acetone (both in less than 15 min). They are relatively stable in nitromethane (3, at least 1 h; 4, 12 h).

The ^{1}H NMR of 3 shows a downfield shift of the thiophene protons relative to free T (Table VIII) as has been observed for other dicationic arene complexes.[30] The BT protons of 4 also shift downfield relative to the free ligand. However, the H2 and H3 resonances show large downfield shifts, H4 and H7 shift to slightly lower field, and H5 and H6 show little change relative to uncoordinated BT.

Cp^*IrL^{2+} (L = T, BT, 3-MeBt, and 2,3-Me_2BT) (5–8). The preparation of 5 from $[Cp^*Ir(acetone)_3](BF_4)_2$ proceeds analogously to that of 3 shown in eq 2. This method has been used by Maitlis and co-workers to synthesize other Ir arene dications.[30] For the Rh complexes refluxing had little effect on the yield, but for Ir the yield is increased approximately twofold when the reactions are refluxed. Complexes 6–8 are synthesized in a similar manner.

Compounds 5–8 have all been characterized by ^{1}H and ^{13}C NMR as well as elemental analysis (Tables V–VII). The solids are all air-stable, but 5 is extremely moisture-sensitive. The Ir complexes are much more stable than the Rh analogues toward ligand displacement. Acetone displaces T from 5 in approximately 2 h at room temperature while 6 will not lose BT even after 12 h in acetone.

The ^{1}H NMR spectra of 6–8 suggest that coordination occurs through the benzene ring of BT, 3-MeBT, and 2,3-Me_2BT. Thus, the H2, H3, C2–CH_3, and C3–CH_3 resonances move further downfield relative to the free ligand upon coordination to Ir, than those of H4–H7 (Table VI).

Conclusion

In all of the Ru, Rh, and Ir complexes the BTs coordinate through the π-system of the benzene ring as in $Cr(CO)_3(BT)$.[15] Even in the case of 2,3-Me_2BT, where the presence of two electron-donating methyl groups might be expected to promote thiophene coordination, the benzene ring was bound.

All of the metals used in these complexes are active HDS catalysts.[31] We are exploring the reactivities of these complexes as possible models for reactions of π-bound T and BTs on catalysts in the HDS process.

Registry No. 1 (A = BF_4), 112068-83-4; 1 (A = PF_6), 112068-98-1; 2, 112068-85-6; 3, 112068-87-8; 4, 112068-89-0; 5, 112068-91-4; 6 (A = BF_4), 112068-93-6; 6 (A = PF_6), 112068-99-2; 7, 112068-95-8; 8, 112068-97-0; BT, 95-15-8; 3-MeBT, 1455-18-1; T, 110-02-1; 2,3-Me_2BT, 4923-91-5; $CpRu(PPh_3)_2Cl$, 32993-05-8; $[CpRu(NCCH_3)_3]PF_6$, 80049-61-2; $[Cp^*RhCl_2]_2$, 12354-85-7; $[Cp^*IrCl_2]_2$, 12354-84-6.

Supplementary Material Available: Tables of least-square planes and bond distances and angles for BF_4^- (1 page); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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Manganese Tricarbonyl and Methylmolybdenum Tricarbonyl Derivatives of the *as*-Indacene Bridging Ligand

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Received July 21, 1987

Deprotonation of 1,6-dihydro-2,7-dimethyl-*as*-indacene (1) with *tert*-butyllithium yields the 2,7-dimethyl-*as*-indacene dianion (2). Reaction of 2 with molybdenum hexacarbonyl followed by methyl iodide yields (2,7-dimethyl-*as*-indacene)bis(methylmolybdenum tricarbonyl) (3). An X-ray structural study of 3 indicates it has a trans disposition of molybdenum groups with respect to the planar tricyclic ligand. Reaction of 2 with bis(pyridine)manganese tricarbonyl bromide at low temperature yields a mixture of cis and trans isomers of (2,7-dimethyl-*as*-indacene)bis(manganese tricarbonyl) that were chromatographically separated. An X-ray structural study of the cis isomer indicates considerable steric interaction between the manganese tricarbonyl groups and a bending of the *as*-indacene bridging ligand to accommodate this.

Introduction

The geometry, electronic structure, and reactivity of polynuclear transition-metal compounds with bridging carbocyclic ligands are areas of general interest.[2] As part of an effort to compare the structure and bonding of the flexible bicyclic fulvalene ligand to the rigid tricyclic *s*- and *as*-indacene ligands, we recently reported improved syntheses of these ligands and the preparation of manganese tricarbonyl complexes of *s*-indacene.[3] Here we report the synthesis of molybdenum and manganese carbonyl complexes of 2,7-dimethyl-*as*-indacene.

