sealed NMR tube containing 11 mg of $(CpMo)_2(SCHCHS)S_2CH_2$, H_2, and $CDCl_3$ was prepared in the same way. Both NMR tubes were heated at 60 °C and the NMR spectra monitored periodically. After about 20 h the hydrogenation of $(CpMo)_2(SCHCHS)S_2CH_2$ to $(CpMo)_2(SCH_2CH_2S)S_2CH_2$ was complete. Only starting material was observed in the reaction of H_2 with IV, even after 7 days of heating. The reaction of IV with H_2 was repeated as described above, with the addition of 1 equiv of I. The products, described in the Discussion, were identified by NMR.

Acknowledgment. This work was supported by the National Institutes of Health, the Department of Energy, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. I, 86163-42-0; II, 93111-39-8; IIIa, 93219-80-8; IIIb, 93111-40-1; IV, 93111-41-2; V, 93111-42-3; VII, 93111-43-4; VIII, 93134-26-0; X, 93111-49-0; $(CpMo)_2(\mu\text{-}SC(C_6H_5)CH(c_6H_5)(\mu\text{-}SCH_3)S_2CH_2$, 93111-44-5; $(CpMo)_2(\mu\text{-}SCHCH(CO_2CH_2CH_3)(\mu\text{-}SCH_3)S_2CH_2$, 93111-45-6; $(CpMo)_2(\mu\text{-}SCH_2CH_2CN)(\mu\text{-}SCH_3)S_2CH_2$, 93111-46-7; $(CpMo)_2(\mu\text{-}SC(CH_3)CH_2)(\mu\text{-}SCH_3)S_2CH_2$, 93111-47-8; $(CpMo)_2(\mu\text{-}SC(CO_2CH_3)CH(CO_2CH_3))(\mu\text{-}SCH_3)S_2CH_2$, 93111-48-9; $[(CpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)(S_2CH_2)]HSO_4$, 93219-82-0; $(CpMo)_2(\mu\text{-}S(B)(\mu\text{-}SCH_3)S_2CH_2$ (B = *sec*-butyl), 93111-50-3; $[(CpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]K$, 93111-51-4; $(CpMo)_2(SCHCHS)S_2CH_2$, 86163-46-4; CH_3I, 74-88-4; CH_3Li, 917-54-4; $LiBHEt_3$, 22560-16-3; $KB(R)_3H$ (R = *sec*-butyl), 54575-49-4; $HC{\equiv}CH$, 74-86-2; $PhC{\equiv}CH$, 536-74-3; C_2H_2, 74-85-1; KC_8, 12081-88-8; $PhC{\equiv}CPh$, 501-65-5; $HC{\equiv}CCO_2Et$, 105-37-3; $H_2C{=}C(H)CN$, 107-13-1; $H_2C{=}C{=}CH_2$, 463-49-0; vinyl bromide, 593-60-2; 1,4-cyclohexadiene, 628-41-1; ethyl iodide, 75-03-6; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available: A perspective drawing of cation II of $[(CpMo)_2(\mu\text{-}S)(\mu\text{-}SCH_3)S_2CH_2]^+$ and tables of observed and calculated structure factors and of atomic thermal parameters (16 pages). Ordering information is given on any current masthead page.

Synthesis, Molecular Structure, and Thermal Chemistry of (η^5-Cyclopentadienyl)dicarbonylrhenacyclopentane†

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Received July 3, 1984

Alkylation of $CpRe(CO)_2H_2$ with 1,4-diiodobutane in the presence of the amine base DBU yields the five-membered rhenacyclopentane 1. The crystal structure of 1 was determined by X-ray diffraction using 767 reflections that were refined to a final R value of 1.90%. The crystals were orthorhombic (space group $P2_12_12_1$) with unit cell parameters $a = 8.0041$, $b = 8.0139$, and $c = 16.6549$ Å. The molecule is disordered at the two β-carbons of the metallacycle ring that each occupy two nearly equivalent positions. Thermolysis of 1 at 100 °C with either PMe_3 or PPh_3 leads quantitatively to methylcyclopropane and $CpRe(CO)_2PR_3$. A kinetic study showed that this reaction was first order in 1 and independent of both phosphine structure and concentration with an average $k_{obsd} = 6.88 \times 10^{-4}\ s^{-1}$. Deuterium labeling studies demonstrated that methylcyclopropane formation proceeds by net β to α hydrogen migration followed by formation of a bond between the β- and the other α-carbon. A ^{13}CO crossover experiment shows that CO dissociation is not occurring on the path to product, suggesting that $\eta^5 \rightleftharpoons \eta^3$ cyclopentadienyl ring slip is occurring to open a vacant coordination site.

Introduction

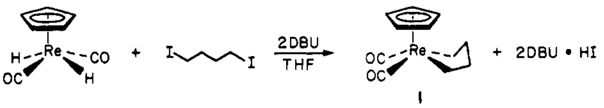
Metallacyclopentanes have been the center of much experimental and theoretical work, particularly regarding their role in olefin dimerization processes.[1-3] The thermal chemistry of metallacyclopentanes consists of β-elimination and reductive elimination processes yielding cyclopentanone, cyclobutane, butenes, or loss of ethylene in 2 + 2 cycloreversion processes.[3,4]

We recently reported the preparation of a new rhenacyclopentane complex (1; Scheme I) from $CpRe(CO)_2H_2$ and its thermolysis to methylcyclopropane via a novel ring contraction process.[5] In this paper we describe the detailed synthesis and characterization of this material as well as mechanistic evidence for transient $\eta^5 \rightleftharpoons \eta^3$ isomerization ("ring slip") of the cyclopentadienyl ring induced by β-elimination.

Results

Synthesis and Structure Determination. When an excess of 1,4-diiodobutane was added to a stirred solution of $CpRe(CO)_2H_2$[6] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF (Scheme I), the solution quickly turned yellow and a white precipitate appeared after several minutes. At this point the infrared spectrum of this

Scheme I



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† Dedicated to the memory of Earl Muetterties, for the guidance, intellectual stimulation, and leadership he provided at Berkeley.

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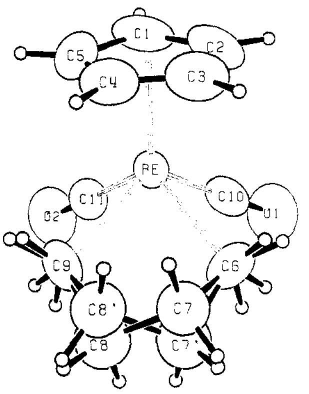


Figure 1. End-on view of metallacycle 1 illustrating the disorder about C7 and C8 of the metallacycle ring.

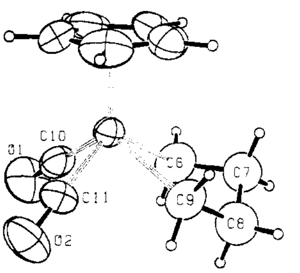


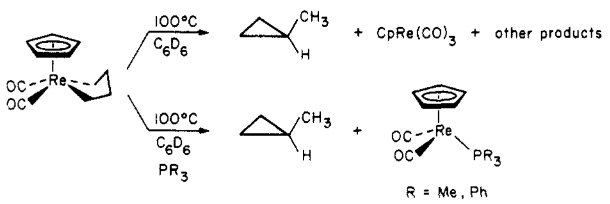
Figure 2. Side-on view of one of the disordered pair shown in Figure 1, illustrating the open-envelope conformation of the metallacycle ring. The angle defined by the intersection of C6–C7–C8 and Re–C6–C8–C9 is 32.7°.

mixture showed that the starting material absorbances at 2005 and 1950 cm^{-1} had been replaced by new bands at 1990 and 1910 cm^{-1}. Chromatography (silica, pentane) and recrystallization from pentane gave the product metallacycle 1 as yellow, air-stable crystals.

The mass spectrum of this material exhibits molecular ions at m/e 362 and 364, with the correct intensity ratios for the two naturally occurring isotopes of rhenium. The solution molecular weight determined by the Signer isothermal distillation method[7] (m/e 363, (calcd 363)) is consistent with a mononuclear structure. The ^{1}H NMR in chloroform-d shows a sharp cyclopentadienyl singlet resonance at 5.32 ppm and four alkyl multiplets at 2.70, 2.20, 1.75, and 1.60 ppm that integrate to two protons each. In benzene-d_6 the ^{1}H NMR spectrum shows a cyclopentadienyl resonance at 4.34 ppm and three alkyl resonances at 2.51, 2.38, and 1.82 ppm in a 2:2:4 intensity ratio due to the overlapping of the two upfield resonances. The gated ^{13}C NMR spectrum (chloroform-d) displays two triplet resonances at 36.59 (J = 126 Hz) and 6.65 (J = 135 Hz) ppm assigned to the alkyl chain and a doublet at 90.25 (J = 181 Hz) ppm assigned to the cyclopentadienyl carbons. The ^{13}CO resonance is seen at 209.3 ppm as a broad singlet due to rhenium quadrupolar coupling. These data are consistent with a four-legged piano stool geometry; the cis relationship of the metallacycle ring carbons renders the ring faces inequivalent.

Confirmation of this geometry was obtained by determination of the crystal and molecular structure by X-ray diffraction. Suitable crystals were grown from toluene/pentane by slow cooling. A total of 839 unique reflections were collected (767 for which $F^2 > 3\sigma F^2$), and the data were refined to a final R value of 1.9%. The molecular structure is illustrated in Figures 1 and 2. Figure 1 provides an end-on view which illustrates the disorder found in the crystal with respect to the locations of C7 and C8 in the metallacycle ring. The two conformations are equally populated. The Cp ring is slightly twisted and destroys any possible mirror plane (considering the disorder). Figure 2 is a side-on view of the molecule showing the open-envelope conformation of the ring. The plane of the flap (C6–C7–C8) is 32.7° out of the plane of the other four atoms (Re–C6–C8–C9) which are coplanar to within 0.01 Å. This flap angle is remarkably similar to that found recently in a dicobalt metallacyclopentane.[8] In that instance the flap was 32.9° out of the plane of the other atoms. In Table I are listed selected bond distances and bond angles.

