (18)
C8	0.0597 (6)	0.3080 (3)	0.4376 (5)	3.81 (17)
C7	$-0.1983$ (6)	0.3975 (4)	0.3697 (5)	5.01 (19)
C6	$-0.3502$ (7)	0.3661 (4)	0.3231 (5)	5.70 (23)
C5	$-0.3624$ (5)	0.2666 (4)	0.3037 (5)	5.23 (20)
C4	$-0.1378$ (5)	0.1482 (3)	0.3518 (4)	3.80 (18)
C12	0.1268 (5)	0.2176 (3)	0.4496 (4)	3.25 (16)
C11	$-0.0972$ (6)	0.3147 (3)	0.3894 (4)	3.51 (17)
C10	$-0.1979$ (5)	0.2343 (3)	0.3468 (4)	3.60 (16)
C9	0.0281 (5)	0.1369 (3)	0.4050 (4)	3.45 (17)
C13	0.2155 (5)	0.2496 (4)	0.2091 (5)	4.09 (17)
C14	0.0246 (6)	0.1058 (3)	0.1237 (6)	3.95 (17)
C15	0.3232 (6)	0.0800 (4)	0.2421 (5)	4.65 (18)
O1	0.2337 (4)	0.3192 (3)	0.1607 (4)	6.12 (14)
O2	$-0.0804$ (4)	0.0837 (2)	0.0225 (4)	5.62 (13)
O3	0.4178 (5)	0.0396 (3)	0.2189 (4)	7.06 (15)

$${}^a B_{\text{eq}} = 8\pi^2[U_{22} \sin^2 \beta + 2U_{13} \cos \beta]/3(1 - \cos^2 \beta)$$

fractured to appropriate lengths and mounted in nitrogen-filled quartz capillaries. The data crystal (approximately  $0.4 \times 0.4 \times 0.4$  mm) was mounted on a Syntex  $P\bar{1}$  four-circle automatic diffractometer with molybdenum X-ray tube and graphite monochromator. Indexing of 15 automatically centered reflections between  $30^{\circ}$  and  $35^{\circ}$  in  $2\theta$  followed by a short preliminary data collection led to the assignment of space group  $P2_1/n$  and least-squares refinement of cell parameters (Mo  $K\alpha$ ,  $0.71069$  Å; Table I). Duplicate data ( $\pm h, \pm k, +l$ ) were collected between  $3.0^{\circ}$  and  $38.0^{\circ}$  in  $2\theta$  at room temperature. A total of 1002 reflections were collected, of which 845 were not systematically absent and greater than  $3\sigma^{20}$  after the usual corrections and averaging ( $R = 3.2\%$ ). No correction for absorption was made.

The initial Patterson map was solved for the Mn position<sup>21</sup> and subsequent least-squares<sup>22a</sup> difference Fourier cycles revealed the remaining heavy atoms. Hydrogen atoms were included in calculated positions ( $d_{\text{C-H}} = 0.95$  Å),<sup>22b</sup> special care being taken in the 5-hydro end of the ligand that the methylene carbon was unambiguously identified before including the hydrogen atoms for it and its immediate neighbors. The thermal parameters for all heavy atoms were treated anisotropically. The model converged to give weighted and unweighted *R* factors of 3.05% and 2.69%,<sup>23</sup>

(20)  $\sigma^2(F_o) = \sigma_c^2 + 0.0004F_o^2$  with  $\sigma_c^2$  from counting statistics.

(21) The scattering factors used for all atoms were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974.

(22) (a) The function minimized in the least-squares procedures was  $\sum w(|F_o| - |F_c|)^2$ . (b) Churchill, M. R. *Inorg. Chem.* 1973, 12, 1213.

(23)  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ . The weighting scheme used for all refinements was based on counting statistics where  $w = 1/\sigma^2(F_o)$ .