Earlier work by Katz and co-workers[4] used the *as*-indacene dianion to prepare bis(*as*-indacene)diiron as a mixture of isomers, with the centrosymmetric isomer

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0276-7333/88/2307-0691$01.50/0

characterized by X-ray crystallography.[5] From an alternative route to the *as*-indacene dianion,[6] Sano and coworkers synthesized (*as*-indacene)bis(cyclopentadienyliron),[7] with a trans disposition of iron atoms, and characterized its oxidized mixed-valence derivative.[8]

Our work with the dianions of both *s*- and *as*-indacene indicates that both are good two-electron-reducing agents, and this complicates their substitution chemistry with easily reduced transition-metal substrates. This problem was circumvented in the *s*-indacene system by preparing trimethyltin derivatives and then carrying out transmetalation reactions with $Mn(CO)_5Br$ to yield manganese carbonyl complexes.[3] Here we report reactions of the 2,7-dimethyl-*as*-indacene dianion with metal complexes that are not easily reduced, $Mo(CO)_6$ and $Mn(CO)_3(py)_2Br$. In the case of the manganese complex, substitution occurs very rapidly and yields both cis and trans isomers.

Experimental Section

General Data. NMR spectra were obtained on a JEOL FX-90Q instrument at 89.56 MHz for ^1H and 22.50 MHz for ^{13}C; chemical shifts are reported in parts per million downfield from internal tetramethylsilane unless otherwise noted. Infrared spectra were obtained by using a Perkin-Elmer 599B spectrophotometer and were calibrated against the 1601 cm^{-1} 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; acetonitrile was distilled from calcium hydride. Deuterioacetone was dried over molecular sieve and purified by vacuum transfer. Alkyllithium reagents were standardized by titration against diphenylacetic acid.[9] Flash chromatography was conducted as described by Still and coworkers,[10] using silica gel (Baker, 40-μm average particle diameter) and the indicated solvent.

Molybdenum hexacarbonyl was obtained from Alfa Products. Manganese pentacarbonyl bromide was obtained from Strem Chemical. Bis(pyridine) manganese tricarbonyl bromide was prepared by the literature procedure.[11] 1,6-Dihydro-2,7-dimethyl-*as*-indacene was prepared as previously reported.[3]

All reactions were carried out under an inert atmosphere using modified Schlenk techniques. Filtration of air-sensitive materials was accomplished by Schlenk techniques or by means of a stainless-steel cannula, pointed at one end to pierce a septum and fitted at the other end with a glass tube, which was capped with filter paper. Solevent was forced through the cannula filter by means of a pressure differential. Samples for spectroscopy were prepared in a Vacuum Atmospheres glovebox under a helium atmosphere.

Electrochemical measurements were carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. A Houston Instruments Model 2000 X-Y recorder was used for plotting cyclic voltammograms. A silver wire was dipped in HNO_3 and then HCl, finally rinsed, and dried. This wire was used as a pseudoreference electrode, and ferrocene was used as an internal standard. A carbon disk electrode (IBM) was used as the working electrode, and a platinum wire was used as the counter electrode.

Preparation of (2,7-Dimethyl-*as*-indacene)bis(methylmolybdenum tricarbonyl). 1,6-Dihydro-2,7-dimethyl-*as*-indacene (353 mg, 1.94 mmol) was dissolved in 100 mL of hexanes and cooled to −78 °C. *t*-Butyllithium (4.0 mmol, 2.0 mL of 2 M solution in pentane) was added; after the solution was warmed to room temperature, solvent was removed to give a yellow solid. This was dissolved in 100 mL of THF and $Mo(CO)_6$ (1.09 g, 3.98 mmol) added. The resulting yellow-orange solution was heated to reflux for 20 h, during which time it turned a dark red-brown. The solution was cooled to room temperature and methyl iodide (0.48 mL, 7.7 mmol) added; there was no marked color change at this point. After the solution was stirred for 1 h at 25 °C, solvent was removed under reduced pressure to give a yellow-brown solid. This was washed with 2 × 10 mL portions of acetonitrile; the remaining yellow solid (0.27 g, 25%) was further purified by recrystallization from acetonitrile. The recrystallized solid is only slightly air sensitive: mp 130 °C dec; ^1H NMR (acetone-d_6) δ 7.00 (br s, 2, H-4,5), 6.04 (m, 2) and 5.95 (m, 2) (H-1,3,6,8), 2.16 (s, 6, RCH_3), −0.35 (s, 6, $MoCH_3$); IR (CH_2Cl_2) 2008, 1932 cm^{-1} ($C\equiv O$). Anal. Calcd for $C_{22}H_{18}Mo_2O_6$: C, 46.34; H, 3.18; Mo, 33.65. Found: C, 46.33; H, 3.18; Mo, 33.68.

