

# Formation of $(\eta^5\text{-C}_9\text{H}_7)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$ and Its Rearrangement to $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\mu\text{-}\eta^2,\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$

Ramin Khayatpoor and John R. Shapley\*

Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received October 13, 1998

**Summary:** UV photolysis of  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  in hexane provides binuclear  $(\eta^5\text{-C}_9\text{H}_7)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  (**1**) (30%) and a small amount (3%) of an indenyl-bridged compound  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\mu\text{-}\eta^2,\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  (**2**). Compound **1** rearranges quantitatively to compound **2** with a half-life in  $\text{CH}_2\text{Cl}_2$  at 25 °C of 25 min.

## Introduction

Photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$  in saturated hydrocarbon solution provides the binuclear compound  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$ ;<sup>1,2</sup> the analogous treatment of  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$  affords both  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$ .<sup>3</sup> Photolysis of the mononuclear rhenium compounds in the presence of ligands, such as THF,<sup>4</sup> benzene,<sup>5</sup> or alkenes,<sup>6</sup> has provided a variety of complexes, e.g.,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2\text{L}$ , with subsequent interesting chemistry. Although the indenyl complex  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\text{THF})$  has been used to form a complex with indene,<sup>7</sup> the indenyl analogues of the binuclear cyclopentadienylrhenium complexes have not been reported. We now report the formation of  $(\eta^5\text{-C}_9\text{H}_7)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  (**1**) together with its unanticipated rearrangement to an indenyl-bridged isomeric compound (**2**) (see Scheme 1).

## Experimental Section

**General Procedures.**  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  was prepared by heating  $\text{Re}_2(\text{CO})_{10}$  (Pressure Chem. Co.) in indene, according to the literature procedure.<sup>8</sup> Hexane used for the photolysis reaction was freshly distilled from sodium. Irradiations were carried out with a water-cooled, 200 W, medium-pressure Hg vapor lamp. IR spectra were recorded with a Perkin-Elmer model 1750 FTIR instrument. NMR spectra were obtained with a Varian Unity 500 spectrometer. 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 at the University of Illinois. Elemental analyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

(1) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65.

(2) Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1981**, *20*, 1139.

(3) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

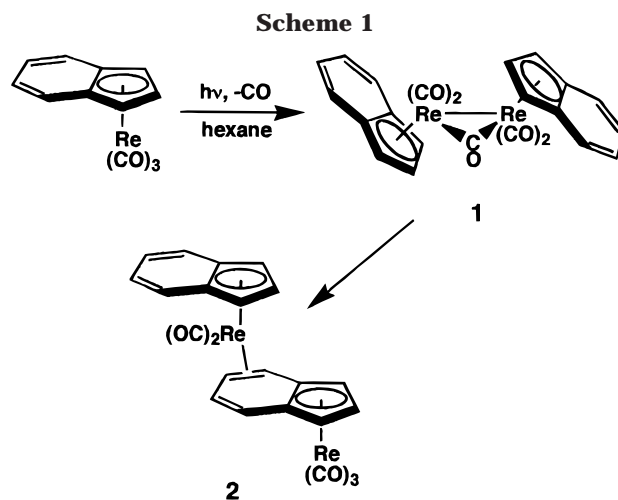
(4) Casey, C. P.; Sakaba, H.; Hazin, P. N.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165.

(5) Van der Heijden, H.; Orpen, A. G.; Pasma, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576.

(6) Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516.

(7) Trifonova, O. I.; Borisenko, A. A.; Ustynyuk, A. Y.; Ustynyuk, N. A. *Russ. Chem. Bull.* **1993**, *42*, 1222.

(8) Zdanovic, V. I.; Lobanova, I. A.; Kolobova, N. E. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1984**, *33*, 1963 (Engl. Trans); *Izv. Akad. Nauk SSSR., Ser. Khim.* **1984**, *33*, 1963.