Scheme II



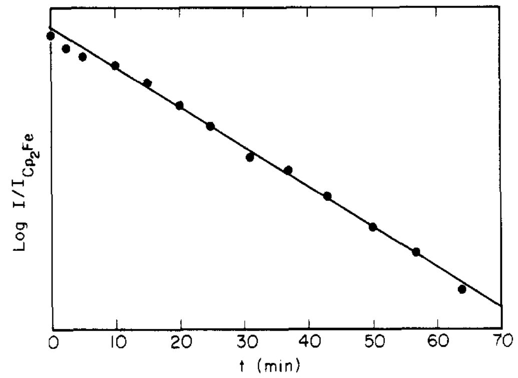


Figure 3. A typical first-order plot for the disappearance of starting material in the thermolysis of metallacycle 1 (1.31 × 10^{-2} M) in the presence of PPh$_3$ (0.147 M); k_{obsd} = 6.96 × 10^{-4} s^{-1}. $I/I_{\mathrm{Cp_2Fe}}$ is the relative intensity of the Cp resonance for 1 measured against an internal standard (ferrocene).

Thermal Chemistry. Thermolysis of metallacycle 1 in benzene-d_6 at 100 °C in a sealed NMR tube was observed to proceed quite rapidly and was complete within 2 h. Several organometallic products were formed, the most abundant (ca. 60%) being CpRe(CO)$_3$. On the basis of the thermolysis of other metallacyclopentane systems, we had expected this reaction to yield butenes and perhaps cyclobutane or cyclopentanone.[3,4] Surprisingly, the major organic product was methylcyclopropane, identified by NMR and GC and formed in 67% yield.

When run in the presence of either PMe$_3$ or PPh$_3$, the reaction became much cleaner, with both methylcyclopropane and CpRe(CO)$_2$PR$_3$ formed as the exclusive products in quantitative yield. The overall thermal reactions are summarized in Scheme II.

A kinetic study of metallacycle decomposition and product formation was performed in the presence of an excess of triphenylphosphine and trimethylphosphine. The reactions were carried out in sealed NMR tubes immersed in the vapor of a boiling water bath. At specified times tubes were withdrawn and rapidly quenched (within 3 s) in a dry ice/acetone slush bath, and the NMR spectra

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Table I. Selected Bond Distances (Å) and Bond Angles (deg)

Intramolecular Distances

atom 1	atom 2	distance
Re	C1	2.269 (8)
Re	C2	2.297 (7)
Re	C3	2.331 (9)
Re	C4	2.332 (7)
Re	C5	2.280 (8)
Re	Cp1[a]	1.978
Re	C6	2.246 (9)
Re	C9	2.255 (8)
Re	C10	1.878 (10)
Re	C11	1.871 (8)
C10	O1	1.186 (11)
C11	O2	1.174 (10)
C6	C7	1.53 (2)
C6	C7′	1.49 (2)
C7	C8	1.49 (3)
C7′	C8′	1.49 (3)
C8	C9	1.51 (2)
C8′	C9	1.56 (2)
C1	C2	1.400 (13)
C2	C3	1.350 (13)
C3	C4	1.368 (13)
C4	C5	1.409 (13)
C5	C1	1.396 (13)

Intramolecular Angles

atom 1	atom 2	atom 3	angle
Cp1[a]	Re	C6	114.5
Cp1[a]	Re	C9	115.3
Cp1[a]	Re	C10	122.2
Cp1[a]	Re	C11	124.8
C6	Re	C9	73.8 (3)
C9	Re	C11	74.5 (3)
C11	Re	C10	80.4 (3)
C10	Re	C6	75.2 (3)
C6	Re	C11	120.1 (4)
C9	Re	C10	121.8 (3)
Re	C10	O1	179.0 (8)
Re	C11	O2	179.5 (7)
Re	C6	C7	109.0 (8)
Re	C6	C7′	114.7 (10)
C6	C7	C8	104.1 (15)
C6	C7′	C8′	108.6 (17)
C7	C8	C9	107.9 (17)
C7′	C8′	C9	102.9 (13)
C8	C9	Re	114.4 (9)
C8′	C9	Re	108.6 (8)
C5	C1	C2	108.4 (8)
C1	C2	C3	107.5 (8)
C2	C3	C4	110.0 (9)
C3	C4	C5	108.0 (8)
C4	C5	C1	106.0 (8)

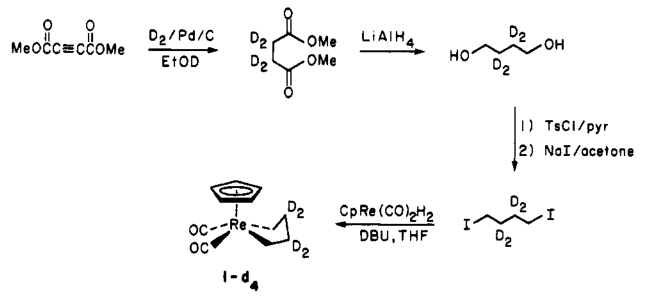
[a] Cp1 is the centroid of the cyclopentadiene ring.

Table II. Observed Rate Constants for the Reaction of Metallacycle 1 with PPh_3 and PMe_3 in C_6D_6 at 100 °C

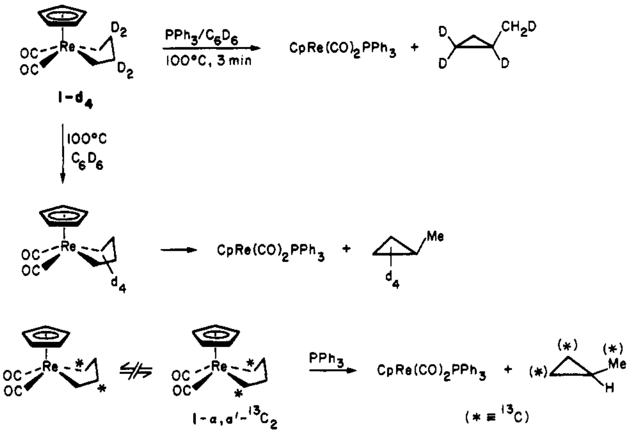
[Re], M	L	[L], M	10^4k_{obsd},[a] s	10^4k_{obsd},[b] s
1.35×10^{-2}	PPh_3	0.396	6.75	6.61
1.35×10^{-2}	PPh_3	4.37×10^{-2}	7.01	6.69
1.31×10^{-2}	PPh_3	0.147	6.96	6.78
2.84×10^{-2}	PPh_3	0.384	6.62	7.15
7.10×10^{-3}	PPh_3	0.142	7.51	6.91
2.13×10^{-2}	PPh_3	0.112	7.24	6.99
2.17×10^{-2}	PPh_3	0.231	6.99	6.18
2.09×10^{-2}	PPh_3	0.301	6.78	6.99
1.78×10^{-2}	PMe_3	1.04[c]	6.84	6.52
1.86×10^{-2}	PMe_3	0.389	6.86	7.20

[a] Measured for disappearance of starting material 1.
[b] Measured for the appearance of product $CpRe(CO)_2PR_3$.
[c] Concentration assuming complete solution in the liquid phase.

Scheme III



Scheme IV



were recorded at room temperature (see Experimental Section for details). The rate data are summarized in Table II. All the runs exhibited good first-order kinetics to greater than 3 half-lives; a typical plot of the log of the relative intensity of the metallacycle Cp resonance vs. time is shown in Figure 3. Changing the phosphine concentration (Table II) demonstrated that the reaction is first order in metallacycle and independent of the phosphine identity and concentration. Measured rate constants were identical within experimental error for both starting material disappearance and product formation.

Deuterium and ^{13}C Labeling Studies. Deuterium labeling studies were used to determine how the α- and β-protons and their respective carbons migrate during the thermolysis reaction. Preparation of complex 1 deuterated in the β-positions (1-d_4) was accomplished as summarized in Scheme III. In ethanol-d_1[9] dimethyl acetylenedicarboxylate was hydrogenated with deuterium gas on Pd/C. Reduction of the resulting dimethyl succinate-d_4 with $LiAlH_4$ yielded 1,4-butanediol-*2,2,3,3*-d_4 that was converted to the corresponding diiodide via the ditosylate. Reaction of the diiodide with $CpRe(CO)_2H_2$ and DBU in THF yielded the deuterated metallacycle 1-d_4. The pure labeled material was obtained by careful recrystallization of the crude product from pentane. In the ^1H NMR spectrum (benzene-d_6) of this material the upfield alkyl resonance does not appear and the two downfield alkyl resonances each appear as a doublet slightly broadened by deuterium coupling with a proton–proton coupling constant of 10.5 Hz. Integration indicated that this material was >96% deuterated at the β-positions.

Thermolysis of 1-d_4 was performed with an excess of PPh_3 in benzene-d_6 as for the unlabeled material but carried only to low conversion in order to minimize label scrambling by secondary reactions (see below). The results

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[9] Hydrogenation with deuterium gas of dimethyl acetylenedicarboxylate in nondeuterated ethanol resulted in substantial incorporation of proton in the product diester.

