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Photolysis of (η^5-C_5Me_5)Re(CO)$_3$ with Alkenes. Synthesis of (η^5-C_5Me_5)Re(CO)$_2$(alkene) Complexes and C–H Activation To Give Allyl Hydrido Derivatives

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Ultraviolet photolysis of Cp*Re(CO)$_3$ or, in some cases, Cp*Re(CO)$_2$(N$_2$) (Cp* = η^5-C$_5$Me$_5$) in the presence of alkenes has been used to synthesize the alkene complexes Cp*Re(CO)$_2$(η^2-alkene) (**1**–**8**) (where alkene = ethene (**1**), propene (**2**), 2-pentene (**3**), 1-octene (**4**), 2-octene (**5**), cyclohexene (**6**), 4-methylcyclohexene (**7**), and cyclooctene (**8**)). The syntheses by various routes of Cp*Re(CO)$_2$(η^2-allene) (**9**), Cp*Re(CO)$_2$(η^2-diene) (**10**, **11**) (diene = 1,3-cyclohexadiene (**10**), 1,4-cyclohexadiene (**11**)), Cp*Re(CO)$_2$(1-methoxy-2-propene) (**2a**), Cp*Re(CO)$_2$(3-methoxycyclohexene) (**6a**), Cp*Re(CO)(PMe$_3$)(propene) (**12**), and Cp*Re(CO)(η^4-1,4-cyclohexadiene) (**13**) are also described. The ^{1}H NMR spectra and the mass spectral fragmentation patterns for these alkene complexes are discussed in detail. In the case of the allene complex **9**, variable-temperature ^{1}H NMR spectra have been measured and the barrier to allene rotation estimated at the coalescence temperature ($\Delta G^{\ddagger}_{223}$ = 9.6 ± 0.2 kcal mol^{-1}). The photolysis of Cp*Re(CO)$_3$ in the presence of propene or the photolysis of **2** itself also yields exo and endo isomers of the allyl hydrido complex Cp*Re(CO)(H)(η^3-C$_3$H$_5$) (**14**) that have been separated by chromatography and fully characterized by analysis, X-ray crystallography, and ^{1}H NMR and mass spectrometry. ^{1}H NMR NOE difference spectra show that the exo and endo structures are retained in solution. The *exo*-**14** isomer converts to the thermodynamically more stable *endo*-**14** in solution in the dark, with an activation barrier E_a = 28.9 ± 3.2 kcal mol^{-1}; however, conversion of *endo*-**14** to *exo*-**14** occurs under UV irradiation. Related allyl hydrido compounds (**15**,**16**) have been observed in the photolysis of Cp*Re(CO)$_3$ with 2-pentene and 1-octene. The bromo complex Cp*Re(CO)(Br)(η^3-C$_3$H$_5$) (**17**) has been synthesized for a comparison with **14** and was isolated exclusively as the endo isomer. The prolonged photolysis of Cp*Re(CO)$_3$ with cyclohexene resulted in no observable cyclohexenyl hydrido product but instead the formation of the dehydrogenation products **10** and **13**.

Introduction

Manganese alkene complexes of the type CpMn(CO)$_2$(alkene) (Cp = C$_5$H$_5$) have been well studied[1-10] including restricted rotation of the alkene,[4] kinetics of substitution,[5] and several crystal structure determinations.[1] The corresponding rhenium complexes CpRe(CO)$_2$(alkene) are far less well established. The review by Caulton[1a] mentions only CpRe(CO)$_2$(η^2-c-C$_5$H$_8$). Although this complex was synthesized earlier, it was properly formulated by Green and Wilkinson, who also described its conversion to CpRe(CO)$_2$(η^2-c-C$_5$H$_8$) by hydrogenation.[11-13] More recently, Perutz has studied its photochemistry.[14] The review by Boag and Kaesz[15] lists these complexes and the binuclear complex Cp(CO)$_2$Re(η-CH$_2$C(Ph)C(Ph)=C=Re(CO)$_2$Cp)[16] but surprisingly mentions no others. Recently, Casey has described a Re–Pt bimetallic complex that reacts stoichiometrically with alkynes to produce CpRe(CO)$_2$(alkene) complexes in high yield for ethene, propene, 2-butene, and stilbene, among others.[17] The cyclooctene complex was synthesized by Butler from CpRe(CO)$_2$(THF) and cyclooctene[18] and the 1-pentene complex has been reported to be formed in ligand-exchange processes.[19]

