

Mono- and Bimetalated Rhenium and Manganese Carbonyl Derivatives of 1,2-Bis(indenyl)ethane

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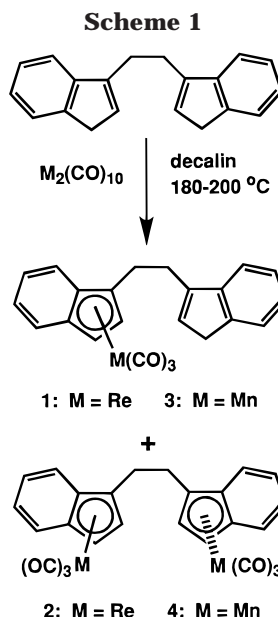
Heating a mixture of $M_2(CO)_{10}$ ($M = Re, Mn$) with 1,2-bis(indenyl)ethane in Decalin at ca. 180 °C provided both monometalated $M(CO)_3\{\eta^5-C_9H_6\}C_2H_4C_9H_7\}$ (**1**, $M = Re$; **3**, $M = Mn$) and bimetalated $(M(CO)_3)_2\{\mu-(\eta^5-C_9H_6)C_2H_4(\eta^5-C_9H_6)\}$ (**2**, $M = Re$; **4**, $M = Mn$) products, which were separated by chromatography, isolated as pure solids, and characterized by a combination of analytical and spectroscopic methods. The bimetalated compounds **2** and **4** were formed as a mixture of *meso* and *rac* diastereomers; the *rac* form of **2** crystallized selectively, and its structure was determined by X-ray crystallography. UV photolysis of **1** and **3** (or **4**) yielded the compounds $M(CO)_2\{\eta^5-C_9H_6\}C_2H_4(\eta^2-C_9H_7)\}$ (**5**, $M = Re$; **6**, $M = Mn$), in which a carbonyl ligand is replaced by the η^2 coordination of the pendant indene group. UV photolysis of **2** gave primarily the rearranged isomer $Re_2(CO)_6\{\mu-(\eta^1:\eta^2-C_9H_6)-C_2H_4(\eta^5-C_9H_6)\}$ (**7**), in which one indenyl group bridges the two Re centers as an $\eta^1:\eta^2$ -vinyl moiety. The molecular structures of compounds **6** and **7** also were determined by X-ray crystallography.

Introduction

We recently reported¹ that photolysis of $(\eta^5-C_9H_7)Re(CO)_3$ provides dinuclear $(\eta^5-C_9H_7)_2Re_2(CO)_4(\mu-CO)$ but that the latter compound undergoes a facile intramolecular rearrangement to give $(\eta^5-C_9H_7)Re(CO)_2(\mu-\eta^2:\eta^5-C_9H_7)Re(CO)_3$, in which the two rhenium centers are positioned on opposite sides of the planar bridging indenyl group. We wondered what would happen if the possibility for this rearrangement were inhibited by a link between the two indenyl moieties. Although such linked indenyl ligands have undergone considerable development in the context of providing chiral environments for mononuclear transition-metal catalysts,² they have received scant attention as ligands for dinuclear compounds.³ We therefore thought it would be interesting to investigate the reaction of $Re_2(CO)_{10}$ (and $Mn_2(CO)_{10}$) with 1,2-bis(indenyl)ethane, and we now report on the resulting mono- and bimetalated compounds as shown in Scheme 1. Photolysis of these compounds leads to further transformations that are depicted in Scheme 2.

Experimental Section

General Procedures. Solvents used for reactions were freshly distilled from sodium; other solvents were reagent



grade. The reactants $Re_2(CO)_{10}$ (Strem), $Mn_2(CO)_{10}$ (Strem), and 1,2-bis(indenyl)ethane (Aldrich) were used as received. Irradiations were carried out with a water-cooled, 200 W medium-pressure Hg vapor lamp. Infrared spectra were obtained with a Perkin-Elmer Model 1750 FTIR instrument. NMR spectra were recorded with Varian Unity 400 and 500 MHz spectrometers. Field desorption (FD) mass spectra were obtained on a Varian-MAT 731 spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences. Elemental analyses were performed by the staff of the School Microanalytical Laboratory.

Synthesis of 1 and 2. To a 1.0 g (1.53 mmol) sample of $Re_2(CO)_{10}$ was added 380 mg (1.47 mmol) of 1,2-bis(indenyl)ethane and 1 mL of Decalin in a 10 mL round-bottom flask. The mixture was degassed under vacuum, and then it was heated under nitrogen with stirring to 190–200 °C for 2 days. The solution formed was initially yellow and then became

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- (2) (a) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233. (b) Wild, F. R. W. P.; Wasuccionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63. (c) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (d) Kaminsky, W.; K  lper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (e) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1263. (f) Verdaguer, X.; Lange, U. E. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1103.
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Scheme 2

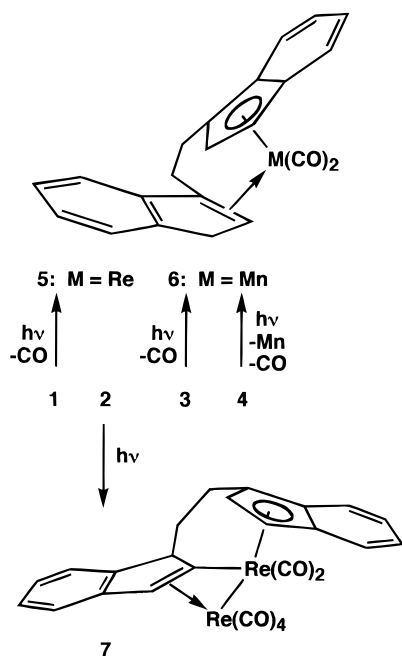


Chart 1

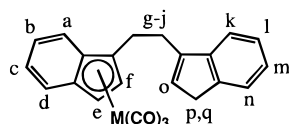
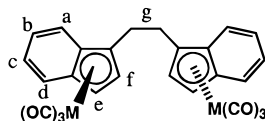