Table III. Interatomic Distances and Bond Angles in (5-Hydro-*s*-indacene)manganese Tricarbonyl (22)

Bond Distances (Å)			
Mn-C3	2.128 (4)	C3-C2	1.398 (6)
Mn-C2	2.107 (4)	C2-C1	1.390 (7)
Mn-C1	2.123 (4)	C1-C12	1.425 (6)
Mn-C12	2.210 (4)	C12-C8	1.420 (6)
Mn-C9	2.218 (4)	C8-C11	1.344 (6)
		Co-C9	1.425 (6)
C11-C7	1.475 (6)	C4-C9	1.425 (6)
C7-C6	1.373 (7)	C9-C12	1.431 (5)
C6-C5	1.435 (7)	C11-C10	1.433 (6)
C5-C10	1.492 (6)	C10-C4	1.343 (5)
Mn-C13	1.800 (6)	C13-O1	1.152 (5)
Mn-C14	1.791 (6)	C14-O2	1.143 (5)
Mn-C15	1.772 (6)	C15-O3	1.152 (5)
Bond Angles (deg)			
C9-C3-C2	107.5 (4)	Mn1-C13-O1	178.5 (4)
C3-C2-C1	109.8 (4)	Mn1-C14-O2	177.4 (4)
C2-C1-C12	107.9 (4)	Mn1-C15-O3	177.6 (4)
C1-C12-C9	107.2 (4)	C11-C7-C6	107.2 (4)
C12-C9-C3	107.5 (4)	C7-C6-C5	112.7 (4)
C1-C12-C8	132.6 (4)	C6-C5-C10	104.5 (4)
C8-C11-C7	130.3 (5)	C5-C10-C11	107.9 (4)
C13-Mn1-C14	94.1 (2)	C10-C11-C7	107.6 (4)
C13-Mn1-C15	93.1 (2)	C5-C10-C4	130.9 (4)
C12-C8-C11		C4-C9-C3	133.2 (4) 8.2 (4)
C8-C11-C10	122.1 (4)	C14-Mn1-C5	92.5 (2)
C11-C10-C4	121.2 (4)		
C10-C4-C9	119.0 (4)		
C4-C9-C12	119.3 (4)		
C9-C12-C9	120.2 (4)		

respectively. The residuals showed no anomalies. In the final difference map, the largest residual peak was 0.33 electron/Å<sup>3</sup>. Final positional and thermal parameters are found in Table II.

(*s*-Indacene)bis(manganese tricarbonyl). Red crystals (parallelepipeds with clean faces) from THF/hexane were glued to glass fibers. The data crystal (approximately 4.0 × 0.4 × 0.3 mm) was mounted on a Syntex P1 four-circle automatic diffractometer with molybdenum tube and graphite monochromator. Indexing of 15 automatically centered reflections between 8° and 25° in 2θ (Mo Kα, 0.710 69 Å) revealed a triclinic cell (Table I). A total of 3746 room-temperature data were collected between 3° and 55° in 2θ—the entire sphere. After the usual corrections and averaging (*R* = 4.0%), there were 1600 unique data greater than 3σ<sup>20</sup> used in the final refinement. No correction was made for absorption.

The structure was solved with MULTAN, which located all the heavy atoms and confirmed our suspicion that the space group was *P*1 with *Z* = 1 ( $\rho_{\text{calcd}} = 1.80$ ;  $\rho_{\text{obsd}} = 1.78$  g/cm<sup>3</sup>). As the model converged rapidly,<sup>22a</sup> H1, H2, and H3 were included in calculated positions, while H4 was included in the position discerned from a difference map. The H4 position was not refined, while the remaining three H atoms remained in calculated ( $d_{\text{C-H}} = 0.95$  Å)<sup>22b</sup> positions. Isotropic thermal parameters for the H atoms were not refined, while the thermal parameter of all heavy atoms were treated anisotropically. The model converged to weighted and unweighted *R* factors<sup>23</sup> of 3.76% and 3.63%, respectively. The residuals showed no anomalies. The largest peak in the final difference Fourier was 0.76 e/Å<sup>3</sup>, close to Mn. Final positional and thermal parameters are found in Table IV.