Preparation of (2,7-Dimethyl-*as*-indacene)bis(manganese tricarbonyl). A solution of 1,6-dihydro-2,7-dimethyl-*as*-indacene (198 mg, 1.09 mmol) in 100 mL of THF was cooled in dry ice/2-propanol and *t*-BuLi (2.2 mmol, 1.1 mL of 2 M solution in pentane) added. The solution was allowed to warm slowly to room temperature; on warming the color turned from light orange to yellow. After being cooled in dry ice/2-propanol again, a solution of $Mn(CO)_3(C_5H_5N)_2Br$ (850 mg, 2.25 mmol) in 60 mL of THF at 0 °C was added to the dilithioindacene solution. The reaction mixture immediately turned a dark red-brown; there was no color change on warming to room temperature. Removal of THF under vacuum gave a red-brown oily solid. Toluene was added and the mixture cannula filtered; removal of solvent gave a yellow-brown solid. This material was dissolved in CH_2Cl_2 and filtered through a silica gel pad; removal of solvent gave a yellow solid, weight 404 mg (81%), whose ^1H NMR spectrum was consistent with a mixture of cis and trans isomers. Flash chromatography (80:20, hexanes/CH_2Cl_2) separated the crude product into two components. These were identified as isomers 4 and 5, with 5 being the compound which elutes first. The yield of the chromatographically pure material was as follows: 5, 219 mg (44%); 4, 68 mg (14%).

Physical Properties. 5: mp 223–223.5 °C; ^1H NMR (acetone-d_6) δ 7.12 (s, 2, H-4,5), 5.49 (d, 2, J = 1.3 Hz), 5.33 (d, 2, J = 1.3 Hz), H-1,3,6,8, 2.05 (s, 6, CH_3); IR (CH_2Cl_2) 2012, 1942 cm^{-1}; MS, m/e (%) 459 (4.1), 458 (M^+, 19.0), 403 (4.0), 402 (20.1), 375 (8.2), 374 (44.5), 319 (16.4), 318 (95.3), 291 (15.4), 290 (M − 6CO, 100), 236 (6.5), 235 (38.3), 181 (12.1), 180 ($C_{14}H_{12}$, 76.1). Anal. Calcd for $C_{20}H_{12}Mn_2O_6$: C, 52.43; H, 2.64; Mn, 23.98. Found: C, 52.37; H, 2.72; Mn, 23.91.

4: mp 202–203 °C; ^1H NMR (acetone-d_6) δ 7.10 (s, 2, H-4,5), 5.86 (d, 2, J = 1.5 Hz) and 5.17 (d, 2, J = 1.5 Hz), H-1,3,6,8, 1.98 (s, 6, CH_3); IR (CH_2Cl_2) 2028, 2008, 1958, 1926 cm^{-1}; MS, m/e (%) 459 (3.8), 458 (M^+, 17.1), 375 (7.8), 374 (1.6), 346 (11.9), 319 (7.4), 318 (44.0), 291 (15.8), 290 (M − 6CO, 100), 236 (4.8), 235 (21.0), 181 (7.5), 180 ($C_{14}H_{12}$, 40.4). Anal. Calcd for $C_{20}H_{12}Mn_2O_6$: C, 52.43; H, 2.64; Mn, 23.98. Found: C, 52.33; H, 2.90; Mn, 24.04.

X-ray Structure of *trans*-(μ-2,7-Dimethyl-*as*-indacene)bis(methylmolybdenum tricarbonyl) (3). Yellow rods grown from an acetonitrile solution were cut to appropriate lengths and mounted in nitrogen-filled quartz capillaries. The data crystal (approximately 0.3 × 0.5 × 1.0 mm) was mounted on a Syntex $P\bar{1}$ four-circle automatic diffractometer with molybdenum tube and graphite monochromator. Lattice parameters were determined by a least-squares refinement on 29 automatically centered reflections between 15° and 34° in 2θ (Mo Kα, 0.71069 Å). A total of 4426 room-temperature $h,k,\pm l$ data were collected between 3° and 50° in 2θ. Systematic absences indicated space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14). No decay was observed. The data were corrected for Lorentz and polarization effects and averaged (R_{av} = 1.6%) to yield 3015 independent reflections greater than 3σ used in the final refinement.[12] No correction was made for absorption.

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[12] $\sigma^2(F_o) = \sigma_c^2 + PF_o^2$ where σ_c^2 is from counting statistics, and P, a factor to downweight stronger intensities, is 0.001 for 3 and 0.0008 for 4.