In the case of the pentamethylcyclopentadienyl (Cp*) analogues of these manganese and rhenium alkene complexes, the literature is fragmentary. The manganese complexes Cp*Mn(CO)$_2$(alkene) have been synthesized for ethene, dibromoethene, and cyclooctene;[10,20,21] there is also a report of electron-transfer complexes with tetracyanoethene.[22] However, as far as we can determine, the only previously reported rhenium analogue Cp*Re(CO)$_2$(alkene) is the mesityl oxide complex.[23] Here, we describe the synthesis and properties of a series of complexes Cp*Re(CO)$_2$(alkene) that are accessible from the photolysis of Cp*Re(CO)$_3$ in the presence of an alkene. In some instances, additional products are observed that result from intramolecular C–H activation of an allylic C–H bond in the alkene complex with formation of an allyl hydrido complex. No comparable C–H activation has been observed, as far as we can ascertain, in the reported cases

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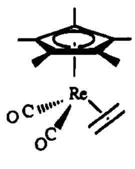
where either CpMn(CO)$_3$, (C_5H_4Me)Mn(CO)$_3$, or (C_5Me_5)Mn(CO)$_3$ has been photolyzed in the presence of an alkene.[5,7,20] However, we are informed that C–H activation is known to occur when mixtures of propene and CpRe(CO)$_3$ are irradiated.[24] Part of this work has been the subject of a communication.[25a]

Experimental Section

General Procedures. All manipulations were carried out under dry N_2 in Schlenk apparatus connected to a switchable double manifold providing a purified nitrogen supply and a low vacuum. Solvents were purified by standard methods and were distilled under nitrogen and used immediately. Reaction yields are based on the rhenium reagent used, unless otherwise specified. Irradiations were carried out with a water-jacketed 200-W Hanovia Model 654A-0360 high-pressure mercury-vapor lamp. The radiation was otherwise unfiltered. The sample was in either a quartz or, where specified, Pyrex tube adjacent to the lamp or else was in a quartz immersion-type reactor and was continuously purged with nitrogen or an appropriate gas. IR spectra were recorded on a Perkin-Elmer 983G instrument for solutions in CaF_2 cells. ^{1}H NMR and NOE spectra were recorded in the NMR Services of SFU by Mrs. M. Tracey on a Bruker WM-400 instrument operating at 400.13 MHz. Electron-impact mass spectra were obtained by Mr. G. Owen on a Hewlett-Packard Model 5985 GC-MS instrument operating at 70 eV. Masses are quoted for the ^{187}Re and ^{79}Br isotopes. Microanalyses were performed by Mr. M. K. Yang of the SFU Microanalytical Laboratory.