## Results

The isolation, characterization and utility of the ligand precursors 1,6-dihydro-2,7-dimethyl-*as*-indacene (11) and dihydro-*s*-indacene (4a,b) is enhanced by the thermal stability of these hydrocarbons, in comparison to dihydrofulvalene, which must be prepared and used in situ.<sup>3h,i</sup> In addition, these hydrocarbons can be selectively deprotonated to yield mono- and dianions which can be isolated. In contrast, neither the isolation nor in situ reaction chemistry of the hydrofulvalene monoanion has yet been reported.<sup>24</sup>

Table IV. Final Positional and Thermal<sup>39</sup> Parameters for C<sub>12</sub>H<sub>8</sub>[Mn(CO)<sub>3</sub>]<sub>2</sub> (23)

atom	x	y	z	<i>B</i> <sub>eq</sub> , Å <sup>2</sup>
Mn1	0.31680 (6)	-0.32296 (4)	0.23033 (4)	2.57 (17)
C1	0.4924 (5)	-0.1690 (3)	0.2746 (3)	3.12 (8)
C2	0.6324 (5)	-0.2342 (4)	0.1316 (3)	3.37 (8)
C3	0.6904 (4)	-0.4279 (4)	0.1648 (3)	3.15 (8)
C4	0.6249 (4)	-0.6627 (3)	0.4302 (3)	2.80 (7)
C5	0.6079 (4)	-0.4874 (3)	0.3342 (3)	2.62 (7)
C6	0.4826 (4)	-0.3247 (3)	0.4045 (3)	2.66 (7)
C7	0.0254 (5)	-0.2075 (4)	0.3461 (3)	3.30 (8)
C8	0.2441 (4)	-0.5259 (3)	0.2369 (3)	3.02 (3)
C9	0.2498 (5)	-0.2221 (3)	0.0493 (3)	3.17 (8)
O1	-0.1504 (4)	-0.1267 (3)	0.4173 (3)	4.m1 (8)
O2	0.2026 (4)	-0.6565 (3)	0.2382 (3)	4.25 (8)
O3	0.2082 (4)	-0.15797 (3)	-0.0678 (2)	4.29 (8)

$${}^a B_{\text{eq}} = 8\pi^2[U_{11}\sin^2\alpha + U_{22}\sin^2\beta + U_{33}\sin^2\gamma + 2U_{12}\cos\gamma\sin\alpha\sin\beta + 2U_{13}\cos\beta\sin\alpha\sin\gamma + 2U_{23}\cos\alpha\sin\beta\sin\gamma]/3(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)$$

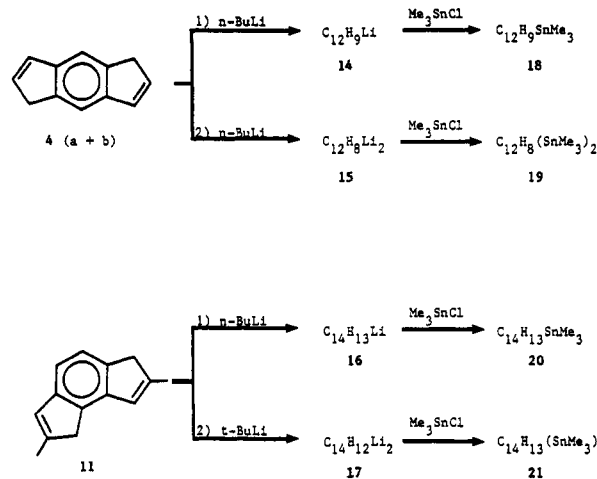


Figure 4. Synthesis of indacene anions and (trimethylstannyl)indacene compounds.

Deprotonation of 11 with 2 equiv of *n*-butyllithium in THF rapidly yields the monoanion 16 followed by very slow formation of the dianion 17. Rapid removal of the second proton was readily accomplished by using *tert*-butyllithium. Similar reaction chemistry was observed by Katz<sup>25</sup> with a related hydrocarbon precursor to an annulated ligand was reported by Katz to be deprotonated to a trianion by *n*-butyllithium.<sup>26</sup> The parent dihydro-*as*-indacene is readily converted to its dianion with *n*-butyllithium,<sup>5</sup> suggesting that the kinetic acidity of this hydrocarbon is significantly reduced by methyl substitution in the 2,6-positions. Selective deprotonation reactions to yield the 1-hydro-2,6-dimethyl-*as*-indacene (16) and 1-hydro-*s*-indacene (14) monoanions together with <sup>1</sup>H NMR analysis indicate that the differences between first and second ionization constants is sufficiently large that solutions of both monoanions do not contain substantial amounts (<5%) of the parent hydrocarbon and dianion. As evidence that this is a thermodynamic rather than a kinetic effect, the monoanion 14 was prepared by reaction of 15 and 4. In their <sup>1</sup>H and <sup>13</sup>C NMR spectral features, the *as*- and *s*-indacene hydrocarbons and anions resemble indene and indenyllithium.<sup>27</sup>