Table I. Crystal Data

	3	4
formula	$C_{22}H_{18}Mo_2O_6$	$C_{20}H_{12}Mn_2O_6$
mol wt (amu)	570.21	458.18
space group	$P2_1/n$	$P2_1/c$
a (Å)	7.697 (1)	11.180 (3)
b (Å)	25.293 (5)	12.089 (3)
c (Å)	11.314 (2)	14.534 (3)
α (deg)	90	90
β (deg)	97.91 (1)	110.69 (2)
γ (deg)	90	90
V (Å^3)	2181.7 (6)	1837.7 (8)
μ (cm^{-1})	11.6	13.5
Z	4	4
ρ_{obsd} (g/cm^3)	1.71	
ρ_{calcd} (g/cm^3)	1.74	1.66
n_{obsd}	3015	2440
$n_{parameter}$	286	261
R	0.038	0.039
R_w	0.035	0.050

Table II. Final Positional and Thermal Parameters for $C_{14}H_{12}[Mo(CH_3)(CO)_3]_2$ (3)

atom	x	y	z	U_{eq},[a] Å^2
Mo1	−0.02398 (5)	0.10403 (2)	−0.36614 (3)	0.0369 (1)
Mo2	0.34753 (5)	0.14537 (2)	0.09465 (3)	0.0332 (1)
C1	0.2015 (6)	0.1607 (2)	−0.2833 (4)	0.039 (1)
C2	0.2618 (6)	0.1316 (2)	−0.3772 (4)	0.043 (2)
C3	0.2662 (6)	0.0776 (2)	−0.3460 (4)	0.049 (2)
C4	0.2113 (6)	0.0273 (2)	−0.1528 (4)	0.046 (2)
C5	0.1766 (6)	0.0326 (2)	−0.0407 (5)	0.046 (2)
C6	0.0825 (6)	0.1004 (2)	0.1124 (4)	0.044 (2)
C7	0.0453 (6)	0.1550 (2)	0.1071 (4)	0.043 (2)
C8	0.0780 (6)	0.1740 (2)	−0.0058 (4)	0.038 (1)
C9	0.2180 (6)	0.0723 (2)	−0.2286 (4)	0.039 (1)
C10	0.1788 (6)	0.1245 (2)	−0.1902 (4)	0.034 (1)
C11	0.1332 (5)	0.1305 (2)	−0.0703 (4)	0.037 (1)
C12	0.1342 (6)	0.0839 (2)	0.0017 (4)	0.033 (1)
C13	0.3216 (7)	0.1558 (3)	−0.4873 (5)	0.067 (2)
C14	−0.0306 (8)	0.1870 (3)	0.2011 (5)	0.064 (2)
C15	−0.1891 (9)	0.0441 (3)	−0.3584 (6)	0.073 (2)
C16	−0.0441 (7)	0.0750 (2)	−0.5298 (5)	0.055 (2)
C17	−0.1634 (6)	0.1598 (2)	−0.4549 (5)	0.051 (2)
C18	0.5038 (7)	0.1917 (2)	0.0158 (5)	0.056 (2)
C19	0.3949 (7)	0.2024 (2)	0.2124 (4)	0.051 (2)
C20	0.4884 (7)	0.1078 (2)	0.2293 (5)	0.054 (2)
C21	−0.2287 (7)	0.1296 (3)	0.2466 (6)	0.074 (2)
C22	0.5484 (7)	0.0921 (2)	0.0178 (5)	0.057 (2)
O1	−0.2839 (8)	0.0100 (2)	−0.3504 (7)	0.126 (3)
O2	−0.0562 (7)	−0.0591 (2)	−0.6250 (4)	0.089 (2)
O3	−0.2374 (6)	0.1931 (2)	−0.5078 (5)	0.087 (2)
O4	0.5925 (7)	0.2184 (2)	−0.0315 (5)	0.099 (2)
O5	0.4260 (7)	0.2352 (2)	0.2819 (4)	0.085 (2)
O6	0.5647 (7)	0.0851 (2)	0.3054 (4)	0.089 (2)

[a] The equivalent isotropic U is defined as $^1/_3$ the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $C_{14}H_{12}[Mo(CH_3)(CO)_3]_2$ (3)

Mo1–C1	2.344 (4)	C3–C2	1.411 (8)
Mo1–C2	2.327 (4)	C3–C9	1.434 (7)
Mo1–C3	2.313 (5)	C4–C9	1.430 (7)
Mo1–C9	2.395 (4)	C5–C4	1.338 (7)
Mo1–C10	2.411 (4)	C5–C12	1.436 (7)
Mo2–C7	2.363 (5)	C6–C12	1.429 (7)
Mo2–C8	2.339 (4)	C7–C6	1.411 (7)
Mo2–C6	2.369 (5)	C7–C14	1.516 (7)
Mo2–C11	2.345 (4)	C8–C7	1.418 (7)
Mo2–C12	2.397 (4)	C8–C11	1.418 (6)
C1–C10	1.424 (6)	C9–C10	1.436 (6)
C2–C1	1.422 (7)	C10–C11	1.455 (6)
C2–C13	1.516 (7)	C11–C12	1.432 (6)
C9–C3–C2	108.7 (4)	C5–C4–C9	121.2 (5)
C3–C2–C1	108.3 (4)	C4–C9–C10	121.6 (4)
C2–C1–C10	107.8 (4)	C11–C8–C7	107.7 (4)
C1–C10–C9	108.3 (4)	C8–C7–C6	108.0 (4)
C10–C9–C3	106.7 (4)	C7–C6–C12	109.2 (4)
C9–C10–C11	117.7 (4)	C6–C12–C11	106.1 (4)
C10–C11–C12	117.5 (4)	C12–C11–C8	108.9 (4)
C11–C12–C5	122.5 (4)	C1–C2–C13	126.7 (5)
C12–C5–C4	119.4 (5)	C6–C7–C14	126.0 (5)