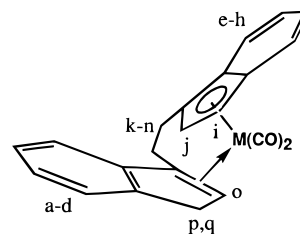
Chart 2



dark. The flask was cooled to room temperature, and its contents were dissolved in a minimal amount of dichloromethane. This solution was applied to a column of neutral alumina (3 × 15 cm). Bands containing the starting materials were eluted with hexane. Elution with hexane–dichloromethane (3:1) gave a band containing compound **1** (355 mg, 0.673 mmol, 22%), and elution with dichloromethane alone gave compound **2** (232 mg, 0.291 mmol, 19%). Data for **1** are as follows. Anal. Calcd for C₂₃H₁₇O₃Re: C, 52.27, H, 3.24. Found: C, 52.43, H, 3.31. MS (FD): *m/z* (¹⁸⁷Re) 528 (M⁺). IR (CH₂Cl₂): ν(CO), 2020 (s), 1924 (br, s) cm⁻¹. ¹H NMR (CDCl₃; see Chart 1 for assignments): δ 7.52–7.04 (8H, m, **a–d** + **k–n**), 6.24 (1H, s (br), **o**), 5.63 (1H, d, *J* = 2.8 Hz, **e** or **f**), 5.60 (1H, d, *J* = 2.8 Hz, **e** or **f**), 3.35 (2H, s (br), **p, q**), 3.27 (1H, m, **g–j**), 3.08 (1H, m, **g–j**), 2.87 (2H, m, **g–j**). Data for **2** are as follows. Anal. Calcd for C₂₆H₁₆O₆Re₂: C, 39.10, H, 2.02. Found: C, 39.36, H, 2.09. MS (FD): *m/z* (¹⁸⁷Re) 798 (M⁺). IR (CH₂Cl₂): ν(CO), 2020 (s), 1926 (br, s) cm⁻¹. ¹H NMR (CDCl₃) (see Chart 2 for assignments): *meso* isomer, δ 7.44 (2H, dm, *J* = 8.4 Hz, **a** or **d**), 7.35 (2H, dm, *J* = 8.4 Hz, **a** or **d**), 7.07 (4H, m, **b** + **c**), 5.58 (2H, dd, *J* = 3.0, 0.8 Hz, **e**), 5.54 (2H, d, *J* = 3.0 Hz, **f**), 3.19 (2H, m, **g**), 2.98 (2H, m, **g**); *rac* isomer, δ 7.43 (4H, m, **a** + **d**), 7.03 (4H, m, **b** + **c**), 5.62 (2H, dd, *J* = 3.0, 0.7 Hz, **e**), 5.52 (2H, d, *J* = 3.0 Hz, **f**), 3.22 (2H, m, **g**), 2.96 (2H, m, **g**).

Synthesis of 3 and 4. A sample of Mn₂(CO)₁₀ (1.0 g, 2.56 mmol) was combined with 1,2-bis(indenyl)ethane (645 mg, 2.50 mmol) and 1.5 mL of Decalin in a 10 mL round-bottom flask under nitrogen, and the flask was heated at ca. 180 °C for 12 h. The reaction mixture was extracted with dichloromethane

Chart 3



and then separated into three bands by thin-layer chromatography (SiO₂, 2:1 C₆H₁₄–CH₂Cl₂). The first band contained organic material and a small amount of Mn₂(CO)₁₀. The second band contained 366 mg (0.923 mmol, 18%) of the monometallated compound **3**. The third band contained 192 mg (0.359 mmol, 14%) of compound **4**. Data for **3** are as follows. Anal. Calcd for C₂₃H₁₇O₃Mn: C, 69.69, H, 4.33. Found: C, 70.09, H, 4.63. MS (FD): *m/z* 396 (M⁺). IR (CHCl₃): ν(CO) 2020 (s), 1934 (br, s) cm⁻¹. ¹H NMR (C₂D₆CO) (see Chart 1 for assignments): δ 7.67–7.15 (8H, m, **a–d** + **e–g**), 6.33 (1H, m, **i**), 5.35 (1H, dd, *J* = 3.0, 0.7 Hz, **k**), 5.31 (1H, d, *J* = 3.0 Hz, **j**), 3.32 (2H, m, **l**), 3.24 (1H, m, **m**), 3.10 (1H, m, **m**), 2.97 (2H, m, **m**). Data for **4** are as follows. Anal. Calcd for C₂₆H₁₆O₆Mn₂: C, 58.43, H, 3.02. Found: C, 59.85, H, 3.26. MS (FD): *m/z* 534 (M⁺). IR (CHCl₃): ν(CO), 2020 (s), 1934 (s, br) cm⁻¹. ¹H NMR (C₂D₆CO) (see Chart 2 for assignments): *meso* isomer, δ 7.57 (4H, m, **a** + **d**), 7.17 (4H, m, **b** + **c**), 5.33 (2H, d, *J* = 3.0 Hz, **e** or **f**), 5.27 (2H, d, *J* = 3.0 Hz, **e** or **f**), 3.25 (2H, m, **g**), 3.11 (2H, m, **g**); *rac* isomer, δ 7.52 (4H, m, **a** + **d**), 7.11 (4H, m, **b** + **c**), 5.37 (2H, dd, *J* = 3.0 Hz, **e** or **f**), 5.22 (2H, d, *J* = 3.0 Hz, **e** or **f**), 3.32 (2H, m, **g**), 3.04 (2H, m, **g**).