**Photolysis of  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  in Hexane. Isolation of Compounds **1** and **2**.** Under a nitrogen atmosphere, to a 100 mL quartz Schlenk flask equipped with a stir bar was added 100 mg (0.26 mmol) of  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  followed by 20 mL of dry hexane. The flask was fitted with a coldfinger, which was charged with dry ice. The flask was placed in close proximity to the Hg lamp for 1 h. During this period solid residue appeared in the flask, and the solution became yellow. The mixture was evaporated in vacuo, and the residue was dissolved in dichloromethane for separation by thin-layer chromatography (silica,  $\text{C}_6\text{H}_{14}:\text{CH}_2\text{Cl}_2$ , 1:2). A dominant, bright yellow band contained compound **1** (29 mg, 0.039 mmol, 30%). Anal. Calcd for  $\text{C}_{23}\text{H}_{14}\text{O}_5\text{Re}_2$ : C, 37.19; H, 1.90. Found: C, 36.96; H, 1.71.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.22 (4H, dd,  $J = 3.0, 6.4$  Hz), 7.14 (4H, dd,  $J = 3.0, 6.4$  Hz), 5.88 (2H, t,  $J = 2.8$  Hz), 5.51 (4H, d,  $J = 2.8$  Hz). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$ , 1947 (s), 1912 (s), 1718 (br,w)  $\text{cm}^{-1}$ . MS (FD):  $m/z$  744 ( $\text{M}^+$ ).

Following identification of **2** as the rearrangement product from **1**, it was determined that a pale green-yellow band, appearing on the TLC plate ahead of the yellow band for **1**, contained a small amount of **2** (3.4 mg, 0.0046 mmol, 3.5%). Anal. Calcd for  $\text{C}_{23}\text{H}_{14}\text{O}_5\text{Re}_2$ : C, 37.19; H, 1.90. Found: C, 36.86; H, 1.86. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$ , 2017 (s), 1964 (m), 1921 (br,s), 1889 (m)  $\text{cm}^{-1}$ . MS (FD):  $m/z$  744 ( $\text{M}^+$ ). For NMR data and assignments see Table 4.

**X-ray Crystallographic Studies.** Yellow needles of **1** suitable for X-ray crystallography were grown from chloroform by diffusion with hexane at  $-14$  °C. Single crystals of **2** were obtained by layering hexane on 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.<sup>9a</sup> The structures were solved by direct methods,<sup>9b</sup> and refinements were made by full-matrix least-

(9) (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.

**Table 1. Crystallographic Data for  $(\eta^5\text{-C}_9\text{H}_7)_2\text{Re}_2(\text{CO})_4(\mu\text{-Co})$  (**1**) and  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\mu\text{-}\eta^2, \eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  (**2**)**

formula	$\text{C}_{23}\text{H}_{14}\text{O}_5\text{Re}_2$	$\text{C}_{23}\text{H}_{14}\text{O}_5\text{Re}_2$
fw	742.74	742.74
space group	$P\bar{1}$	$P2_1/n$
cryst syst	triclinic	monoclinic
<i>a</i> (Å)	8.8331(3)	7.4493(2)
<i>b</i> (Å)	10.5851(3)	11.9832(4)
<i>c</i> (Å)	10.8827(3)	22.5539(6)
$\alpha$ (deg)	74.415(1)	90
$\beta$ (deg)	89.765(1)	91.07(1)
$\gamma$ (deg)	85.515(1)	90
<i>V</i> , Å <sup>3</sup>	976.96(5)	2012.9(1)
<i>Z</i>	2	4
temp (K)	198 (2)	198 (2)
wavelength (Å)	0.710 73	0.710 73
$\rho$ calc (g cm <sup>-3</sup> )	2.525	2.451
cryst size (mm <sup>3</sup> )	0.01 × 0.08 × 0.60	0.10 × 0.24 × 0.34
$\mu$ (mm <sup>-1</sup> )	12.413	12.049
trans coeffs, max/min	0.8802/0.2404	0.3015/0.0777
no. reflns collected	6259	12896
no. ind reflns	4367	4830
<i>R</i> <sub>int</sub>	0.0778	0.0405
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0545	0.0273
	0.1317	0.0662

$$^a R_1 = \sum |F_o - F_c| / \sum F_o; wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}.$$