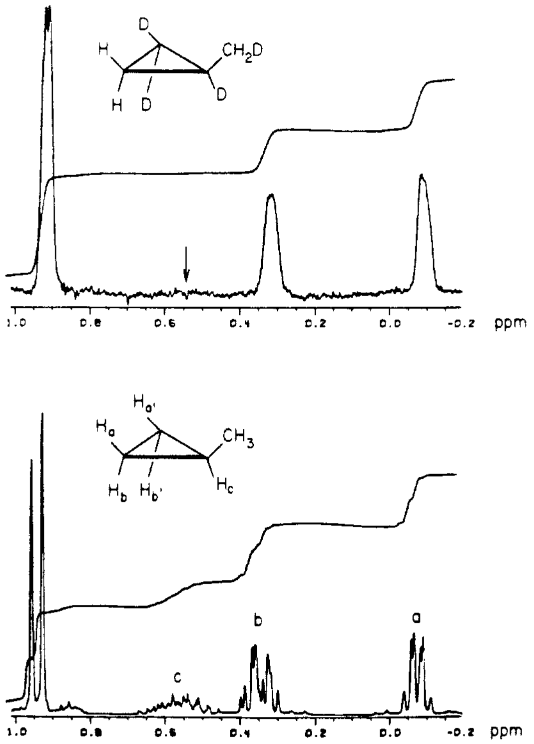
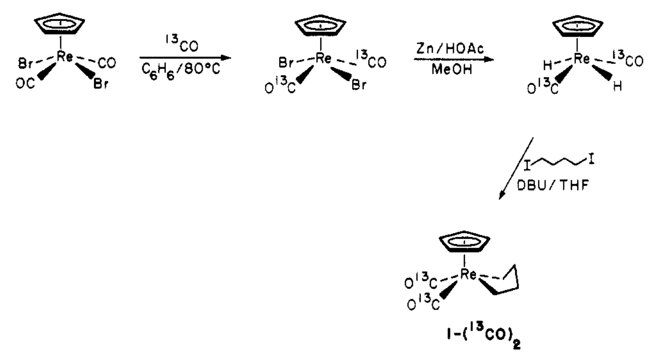


Figure 4. ^{1}H NMR spectra (200 MHz, benzene-d_6) of the volatile products from the thermolysis of 1-d_4 at 100 °C, 3 min (top), and of methylcyclopropane (bottom). The chemical shifts are in parts per million downfield of Me_4Si.

obtained are illustrated in Scheme IV. The volatile materials produced after 3 min at 100 °C (ca. 12% conversion) were vacuum transferred into an NMR tube which was then sealed under vacuum. The ^{1}H NMR spectrum of this material is shown together with the spectrum of authentic methylcyclopropane in Figure 4. The absence of the broad resonance at 0.55 ppm shows that this position is >90% deuterium substituted in the product. Integration of the remaining three resonances shows a 2:2:1 intensity ratio that is consistent with the labeling pattern illustrated in Figure 4. At longer reaction times a broad 0.55 ppm resonance begins to grow in. Simultaneously, one observes scrambling of the deuterium label into the α-positions of the unreacted starting material, along with hydrogen incorporation at the β-positions. GC–MS of the methylcyclopropane product isolated after longer reaction times (e.g., 35 min at 100 °C, 75% conversion) confirm that it is still d_4. Thus only intramolecular processes are taking place in both the scrambling and the methylcyclopropane forming reactions.

The α-^{13}C-labeled metallacycle 1-α,α'-$^{13}C_2$ was prepared in order to determine whether rearrangement of the carbon framework was responsible for the deuterium scrambling. The synthesis began with succinic-*1,4*-$^{13}C_2$ acid which was treated with diazomethane to yield dimethylsuccinate-*1,4*-$^{13}C_2$. Conversion to the metallacycle was accomplished as shown in Scheme III for 1-d_4. Thermolysis of 1-α,α'-$^{13}C_2$ with excess PPh_3 in benzene-d_6 was performed in a glass bomb at 100 °C. The unreacted metallacycle was examined by ^{13}C{^{1}H} NMR after 20 and 40 min and displayed only α-^{13}C resonances. The methylcyclopropane formed in the reaction was removed after 20 and 40 min, and these were individually examined by ^{13}C{^{1}H} NMR. Both samples were identical, displaying only the resonances assigned to the primary and secondary carbons of methylcyclopropane. A carbon scrambling process would generate β-^{13}C resonances in the starting material and thus ^{13}C labeling of the tertiary carbon of methylcyclopropane. Since these signals are absent no carbon rearrangement is occurring.

Scheme V



1-(^{13}CO)$_2$

The labeling results show that the thermolysis of 1 to methylcyclopropane proceeds with net β to α hydrogen transfer followed by α' to β carbon–carbon bond formation. Furthermore, it is clear that rearrangement of the carbon framework is not responsible for the deuterium scrambling observed (Scheme IV).

Carbonyl-Labeled Crossover Studies. Because the thermolysis reactions were run in the absence of added carbon monoxide, the production of $CpRe(CO)_2PR_3$ as the major organometallic product suggested that CO does not dissociate from the rhenium center during the reaction. In order to confirm this and to provide more information on the role of CO in the thermolysis of metallacycle 1, a crossover experiment using a mixture of 1 and 1 that was labeled at both carbonyls with ^{13}Co [1-(^{13}CO)$_2$] was performed.

Because no substitution of CO by PR_3 was observed when 1 was heated in the presence of phosphines, exchange of CO was likely to be difficult at the metallacycle stage. Thus, we attempted to incorporate ^{13}CO into the system by substitution of the carbonyls in $CpRe(CO)_2H_2$. In a sealed NMR tube a benzene-d_6 solution of $CpRe(CO)_2H_2$ was heated to 110 °C under ^{13}CO (350 torr at −196 °C). Surprisingly, $CpRe(CO)_3$ was the only product observed by NMR (50% conversion after 50 min). Mass spectral analysis of this material showed it to be 87% ^{13}C and 12% $^{13}C_2$, indicating incorporation of one new CO into the molecule. In contrast, when a benzene-d_6 solution of $CpRe(CO)_2H_2$ was heated at 110 °C in the presence of PMe_3, $CpRe(CO)(PMe_3)H_2$ was cleanly formed. When heated in the absence of phosphine, $CpRe(CO)_2H_2$ appears to be indefinitely stable.

Since incorporation of ^{13}CO into the dihydride appeared to be impossible, exchange of CO in $CpRe(CO)_2Br_2$[10,11] was attempted. When a benzene-d_6 solution of *trans*-CpRe(CO)$_2$Br$_2$ was heated at 80 °C under ^{13}CO (350 torr at −196 °C) in a sealed NMR tube, rapid incorporation of ^{13}CO was observed by ^{13}C NMR. Periodic integration of the relative intensities of coordinated (183.98 ppm) vs. free (184.38 ppm) ^{13}CO indicated that the reaction mixture had reached equilibrium after ca. 5 h. Thus, preparation of 1-(^{13}CO)$_2$ was finally accomplished by the route illustrated in Scheme V. In a sealed glass vessel a benzene solution of *trans*-CpRe(CO)$_2$Br$_2$ was exchanged with high purity ^{13}CO at 80 °C. Mass spectral analysis indicated >98% double ^{13}CO substitution after three exchange cycles. After conversion to the dihydride in 72% yield by reduction with Zn/HOAc in MeOH,[12] the ^{1}H NMR spectrum (benzene-d_6) displayed

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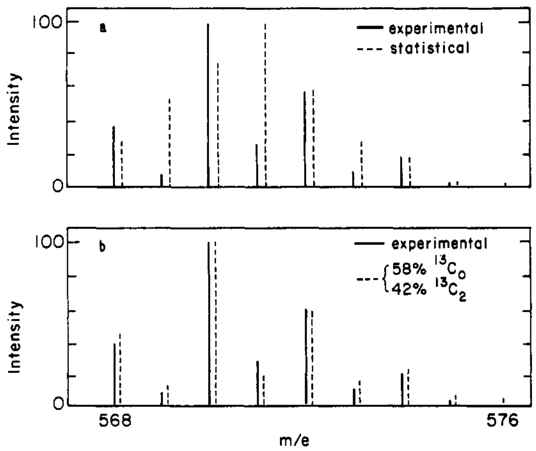


Figure 5. Comparison of experimental (solid line) and simulated (dotted line) mass spectra for the molecular ion region of ^{13}CO-labeled $CpRe(CO)_2PPh_3$ formed on decomposition of 54% 1 and 46% $1\text{-}(^{13}CO)$ in the presence of excess PPh_3: (a) experimental vs. a statistically calculated mixture (based on the starting ratio of 1 and $1\text{-}(^{13}CO)$) of 0.29:0.50:0.21 unlabeled, singly and doubly labeled phosphine complex; (b) experimental vs. calculated spectrum for a 58%/42% mixture of unlabeled and doubly labeled product.

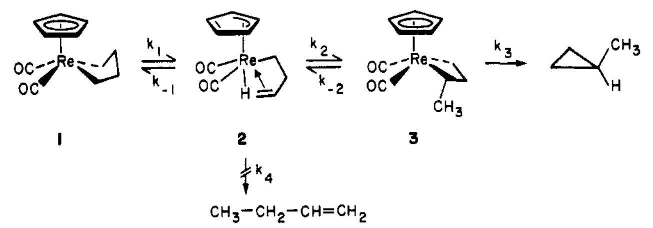
Scheme VI

$$\underset{54\%}{1} + \underset{46\%}{1\text{-}(^{13}CO)_2} \xrightarrow[100\,°C]{PPh_3/C_6H_6} \left\{\begin{array}{ll} CpRe(CO)_2PPh_3 & 58\% \\ CpRe(^{13}CO)(CO)PPh_3 & <4\% \\ CpRe(^{13}CO)_2PPh_3 & 42\% \end{array}\right.$$

a cyclopentadienyl singlet resonance at 4.32 ppm and a hydride triplet at −9.82 (J_{HC} = 12.8 Hz) ppm due to coupling to two ^{13}CO ligands. A triplet at 194.88 (J_{CH} = 12.4 Hz) ppm in the ^{13}C NMR spectrum was assigned to the carbonyl ligands coupled to the two hydride ligands. The observation of triplets for the ^{13}CO and hydride resonances is in agreement with the trans arrangement of ligands shown in Scheme V and assigned by Graham and Hoyano.[6] The metallacycle $1\text{-}(^{13}CO)_2$ was prepared analogously to the unlabeled material. The mass spectrum of the product $1\text{-}(^{13}CO)_2$ indicated it to be >98% doubly ^{13}CO substituted. The infrared spectrum of this material shows two carbonyl bands shifted by the appropriate amount for ^{13}C substitution at 1950 (s) and 1880 (vs) cm^{-1}. Two additional bands are seen at 1933 (m) and 1850 (m) cm^{-1} attributed to $(^{13}C^{18}O)(^{13}C^{16}O)$-containing The ^1H NMR spectrum is identical with that of the unlabeled metallacycle.