Photolysis of 1. A 100 mg (0.190 mmol) sample of **1** was dissolved in 10 mL of diethyl ether in a quartz flask. The flask was irradiated for 45 min with a constant purge of nitrogen. Then the solution was evaporated, and the residue was separated by preparative TLC (2:1 hexane–dichloromethane). A band following the unreacted starting material was isolated and contained 42 mg (0.083 mmol, 44%) of **5**. Anal. Calcd for C₂₂H₁₇O₂Re: C, 52.89, H, 3.43. Found: C, 53.10, H, 3.49. MS (FD): *m/z* 500 (M⁺). IR (CHCl₃): ν(CO), 1960 (s), 1890 (s) cm⁻¹. ¹H NMR (CDCl₃, major isomer; see Chart 3 for assignments): δ 7.0–7.8 (8H, m, **a–d**, **e–h**), 5.93 (1H, d, *J* = 2.6 Hz, **i**), 5.63 (1H, d, *J* = 2.6 Hz, **j**), 3.87 (1H, d, *J* = 5.3 Hz, **o**), 3.66 (1H, ddd, *J* = 14.7, 5.6, 1.2 Hz, **k, l, m**, or **n**), 3.52 (1H, dd, *J* = 19.5, 5.3 Hz, **p** or **q**), 3.41 (1H, ddd, *J* = 13.8, 12.9, 7.3 Hz, **k, l, m**, or **n**), 2.98 (1H, d, *J* = 19.5 Hz, **q** or **p**), 2.64 (1H, ddd, *J* = 14.5, 7.3, 1.5 Hz, **k, l, m**, or **n**), 2.47 (1H, ddd, *J* = 14.2, 12.9, 5.6 Hz, **k, l, m**, or **n**).

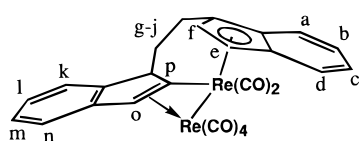
Photolysis of 3. With a procedure analogous to that for **1**, starting with 100 mg (0.252 mmol) of **3** yielded 29 mg (0.081 mmol, 32%) of **6**. Anal. Calcd for C₂₂H₁₇O₂Mn: C, 71.74, H, 4.65. Found: C, 71.36, H, 4.89. MS (FD): *m/z* 368 (M⁺). IR (C₆H₁₄): ν(CO), 1971 (s), 1912 (s) cm⁻¹. ¹H NMR (C₂D₆CO) (major isomer, see Chart 3 for assignments): δ 6.92–7.72 (8H, m, **a–d**, **e–h**), 5.49 (1H, d, *J* = 2.6 Hz, **i**), 5.04 (1H, d, *J* = 2.4 Hz, **j**), 4.31 (1H, d, *J* = 4.5 Hz, **o**), 3.84 (1H, m, **k, l, m**, or **n**), 3.34 (1H, dd, *J* = 21, 4.5 Hz, **p** or **q**), 3.20 (1H, m, **k, l, m**, or **n**), 2.82 (1H, d, *J* = 21 Hz, **k, l, m**, or **n**), 2.50 (2H, m, **k, l, m**, or **n**).

Photolysis of 2. A 100 mg (0.126 mmol) sample of **2** was dissolved in 20 mL diethyl ether. The solution was exposed to UV light under N₂ purge for 60 min. The solution was then separated by preparative TLC (2:1 hexane:dichloromethane). A bright yellow band adjacent to a band for the starting material was isolated and contained 53 mg (0.067 mmol, 53%) of **7**. Anal. Calcd for C₂₆H₁₆O₆Re₂: C, 39.10, H, 2.02. Found: C, 39.24, H, 2.48. MS (FD M⁺): *m/z* (¹⁸⁷Re) 798. IR (CH₂Cl₂): ν(CO), 2083 (m), 1995 (s), 1980 (s), 1952 (s), 1881 (s) cm⁻¹. ¹H NMR (CDCl₃) (major isomer, see Chart 4 for assignments): δ 7.0–7.8 (8H, m, **a–d**, **k–n**), 5.92 (1H, d, *J* = 2.4 Hz, **e** or **f**),

Table 1. Crystallographic Data for **2**, **6**, and **7**

	2-rac	6	7
formula	C ₂₆ H ₁₆ O ₆ Re ₂	C ₂₂ H ₁₇ MnO ₂	C ₂₇ H ₁₈ O ₆ Cl ₂ Re ₂
fw	796.79	368.30	881.7
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
cryst syst	triclinic	monoclinic	monoclinic
<i>a</i> (Å)	12.1583(5)	9.3855(1)	22.3562(5)
<i>b</i> (Å)	13.2178(4)	7.7889(1)	11.5812(3)
<i>c</i> (Å)	15.5840(6)	2.8777(4)	20.3625(5)
α (deg)	77.781(1)	90	90
β (deg)	70.097(1)	99.644(1)	111.227(1)
γ (deg)	88.776(1)	90	90
<i>V</i> (Å ³)	2298.0(2)	1648.68(1)	4914.4(2)
<i>Z</i>	4	2	8
temp (K)	198(2)	198(2)	198(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
ρ (calcd) (g cm ⁻³)	2.303	0.742	2.378
cryst size (mm ³)	0.06 × 0.15 × 0.22	0.28 × 0.40 × 0.42	0.06 × 0.06 × 0.11
μ (mm ⁻¹)	10.566	0.406	10.104
transmissn coeff, max/min	0.5542/0.1454	0.8227/0.7365	0.5963/0.4950
no. of rflns collected	14642	10 400	15 791
no. of indep rflns	10352	3909	5883
<i>R</i> _{int}	0.0524	0.0253	0.0687
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0346	0.0286	0.0461
w <i>R</i> 2 ^b	0.1058	0.0943	0.1180

^a $R1 = \sum |(F_o - F_c)| / \sum F_o$. ^b $wR2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum (w(F_o^2)^2) \}^{1/2}$.