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1**

Re1–Re2	2.9848(8)		
Re1–C300	2.07(2)	Re2–C300	2.09(1)
Re1–C11	2.29(2)	Re2–C21	2.25(2)
Re1–C12	2.26(2)	Re2–C22	2.26(2)
Re1–C13	2.29(2)	Re2–C23	2.30(2)
Re1–C14	2.39(1)	Re2–C24	2.42(2)
Re1–C19	2.39(2)	Re2–C29	2.41(2)
Re1–C300–Re2	91.6(6)	C19–Re1–Re2	101.3(3)
C14–Re1–Re2	115.0(3)	C23–Re2–Re1	104.1(5)
		C24–Re2–Re1	98.7(4)

**Table 3. Selected Bond Distances (Å) and Angles (°) for Compound 2**

Re1–C1	2.276(6)	Re2–C10	2.295(6)
Re1–C2	2.286(6)	Re2–C11	2.284(6)
Re1–C3	2.319(6)	Re2–C12	2.293(6)
Re1–C4	2.381(6)	Re2–C13	2.352(5)
Re1–C9	2.354(5)	Re2–C18	2.342(5)
Re1–C14	2.252(5)	Re1–C15	2.286(5)
C13–C14	1.465(7)	C4–C5	1.419(9)
C14–C15	1.436(8)	C5–C6	1.348(9)
C15–C16	1.448(9)	C6–C7	1.425(9)
C16–C17	1.339(9)	C7–C8	1.353(9)
C17–C18	1.454(8)	C8–C9	1.428(8)
C13–C18	1.424(8)	C4–C9	1.439(8)
C13–C14–Re1	119.1(4)	C16–C15–Re1	119.0(4)
C5–C4–Re1	123.2(4)	C14–C13–Re2	125.9(4)
C8–C9–Re1	119.7(4)	C17–C18–Re2	124.3(4)

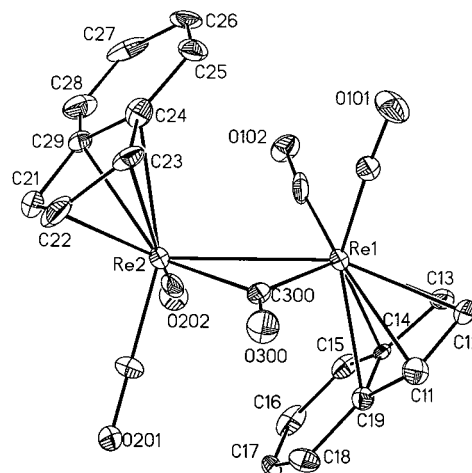
squares based on  $F^2$ . Hydrogen atoms were fixed on calculated positions. Crystallographic details for the studies of **1** and **2** are summarized in Table 1. Bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

**Conversion of 1 to 2.** Solutions of compound **1** were observed to convert quantitatively to compound **2** by IR or by NMR spectroscopy. In dichloromethane the rate of conversion as monitored by IR spectroscopy was unchanged over a 10-fold change in the initial concentration of **1**. A representative set of spectra is shown in Figure 3.

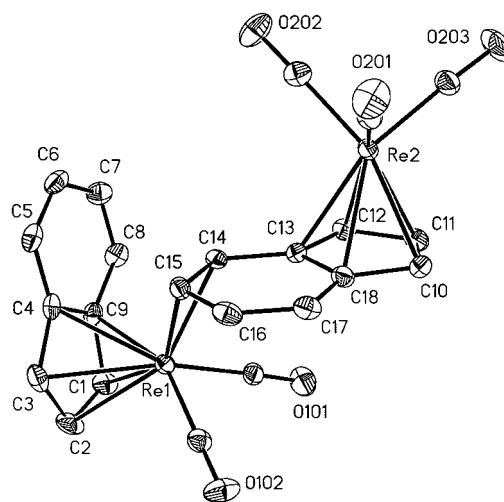
## Results and Discussion

### Synthesis and Spectroscopic Characterization of 1 and 2.

Photolysis of  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  in hexane



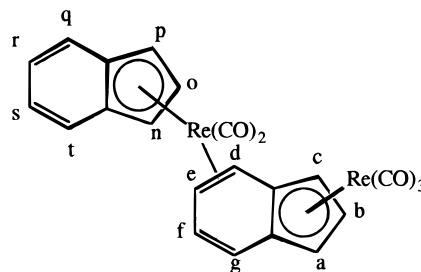
**Figure 1.** ORTEP diagram of compound **1** (30% thermal ellipsoids).