Table IV. Positional and Thermal Parameters for $C_{14}H_{12}[Mn(CO)_3]_2$ (4)

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Mn1	−0.22905 (5)	0.13196 (5)	0.16145 (4)	0.0322 (2)
Mn2	−0.61838 (5)	0.27097 (5)	0.11534 (4)	0.0347 (2)
O1	−0.1596 (4)	0.1204 (3)	0.3755 (2)	0.076 (1)
O2	−1.0597 (3)	−0.0544 (3)	0.1684 (3)	0.075 (1)
O3	−0.4443 (3)	−0.0203 (3)	0.1274 (3)	0.066 (1)
O4	−0.4513 (3)	0.1895 (3)	0.3078 (2)	0.064 (1)
O5	−0.7403 (3)	0.0543 (3)	0.0604 (2)	0.064 (1)
O6	−0.8099 (4)	0.3347 (4)	0.1989 (3)	0.090 (2)
C1	−0.2873 (3)	0.1997 (3)	0.0167 (3)	0.035 (1)
C2	−0.1526 (3)	0.2084 (3)	0.0611 (3)	0.037 (1)
C3	−0.1243 (4)	0.2749 (3)	0.1472 (3)	0.040 (1)
C4	−0.2667 (4)	0.3948 (3)	0.2165 (3)	0.044 (1)
C5	−0.3842 (4)	0.4383 (3)	0.1941 (3)	0.048 (1)
C6	−0.6170 (4)	0.4368 (3)	0.2165 (3)	0.044 (1)
C7	−0.6816 (4)	0.3681 (4)	−0.0168 (3)	0.047 (1)
C8	−0.5916 (4)	0.2880 (2)	−0.0239 (3)	0.039 (1)
C9	−0.2425 (3)	0.3134 (2)	0.1520 (3)	0.037 (1)
C10	−0.3436 (3)	0.2666 (3)	0.0720 (3)	0.031 (1)
C11	−0.4718 (3)	0.3074 (3)	0.0524 (3)	0.034 (1)
C12	−0.4879 (4)	0.3991 (3)	0.1099 (3)	0.041 (1)
C13	−0.0554 (4)	0.1611 (4)	0.0228 (3)	0.050 (2)
C14	−0.8170 (4)	0.3801 (5)	−0.0863 (4)	0.070 (2)
C15	−0.1875 (4)	0.1268 (4)	0.2920 (3)	0.048 (1)
C16	−0.1226 (4)	0.0179 (4)	0.1669 (3)	0.047 (1)
C17	−0.3612 (4)	0.0401 (3)	0.1407 (3)	0.041 (1)
C18	−0.5165 (4)	0.2210 (4)	0.2324 (3)	0.043 (1)
C19	−0.6913 (4)	0.1388 (4)	0.0812 (3)	0.042 (1)
C20	−0.7347 (4)	0.3091 (4)	0.1664 (4)	0.053 (2)

[a] The equivalent isotropic U is defined as $^1/_3$ the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The initial Patterson map was solved for two Mo positions.[13–16] Subsequent least-squares, difference Fourier cycles located all the remaining heavy atoms.[17] Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å[18]) with unrefined isotropic thermal parameters. Thermal parameters of all non-hydrogen atoms were treated anisotropically. The rotational orientation of the hydrogen atoms on each methyl group was refined. The model converged to unweighted and weighted R factors of 0.0354 and 0.0379, respectively.[19] In the final difference Fourier, the largest residual peak was 0.9 electron/Å^3, within 1.15 Å of a molybdenum atom. Final positional and thermal parameters are found in Table II.

X-ray Structure of *cis*-(μ-2,7-Dimethyl-*as*-indacene)bis(manganese tricarbonyl) (4). Yellow prisms were obtained by cooling a saturated solution in 50:50 toluene/hexanes. The data crystal, approximately 0.4 × 0.4 × 0.5 mm, was mounted on a Syntex P$\bar{1}$ four-circle automatic diffractometer with molybdenum

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[13] Programs were contained in our derived from Syntex data reduction routines, the MULTAN 78 package,[14] the Northewestern University Crystallographic Computing Package of Dr. J. A. Ibers, or the SHELX Package.[15]

[14] Main, P. Multan 78, A System of Computer Programs for the Automatic Solution of Crystal Structures; Department of Physics, University of York: York, England, 1978.