Chart 4

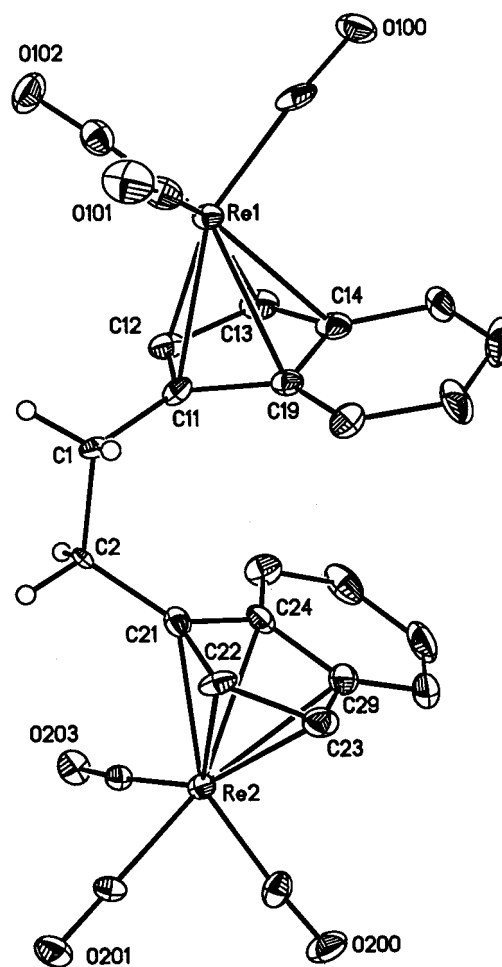
5.76 (1H, d, *J* = 2.4 Hz, **e** or **f**), 5.0 (1H, s, **o**), 4.28 (1H, d, *J* = 11.4 Hz, **p**), 3.0 (3H, m, **h–j**), 2.83 (1H, m, **g**).

Another band with an *R_f* value lower than that of the starting material contained a small amount of compound **8**. MS (FD): *m/z* (¹⁸⁷Re) 768. IR (CH₂Cl₂): ν (CO) 2017 (s), 1955 (m), 1921 (s, br), 1881 (m) cm⁻¹.

Photolysis of 4. A small sample of **4** (ca. 10 mg) was dissolved in hexane (50 mL) in a quartz Schlenk tube. The solution was stirred and exposed to UV light for 15 min. The reaction mixture consisted of an orange solution and a fluffy, pale precipitate. The IR spectrum of the orange solution showed only the presence of **6**: ν (CO) 1968 (s), 1917 (s) cm⁻¹. The separated precipitate proved intractable in that no solvent was found to dissolve it. Similar behavior was observed when **4** was irradiated in THF or dichloromethane.

X-ray Crystallographic Studies. Single crystals of **2** suitable for X-ray crystallography formed after leaving the evaporated residue of the compound for several days at room temperature. Single crystals of **6** were obtained by layering hexane on a dichloromethane solution at room temperature. Single crystals of **7** were obtained by slow evaporation of a dichloromethane solution at room temperature. X-ray diffraction data were obtained on a Siemens Platform/CCD automated diffractometer. All data processing was performed with the integrated program package SHELXTL.^{4a} The structures were solved by direct methods,^{4b} and refinements were made by full-matrix least squares based on *F*². Hydrogen atoms were fixed on calculated positions. Crystallographic details for the studies of **2**, **6** and **7** are summarized in Table 1. Bond distances and angles for **2**, **6**, and **7** are listed in Tables 2–4, respectively. Structural diagrams for compounds **2**, **6**, and **7** are depicted in Figures 1, 2, and 3, respectively, with 30% thermal ellipsoids.

(4) (a) Sheldrick, G. M. SHELXTL-PC, version 5.0; Siemens Industrial Automation, Inc., Madison, WI, 1994. (b) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.



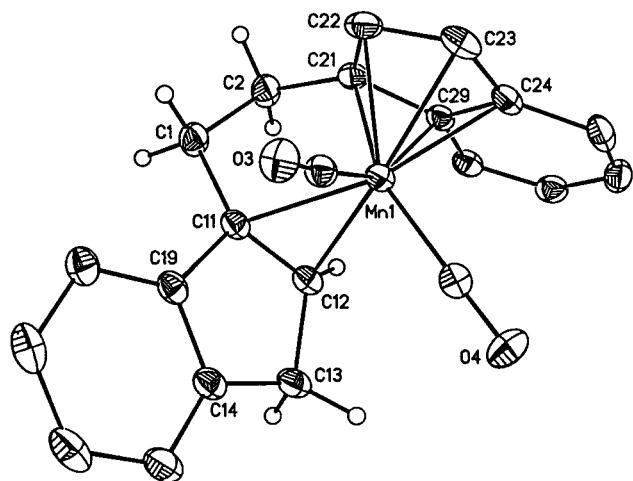


Figure 2. Structural diagram of **6**. Selected hydrogen atoms are shown in calculated positions.