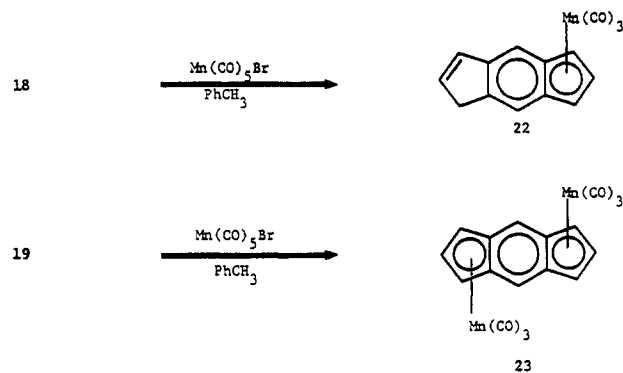
Our initial exploratory reaction chemistry with the *s*-indacene ligand system involved reaction of its dianion 15

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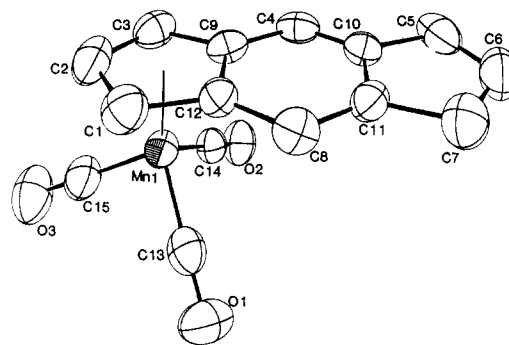


**Figure 5.** Synthesis of (*s*-indacene)manganese tricarbonyl compounds by transmetalation.

with 2 equiv of  $(C_5H_5)Fe(CO)_2Br$ <sup>28</sup> to yield  $[(C_5H_5)Fe(CO)_2]_2$  and uncharacterized and intractable organic material. A related reaction with  $Mn(CO)_5Br$  yielded  $Mn_2(CO)_{10}$  and similar organic material. In order to avoid apparent redox reaction leading to metal-metal bonded products and uncoordinated oxidized hydrocarbons, we synthesized mono- and bis(trimethyltin) derivatives of the *as*- and *s*-indacene ligands for use in transmetalation reactions.<sup>29,30</sup>

The tin reagents are readily prepared from the *as*- and *s*-indacene mono- and dianions to yield slightly air-sensitive solids or oils. In solution at 38 °C, they exhibit 90-MHz <sup>1</sup>H NMR spectra that indicate that they are stereochemically nonrigid  $\sigma$ -bonded trimethyltin compounds undergoing sigmatropic rearrangements. While this fluxional behavior has been well-studied in the indenyltrialkyltin system,<sup>31</sup> it remains unexplored in the *as*- and *s*-indacene systems. The existence of mixed *cis* and *trans* isomers with respect to the hydrocarbon plane of the bis(trimethylstannyl)-*s*-indacene is supported by variable-temperature (VT) <sup>1</sup>H NMR studies in which the observed singlet at  $\delta$  -0.09 for the  $Sn(CH_3)_3$  protons at 38 °C, changes to four closely spaced singlets from  $\delta$  -0.08 to -0.11, on cooling to -34 °C. While the VT NMR studies are not complete, there is no evidence of intermolecular interconversion of *cis* and *trans* isomers. The intriguing question of correlated rearrangements of trimethyltin groups in either stereoisomer of the *as*- and *s*-indacene ligands remains open. In related work<sup>24</sup> we have prepared the bis(trimethylstannyl)fulvalene and demonstrated its utility in transmetalation reactions to yield the known (fulvalene)bis(manganese tricarbonyl).<sup>32</sup>