A mixture of 54% 1 and 46% $1\text{-}(^{13}CO)_2$ was thermolyzed at 100 °C in benzene with a fivefold excess of PPh_3. After 20 min (43% conversion) the solvent was removed under vacuum and the reaction mixture analyzed directly by mass spectroscopy. The $CpRe(CO)_2PPh_3$ region of the mass spectrum (*m/e* 568–575) was fit by matrix least-squares analysis[13] to a mixture containing 57 ± 3% $CpRe(CO)_2PPh_3$ and 43 ± 3% $CpRe(^{13}CO)_2PPh_3$, whose individual spectra were computer generated. Comparisons of the experimental mass spectrum to calculated spectra are shown in Figure 5. By this analysis, the maximum amount of the crossover product $CpRe(CO)(^{13}CO)PPh_3$ that could have been present is 4%. This result is illustrated in Scheme VI. Thus, in at least 92% of the product $CpRe(CO)_2PPh_3$ the $Re(CO)_2$ moiety has remained intact throughout the entire reaction.

Scheme VII



Discussion

These results provide the first example of the conversion of a five-membered metallacycle to methylcyclopropane. We propose that this transformation involves the conversion of a four-carbon chain containing rhenium–carbon bonds at C1 and C4 to a chain having such bonds at C1 and C3; simultaneously, rearrangement of a hydrogen atom from C2 to C1 must take place. The deuterium labeling studies discussed above reveal that in fact, much more extensive hydrogen scrambling occurs during thermolysis of 1, but experiments utilizing metallacycles containing ^{13}C in the ring demonstrate that the carbon atom connectivity does not change.

A β-elimination/readdition mechanism is the simplest way to account for this set of bonding changes. Because β-elimination normally requires the generation of a new coordination site, this primary step often follows initial dissociation of a dative ligand (e.g., CO) from the metal center. An unusual result of these studies, therefore, comes from our ^{13}CO crossover experiments, which clearly require that no such dissociation occurs during the thermolysis of metallacycle 1.

In order to account for this result and avoid the generation of 20-electron intermediates during the course of the rearrangement, we propose that $\eta^5 \rightleftharpoons \eta^3$ isomerization (or "ring slip") of the cyclopentadienyl ring occurs to generate the site of coordinative unsaturation. As shown in Scheme VII, it is most economical to assume that this happens as hydrogen is transferred to the metal center, generating butenyl hydride 2. Alkene insertion into the rhenium–hydride bond of 2 can proceed either to regenerate 1 or to form metallacyclobutane 3.[14] This material rapidly reductively eliminates methylcyclopropane, leaving a $CpRe(CO)_2$ fragment which subsequently reacts rapidly with phosphine.

Our results provide the first strong evidence for the involvement of cyclopentadienyl "ring slip" in an organometallic rearrangement process, but there is significant precedent for it in substitution reactions. Basolo and Schuster-Woldan suggested it many years ago as a way to account for the rapid bimolecular kinetics observed in the exchange of $CpRh(CO)_2$ with labeled carbon monoxide.[15] Subsequent studies of substituted systems have provided interesting information about the effects of various substituents on promoting this isomerization.[16,17] Recently

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(12) (a) Moss, J. R.; Graham, W. A. G. *Inorg. Chem.* 1977, *16*, 75; (b) Shapley, J. R.; Adair, P. C.; Lawson, R. J.; Pierpont, C. G. *Ibid.* 1982, *21*, 1702.

(13) Hamilton, W. C. "Statistics in Physical Science"; Ronald Press: New York, 1964.

(14) An alternative to the alkene insertion step to give metallacyclobutane 3 is a homoallylic rearrangement to give the cyclopropylmethyl hydride $CpRe(CO)_2(H)(CH_2CH(CH_2)_2)$ that reductively eliminates methylcyclopropane. These two paths are equivalent in the overall transformation occuring and differ only in the sequence of the C-H and C-C bond formation processes and thus they are difficult to distinguish. This possibility was suggested to us by Prof. J. A. Kampmeier. For a discussion of but-3-en-1-yl metal complexes see Brown, J. M.; Mertis, K. *J. Chem. Soc., Perkin Trans 2* 1973, 1993.

(15) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* 1966, *88*, 1657.

(16) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* 1975, *92*, 245.

Casey, O'Conner, Jones, and Haller demonstrated stoichiometric conversion of η^5-CpRe(CO)$_3$ to η^1-CpRe(CO)$_3$(PMe$_3$)$_2$ in the presence of PMe$_3$.[18] This demonstrates that the ring-slip metal-activation mechanism is accessible to cyclopentadienylrhenium complexes.[19] In addition, the bimolecular kinetics observed by Casey and Jones provide support for the idea that ring slip may be concerted with delivery of an incoming ligand to the metal center. However, the kinetic results show that in our system the β-elimination-induced ring slip is favored over a possible ring slip induced by either PPh$_3$ or PMe$_3$.

Perhaps the most interesting aspect of the mechanism in Scheme VII is the fact that the combined alkene insertion and cyclopropane reductive elimination sequence, leading to methylcyclopropane, occurs at a rate more rapid than the processes that might lead to β-elimination and extrusion of alkene. That is, intermediate **2** undergoes alkene insertion faster than C–H reductive elimination ($k_2 > k_4$), but C–C reductive elimination (k_3) must be faster than the combination of β-elimination/C–H reductive elimination ((k_{-2})(k_4) and the similar process which would lead to internal alkene) that would produce 1-butene. This is rather unusual, considering the relative ease with which other hydridoalkyl complexes undergo reductive elimination in comparison to dialkyl complexes. Thus, the presence of the third-row metal in this system does not simply produce an overall stabilization of the hydridoalkyl complex **2**—rather, it retards k_4 but does not cause appreciable problems in either the alkene insertion or C–C reductive elimination steps.[20] Now that these variable effects on the different processes involved can be identified, perhaps some progress can be made in understanding their physical causes.

This work also provides support for the mechanism proposed by McLain, Sancho, and Schrock in their study of the conversion of tantalum metallacyclopentanes to alkenes.[21] In order to explain a deuterium labeling pattern inconsistent with simple β-elimination to give alkenyl hydride complex, followed by reductive elimination of alkene, ring contraction to a metallacyclobutane was postulated. This is directly analogous to the process we have suggested in Scheme VII for the decomposition of **1**, except that the tantalum intermediate analogous to **3** undergoes hydrogen shift and extrusion of alkene, rather than direct C–C reductive elimination of cyclopropane. In addition, the lower electron count of the tantalum system avoids the necessity of postulating an $\eta^5 \rightleftharpoons \eta^3$-Cp isomerization similar to that suggested for the rhenium reaction.

The factors that control the cyclopropane forming step are still unclear. However, if a means can be found to trap the final organometallic product CpRe(CO)$_2$ with ethylene and reconvert it to metallacycle,[22] the possibility exists of developing a catalytic method for converting ethylene to methylcyclopropane. The fact that methylcyclopropane is stable to reaction with the rhenium complexes studied here and that the proposed catalytic conversion is calculated to be exothermic despite the formation of a small ring[23] makes such a process a feasible possibility. This would be a very rare example of the catalytic oligomerization of an alkene to a strained ring compound, and efforts are under way aimed at finding a means to effect it.

Finally, the rhenium metallacyclobutane-to-metallacyclopropane ring contraction observed here, along with the very similar transformation observed earlier for tantalum by Schrock et al.,[21] suggests that such rearrangements may be general processes. Thus they may be accessible in the thermal decomposition reactions of metallacycles formed from other metals.

Experimental Section

General Data. CpRe(CO)$_3$ was prepared from Re$_2$(CO)$_{10}$ (Strem) by the method described by Green and Wilkinson.[24] All anionic rhenium complexes or those containing hydride ligands were at least mildly air sensitive and were stored and handled in a nitrogen filled Vacuum Atmosphere 553-2 inert-atmosphere glovebox equipped with an MO-40-1 inert-gas purifier.

^{1}H NMR spectra were recorded at 200, 250, or 300 MHz with the Fourier transform NMR spectrometers at the University of California, Berkeley (UCB), NMR facility, and are reported in units of parts per million (δ) downfield from tetramethylsilane (Me$_4$Si). The internal standard for spectra recorded in chloroform-*d* is Me$_4$Si. For spectra recorded in benzene-d_6, acetone-d_6, acetonitrile-d_3, and THF-d_8 the internal standard is the residual proton resonance occurring at δ 7.15, 2.03, 1.93, and 1.73, respectively.