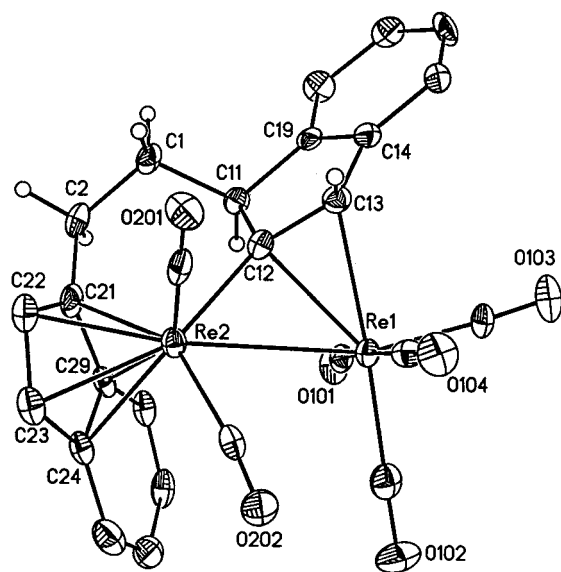
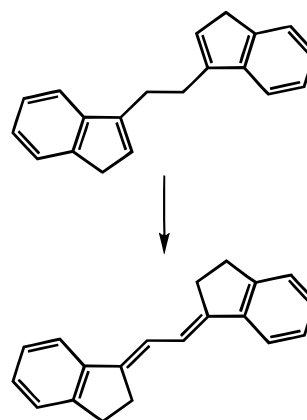


Figure 3. Structural diagram of **7**. Selected hydrogen atoms are shown in calculated positions.

Scheme 1. No appreciable metalation occurred at lower temperatures. This direct procedure was based on the preparation of $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$ by heating $\text{Re}_2(\text{CO})_{10}$ with indene as the solvent.⁵ In the case of 1,2-bis(indenyl)ethane some amount of refluxing solvent must be added to wash sublimed $\text{Re}_2(\text{CO})_{10}$ back into the flask, but if the mixture of reactants was not relatively concentrated, lower yields were obtained. When the molar ratio of the ligand to $\text{Re}_2(\text{CO})_{10}$ was 1:1, production of the bimetalated product **2** was favored. Higher amounts of ligand in the reaction mixture increased the relative yield of the monometalated product **1**; however, even when a 2-fold excess of ligand was used, there was a small amount of **2** present. Thus, it is likely that each indenyl unit reacts independently; i.e., whether one unit is already metalated does not seem to be an important factor.

The synthesis of the Mn analogues **3** and **4** was undertaken by the same method, by heating $\text{Mn}_2(\text{CO})_{10}$ with the ligand at high concentration in Decalin. A

Scheme 3



heating time of ca. 12 h seemed to give the optimum yield in this case; if the heating was prolonged, the yield diminished as large amounts of insoluble residue appeared.

One interesting feature of these reactions, which may limit the possible yields of organometallic products, was revealed upon examination by ^1H NMR of the chromatography band thought to contain only unreacted 1,2-bis(indenyl)ethane. The spectrum showed that a significant amount of a new organic compound was present. In one reaction with $\text{Re}_2(\text{CO})_{10}$, in which 1,2-bis(indenyl)ethane was used in significant excess, the extracted band containing the organic material was evaporated, and crystals of the new compound formed spontaneously. The FD mass spectrum of the compound showed it to have the same mass (258) as 1,2-bis(indenyl)ethane, and its ^1H NMR spectrum clearly showed it to be the isomeric compound (*E,E*)-bis(indanylindenyl)ethane (see Scheme 3). This compound was prepared previously in a multistep synthesis starting with 1-indanone.⁶ However, the action of the metal carbonyl on 1,2-bis(indenyl)ethane causes a double allylic 1,3-hydrogen shift that brings the endocyclic double bonds into exocyclic conjugation. In some reactions we observed that as much as 50% of the 1,2-bis(indenyl)ethane charged was transformed into the new isomer, but the reaction appears to be stoichiometric, not catalytic. We obtained no evidence for metal complexes of this diene isomer.

An alternative synthetic approach to **2** was explored briefly. A solution of $\text{Re}(\text{CO})_5\text{Br}$ was heated under reflux for 18 h in THF to give a solution containing $\text{Re}_2(\text{CO})_6(\text{THF})_2(\mu\text{-Br})_2$.⁷ Then 1,2-bis(indenyl)ethane in THF was treated with 2 equiv of *n*-butyllithium, and this solution was added to the previous one, followed by heating the mixture under reflux. However, the yields of **1** and **2** obtained following chromatographic workup (25% and 24%, respectively) were comparable with those obtained by the direct reaction method.

The mixture of mono- and bimetalated products can be separated conveniently by chromatography, as the R_f values for each product and the starting materials differ considerably. As expected, the dinuclear products **2** and **4** each form two diastereomers, *meso* and *rac*. Our

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attempts to separate the diastereomers by either column or thin-layer chromatography were not successful. However, the solubilities of the *rac* diastereomers were observed to be higher in aromatic hydrocarbons, diethyl ether, and chloroform, and therefore at least partial separation of the diastereomers could be achieved by selective extraction.

Spectroscopic Characterization of Compounds 1–4.

The $\nu(\text{CO})$ IR spectra of compounds **1** and **2** are indistinguishable from each other as well as from that of $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$. These spectra consist of a sharp band at higher frequency, ca. 2020 cm^{-1} , and a broad band near 1920 cm^{-1} in typical solvents. A similar situation obtains for the manganese analogues. Thus, the IR spectra are not particularly useful in following the course of reaction in either case.