The transmetalation reaction of the (trimethylstannyl)-5-hydro-*s*-indacene (18) with  $Mn(CO)_5Br$  in toluene at 60 °C is complete in 2 h, while the bis(trimethylstannyl)-*s*-indacene (19) requires 24 h to yield the (*s*-indacene)bis(manganese tricarbonyl). The analogous mono- and bis(trimethylstannyl)-2,6-dimethyl-*as*-indacene derivatives did not react under the same conditions and yielded only decomposition products at higher temperatures and prolonged reaction times. Use of the potentially more reactive  $[Mn(CO)_4Br]_2$ <sup>32</sup> starting material was also



**Figure 6.** Structure of  $(C_{12}H_9)Mn(CO)_3$  (22).

unsuccessful in yielding significant quantities of a tractable organomanganese compound.

Structural studies of the (*s*-indacene)-*trans*-bis(manganese tricarbonyl) product isolated indicate that the ligand bonds in a symmetrical  $\eta^5:\eta^5$ -manner (Figure 1; 5a). Although the transmetalation reaction to form this product may proceed via  $\eta^1$  to  $\eta^3$  to  $\eta^5$  bonding modes, with sequential loss of CO ligands, an intermediate  $\eta^3-Mn(CO)_4:\eta^5-Mn(CO)_3$  was not observed. An alternative approach to such structures might involve ligand (L) addition reactions with tertiary phosphines to yield a  $\eta^3-Mn(CO)_3L$  moiety. Ongoing synthetic and structural studies of manganese and molybdenum derivatives of the *as*-indacene ligand seek to further develop an understanding of the structure and bonding in related bridging ligands.<sup>33</sup>

Crystals of both the (*s*-indacene)mono- and (*s*-indacene)bis(manganese tricarbonyls) were grown and single-crystal X-ray structure determinations performed.

**Structure of (5-Hydro-*s*-indacene)manganese Tricarbonyl (22).** The crystal structure consists of discrete molecular units at general positions in the unit cell. The closest intermolecular contact is 2.43 Å between H3 and H6. Excluding H-H interactions, the closest intermolecular contact is 2.95 Å between O2 and O2. The molecular structure consists of Mn coordinated by three CO groups and a  $C_5$  ring in the *s*-indacene monoanion, much the same as seen in  $(C_5H_5)Mn(CO)_3$ .<sup>34a</sup> The pattern of bond lengths in the indacene ligand indicates localized double bonds between C8 and C11, C10 and C4, and C7 and C6. The closest intramolecular nonbonded contact is 1.55 Å between H51 and H52. Excluding H atoms, the closest contact is 2.28 Å between C2 and both C12 and C9. The indacene ligand is essentially planar, the average deviation from planarity of the 12-membered plane being 0.04 Å. The Mn is 1.76 Å from the plane formed by the ring to which it is bound. Pertinent bond distances and angles are found in Table III.

The pattern of Mn-C ring distances is typical of those found in indenylmetal structures.<sup>35-40</sup> While the average

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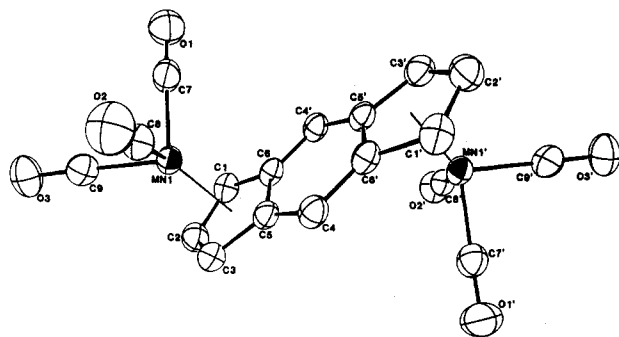


Figure 7. Structure of  $C_{12}H_8[Mn(CO)_3]_2$  (23).