^{13}C{^{1}H} and gated ^{13}C NMR spectra were recorded at 75.5 MHz and are reported in units of parts per million downfield from Me$_4$Si with the solvent ^{13}C resonance serving as the internal standard: chloroform-*d* (77), benzene-d_6 (128). Solution infrared spectra were recorded in 0.1 mm NaCl cells on a Perkin-Elmer Model 283 spectrophotometer. Electron-impact mass spectra were recorded at the UCB mass spectral facility on an AEI MS 12 mass spectrometer. Fitting of mass spectral data was performed by matrix least-squares analyses.[13] Elemental analyses were performed by the UCB microanalytical laboratory. Melting points were taken in glass capillary tubes in a Thomas-Hoover capillary melting point apparatus and are not corrected.

Benzene, THF, and toluene were distilled from Na/benzophenone under a nitrogen atmosphere. UV-grade hexane was distilled from LiAlH$_4$. Acetone-d_6 and acetonitrile-d_3 were vacuum transferred from 3A sieves. Benzene-d_6 and THF-d_8 were vacuum transferred from Na/benzophenone. Pentane was vacuum transferred from a sodium mirror. Carbon monoxide (99.58% ^{13}C, 17.75% ^{18}O, 1.13% ^{17}O) was obtained from Bio-Rad. Trimethylphosphine (Strem) was dried over a sodium mirror and vacuum transferred prior to use. Triphenylphosphine (Mallinckrodt), 1,4-diiodobutane, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (both from Aldrich) were used as received. Ferrocene was purchased from Aldrich and was sublimed prior to use. Methylcyclopropane was purchased from Columbia Organic Chemicals. All other solvents and reagents were reagent grade and were used without purification.

CpRe(CO)$_2$Br$_2$. Bromination of CpRe(CO)$_3$ was carried out by a modification of the route described by King and Reimann.[11] In a 250-mL Erlenmeyer flask equipped with a magnetic stir bar and a nitrogen purge was placed CpRe(CO)$_3$ (5.82 g, 17.4 mmol) and 50 mL of CF$_3$CO$_2$H (Aldrich). This mixture was stirred, and a solution of pyridinium hydrobromide perbromide (5.77 g, 18.0 mmol, Alfa) in 50 mL of CF$_3$CO$_2$H was added over 20 min. Evolution of gas was evident. After the addition was complete, the reaction mixture was poured into 700 mL of water. A pale orange precipitate immediately formed which was filtered and

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[17] Rerek, M. E.; Ji, L.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372.

[18] (a) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535. (b) See also: Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6156.

[19] For other examples of cyclopentadienyl ring slip see: (a) Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. J. *J. Organomet. Chem.* **1978**, *145*, 329. (b) Reference 18b and the references cited therein.

[20] Attempts to prepare the butenyl hydride CpRe(CO)$_2$(H)(CH$_2$CH$_2$CHCH$_2$) in an attempt to independently form hydrido alkyl **2** have not been successful, but neither have they led to formation of methylcyclopropane.

[21] McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.

[22] Preliminary results show that when **1** is thermalized at 100 °C in benzene-d_6 under ca. 1 atm of ethylene CpRe(CO)$_2$(C$_2$H$_4$) is cleanly formed. However, this material does not form either **1** or methylcyclopropane upon heating under 1 atm of ethylene up to 190 °C. Experiments utilizing higher pressures of ethylene are in progress.

[23] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1974.

[24] Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4314.

washed with water. After being dried under aspirator suction, the crude product was adsorbed on 20 g of silica by dissolving it in ca. 50 mL of CH_2Cl_2, adding the silica, and then removing the solvent under vacuum. This material was loaded in a 6 × 40 cm column containing 300 g of SiO_2·60 (70–230 mesh, E. Merck) and eluted with 2:1 hexane/CH_2Cl_2. Three fractions were collected: a clear, colorless forerun, a bright red-orange fraction, and a brown fraction that eluted with CH_2Cl_2. These were stripped of solvent under vacuum and yielded, respectively, $CpRe(CO)_3$ (3.55 g, 10.6 mmol, 61%), *trans*-$CpRe(CO)_2Br_2$ (2.32 g, 4.97 mmol, 28%), and *cis*-$CpRe(CO)_2Br_2$ (0.90 g, 1.93 mmol, 11%, yields based on starting $CpRe(CO)_3$). Use of Br_2 or more than 1 equiv of pyridinium hydrobromide perbromide substantially reduced the total yield of recovered rhenium. For *trans*-$CpRe(CO)_2Br_2$: ^1H NMR (acetone-d_6) δ 6.01 (s); ^1H NMR (benzene-d_6) δ 4.51; IR (CH_2Cl_2) 2070 (m), 2005 (s) cm^{-1} [lit.[11] ^1H NMR (acetone-d_6) δ 6.00 (s); IR (CH_2Cl_2) 2074, 1998 cm^{-1}]. For *cis*-$CpRe(CO)_2Br_2$: ^1H NMR (acetone-d_6) δ 6.45 (s); ^1H NMR (benzene-d_6) δ 4.62; IR (CH_2Cl_2) 2053 (s), 1982 (s) cm^{-1} [lit.[11b] ^1H NMR (acetone-d_6) δ 6.40 (s); IR (CH_2Cl_2) 2056, 1975 cm^{-1}].

$CpRe(CO)_2H_2$. In a 500-mL Erlenmeyer flask, under a continuous purge of nitrogen, 3.22 g of $CpRe(CO)_2Br_2$ (6.89 mmol, mixture of both cis and trans isomers) was stirred in 300 mL of MeOH. Acetic acid (8 mL, 139 mmol, Mallinckrodt) was added, followed by 5.95 g of zinc dust (91 mmol, Mallinckrodt). This mixture was stirred until all of the $CpRe(CO)_2Br_2$ had dissolved and then for 5 min longer. The solvent was then removed under vacuum and the residue was triturated with 50 mL of water. The aqueous mixture was extracted with pentane (5 × 50 mL). The combined pentane extracts were stripped of solvent under vacuum, and the remaining oil was sublimed (50 °C, 0.01 torr) to yield clear colorless crystals of $CpRe(CO)_2H_2$ (1.68 g, 5.43 mmol) in 79% yield based on $CpRe(CO)_2Br_2$. These were determined to be pure by NMR: IR (hexane) 2016 (s), 1960 (vs) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.35 (s, 5 H), −9.68 (s, 2 H); mp (N_2) 34.5–35.5 °C [lit.[6] IR (heptane) 2022 (m), 1954 (s), cm^{-1}; ^1H NMR (benzene-d_6) δ 5.28 (s, 5 H), −9.26 (s, 2 H); mp 36–37 °C].

(η^5-Cyclopentadienyl)dicarbonylrhenacyclopentane (1). In a glovebox a 100-mL round bottom flask was charged with a solution of $CpRe(CO)_2H_2$ (0.49 g, 1.57 mmol) and DBU (1.02 g, 6.73 mmol) in 20 mL of THF. To this a solution of 1,4-butanediiodide (0.97 g, 3.12 mmol) in 10 mL of THF was added dropwise over 5 min. The colorless mixture turned bright yellow during the addition and a white precipitate (DBU·HI) soon formed. The IR spectrum of an aliquot removed at this point displayed three intense bands at 1985, 1905 (vs, product), and 1618 (s, DBU) cm^{-1}. The reaction mixture was removed from the glovebox and worked up in the air. The solvent was removed under vacuum, and the residue was triturated with water (20 mL) and pentane (50 mL). The aqueous layer was then extracted with pentane (2 × 50 mL). The combined organic layers were dried ($MgSO_4$) and stripped of solvent under vacuum leaving a mixture of yellow 1 and excess diiodide. Chromatography (silica, pentane, 4 × 19 cm) yielded a faint yellow band that was collected and stripped under vacuum. Recrystallization from pentane (−60 °C) yielded 0.35 g of yellow air-stable crystals of 1 which were pure by NMR (61% yield based on $CpRe(CO)_2H_2$): ^1H NMR (chloroform-*d*) δ 5.32 (s, 5 H), 2.70 (m, 2 H), 2.20 (m, 2 H), 1.75 (m, 2 H), 1.00 (m, 2 H); ^1H NMR (benzene-d_6) δ 4.34 (s, 5 H), 2.51 (m, 2 H), 2.38 (m, 2 H), 1.82 (m, 4 H); ^{13}C NMR (gated, chloroform-*d*) δ 209.3 (br s), 90.25 (d, J = 181 Hz), 36.59 (t, J = 125.5 Hz), 6.65 (t, J = 135 Hz); IR (THF) 1990 (s), 1910 (s) cm^{-1}; IR (pentane) 2035 (w), 1998 (s), 1945 (m), 1930 (vs) cm^{-1}; mass spectrum (70 eV), *m/e* 362/364 (M^+, $^{185}Re/^{187}Re$); mp (N_2) 88.5–90 °C; M_r (Signer isothermal distillation method,[7] Me_2O solvent) 363 (calcd 363). Anal. Calcd for $C_{11}H_{13}O_2Re$: C, 36.35; H, 3.61. Found: C, 36.02; H, 3.53.

Thermolysis of 1 with Excess PPh_3. A mixture of 1 (7 mg, 19.2 × 10^{-6} mol), ferrocene (2 mg, internal standard), and PPh_3 (35 mg, 133 × 10^{-6} mol) were placed in an NMR tube attached to a ground glass joint. Benzene-d_6 (0.68 mL) were vacuum transferred in. The tube was sealed off under vacuum. A ^1H NMR spectrum was recorded to determine the relative intensities of the ferrocene and metallacycle Cp resonances.

The tube was immersed in a 100 °C bath and periodically removed to record a ^1H NMR spectrum. The solution became bright yellow, and a new resonance at 4.52 ppm appeared as the starting material Cp resonance at 4.34 ppm disappeared. Resonances due to methylcyclopropane appeared in the +1 to −0.1 ppm region. No other resonances appeared. After 2 h at 100 °C integration of the ^1H NMR spectrum indicated that the starting material had been quantitatively converted to the new Cp resonance. The tube was cracked open, and the volatile components were collected under vacuum. This mixture was found to contain only benzene-d_6 and a volatile component that was identical with authentic methylcyclopropane by NMR, GC, and GC–MS.