Gas or liquid alkene, decacarbonyldirhenium (Strem Chemicals), and trimethylphosphine (Alfa) were used directly as purchased. Cp*Re(CO)$_3$ was synthesized by the method used by Gladysz.[26] The dinitrogen complexes Cp*Re(CO)$_2$(N_2) and Cp*Re(CO)(N_2)(PMe$_3$) were synthesized as described previously.[27] Bromoform was dried over anhydrous calcium chloride and then passed through a neutral-alumina column to remove final traces of water, collected under N_2, and used immediately. The complex [Cp*Re(CO)$_2$(η^3-C_3H_5)][BF$_4$] was synthesized from the reaction of the propene complex 2 with [Ph$_3$C][BF$_4$].[28] The corresponding complex [Cp*Re(CO)$_2$(η^3-C_6H_9)][BF$_4$] was synthesized from the cyclohexene complex 6 and [Ph$_3$C][BF$_4$].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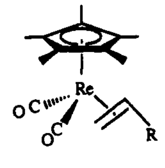
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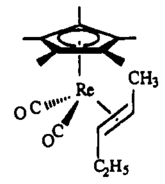
(b) CH_2OCH_3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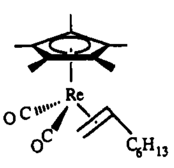
trans & cis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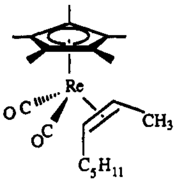
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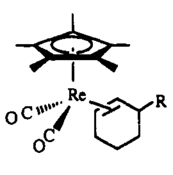
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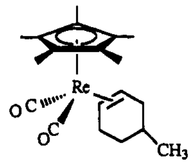
(b) OMe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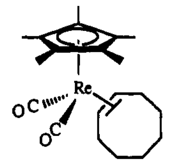
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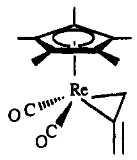
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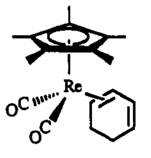
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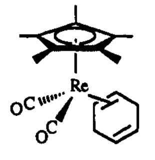
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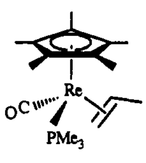
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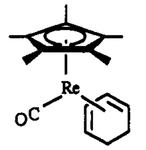
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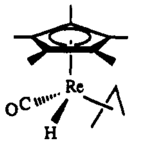
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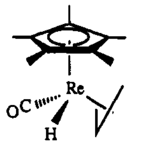
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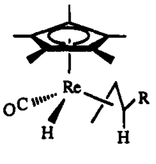
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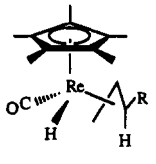
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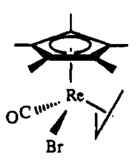
17 *endo*

Preparation of Complexes. Cp*Re(CO)$_2$(η^2-C_2H_4) (1). Method 1. A solution of Cp*Re(CO)$_3$ (100 mg, 0.246 mmol) in freshly distilled hexane (50 mL) was saturated with dry ethene gas for 15 min and then irradiated in quartz at 0 °C for 20 min under a continuous ethene purge. The IR spectrum of the resulting brown solution exhibited ν(CO) bands at 1964 and 1894 cm^{-1} assignable to complex 1 and indicated some residual tricarbonyl. The solution was filtered through Celite to remove solid decomposition products, reduced in volume, and then chromatographed on an acidic alumina column, eluting with hexane. The residual Cp*Re(CO)$_3$ eluted first and then complex 1, which was obtained as a white solid, mp 126–127 °C. Yield: 28 mg (0.086 mmol, 28.0%).

Method 2. A solution of Cp*Re(CO)$_2$(N_2) (70 mg, 0.172 mmol) was saturated with ethene as above and irradiated in quartz under ethene at 0 °C for 20 min. Workup as above gave complex 1 (35 mg, 0.086 mmol, 50%).

Photolysis of Cp*Re(CO)$_3$ with Propene. A solution of Cp*Re(CO)$_3$ (800 mg, 1.907 mmol) in about 100 mL of freshly distilled hexane was irradiated in a quartz immersion reactor at 0 °C for 1 h with a propene purge. This resulted in an IR spectrum having strong absorptions at 1961 and 1890 cm^{-1} for the propene complex 2 and weaker ones at 1904 and 1912 cm^{-1} for the allylhydrido complexes *exo*-14 and *endo*-14, respectively, plus residual absorptions from Cp*Re(CO)$_3$. Further irradiation for

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another 30 min intensified the absorptions from *exo*-**14** and *endo*-**14** relative to **2**. After removal of the solvent under vacuum at room temperature, the residual brown solid was redissolved in hexane and transferred to a neutral-alumina column (25 cm × 1 cm) and eluted with hexane. Four fractions were eluted and isolated, in the order Cp*Re(CO)$_3$, complex **2**, complex *endo*-**14**, and finally *exo*-**14**. Complex **2** was recrystallized at –78 °C from hexane; *exo*-**14** and *endo*-**14** were separately recrystallized at –78 °C from hexane–diethyl ether (1:2). Yields: **2** white microcrystals, mp 109–110 °C, 310 mg (0.738 mmol, 37.5%); *exo*-**14** white microcrystals, 105 mg (0.268 mmol, 13.6%); *endo*-**14** white microcrystals, 49 mg (0.125 mmol, 6.3%).