Table V. Interatomic Distances and Bond Angles in (*s*-Indacene)bis(manganese tricarbonyl) (23)

Bond Distances (Å)			
Mn1-C1	2.125 (2)	C7-O1	1.132 (3)
Mn1-C <sub>2</sub>	2.126 (3)	C8-O2	1.149 (3)
Mn1-C3	2.131 (2)	C9-O3	1.144 (3)
Mn1-C5	2.250 (2)	C1-C2	1.408 (4)
Mn1-C6	2.247 (2)	C2-C3	1.415 (4)
Mn1-C7	1.814 (3)	C3-C5	1.428 (3)
Mn1-C8	1.798 (3)	C5-C4	1.400 (3)
Mn1-C9	1.778 (2)	C5-C6	1.453 (3)
		C6-C1	1.440 (3)
		C6-C4'	1.398 (3)
Bond Angles (deg)			
C6-C1-C2	107.9 (2)	Mn1-C7-O1	175.6 (3)
C1-C2-C3	109.2 (2)	Mn1-C8-O2	178.4 (2)
C2-C3-C5	108.1 (2)	Mn1-C9-O3	179.0 (2)
C3-C5-C4	131.7 (2)	C5-C4-H4	119.2 (2)
C3-C5-C6	107.4 (2)	C7-Mn1-C8	97.1 (1)
C5-C6-C1	107.0 (2)	C8-Mn1-C9	89.2 (1)
C4-C5-C6	120.9 (2)	C7-Mn1-C9	91.4 (4)
C5-C4-C6'	117.7 (2)		
C5-C6-C4'	121.4 (2)		

Mn-C ring distance is close to that of numerous compounds of the general formula  $(C_5H_5)Mn(CO)_{3-x}L_x$ ,<sup>34</sup> the range of the Mn-C distances is roughly twice as large. Typical indenylmetal complexes exhibit two longer and three shorter Mn-C ring distances, as does 22. Thus, there is apparent slippage of the metal parallel to the ligand

plane and toward C2. The projection of the Mn on the ring plane is shifted ca. 0.07 Å toward C2 from the ring center.

Significant double-bond localization between C<sub>4</sub>-C<sub>10</sub> and C<sub>8</sub>-C<sub>11</sub> is readily apparent with the crystallographic data available. Precisely determined structures of metal-indenyl complexes generally show a similar pattern of bond length in the six-membered ring.<sup>35-40</sup>

**Structure of (*s*-Indacene)bis(manganese tricarbonyl) (23).** The crystal structure consists of discrete molecular units centered on the inversion center at  $1/2, 1/2, 1/2$  in  $P\bar{1}$ . The closest intermolecular contact is 3.20 Å between O1 and C1. The molecular structure consists of the *s*-indacene dianion coordinated to two manganese tricarbonyl units through the five-membered rings, much the same as in  $(C_5H_5)Mn(CO)_3$ .<sup>34a</sup> The closest intramolecular nonbonded contact is 2.041 Å between C5 and H4. The manganese is 1.80 Å from the least-squares plane of the C<sub>5</sub> ring to which it is coordinated. The average deviation from this plane is 0.02 Å. The inversion center is very nearly in the plane defined by C4, C5, and C6, as evidenced by the very small average deviation from the C<sub>6</sub> ring that includes the three above carbon atoms and their inversion related neighbors (0.0002 Å). The angles between the C<sub>6</sub> ring plane and the two C<sub>5</sub> rings planes are nearly identical (0.20° and 0.18°). Thus the ligand is very nearly planar, with the C<sub>6</sub> ring centered on the inversion center and the C<sub>5</sub> rings tilted at small angles from it.

The pattern of Mn-C<sub>ring</sub> distances is typical of indenylmetal structures<sup>35-40</sup> as it was in the monomanganese compound 22; i.e., the metal is displaced toward C2. The projection of Mn on the ring plane is shifted ca. 0.11 Å toward C2 from the ring center. Bond distances and angles are found in Table V.

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**Supplementary Material Available:** Tables of calculated hydrogen positions, anisotropic thermal parameters, and least-squares planes for 22 and 23 (6 pages); listings of structure factors for 22 and 23 (13 pages). Ordering information is given on any current masthead page.