The nonvolatile component was purified by chromatography (silica, hexane/CH_2Cl_2, 1:1) and isolated as a white crystalline solid in 84% isolated yield (based on 1) which was identified to be $CpRe(CO)_2PPh_3$ by its melting point and IR spectrum: mp 235–237 °C; IR (CH_2Cl_2) 1925 (s), 1855 (s) cm^{-1}; ^1H NMR (benzene-d_6) δ 7.56 (m, 6 H), 7.02 (m, 9 H), 4.52 (s, 5 H); MS (70 eV) *m/e* 570 (M^+, base). [lit.[25] mp 234–235 °C; IR (CH_2Cl_2) 1930 (s), 1859 (s) cm^{-1}].

In order to determine the yield of methylcyclopropane, an NMR tube was charged with 1 (17.3 mg, 47.6 × 10^{-6} mol), ferrocene (4 mg, internal standard), and PPh_3 (61.2 mg, 2.34 × 10^{-4} mol). Benzene-d_6 (0.78 mL) and methylcyclopropane (10.35 torr, 65.1 mL at 24 °C, 36.3 × 10^{-6} mol) were vacuum transferred in, and the tube was sealed under vacuum. An ^1H NMR spectrum was recorded and integrated. After the tube was heated at 100 °C for 1 h, another ^1H NMR spectrum was recorded and integrated. From the relative intensities of the methylcyclopropane resonances in the spectra of unreacted and fully reacted materials and the ratio of 1 to added methylcyclopropane the yield of methylcyclopropane was calculated as 96% based on 1.

Thermolysis of 1 with Excess PMe_3. In an NMR tube charged with 1 (4.5 mg, 12.3 × 10^{-6} mol) and ferrocene (1 mg, internal standard). Benzene-d_6 (0.66 mL) and PMe_3 (2.57 × 10^{-4} mol) were condensed in, and the tube was sealed under vacuum. A ^1H NMR spectrum was recorded to determine the relative intensities of the ferrocene and metallacycle Cp resonances. The tube was heated at 100 °C, and NMR spectra were periodically recorded at room temperature. A new Cp resonance at 4.57 (d, 5 H, J = 0.5 Hz) ppm and bound phosphine at 1.20 (d, 9 H, J = 9.4 Hz) ppm appeared. The characteristic methyl doublet at 0.94 (J = 5.8 Hz), ppm and multiplets at 0.35 and −0.04 ppm due to methylcyclopropane also appeared. After the mixture was heated for 2 h, integration of the ^1H NMR spectrum indicated that 1 had been quantitatively converted to the new Cp resonance. The tube was opened, and the volatile components were removed under vacuum. The remaining material was chromatographed in the air (silica, CH_2Cl_2/pentane, 1:1), yielding a white crystalline product. This material was identified as $CpRe(CO)_2PMe_3$ by ^1H NMR, IR, and melting point and was isolated in 84% yield based on 1: ^1H NMR (benzene-d_6) δ 4.57 (d, 5 H, J = 0.5 Hz), 1.20 (d, 9 H, J = 9.4 Hz); IR (THF) 1923, 1855 cm^{-1}; mp (N_2) 98–99 °C [lit.[18a] ^1H NMR (benzene-d_6) δ 4.56 (d, 5 H, J = 0.6 Hz), 1.20 (d, 9 H, J = 9.4 Hz); IR (THF) 1929 (s), 1859 (s) cm^{-1}; mp (sealed capillary) 99–100 °C].

Thermolysis of 1 without Added Ligand. This experiment was performed in a manner identical with the thermolysis with PPh_3. The thermolysis was again monitored by ^1H NMR spectroscopy. Several Cp resonances as well as a number of alkyl resonances appeared during the course of the reaction as the solution became dark brown. The predominant organic product was methylcyclopropane which was identified by its characteristic ^1H NMR spectrum. The major organometallic product that accounted for 60% of the Cp resonance intensities was isolated by chromatography (silica, hexane/benzene, 10:1) and identified to be $CpRe(CO)_3$ by comparison of its ^1H NMR and IR spectra with those of an authentic sample:[24] ^1H NMR (benzene-d_6) δ 4.31 (s); IR (hexane) 2030 (s), 1945 (vs) cm^{-1}.

The yield of methylcycloproprane was determined by the method previously described for the thermolysis with PPh_3 to be 66% based on 1.

Kinetics. A standard solution of 1 (8.24 × 10^{-2} M) and ferrocene (3.95 × 10^{-2} M, internal standard) was made up in methylene chloride. An appropriate volume of this solution was syringed into an NMR tube sealed to a ground glass joint, and

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(25) Nesmeyanov, A. N.; Kolobova, N. E.; Makarov, Yu. V.; Lokshin, B. V.; Rusach, E. B. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1976**, *3*, 629.

the methylene chloride was removed under vacuum. Triphenylphosphine was weighed into the tube or trimethylphosphine was condensed in, and benzene-d_6 was vacuum transferred into the tube which was then sealed under vacuum. A kinetic experiment was performed by immersing a tube in the vapor of a bath of refluxing water (100 ± 0.5 °C). At given time intervals (5 min) the tube was taken out of the bath and cooled in a dry ice/acetone slush. The contents of the tube froze within 3 s after removal from the bath. At room temperature the ^{1}H NMR spectrum was recorded. The NMR tube was then returned to the bath. The relative cyclopentadienyl resonance intensities of product $CpRe(CO)_2PR_3$ and starting material 1 were integrated against the internal standard ferrocene. At least 12 (10 for the PMe_3 experiments) data points over greater than 3 half-lives were obtained in this manner. The data was plotted in the appropriate first order plot as shown in Figure 3. The kinetic results are summarized in Table II.

Preparation of Butane-1,4-ditosylate-*2,2,3,3-d*$_4$. In a 500-mL two-neck round bottom flask equipped with a magnetic stir bar 1.65 g of Pd/C (10%, Englehard) was stirred in EtOD (200 mL, 99.5 atom % D, Aldrich). A balloon was fitted to one joint and a septum to the other. Dimethyl acetylenedicarboxylate (20 mL, 23.2 g, joint mol, "DMAD" Aldrich) was added by syringe. Deuterium gas was admitted through the septum periodically to keep the balloon filled. The reaction mixture quickly became warm as gas was consumed. After 2 h the mixture had cooled to room temperature. The Pd/C was removed by filtration, and the EtOD was removed from the crude product under vacuum. The remaining yellow oil was distilled (bp 79–81 °C (10 torr) to yield clear, colorless dimethylsuccinate-*2,2,3,3-d*$_4$ (18.7 g, 77% yield based on DMAD) which was pure by NMR: ^{1}H NMR (chloroform-d_6) δ 3.70 (s, Me), 2.61 (br s, residual succinate protons). Integration of the 2.61 ppm residual proton resonance against the methyl singlet indicated >98% deuteration at the succinate carbons.

Reduction of the diester to the diol was accomplished in the following manner. A 500-mL one-neck round-bottom flask was charged with 250 mL of anhydrous diethyl ether (Mallinckrodt), a magnetic stir bar, and $LiAlH_4$ (5.25 g, 0.14 mmol, Alfa). A pressure-equalizing addition funnel containing a solution of dimethylsuccinate-d_4 (5.34 g, 35.6 mmol) in 50 mL of diethyl ether was attached to the flask. The flask was cooled to −76 °C, and the diester was added dropwise to the stirred $LiAlH_4$ mixture. The addition was complete within 30 min, and the reaction mixture was warmed to room temperature over 40 min. After being quenched with a small amount of saturated aqueous Na_2SO_4, the reaction mixture was stirred with saturated aqueous potassium sodium tartrate (ca. 100 mL, Aldrich) until nearly all of the salts had dissolved. After continuous extraction with Et_2O for 20 h the Et_2O extract was dried with $MgSO_4$ and stripped of solvent under vacuum, yielding 2.74 g of product as a clear, colorless oil (82% yield based on dimethylsuccinate): ^{1}H NMR (chloroform-d_6) δ 3.68 (s, 2 H), 2.52 (s, 1 H), 1.68 (br s, residual proton). Integration of the peak intensities showed that the material was pure and >96% deuterated at the β-carbons.

Preparation of the ditosylate was performed as described by Laasko and Reynolds.[26] The crude product was recrystallized from CH_2Cl_2/Et_2O and isolated in 39% yield based on dimethylsuccinate-*2,2,3,3-d*$_4$: ^{1}H NMR (chloroform-d_6) δ 7.76 (s, 4 H, J = 8.3 Hz), 7.35 (d, 4 H, J = 8 Hz), 3.98 (s, 4 H), 2.46 (s, 6 H), 1.68 (br s, residual proton). Integration indicated that this material was pure and >95% deuterated: mp 80.5–81.5 °C (lit.[26] 81–82 °C).

Preparation of 1,4-Diiodobutane-*2,2,3,3-d*$_4$. In a 100-mL round-bottom flask 1,4-butaneditosylate-*2,2,3,3-d*$_4$ (3.11 g, 7.7 mmol) was dissolved in 60 mL of a 0.50 M solution of NaI in acetone. This mixture was stirred and refluxed for 3 h during which time a white crystalline precipitate appeared. The reaction mixture was cooled, and 10 mL of H_2O was added. The acetone was removed under vacuum, and the resulting aqueous mixture was extracted with 2 × 50 mL of pentane. The combined pentane extracts were washed with saturated aqueous $Na_2S_2O_3$ (10 mL) and then dried ($MgSO_4$). The pentane was removed under vacuum, yielding 2.43 g of 1,4-diiodobutane-*2,2,3,3-d*$_4$ which was pure by NMR (yield 100% based on ditosylate): ^{1}H NMR (chloroform-d) δ 3.18 (s), 1.92 (br s, residual proton). Integration of the NMR spectrum indicated >96% deuteration at the β-carbon positions. For 1,4-diiodobutane-d_0 (Aldrich): ^{1}H NMR (chloroform-d) δ 3.20 (m, 1 H), 1.95 (m, 1 H).