The ^1H NMR spectra of the products, however, are quite informative. Chart 1 shows the categories of protons for the monometalated compounds **1** and **3**, and the specific assignments are given in the Experimental Section. Although the aromatic proton signals fall in the same region for both the metalated and nonmetalated indenyl moieties, the signals for the protons on the five-membered rings are quite distinct. A characteristic feature in the spectra of both **1** and **3** is a broad singlet near δ 6.3, which corresponds to the vinylic proton **o** on the nonmetalated ring. The methylene protons **p** and **q** on this ring also are observed as a broad singlet, despite their inequivalence, and this signal appears considerably upfield near δ 3.3. In contrast, the signals for the two protons **e** and **f** on the metalated ring appear as coupled doublets close together near δ 5.3.

Chart 2 depicts the categories of protons for the diastereomers of the bimetalated compounds **2** and **4**, and specific assignments are given in the Experimental Section. The signals for the various groups of protons occur in very similar regions for the two diastereomers, but individual assignments for *meso* vs *rac* diastereomers became possible after determining the structure of **2-rac** by X-ray crystallography (vide infra). The clearest separation in signals for the two diastereomers occurs for the two protons **e** and **f** on the metalated five-membered rings. These signals appear in the δ 5–6 region, and one pair of doublets arises from each diastereomer. The relative intensity of these doublet pairs indicates the diastereomer abundance ratio. Equal intensities for these pairs of signals were invariably observed following initial isolation of compounds **2** or **4**; hence, their formation was not diastereoselective.

X-ray Crystal Structure Study of 2-rac. Evaporation of the solution containing **2** after extraction of the chromatography band left a residue that appeared to be a powder, but discrete single crystals formed after letting the residue stand several days. These crystals were exclusively of one habit and proved to contain only the *rac* isomer, even though the residue always contained both diastereomers.

The molecular structure of **2-rac** is shown in Figure 1. Selected distances are given in Table 2. Each of the two $\text{Re}(\text{CO})_3$ units is coordinated in an η^5 mode to the five-membered ring of an indenyl moiety. The indenyl–rhenium complexes are oriented respectively “head-to-head”, with the $\text{Re}(\text{CO})_3$ units pointed away from one another. The conformation of these two substituents on

Table 2. Selected Bond Distances (Å) for 2-rac

Re1–C11	2.30(1)	Re2–C21	2.31(1)
Re1–C12	2.29(1)	Re2–C22	2.30(1)
Re1–C13	2.29(1)	Re2–C23	2.30(1)
Re1–C14	2.35(1)	Re2–C24	2.36(1)
Re1–C19	2.38(1)	Re2–C29	2.34(1)
C11–C1	1.48(1)	C21–C2	1.47(1)
C1–C2	1.54(1)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 6

Mn1–C21	2.138(2)	Mn1–C11	2.222(2)
Mn1–C22	2.121(2)	Mn1–C12	2.185(2)
Mn1–C23	2.136(2)	Mn1–C3	1.769(2)
Mn1–C24	2.220(2)	Mn1–C4	1.790(2)
Mn1–C29	2.227(2)		
C11–C12	1.410(2)	C21–C22	1.418(3)
C12–C13	1.517(2)	C22–C23	1.416(3)
C13–C14	1.513(3)	C23–C24	1.420(3)
C14–C19	1.400(2)	C24–C29	1.437(2)
C19–C11	1.490(2)	C29–C21	1.445(2)
C11–C1	1.518(2)	C21–C2	1.497(3)
C1–C2	1.537(3)		
C11–C1–C2	111.50(15)	C21–C2–C1	108.3(2)
Mn1–C11–C19	115.73(11)	Mn1–C12–C13	121.19(12)
C21–Mn1–C22	38.90(7)	C22–Mn1–C23	38.86(8)
C23–Mn1–C24	38.00(7)	C24–Mn1–C29	37.70(6)
C29–Mn1–C21	38.62(6)	C11–Mn1–C12	37.32(6)

the ethano bridge is gauche, and they are clearly related by an approximate molecular (not crystallographic) 2-fold rotation axis. The Re–C distances for each η^5 ring have an average value of $2.32(2)\text{ Å}$, which compares very well with data for similar indenyl–Re compounds, such as $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\mu\text{-}\eta^2\text{:}\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$ ¹ and (trindenyl)[$\text{Re}(\text{CO})_3$]₃.⁸ The relatively small “ring slip” values for compound **2** (0.072 Å for Re1 and 0.054 Å for Re2) also indicate symmetrical bonding, consistent with related compounds.

Photolysis of Compounds 1–4. The synthesis of bimetalated compounds **2** and **4** was undertaken with the original goal of investigating the possible formation of metal–metal-bonded compounds via photolysis, as in the case of $[(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2](\mu\text{-CO})$ from $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$.¹ Since the monometalated compounds **1** and **3** were also obtained in the preparations, the photolysis of all four compounds has been investigated, and the results are depicted in Scheme 2. Photolysis of **1** and **3** gave compounds **5** and **6**, respectively, in which the pendant indene moiety is wrapped around the metal center to become η^2 -coordinated. Photolysis of **2** did indeed lead to the dinuclear compound **7**, but formation of the metal–metal bond was accompanied by significant rearrangement of one indenyl group to become a bridging vinylic ligand. Finally, photolysis of **4** also gave **6** in low yield as the only observable product.