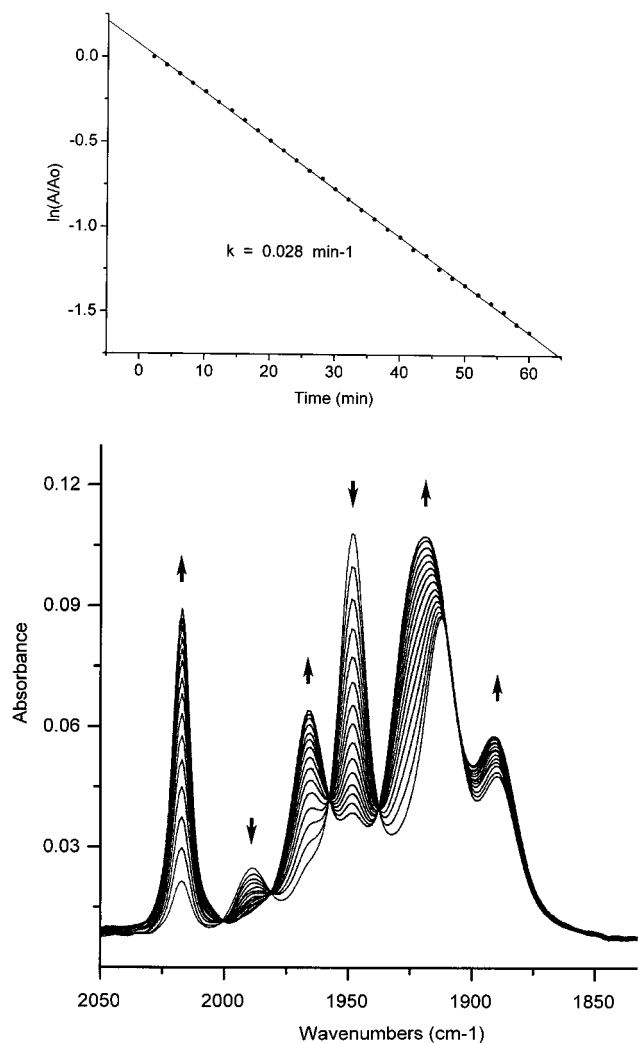
**Figure 2.** ORTEP diagram of compound **2** (30% thermal ellipsoids).

**Table 4. NMR Data and Assignments for Compound 2**

<sup>1</sup> H signal (mult)	<sup>13</sup> C signal	assignment
2.57 (dd)	45.37	e
3.01 (dd)	42.35	d
5.15 (t)	82.84	b
5.35 (ddd)	77.26	c
5.51 (m)	75.96	a
5.87 (m)	88.20	o
5.91 (m)	71.95	n, p
6.16 (d)	114.96	g
6.71 (d)	134.60	f
7.20; 7.21; 7.29 (m)	126.78; 122.21; 122.21	q, r, s, t



leads primarily to the formation of Re–Re bonded compound **1** as well as a small amount of compound **2**. The isolation of compound **1** is dependent on its insolu-



**Figure 3.** Bottom: IR spectra for conversion of **1** to **2** in dichloromethane. Top: Plot for absorbance data at 1948  $\text{cm}^{-1}$ .

bility in the hydrocarbon solvent, since it precipitates during the photolysis reaction. However, compound **2** also is only slightly soluble in hexane, and therefore a chromatographic separation is necessary. Analogous photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$  in cyclohexane gave only  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$ ,<sup>1</sup> whereas the same procedure starting with  $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$  gave a mixture of singly and triply bridged compounds  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\mu\text{-CO})_3$ .<sup>3</sup> Recent spectroscopic studies on the photolysis of  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$  in alkane solvents have provided evidence for relatively long-lived alkane complexes, which are likely intermediates in the formation of the isolated dinuclear product.<sup>10</sup>