Preparation of 1-*d*$_4$. $CpRe(CO)_2H_2$ was alkylated with 1,4-diiodobutane-*2,2,3,3-d*$_4$ in THF as described above for the unlabeled material. The crude 1-d_4 was initially purified by chromatography (pentane, silica) followed by recrystallization from pentane to yield yellow crystals. However, the ^{1}H NMR (benzene-d_6) spectrum displayed three broad multiplets at 2.47 (1 H), 2.34 (1 H), 1.80 (2 H) ppm. This was indicative of complete scrambling of the deuterium label. We assume exposure to silica in some way induced this rearrangement.

In order to avoid this scrambling, the reaction was repeated and the fully labeled material purified by careful recrystallization. Yellow crystals of 1-d_4 which were pure by NMR were obtained by cooling a filtered pentane solution of crude 1-d_4 to −60 °C and filtering: ^{1}H NMR (benzene-d_6) δ 4.34 (s, 5 H), 2.49 (d, 2 H, J = 10.5 Hz), 2.35 (d, 2 H, J = 10.6 Hz). Integration of the 1.8 ppm residual proton region against the 2.4 ppm region indicated that the product was >95% deuterated at the β-carbons.

Thermolysis of 1-*d*$_4$ with Excess PPh$_3$. A 12-mL glass bomb equipped with a Teflon vacuum valve was charged with 1-d_4 (49.5 mg, 0.13 mmol), PPh_3 (0.328 g, 1.3 mmol), and a magnetic stir bar. The bomb was evacuated, and benzene-d_6 (1.5 mL) was vacuum transferred in. The bomb was closed and immersed in a 100 °C bath for 3 min. After being cooled, 0.45 mL of the volatile reaction solution was vacuum transferred into an NMR tube which was then sealed under vacuum. The ^{1}H NMR spectrum of this solution showed the following methylcyclopropane signals (benzene-d_6): δ 0.90 (br d, 2 H, CH_2D), 0.31 (br s, 1 H, H_a), −0.10 (br s, 1 H, H_b). This NMR spectrum and labeling scheme is illustrated in Figure 4.[27] Integration of the 0.65 ppm region against the other resonances showed >95% deuterium substitution at this position. Volatiles were removed from the same reaction mixture after longer periods of thermolysis by the same technique. The NMR spectra showed a similar labeling pattern but with increasing amounts of proton signal in the 0.65 ppm region. A GC–mass spectrum of the methylcyclopropane in this solution confirmed that it was >90% d_4.

A separate experiment was performed to observe the metallacycle resonances during the thermolysis. In an NMR tube were placed 1-d_4 (4.1 mg, 1.1 × 10^{-5} mol), PPh_3 (21.1 mg, 81 mmol), and ferrocene (1.4 mg, 7.5 × 10^{-6} mol). Benzene-d_6 was vacuum transferred into the tube which was then sealed under vacuum. The tube was immersed in a 100 °C bath and removed every 5 min for an NMR spectrum. Clean formation of $CpRe(CO)_2PPh_3$ was observed. Formation of labeled methylcyclopropane was observed as in the above experiment with gradual growth of the broad methylcyclopropane C–H resonance at 0.65 ppm. Also observed was the increase in the metallacycle resonance at 1.8 ppm due to hydrogen incorporation at the β-carbons. The metallacycle appeared to be completely scrambled after ca. 2 half-lives as judged by integration of the β-carbon region (1.8 ppm) against the α-carbon region (2.5–2.35 ppm).

Preparation of 1-α-^{13}*C*. Succinic-*1,4*-$^{13}C_2$ acid (0.50 g, 4.3 mmol, 90% ^{13}C, Merck, Sharpe and Dohme Isotopes) was diluted with unlabeled succinic acid (0.68 g, 5.8 mmol). This mixture was dissolved in 100 mL of THF and treated with an ethereal solution of diazomethane until a faint yellow color persisted. Removal of the solvent under vacuum yielded dimethylsuccinate-*1,4*-$^{13}C_2$ which was pure by NMR: ^{1}H NMR (chloroform-d) δ 3.70 (s and d, 6 H, J = 3.6 Hz), 2.64 (s, 4 H); IR (Et_2O) 1748 (^{12}CO), 1706 (^{13}CO). From the relative areas of the ^{13}C and ^{12}C carbonyl bands the product was determined to be 41% ^{13}C substituted. The diester was converted to the corresponding 1,4-diiodobutane-*1,4*-$^{13}C_2$ via the same procedure used for the deuterated analogue. The product was isolated as a slightly yellow oil which was pure by NMR in 12.5% overall yield from succinic acid: ^{1}H NMR (chloroform-d) δ 3.20 (mult and d of mult, 1 H, J = 150.4 Hz),

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(26) Laasko, T. M.; Reynolds, D. D. *J. Am. Chem. Soc.* **1951**, *73*, 3518.

(27) The assignments of the proton resonances in methylcyclopropane are based on: Crawford, R. J.; Erickson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 3907.

1.95 (m, 1 H). Integration of the ^{13}C satellite resonances indicated 41% ^{13}C substitution.

Metallacycle 1-α-^{13}C was prepared via the route used to prepare 1-d_4 and was isolated by recrystallization from pentane at −76 °C: ^{1}H NMR (benzene-d_6) δ 4.34 (s, 5 H), 2.51, 2.38 (2 mult and d of 2 mult, 4 H, J = 132 Hz), 1.82 (m, 4 H); ^{13}C{^{1}H} NMR (benzene-d_6) δ 6.71 (t, J = 132 Hz). This material was pure by both ^{13}C and ^{1}H NMR.

Thermolysis of 1-α-^{13}C. In a glass bomb sealed with a Teflon valve were placed 1-α-^{13}C (20 mg, 5.5×10^{-5} mol) and PPh$_3$ (82 mg, 3.1×10^{-4} mol). Benzene-d_6 (1.5 mL) was vacuum transferred into the bomb which was the closed under vacuum. The bomb was immersed in a 100 °C bath for 20 min and then cooled at ambient temperature. The methylcyclopropane formed in the reaction was removed together with 0.5 mL of the benzene-d_6 and condensed into an NMR tube which was then sealed. The ^{13}C{^{1}H} NMR spectrum of this material showed resonances at 19.47 and 5.97 ppm due to the primary and secondary carbons in methylcyclopropane. No signal at 5.23 ppm, assigned to the tertiary carbon, was observed. The nonvolatile reaction mixture was pipetted into an NMR tube under nitrogen. The ^{13}C{^{1}H} NMR spectrum of this material displayed only the α-carbon resonance at 6.71 ppm. No resonance assigned to the β-carbon was observed to within 3% of the α-carbon resonance intensity. The reaction mixture was returned to the bomb and degassed by three freeze–pump–thaw cycles. Additional benzene-d_6 (0.5 mL) was vacuum transferred into the bomb. The bomb was heated to 100 °C for 20 min, and analysis of the volatiles and nonvolatiles was performed as described with identical results.

Preparation of CpRe(^{13}CO)$_2$H$_2$. In a 154-mL glass vessel equipped with a magnetic stir bar and sealed with a Teflon vacuum valve was placed *trans*-CpRe(CO)$_2$Br$_2$ (500 mg, 1.07 mmol). The vessel was evacuated and 15 mL of benzene was vacuum transferred in. The vessel was immersed in liquid nitrogen and filled with 300 torr of ^{13}CO. The vacuum valve was closed, and the vessel was immersed in an 80 °C bath for 2.5 h. The red solution was rapidly stirred to ensure good gas/liquid equilibrium. After the solution was cooled, the benzene and remaining CO were removed under vacuum. Fresh benzene and ^{13}CO were added, and the procedure was repeated. After three exchanges had been performed, the solvent was removed under vacuum, yielding a red crystalline product. A mass spectrum of this material showed a mass envelope of the molecular ion consistent with >99% disubstituted material (i.e., CpRe(^{13}CO)$_2$Br$_2$). This dibromide was converted to CpRe(^{13}CO)$_2$H$_2$, identical with the unlabeled material in 72% yield (pure by NMR): IR (pentane) 1975 (s), 1960 (m, ^{18}O), 1915 (vs), 1885 (s, ^{18}O) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 4.32 (s, 5 M), −9.82 (t, 2 H, J_{CH} = 12.8 Hz); ^{13}C NMR (benzene-d_6, gated) δ 194.88 (t, J_{CH} = 12.4 Hz).

Preparation of 1-(^{13}CO)$_2$. Conversion of CpRe(^{13}CO)$_2$H$_2$ to 1-[^{13}CO]$_2$ was accomplished as for the unlabeled material: IR (pentane) 1950 (vs), 1933 (w, ^{18}O), 1880 (vs), 1850 (w, ^{18}O) cm^{-1} (see text for assignments). The ^{1}H NMR spectrum (benzene-d_6) was identical with that of the unlabeled material and showed the product to be pure. The mass spectrum exhibited molecular ions at m/e 364 (47.4%), 366 (100%), and 368 (32.5%). Analysis of the relative peak intensities in the molecular ion envelope indicated that the product was 99% (^{13}CO)$_2$ substituted and 1% (^{13}CO)$_1$ substituted.