Characterization of Compounds 5 and 6. Figure 2 shows the molecular structure of **6** derived from X-ray crystallographic analysis. One carbonyl ligand is lost from the Mn center in **3**, and it is replaced in **6** by coordination of the double bond of the pendant indene moiety. Selected distances and angles for the structure are given in Table 3. The Mn–C distances to the carbon atoms of the η^5 -coordinated ring range from $2.121(2)$ to $2.227(2)\text{ Å}$ (with slip value $\Delta = 0.092\text{ Å}$), which are

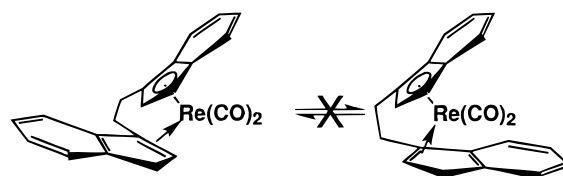
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comparable to those for related compounds.⁹ The Mn–C distances of the η^2 -olefin are significantly shorter, at 1.769(2) and 1.790(2) Å, but these values are comparable to similar bonds in [CpMn(CO)₂]₂(μ - η^2 : η^2 -cyclopentadiene)^{9a} and CpMn(CO)₂(η^2 -C₈H₈).^{9b} Analogous indenyl–indene compounds (η^5 -C₉H₇)M(CO)₂(η^2 -C₉H₈) (M = Mn,¹⁰ Re¹¹) have been reported previously, but to our knowledge no X-ray structures are available.

Two diastereomers are possible for **6** (and **5**), since coordination of the indene olefinic group can occur at either of its two faces. The solid-state structure observed for **6** is the “*rac*-like” diastereomer; i.e., the isomer in which the two six-membered rings would be related by a 2-fold axis if the two indenyl moieties were chemically identical. A mixture of diastereomers is generated in the synthesis of **6**, as indicated by the ¹H NMR spectrum of the product, but dissolving crystals of **6** for an NMR spectrum identified the major product as the “*rac*-like” diastereomer. The ¹H NMR spectra of the diastereomers of **5** are very similar in appearance to those of **6**, and we assume analogous structures. The ¹H NMR assignments for the major isomers of compounds **5** and **6** are displayed in Chart 3. The most notable changes in the ¹H NMR spectra for **5** and **6** in comparison with those for **1** and **3** are, as expected, in the signals for the protons on the five-membered ring that has become coordinated. The signal for vinylic proton **o** is shifted dramatically upfield (from ca. δ 6.3 to ca. δ 3.9), the signals for the inequivalent methylene protons **p** and **q** become significantly separated, with a large geminal coupling (ca. 20 Hz), and **o** is coupled observably (ca. 5 Hz) with only one of the **p**, **q** set. Similar differential coupling due to the angular relationships among an analogous set of vicinal protons is characteristic of cyclopentadiene (η^4 -C₅H₆) ligands.¹²

The relative yields of the diastereomers of **5** or **6** from the photolysis of **1** or **3** in hexane or ether was ca. 2:1 in favor of the “*rac*-like” diastereomer. Interestingly, however, photolysis of **1** in THF gave a sample of **5** in which the proportion of the major isomer was increased to 5:1. The higher diastereoselectivity in THF is likely due to formation of the relatively stable solvated intermediate Re(CO)₂(THF){(η^5 -C₉H₆)C₂H₄(C₉H₇)}, which allows complete equilibration of the rotamers involving the dangling indene group and then promotes preferential formation of the more stable diastereomer. In a related reaction involving the photolysis of Mo(CO)₃-(CH₃){(η^5 -C₅H₄)C₂H₄(C₉H₇)}, which has a dangling ethanoindene moiety attached to a cyclopentadienyl ligand, a 4:1 ratio of diastereomers for the η^2 -olefin product Mo(CO)₂(CH₃){(η^5 -C₅H₄)C₂H₄(η^2 -C₉H₇)} was observed.¹³

Scheme 4

Table 4. Selected Bond Distances (Å) and Angles (deg) for **7**

Re1–Re2	2.9843(6)	Re2–C21	2.334(10)
Re1–C13	2.370(10)	Re2–C22	2.277(10)
Re1–C12	2.292(9)	Re2–C23	2.275(10)
Re2–C12	2.122(10)	Re2–C24	2.360(10)
		Re2–C29	2.416(10)
Re1–C101	1.994(11)	Re1–C102	1.950(13)
Re1–C103	1.908(10)	Re1–C104	2.020(11)
Re2–C201	1.869(12)	Re1–C202	1.936(11)
C11–C12	1.56(1)	C21–C22	1.39(2)
C12–C13	1.41(1)	C22–C23	1.42(2)
C13–C14	1.49(1)	C23–C24	1.42(2)
C14–C19	1.39(1)	C24–C29	1.44(1)
C19–C11	1.54(1)	C29–C21	1.44(2)
C1–C11	1.53(1)	C2–C21	1.51(2)
C1–C2	1.52(2)		
Re1–C12–Re2	85.0(3)	C12–Re1–Re2	45.1(3)
C101–Re1–C104	174.9(4)	C12–Re2–Re1	49.9(3)
C21–Re2–C22	35.0(4)	C22–Re2–C23	36.2(4)
C23–Re2–C24	35.7(4)	C24–Re2–C29	35.1(3)
C29–Re2–C21	35.1(4)	C12–Re1–C13	35.2(3)

Interestingly, the diastereoselective preparation of the related mononuclear *ansa* derivatives, such as ZrCl₂·{(η^5 -C₉H₆)C₂H₄(η^5 -C₉H₆)},^{2b} can vary considerably depending on the reaction conditions and the specific reagents used, but the *rac* form is typically favored by at least a 2:1 ratio.^{2e}

The enrichment of the major isomer of **5** resulting from its preparation in THF made it easier to obtain a relatively pure (ca. 95%) sample of this “*rac*-like” diastereomer by fractional precipitation. This sample was heated for several hours in refluxing octane in order to probe for possible equilibration between the diastereomers of **5** (see Scheme 4). Monitoring the reaction periodically by its ¹H NMR spectrum showed that **5** gradually decomposed, but no evidence for the formation of the “*meso*-like” diastereomer was obtained. Another reaction examined was the possibility of converting **5** to an *ansa*-metallocene complex, e.g., [Re(CO)(η^5 -C₉H₆-CH₂)₂]⁺, by treatment with [CPh₃]⁺; this was not successful, however, as only decomposition of **5** and no new product were observed.