[15] Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

[16] Scattering factors were taken from: *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

[17] The function minimized in all least-squares procedures was $\sum w(|F_o| - |F_c|)^2$.

[18] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[19] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The weighting scheme used for all refinements was based on counting statistics where $w = 1/\sigma^2(F_o)$; $\sigma^2(F_o)$ is defined in ref 12.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for $C_{14}H_{12}[Mn(CO)_3]_2$ (4)

Mn1–C3	2.137 (4)	C2–C13	1.498 (6)
Mn1–C2	2.143 (4)	C1–C10	1.434 (5)
Mn1–C1	2.134 (4)	C8–C7	1.426 (6)
Mn1–C9	2.200 (4)	C8–C11	1.424 (5)
Mn1–C10	2.192 (4)	C6–C7	1.420 (7)
Mn2–C8	2.158 (4)	C7–C14	1.501 (6)
Mn2–C7	2.147 (5)	C6–C12	1.432 (6)
Mn2–C6	2.136 (4)	C5–C4	1.343 (6)
Mn2–C11	2.185 (4)	C5–C12	1.438 (6)
Mn2–C12	2.148 (4)	C4–C9	1.449 (6)
C3–C2	1.426 (6)	C9–C10	1.422 (5)
C3–C9	1.426 (5)	C10–C11	1.446 (5)
C2–C1	1.416 (5)	C11–C12	1.437 (6)
C9–C3–C2	107.8 (3)	C5–C4–C9	119.9 (4)
C3–C2–C1	108.2 (3)	C4–C9–C10	121.5 (3)
C2–C1–C10	108.9 (3)	C11–C8–C7	109.0 (4)
C1–C10–C9	107.6 (3)	C8–C7–C6	107.1 (4)
C10–C9–C3	108.2 (4)	C7–C6–C12	109.1 (4)
C9–C10–C11	118.1 (3)	C6–C12–C11	107.1 (4)
C10–C11–C12	117.9 (3)	C12–C11–C8	107.7 (3)
C11–C12–C5	121.3 (3)	C3–C2–C13	125.2 (4)
C12–C5–C4	120.2 (4)	C6–C7–C14	126.9 (4)

tube and graphite monochromator. Lattice parameters were determined by a least-squares refinement on 15 reflections between 13° and 36° in 2θ. A total of 3449 room-temperature $h,k,\pm l$ data were collected between 3° and 50° in 2θ. Systematic absences indicated space group $P2_1/c$. Two reflections were remeasured after each 100 reflections; no decay was observed. The data were corrected for Lorentz and polarization effects and yielded 2440 independent reflections greater than 3σ which were used in the final refinement.[12] No correction was made for absorption. The manganese atoms were located by using the Multan[14] program. Carbon and oxygen atoms were located by using DIRDIF[20] and least-squares, difference Fourier refinements.[17] Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å[18]) with unrefined isotropic thermal parameters. Thermal parameters of all non-hydrogen atoms were treated anisotropically. The rotational orientation of the hydrogens of the two methyl groups was refined. The model converged to weighted and unweighted R factors of 0.039 and 0.050, respectively.[19] The highest residual electron density peak was 0.41 e/Å^3. Final positional and thermal parameters are found in Table V.

Results

We recently reported[3] a relatively efficient organic synthesis of 1,6-dihydro-2,7-dimethyl-*as*-indacene (1), which enabled us to prepare the 1-hydro-2,7-dimethyl-*as*-indacene monanion, the 2,7-dimethyl-*as*-indacene dianion (2), and their mono- and bis(trimethyltin) derivatives, in synthetically useful quantities.

The reaction of 2 with 2 equiv of $Mo(CO)_6$ requires approximately 20 h in refluxing THF to yield the intermediate (2,7-dimethyl-*as*-indacene)bis(molybdenum tricarbonyl) dianion. This was not isolated but reacted further with CH_3I to yield the bis(methylmolybdenum tricarbonyl) derivative 3 as shown in Figure 1. Solution IR spectra of 3 exhibit only two metal carbonyl stretching bands (ν_{CO} = 2008, 1932 cm^{-1} (in CH_2Cl_2)) which can be compared to those of indenylmethylmolybdenum tricarbonyl (2024, 1945, 1911 cm^{-1} (in halocarbon mull)).[21] This indicates that the two $Mo(CO)_3$ groups are not vibrationally coupled and suggests a trans disposition of the metals with respect to the plane of the tricyclic ligand.