The  $\nu_{\text{CO}}$  IR bands for **1** are observed at 1947, 1912, and 1718  $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solution, confirming the existence of a bridging carbonyl. The analogous bands occur for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  at 1956, 1923, and 1740  $\text{cm}^{-1}$  in cyclohexane<sup>1</sup> and for  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  at 1930, 1901, and 1714  $\text{cm}^{-1}$  in hexane.<sup>3</sup> The pattern and positions of  $\nu_{\text{CO}}$  IR bands for **2** suggest the presence of independent  $\text{Re}(\text{CO})_3$  (2017 s, 1921 s, br  $\text{cm}^{-1}$ ) and  $\text{Re}(\text{CO})_2$  (1964 m, 1889 m  $\text{cm}^{-1}$ ) units in the

molecule, which is consistent with the structure established by X-ray crystallography. The NMR data obtained for **1** and **2** will be discussed below, after consideration of the molecular structures.

**Molecular Structure of 1.** A structural diagram for **1** is shown in Figure 1, and selected structural data are given in Table 2. The overall features of the structure of **1** are closely analogous to those of the cyclopentadienyl compound  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$ ,<sup>1</sup> with a trans disposition of  $\eta^5$ -indenyl groups relative to the central  $\text{Re}_2(\mu\text{-CO})$  core. The Re–Re distances for these mono-bridged compounds (2.985 Å for **1** and 2.96 Å for the Cp compound<sup>1</sup>) are slightly shorter than the values for the unbridged Re–Re bonds in  $\text{Re}_2(\text{CO})_{10}$  (3.041 Å)<sup>11a</sup> and  $\text{Re}_2(\text{CO})_8(\text{PMe}_2\text{Ph})_2$  (3.044 Å)<sup>11b</sup> but longer than the doubly bridged Re–Re distance in  $\{\text{Cp}^*\text{Re}(\text{CO})\}_2(\mu\text{-CO})-(\mu\text{-}\eta^2, \eta^2\text{-C}_2(\text{CO}_2\text{Me})_2)$ .<sup>12</sup> The Re–C distances for the bridging carbonyl of 2.07(1) and 2.09(1) Å are closely comparable with those found for other compounds with essentially symmetrical  $\text{Re}_2(\mu\text{-CO})$  moieties.<sup>1,3,12,13</sup>

The Re–C distances to the indenyl ring carbons in **1** show the typical pattern of longer distances to the ring fusion carbons (average 2.39(2) Å for Re1; average 2.42(3) Å for Re2) than to the three “allylic” carbons (average 2.28(3) Å for Re1; average 2.27(3) Å for Re2). These differences are similar to values found for the mononuclear Re complex  $(\eta^5\text{-C}_9\text{H}_7)\text{ReH}_2(\text{PPh}_3)_2$ , which range from 0.10 to 0.15 Å.<sup>14</sup> Similar slip distortion values ( $\Delta$ ) have been reported recently for both mononuclear and binuclear indenyl iridium compounds,<sup>15a</sup> but a much more pronounced distortion ( $\Delta$  ca. 0.3 Å) was found for the indenyl ligands in the cluster  $(\eta^5\text{-C}_9\text{H}_7)_3\text{Ir}_3(\mu\text{-CO})_3$ .<sup>15b</sup>

**Molecular Structure of 2.** A structural diagram for compound **2** is shown in Figure 2, and selected bond distances and angles are listed in Table 3. This complex features the coordination of a  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})$  fragment to the six-membered ring of the indenyl ligand of a  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$  moiety, with the metal centers situated on opposite sides of the plane defined by the bridging indenyl ligand (anti configuration). The Re–C distances to the coordinated five-membered rings are somewhat more regular than in **1** ( $\Delta = 0.07$  Å for Re1 and 0.06 Å for Re2), and the Re–C distances to the coordinated double bond are comparable (Re1–C14 = 2.252(5) Å and Re1–C15 = 2.286(5) Å). The C–C bond distance of 1.436(8) Å for the coordinated atoms C14 and C15 is longer than those of other six-membered ring C–C distances in **2**, i.e., C5–C6 = 1.348(9), C7–C8 = 1.353(9), and C16–C17 = 1.339(9) Å, respectively, as well as all the corresponding uncoordinated C–C distances in **1**.