Photolysis of Cp*Re(CO)$_3$ with 2-Pentene. A solution of Cp*Re(CO)$_3$ (100 mg, 0.246 mmol) and 3 mL of 2-pentene (a mixture of cis and trans isomers, ratio [cis]:[trans] ≈ 1:3.5 calculated by GC) in about 60 mL of hexane was irradiated in quartz for 30 min at 0 °C. At this time the IR showed ν(CO) absorptions at 1955 and 1884 cm^{-1} assignable to **3** (which were slightly less intense than the absorptions from unreacted tricarbonyl) and there was a significant amount of solid decomposition product. A weak band at 1891 cm^{-1} was also present, indicating one or more allyl hydrido complexes. Chromatography on a neutral-alumina column gave complex **3** and ca. 8 mg of Cp*Re(CO)(H)(η^3-C$_5$H$_9$) (**15**) as white solids. Complex **3** was shown by ^{1}H NMR spectroscopy to be a mixture of *cis*-**3** and *trans*-**3** isomers (ratio = *cis*-**3**:*trans*-**3** 1:1.7). Yield: **3** 35 mg (0.078 mmol, 31.7%).

A larger scale synthesis with a longer irradiation time was employed to obtain a greater yield of the allyl hydrido complex **15**. Cp*Re(CO)$_3$ (200 mg, 0.493 mmol) and 4 mL of 2-pentene (a similar mixture of cis and trans isomers) were irradiated in hexane in a quartz tube for 60 min at 0 °C. Following chromatography on a neutral-alumina column with hexane as eluant, the allyl hydrido complex **15** was separated from the 2-pentene complex **3** and the residual Cp*Re(CO)$_3$ as above and was isolated as a white solid. Yields: **15** 45 mg (0.107 mmol, 21.7%); **3** 58.9 mg (0.132 mmol, 26.7%). Complex **15** was identified as a mixture of isomers (by NMR spectroscopy) that could not be separated further and decomposed in a few days. ^{1}H NMR (hydride region): δ –8.98 (weak), –9.32 (strong), –9.45 (medium) (exo isomers); δ –11.58 (medium), –11.68 (v weak) (endo isomers).

Photolysis of Cp*Re(CO)$_3$ with 1-Octene. Cp*Re(CO)$_3$ (100 mg, 0.246 mmol) and 1-octene (3 mL) were irradiated at 0 °C in hexane (50 mL) for 30 min. Chromatography yielded complex **4**, 27 mg (0.055 mmol, 22.4%), and the octenyl hydrido complex Cp*Re(CO)(H)(η^3-C$_8$H$_{15}$) (**16**), 8 mg (0.017 mmol, 7.0%).

Cp*Re(CO)$_2$(η^2-*cis*-2-C$_8$H$_{16}$) (5). A solution of [Cp*Re(CO)$_2$(η^3-C$_8$H$_{15}$)][BF$_4$] (10 mg, 0.017 mmol) in 5 mL of THF was vigorously stirred, while a solution of NaBH$_4$ (1 mg, 0.026 mmol) in 1 mL of water was added dropwise at room temperature. After 12 h of stirring, the solution was dried under vacuum; then the residual solid was washed with hexane (3 × 5 mL). The hexane solution was filtered through a short Celite column and concentrated to about 5 mL by rotary evaporation. The hexane solution was checked by IR (ν(CO)), showing two sets of absorptions at 1960 and 1888 cm^{-1} for the 1-octene complex (**4**) and at 1955 and 1883 cm^{-1} for the 2-octene complex (**5**) in approximate 1:1 ratio. Following chromatography on an acidic alumina column, eluting with hexane, complexes **4** and **5** were isolated.