Characterization of Compound 7. The photolysis of **2** in diethyl ether leads predominantly to a product of the same formula, compound **7**, which has been fully characterized by spectroscopic and crystallographic data. The molecular structure of **7** is depicted in Figure 3. Selected interatomic distances and angles are given in Table 4. The overall result of photolyzing **2** is indeed the formation of a Re–Re bond, but one indenyl ligand is modified, with a proton moving from C2 to C1, resulting in an η^1 : η^2 -vinyl ligand bridging the two metal centers. Although the total number of carbonyl ligands is unchanged from **2**, they are unevenly distributed in **7**, with two bound to one center and four bound to the other.

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The Re–Re bond distance of 2.9843(6) Å in **7** is longer than that in related compounds containing a Re–Re bond and a bridging $\eta^1:\eta^2$ -vinyl group. For example, this distance is 2.881(1) Å in $\text{Re}_2(\text{CO})_7(\text{C}_8\text{H}_2\text{Ph}_2\text{Fc}_2)$,¹⁴ 2.8868(7) Å in $\text{Re}_2(\text{CO})_7[\mu\text{-C}(\text{Me})\text{C}(\text{NMe}_2)\text{C}(\text{NMe}_2)\text{-C}(\text{Me})]$,¹⁵ 2.878(1) Å in $\text{Re}_2(\text{CO})_5(\text{C}_4\text{Ph}_4)(\text{C}_2\text{Ph}_2)$,¹⁶ and 2.874(1) Å in $\text{Re}_2(\mu\text{-}\eta^1:\eta^1:\eta^4\text{-C}_4\text{Ph}_4)(\text{CO})_7$.¹⁷ It is also somewhat longer than the value of 2.928(1) Å in the α,β -unsaturated bimetallic compound $\text{Cp}^*(\text{CO})_2\text{Re}\{\mu\text{-}\eta^1:\eta^3\text{-CH=C}[\text{C}(\text{CH}_3)=\text{CH}_2]\text{CO}\}\text{Re}(\text{CO})\text{Cp}^*$.¹⁸ For comparison, the distance in $\text{Re}_2(\text{CO})_{10}$ is 3.041 Å.¹⁹ In the $\text{Re}(\text{CO})_4$ unit, the Re–C distances for the trans carbonyls are longer than the others, by a value of ca. 0.1 Å. The shortest Re–C(carbonyl) distance is for the carbonyl trans to the Re–Re bond. These distances are comparable to those for $\text{Re}(\text{CO})_4$ groups in similar compounds.^{14–17}

The IR spectrum of compound **7** has a relatively complicated appearance due to the presence of both a $\text{Re}(\text{CO})_4$ group and a $\text{Re}(\text{CO})_2$ group. The lower frequency peaks at 1952 and 1881 cm^{-1} clearly belong to the $\text{Re}(\text{CO})_2$ center, whereas the higher frequency bands at 2083, 1995, and 1980 cm^{-1} are due to the $\text{Re}(\text{CO})_4$ center. The latter IR frequencies are comparable to the relatively high stretching frequencies seen for $\text{Re}_2(\text{CO})_{10}$.

The ^1H NMR spectrum of the isolated compound **7** indicated formation of a large excess of one diastereomer. This species is assumed to have the same configuration as that established for the crystalline material, and the key for NMR peak assignment is shown in Chart 4. Interestingly, the observed structure can be viewed as a “*meso*-like” configuration.

Although **7** has the same number of carbonyls and the same overall molecular formula as **2**, our limited mechanistic observations suggest that the reaction involves initial loss of carbon monoxide. In the first place, the concentration of **2** must be relatively high (100

mg/10 mL) to form **7** in significant yield. At a ca. 100-fold-diluted level (5 mg/70 mL), no **7** was obtained. Second, for the photolysis in diethyl ether, an IR peak at 1844 cm^{-1} was observed prior to the appearance of any peak due to **7**. This peak is attributable to a $\text{Re}(\text{CO})_2$ center lightly stabilized by a coordinated ether molecule. Facile loss of the ether ligand presumably would allow insertion of this Re center into a C–H bond of the η^5 -indenyl ligand on the second Re center, which would be followed by hydrogen migration, Re–Re bond formation, and capture of adventitious CO from solution to form **7**. Analogous insertion into a $\eta^5\text{-C}_5\text{H}_5$ ligand is well established,²⁰ and a vinylic ligand bridging two metal–metal-bonded Re carbonyl centers has been reported numerous times.²¹

In some of the photolytic reactions of **2**, the minor product **8** was also isolated. The mass spectrum of this compound indicated that it had one less carbonyl ligand than **7**. The IR spectrum consisted of two sets of peaks, analogous in appearance to the spectrum of $(\eta^5\text{-C}_9\text{H}_7)\text{-Re}(\text{CO})_2(\mu\text{-}\eta^2:\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$.¹ The ^1H NMR spectrum of **8** contains features suggesting similar η^2 coordination of a six-membered ring, but the spectrum also indicates that a variety of diastereo- and/or regioisomers is present, so that no specific structures can be established.

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Supporting Information Available: Figures and tables giving details of the crystallographic studies for compounds **2-rac**, **6**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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