The ability of a  $\text{Cp}^*\text{Re}(\text{CO})_2$  fragment to form an  $\eta^2$  complex with benzene has been well demonstrated by the characterization of the doubly coordinated benzene-

(11) (a) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609. (b) Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2277.

(12) Casey, C. P.; Carino, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617.

(13) Casey, C. P.; Carino, R. S.; Sakaba, H.; Hayashi, R. K. *Organometallics* **1996**, *15*, 2640.

(14) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1993**, *115*, 965.

(15) (a) Comstock, M. C.; Shapley, J. R. *Organometallics* **1997**, *16*, 4816. (b) Comstock, M. C.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 3805.

(10) (a) Sun, X.-Z.; Grills, D. C.; Nikiforov, S. M.; Poliakov, M.; George, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 7521. (b) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.

bridged complex  $\{\text{Cp}^*\text{Re}(\text{CO})_2\}_2(\mu\text{-}\eta^2, \eta^2\text{-C}_6\text{H}_6)$ .<sup>5</sup> Numerous other examples of especially stable alkene complexes of this and related  $(\eta^5\text{-L})\text{Re}(\text{CO})_2$  fragments have been reported, including a variety of  $\text{Cp}^*\text{Re}(\text{CO})_2(\eta^2\text{-alkene})$  complexes,<sup>6</sup> the indene complex  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\eta^2\text{-C}_9\text{H}_8)$ , and the seminal cyclopentadiene complex  $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_5\text{H}_6)$ , which is sufficiently stable to be catalytically hydrogenated to the cyclopentene complex  $\text{CpRe}(\text{CO})_2(\eta^2\text{-C}_5\text{H}_8)$ .<sup>16</sup> In recent years the indenyl ligand has been used to bridge two metal centers, with both homo-<sup>17</sup> and heterobimetallic<sup>18–20</sup> examples. However, in these compounds, particularly when the two metal centers adopt the anti configuration, one center is clearly  $\eta^6$  coordinated, the other is  $\eta^5$  coordinated, and the two metal atoms lie in the mirror plane perpendicular to the mean plane of the indenyl ligand. Compound **2** is the only example, to our knowledge, of a bridging indenyl ligand displaying an unsymmetrical  $\eta^2$  coordination mode of its six-membered ring.

**NMR Characterization Data.** The <sup>1</sup>H NMR spectrum of **1** shows the signals expected for a  $\eta^5\text{-C}_9\text{H}_7$  ring in a symmetrical environment. Since this result is not consistent with the solid-state structure, it is likely that the rapid carbonyl scrambling/enantiomerization process proposed<sup>2</sup> to occur for the analogous  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Re}_2(\text{CO})_4(\mu\text{-CO})$  compound is also occurring here.

The NMR spectra obtained for **2** are complex but can be straightforwardly interpreted on the basis of the crystal structure. The <sup>1</sup>H and <sup>13</sup>C NMR assignments for **2** are summarized in Table 4. The two proton signals shifted upfield to  $\delta$  3.01 and 2.57 are assigned to the protons on the  $\eta^2$  coordinated carbons C14 and C15. (Upfield shifts to  $\delta$  4.14 and 2.85 are observed for a  $\mu\text{-}\eta^2, \eta^2\text{-C}_6\text{H}_6$  ligand.<sup>5</sup>) Combined decoupling/COSY experiments revealed the signals due to the remaining protons on the bridging indenyl ligand, and correlation (HMBC and HMQC) experiments established unambiguous assignments.