Photolysis of Cp*Re(CO)$_3$ with Cyclohexene. A solution of Cp*Re(CO)$_3$ (900 mg, 2.21 mmol) and about 5 mL of cyclohexene in 250 mL of hexane was irradiated in a quartz immersion reactor at 0 °C for 1 h. The resulting brown solution showed IR absorptions at 1952 and 1881 cm^{-1} assignable to **6** and a band at 1891 cm^{-1} that intensified relative to the others on continued irradiation. The solution was filtered through a short Celite column to remove solid decomposition products, reduced in volume under vacuum, and then chromatographed on a neutral-alumina column (25 cm × 1 cm) with hexane as eluant. Four fractions were eluted and isolated. These were, in order, Cp*Re(CO)$_3$, complex **6** (ν(CO) 1952 and 1881 cm^{-1}), complex **10** (the η^2-1,3-cyclohexadiene complex) (ν(CO) 1960 and 1891 cm^{-1}), and as the final fraction, complex **13** (the η^4-1,3-cyclohexadiene complex) (ν(CO) 1891 cm^{-1}). Yields: **6** 117 mg (0.254 mmol, 11.4%); **10** 93 mg (0.203 mmol, 9.2%); **13** ca. 5 mg.

Photolysis of Cp*Re(CO)$_3$ and 4-Methylcyclohexene. Irradiation of a solution of Cp*Re(CO)$_3$ (100 mg, 0.246 mmol) with 4-methylcyclohexene (3 mL) in hexane (50 mL) for 90 min resulted in an IR spectrum containing ν(CO) bands at 1952 and 1881 cm^{-1} for complex **7** that were slightly more intense than those of residual tricarbonyl. An absorption at 1890 cm^{-1} was also present, roughly equal in intensity to the absorptions of **7**. Following chromatography on a 25-cm column of neutral alumina, eluting with hexane, only complex **7** (49 mg, 0.103 mmol, 42%) and the tricarbonyl were recovered. Other products were apparently unstable and decomposed during the chromatography.

Photolysis of Cp*Re(CO)$_3$ and Cyclooctene. Complex **8** was prepared from Cp*Re(CO)$_3$ and cyclooctene by following the procedure used for **6**. Chromatography yielded complex **8**, 34 mg (0.070 mmol, 14.2%), mp 188–189 °C, and the known complex Cp$_2$Re$_2$(CO)$_5$, which was identified on the basis of the following spectroscopic properties: IR (hexane) (ν(CO)) 1971 (w), 1930 (s), 1901 (s), 1877 (w), 1714 (m); MS (EI) *m/z* 726 [M]$^+$; ^{1}H NMR (C$_6$D$_6$) δ 1.86 ppm (Cp*). These data are comparable with those reported by Hoyano and Graham.[29]

Cp*Re(CO)$_2$(η^2-C$_3$H$_4$) (9). Cp*Re(CO)$_3$ (90 mg, 0.222 mmol) was dissolved in about 100 mL of freshly distilled THF and irradiated at 0 °C with a nitrogen purge for 90 min. At this time, the IR spectrum showed that two new absorptions at 1893 and 1823 cm^{-1} for the THF complex Cp*Re(CO)$_2$(THF) were more intense relative to those of Cp*Re(CO)$_3$. The solution of Cp*Re(CO)$_2$(THF) in THF was then stirred vigorously (no irradiation) and allene gas was bubbled for 1 h until the two ν(CO) bands for Cp*Re(CO)$_2$(THF) disappeared. The solution was filtered through a short column (1.5 cm × 2 cm) of silica gel G60 and dried under vacuum. The residual brown solid was dissolved in hexane and chromatographed on a neutral-alumina column (30 cm × 1 cm) with hexane as an eluant. Following chromatography, the unreacted starting material Cp*Re(CO)$_3$ (18 mg, 0.044 mmol) was recovered, and complex **9** was isolated. Yield: 50 mg (0.120 mmol, 67.4%).

Cp*Re(CO)$_2$(η^2-1,3-C$_6$H$_8$) (10). Method 1. Complex **10** was isolated in 9.2% yield from the photochemical reaction of Cp*Re(CO)$_3$ with cyclohexene (see the above preparation of complex **6**) or was directly formed by photolysis of the cyclohexene complex **6**.