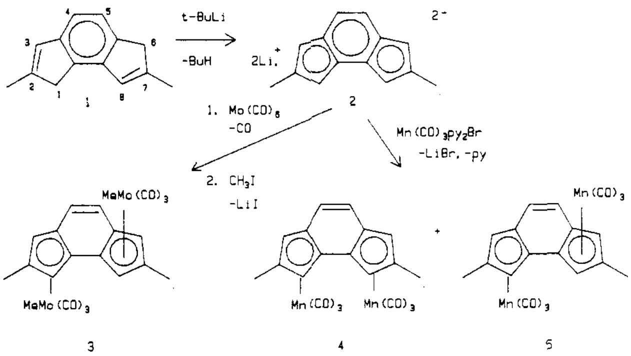

Figure 1. Synthesis of molybdenum and manganese carbonyl derivatives of the 2,7-dimethyl-*as*-indacene ligand.

Proton NMR spectra are consistent with this formulation of 3, which was confirmed by X-ray crystallography (see below), and give no evidence that any of the cis isomer is formed in this reaction.

In the *s*-indacene ligand system, trimethyltin derivatives were used in transmetalation reactions with $Mn(CO)_5Br$ to yield mono- and bis(manganese tricarbonyl) derivatives.[13] This approach successfully avoided redox reactions of the *s*-indacene dianion with $Mn(CO)_5Br$ that yield only $Mn_2(CO)_{10}$ and uncharacterized hydrocarbon products. However, the transmetalation reaction of 1,6-bis(trimethylstannyl)-1,6-dihydro-2,7-dimethyl-*as*-indacene[3] with $Mn(CO)_5Br$ does not yield characterizable products. An alternate approach is to use $Mn(CO)_3(py)_2Br$ as the starting material in reactions with dianion 2. This complex should be more difficult to reduce than $Mn(CO)_5Br$ due to the greater σ-donating ability of the pyridine ligand relative to CO.[22] In addition, the pyridine ligands should be much more labile than CO and this should increase the rate of product formation.

The reaction of dianion 2 with $Mn(CO)_3(py)_2Br$ in THF at −78 °C is apparently complete within a few seconds of mixing. The crude product consists of two compounds present in unequal amounts. These were separated by column chromatography, and mass spectral and chemical analyses confirm that these are isomers. The major isomer elutes first from the column and exhibits two metal carbonyl bands (ν_{CO} = 2012, 1942 cm^{-1} (in CH_2Cl_2)) in the infrared spectrum. This compares well with the spectra observed for (fulvalene)bis(manganese tricarbonyl) (2000, 1925 cm^{-1} (in KBr),[23] and the more closely related indenylmanganese tricarbonyl (2030, 1949, 1940 cm^{-1} (in cyclohexane)[24] and *trans*-(*s*-indacene)bis(manganese tricarbonyl) (2004, 1945 cm^{-1} (in CH_2Cl_2)).[3] This is consistent with a trans disposition of $Mn(CO)_3$ groups that are not vibrationally coupled, as depicted in structure 5 in Figure 1.

The minor isomer exhibits four metal carbonyl bands in the IR spectrum (2028, 2008, 1958, 1926 cm^{-1} (in CH_2Cl_2)) consistent with a structure with a cis disposition of two vibrationally coupled $Mn(CO)_3$ groups (4 in Figure 1). This is similar to the five band metal carbonyl spectrum exhibited by fulvalenedimolybdenum hexacarbonyl[25]

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(20) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A.; Noordik, J. H.; Buerskens, G.; Parthasarthi, V.; BruinsSlot, H. J.; Haltiwanger, R. C. DIRDIF, Technical Report 1983/1; Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

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(22) This is supported by cyclic voltammetric studies that showed irreversible reductions for both compounds in THF. $Mn(CO)_5Br$ was reduced at a potential of −1.7 V vs SCE, and $Mn(CO)_3(py)_2Br$ was reduced at −2.5 V.

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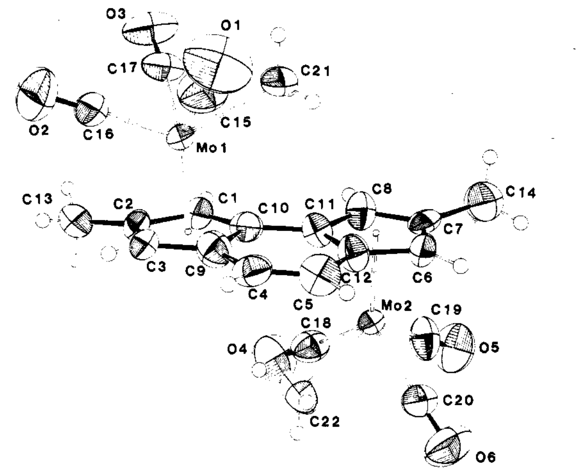

Figure 2. ORTEP[45] drawing of *trans*-(μ-2,7-dimethyl-*as*-indacene)bis(methylmolybdenum tricarbonyl) (3). Thermal ellipsoids for non-hydrogen atoms are shown at the 50% probability level.