**Conversion of 1 to 2.** We first observed the conversion of **1** to **2** in a CDCl<sub>3</sub> NMR solution kept at  $-14^\circ\text{C}$  for several days. However, we saw no evidence of the conversion with compound **1** in crystalline form. At room temperature the conversion can be conveniently followed by solution IR, and Figure 3 shows a set of spectra in CH<sub>2</sub>Cl<sub>2</sub>. The computed rate constant is  $0.028\text{ min}^{-1}$ , corresponding to a half-life of 25 min. The conversion follows a first-order rate law for more than two half-lives, and the rate is independent of the initial concentration of **1** over a 10-fold range. In comparison, the half-life in CHCl<sub>3</sub> is ca. 1 h, in THF is ca. 10 min, and in acetone is comparable with the time for sample preparation. In a nearly saturated THF solution of PPh<sub>3</sub>,

complex **1** forms only **2**, with no evidence by IR of the formation of either  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\text{THF})$  or  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2(\text{PPh}_3)$ .<sup>21</sup> Thus, the conversion of **1** to **2** appears to be entirely intramolecular with no unsaturated intermediate or separation into mononuclear fragments. There are, however, significant mechanistic puzzles. In **1** the two Re centers are necessarily oriented on *the same side of* either indenyl ligand, and therefore rearrangement and coordination of both Re centers to *one* indenyl ligand, for example in  $\eta^2, \eta^5$  fashion, should give a syn configuration rather than the anti configuration actually observed for **2**. It would appear that the  $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_2$  fragment migrates in some fashion to the opposite side of the bridging indenyl ligand, but there is no obvious charge separation to explain the effect of solvent polarity. A potentially analogous anti-to-syn isomerization of the heterobimetallic compound  $\text{Cr}(\text{CO})_3(\mu\text{-}\eta^2, \eta^2\text{-C}_9\text{H}_7)\text{Rh}(\text{NBD})$  is catalyzed by adventitious “[Rh(NBD)][BF<sub>4</sub>]<sup>−</sup>”, which was proposed to induce a sequence of [1,3]-hydrogen shifts across the five-membered ring while the original Rh center migrates via an  $\eta^1\text{-C}_9\text{H}_7$  coordination mode.<sup>20</sup> However, there is no evidence for any such catalysis in the conversion of **1** to **2**. On the other hand, the detailed studies of Peng and Gladysz<sup>22</sup> on the equilibration of chiral rhenium alkene complexes provide a compelling precedent. These workers showed that interconversion of diastereomeric complexes of the formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+$ , which differ in the alkene enantioface bound to rhenium, most likely occurs by migration of the rhenium complex fragment “through” the alkene plane via a C–H  $\sigma$ -bond complex; this happens cleanly even at  $95^\circ\text{C}$  in the presence of excess triphenylphosphine. An analogous pathway can readily be proposed for the syn-to-anti migration necessary for the ultimate formation of **2**. However, in the absence of further experimental evidence or theoretical guidance, details of the overall mechanism for converting **1** to **2** remain speculative.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (CHE 9414217). We thank Dr. Scott R. Wilson for X-ray crystallographic data collection and Dr. Udo Brand for help with the structure solutions. We also thank Dr. Vera Mainz for help with 2-D NMR experiments. NMR spectra were obtained in the Varian Oxford Instrument Center for Excellence in NMR Laboratory; funding for NMR instrumentation was provided in part from the W.M. Keck Foundation, the National Institutes of Health, and the National Science Foundation.

**Supporting Information Available:** Tables of positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM9808514

- (16) Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4314.  
 (17) Kudinov, A. R.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovskii, A. I.; Rybinskaya, M. I. *J. Organomet. Chem.* **1991**, 421, 421.  
 (18) Bonifaci, C.; Cecon, A.; Gambaro, A.; Ganis, P.; Santi, S.; Valle, G.; Venzo, A. *J. Organomet. Chem.* **1995**, 492, 35.  
 (19) Bonifaci, C.; Cecon, A.; Santi, S.; Mealli, C.; Zoellner, R. W. *Inorg. Chim. Acta* **1995**, 240, 541.  
 (20) Bonifaci, C.; Cecon, A.; Gambaro, A.; Ganis, P.; Santi, S.; Venzo, A. *Organometallics* **1995**, 14, 2430.

- (21) Kolobova, N. E.; Lobanova, I. A.; Zdanovic, V. I.; Petrovskii, P. V. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1981**, 5, 935.  
 (22) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, 114, 4174.