Crossover Experiment. A mixture of 1 (3.3 mg, 9.1×10^{-6} mol) and 1-(^{13}CO)$_2$ (3.0 mg, 8.2×10^{-6} mol) was placed in a small glass bomb closed with a Teflon vacuum valve and equipped with a magnetic stir bar. In order to determine the extract ratio of these two materials, enough methylene chloride was added to dissolve all of the metallacycle (to ensure homogeneous sampling) and a small sample of this material was taken out for mass spectral analysis. The molecular ion region for 1 (ca. m/e 364) was found to be due to a mixture of 1 (54% ± 4%) and 1-(^{13}CO)$_2$ (46% ± 4%). The methylene chloride was removed from the bulk of the material under vacuum. Triphenylphosphine (21.3 mg, 81.3×10^{-6} mol) was added as a solid, and benzene (1 mL) was vacuum transferred in. The bomb was closed off under vacuum and then immersed in a 100 °C bath for 20 min. The solvent was removed under vacuum, yielding a sticky oil that crystallized under continued pumping. This mixture was analyzed directly by mass spectroscopy. The molecular ion region for the product CpRe(CO)$_2$PPh$_3$ (m/e 567–576) is shown in Figure 5. Analysis of the relative peak intensities indicated a mixture of 58% ± 3% unlabeled and 42% ± 3% doubly labeled CpRe(CO)$_2$PPh$_3$, with less than 4% of the singly ^{13}CO-substituted product present.

Table III. Crystal and Data Collection Parameters for C$_{11}$H$_{13}$O$_2$Re

(A) Crystal Parameters at 25 °C[a,b]

a = 8.0041 (7) Å
space group: $P2_12_12_1$ (No. 19)
b = 8.0139 (7) Å
fw: 363.43 amu
c = 16.6549 (13) Å
Z = 4
V = 1068.3 (3) Å^3
d(calcd) = 2.26 g cm^{-3}
size: 0.17 × 0.18 × 0.30 mm
μ(calcd) = 115.0 cm^{-1}

(B) Data Measurement Parameters

diffractometer: Enraf-Nonius CAD-4[28]
radiation: Mo Kα (λ = 0.710 73 Å)
monochromator: highly oriented graphite ($2\theta_m$ = 12.2)
detector: crystal scintillation counter, with PHA
aperture–crystal = 173 mm. vertical aperture = 3.0 mm
horizontal aperture = (2.0 + 1.0 tan θ) mm (variable)
reflctns measd: $+h,+k,+l$
2θ range: 3–45
scan type: θ–2θ
scan speed: 0.6–6.7 (θ, deg/min)
scan width: $\Delta\theta$ = 0.5 + 0.347 tan θ
background: measd over an additional 0.25($\Delta\theta$) added to each end of the scan
no. of refctns collected: 885
no. of unique reflctns: 839
intensity stds: (515), (0,0,10), (354); measured every 2 h of X-ray exposure time; over the period of data collection 15% decay in intensity was observed
orientation: 3 reflctns were checked after every 250 measurements; crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°; reorientation was not necessary during data collection

[a] Unit-cell parameters and their esds were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 29° and 32°. [b] In this and all subsequent tables the esds of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

Crystal and Molecular Structure of (η^5-Cyclopentadienyl)dicarbonylrhenacyclopentane (1). Clumps of clear yellow crystals of the compound were obtained by slow crystallization from toluene/pentane. Fragments cleaved from the tips of some of these crystals were mounted on glass fibers by using polycyanoacrylate cement. Preliminary precession photographs indicated orthorhombic Laue symmetry and yielded preliminary cell dimensions. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam.[28] Automatic peak search and indexing procedures yielded a reduced primitive cell with a approximately equal to b. Careful inspection of the intensities of the reflections and determination of systematic absences indicated that the space group was orthorhombic and that the space group was $P2_12_12_1$ (No. 19). The final cell parameters and specific data collection parameters are given in Table III.

The 885 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards showed a monotonic isotropic decrease to 85% of the original intensity over the data collection period. The data were corrected for this decay. Inspection of the azimuthal scan data showed a variation I_{min}/I_{max} = 0.88 for the average curve. An absorption correction based on the measured shape and size of the crystal and a 10 × 10 × 8 Gaussian grid of internal points was applied to the data after solution of the structure, but before the final refinement cycles (T_{max} = 0.249, T_{min} = 0.188). Removal of systematically absent data left 839 unique data.

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(28) For a summary of the equipment and data reduction formulae used in this structure determination, see: Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5845.

Table IV. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re	0.21072 (3)	0.00484 (3)	0.11366 (2)	2.931 (6)
O1	0.2236 (7)	0.3807 (7)	0.1471 (4)	7.3 (2)
O2	0.5474 (7)	0.0860 (7)	0.0381 (4)	6.5 (2)
C1	0.0507 (9)	−0.016 (1)	0.0016 (5)	5.4 (2)
C2	−0.0575 (9)	0.0216 (9)	0.0652 (6)	5.9 (2)
C3	−0.057 (1)	−0.110 (1)	0.1156 (6)	5.7 (2)
C4	0.049 (1)	−0.2310 (9)	0.0874 (6)	5.4 (2)
C5	0.121 (1)	−0.172 (1)	0.0156 (6)	5.7 (2)
C6	0.176 (1)	0.029 (1)	0.2470 (5)	5.3 (2)
C7	0.213 (2)	−0.139 (2)	0.287 (1)	5.2 (4)[b]
C7′	0.288 (2)	−0.078 (2)	0.296 (1)	5.8 (4)[b]
C8	0.388 (2)	−0.178 (2)	0.261 (1)	6.0 (4)[b]
C8′	0.320 (2)	−0.236 (2)	0.251 (1)	5.6 (4)[b]
C9	0.394 (1)	−0.1732 (9)	0.1704 (6)	4.8 (2)
C10	0.2188 (8)	0.235 (1)	0.1334 (5)	4.5 (2)
C11	0.4174 (9)	0.0543 (8)	0.0669 (5)	3.9 (2)

[a] Anisotropically refined atoms are given in the form of an isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$. [b] Atoms refined with isotropic thermal parameters. These atoms also have occupancies of 0.5.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. The enantiomorphic structure was tested following the application of the absorption correction and gave a significant increase in all residuals.

The refinement of C7 and C8 with anisotropic thermal parameters led to bond distances and angles that were not realistic and to thermal parameters that were extreme. Therefore an attempt to fit the electron density with a disordered model was undertaken. Refinement of the disordered atoms with isotropic thermal parameters and all other atoms as before led to residuals that were identical (with two fewer parameters) and yielded much better distances and angles. The assumption that all occupancy factors were equal to 0.5 is supported by the equivalence of the thermal parameters for the two sets of atoms. In a difference Fourier map calculated following refinement of this model, peaks corresponding to the expected positions of some of the hydrogen atoms were found. Hydrogens were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry (including the disordered hydrogens) but were not refined in least squares. They were assigned isotropic thermal parameters 1–2 Å^2 larger than the equivalent B_{iso} of the atom to which they were bonded. In the final cycles of least squares an extinction coefficient was included in the refinement. Its final value, 3.3×10^{-7}, corresponds to a 16% correction on F for the reflection with the largest intensity.

The final residuals for 126 variables refined against the 767 data for which $F^2 > 3\sigma F^2$ were R = 1.90%, wR = 2.34%, and GOF = 1.304. The R value for all 839 data was 2.36%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.02 during most of the refinement and adjusted to 0.03 for the final cycles. The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $(\sin\theta/\lambda$, $|F_0|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peaks in the final difference Fourier map had electron densities of 0.9 e$^-$/A^3 and were located near the rhenium atom. The positional parameters of the non-hydrogen atoms are given in Table IV. The thermal parameters of the non-hydrogen atoms, the positional and thermal parameters of the hydrogen atoms, and a listing of the values of F_0 and F_c will be published separately as supplementary material.

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Registry No. 1, 87145-50-4; 1-*α*-^{13}C, 93110-97-5; 1-*α*,*α*′-^{13}C, 93110-98-6; 1-d_4, 93110-96-4; CpRe(CO)$_3$, 12079-73-1; *cis*-CpRe(CO)$_2$Br$_2$, 57194-43-1; *trans*-CpRe(CO)$_2$Br$_2$, 57195-35-4; CpRe(CO)$_2$H$_2$, 78809-05-9; PPh$_3$, 603-35-0; CpRe(CO)$_2$PPh$_3$, 42766-75-6; PMe$_3$, 594-09-2; CpRe(CO)$_2$PMe$_3$, 84521-32-4; *trans*-CpRe(^{13}CO)$_2$Br$_2$, 93110-99-7; *trans*-CpRe(^{13}CO)$_2$H$_2$, 93111-00-3; 1,4-butanediiodide, 628-21-7; methylcyclopropane, 594-11-6; dimethyl acetylenedicarboxylate, 762-42-5; dimethylsuccinate-*2,2,3,3*-d_4, 30994-23-1; butane-1,4-diol-*2,2,3,3*-d_4, 38274-25-8; butane-1,4-ditosylate-*2,2,3,3*-d_4, 93085-35-9; 1,4-diiodobutane-*2,2,3,3*-d_4, 38274-26-9; succinic acid-*1,4*-$^{13}C_2$, 79864-95-2; dimethylsuccinate-*1,4*-$^{13}C_2$, 79341-56-3; 1,4-diiodobutane-*1,4*-$^{13}C_2$, 79864-97-4; (methyl-d_1)cyclopropane-*1,2,2*-d_3, 93085-33-7; (methyl-^{13}C)cyclopropane-*2,3*-$^{13}C_2$, 93085-34-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms, and calculated and observed structure factors from the X-ray diffraction study of 1 (7 pages). Published in the archival edition of the journal, available in some libraries. Ordering information is given on any current masthead page.