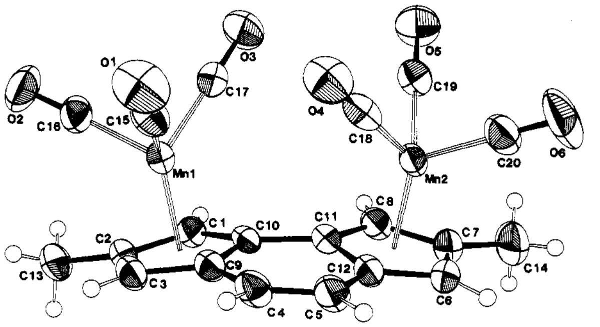

Figure 3. ORTEP[45] drawing of *cis*-(μ-2,7-dimethyl-*as*-indacene)-bis(manganese tricarbonyl) (4). Thermal ellipsoids for non-hydrogen atoms are shown at the 50% probability level.

which contains a metal–metal bonded and vibrationally coupled $Mo_2(CO)_6$ group.

X-ray Structure of 3 and 4

Crystal data for compounds 3 and 4 are given in Table I. The crystal structure of 3 consists of discrete molecular units at general positions in the unit cell; a perspective view of the molecule and the atom numbering scheme are shown in Figure 2. Selected bond lengths and angles with estimated standard deviations are presented in Table III. The closest intermolecular contact in the structure is 2.40 Å between H5 and O2. The molecular structure consists of molybdenum atoms coordinated by three CO groups, a methyl carbon atom, and a C_5 ring of the *as*-indacene ligand. The molybdenum atoms are trans with respect to the tricyclic ligand. This structure is similar to other reported structures that contain the (indenyl)-[26] and (cyclopentadienyl)$Mo(CO)_3R$[27–31] moiety.

The crystal structure of 4 consists of discrete molecular units at general positions in the unit cell; a perspective view of the molecule and the atom numbering scheme are shown in Figure 3. Selected bond lengths and bond angles are presented in Table V. The molecular structure consists of two manganese atoms, each coordinated by three CO ligands and one C_5 ring of the *as*-indacene ligand and oriented cis with respect to the tricyclic ligand. This structure is similar in Mn–C and C–C bond lengths to that of *trans*-(*s*-indacene)bis(manganese tricarbonyl).[3] The structure is also consistent with the previously reported features of indenyl-[33] and cyclopentadienylmanganese tricarbonyl[34–36] compounds.

In both 3 and 4 the C4–C5 bond length is consistent with a localized double bond at 1.34 Å. In both structures, the metal is displaced from the center of the five-membered ring in the direction of C2 and C7, respectively. The difference between the average metal–carbon distance to C1, C2, and C3 and C6, C7, and C8 and those to the ring-junction carbons is 0.04 Å in both 3 and 4. In both 3 and 4 the carbon atoms of each five-membered ring are essentially coplanar. Both observations are consistent with previously reported structures of (η^5-indenyl)metal compounds.[26,33,37–41] This stands in contrast to (η^3-indenyl)-metal compounds, and structures approaching this bonding mode, in which the metal–carbon distance to the allylic carbon atoms is shorter than that to the ring-junction atoms by >0.2 Å, and the five-membered ring is significantly distorted from planarity.[42–44]

The most significant difference between structures 3 and 4 is the planarity of the *as*-indacene ligand in 3 and its deformation from planarity due to steric interactions in 4. In 3, the greatest deviation from the C1–C12 least-squares plane is less than 0.05 Å. In 4, the dihedral angles between the planes defined by the three rings are plane 1 (C-1,2,3,9,10) to plane 3 (C-4,5,9,10,11,12), 12.6 (2)°; plane 2 (C-6,7,8,11,12) to plane 3, 7.0 (2)°; plane 1 to plane 2, 19.6 (2)°.

Acknowledgment. We gratefully acknowledge the assistance of Dr. D. L. DuBois for carrying out the electrochemical measurements and for many helpful discussions. This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences, Division of Chemical Sciences.

Registry No. 1, 106161-69-7; 2·2Li, 106161-74-4; 3, 112139-05-6; 4, 112317-43-8; 5, 112139-06-7; $Mn(CO)_3Py_2Br$, 14881-44-8; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available: Tables of calculated hydrogen positions, anisotropic thermal parameters, and least-squares planes for 3 and 4 (6 pages); listings of structure factors for 3 and 4 (24 pages). Ordering information is given on any current masthead page.

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