Method 2. A solution of Cp*Re(CO)$_2$(N$_2$) (175 mg, 0.431 mmol) and 1,3-cyclohexadiene (1 mL) in hexane (200 mL) was irradiated at 0 °C for 15 min, reduced in volume, and chromatographed on a neutral-alumina column. Elution with hexane removed the tricarbonyl complex Cp*Re(CO)$_3$ also formed, a small amount of unreacted Cp*Re(CO)$_2$(N$_2$), and then the pure complex **10**. Yield: 101 mg (0.220 mmol, 51.0%), mp 155–157 °C.

Cp*Re(CO)$_2$(η^2-1,4-C$_6$H$_8$) (11). This was synthesized by photolysis of Cp*Re(CO)$_2$(N$_2$) with 1,4-cyclohexadiene in a procedure similar to method 2 for complex **10**. Yield: 130 mg (0.284 mmol, 53.7%), mp 138–139 °C.

Cp*Re(CO)(PMe$_3$)(η^2-C$_3$H$_6$) (12). The dinitrogen complex Cp*Re(CO)(PMe$_3$)(N$_2$) (100 mg, 0.22 mmol) in hexane (60 mL) at 0 °C was purged with propene and irradiated in quartz for 20 min. The IR spectrum showed disappearance of the starting material and a strong ν(CO) band at 1845 cm^{-1} for **12**. Other weak ν(CO) absorptions were observed at 1923 and 1860 cm^{-1} (Cp*Re(CO)$_2$(PMe$_3$)), 1912 and 1904 cm^{-1} (*endo*- and *exo*-**14**), and 1961 and 1890 cm^{-1} (**2**). The solution was filtered through Celite, reduced in volume, and chromatographed on silica gel 60G. Elution with hexane removed first Cp*Re(CO)$_2$(PMe$_3$), second the propene complex **2**, third *exo*- and *endo*-**14**, and finally complex **12**. Yield of **12**: 37 mg (0.08 mmol, 36%), mp 93–94 °C.

Cp*Re(CO)(η^4-1,3-C$_6$H$_8$) (13). Complex **13** was isolated in small yield as a byproduct in the synthesis of the cyclohexene complex **6** described above. Complex **13** is not stable in solution in hexane even when stored under an atmosphere of N$_2$ in the freezer.

Cp*Re(CO)$_2$(η^2-C$_3$H$_5$OMe) (2a). A solution of [Cp*Re(CO)$_2$(η^3-C$_3$H$_5$)][BF$_4$][28] (30 mg, 0.059 mmol) in methanol (10 mL) was stirred under nitrogen at room temperature (IR: 2051, 1998 cm^{-1} ν(CO), endo isomer; 2035, 1979 cm^{-1} ν(CO) exo isomer). Solid NaOMe (4 mg, 0.07 mmol) was added, and after 2 h, the spectrum showed ν(CO) 1958 and 1883 cm^{-1} for the product. Solvent was removed under vacuum, and the residual white solid was extracted with 3 × 15 mL portions of hexane. The hexane extract was filtered through a short column of Celite. Removal of hexane gave a white solid. Yield 16 mg (0.036 mmol, 60%).

$Cp^*Re(CO)_2(\eta^3\text{-}C_6H_9OMe)$ (6a). A solution of $[Cp^*Re(CO)_2(\eta^3\text{-}C_6H_9)][BF_4]$ (30 mg, 0.055 mmol) in methanol (10 mL) was stirred at −78 °C, and solid NaOMe (4 mg, 0.07 mmol) was added. After 24 h, the IR spectrum showed the reaction to be virtually complete by the disappearance of ν(CO) bands at 2024 and 1962 cm^{-1} for the starting material and the appearance of ν(CO) bands at 1946 and 1873 cm^{-1} for the product. Removal of the solvent under vacuum gave a white solid, which was extracted with 3 × 15 mL portions of hexane. The extract was filtered through a short column of Celite; then removal of the hexane gave the product. Yield: 16 mg (0.033 mmol, 60%). At room temperature, the reaction resulted in the formation of both **6a** and the η^2-cyclohexadiene complex (**10**).

$Cp^*Re(CO)(Br)(\eta^3\text{-}C_3H_5)$ (17). The allyl hydrido complex **14** (42 mg, 0.107 mmol; a mixture of exo and endo isomers, ratio exo:endo = 3:1) was dissolved in bromoform (10 mL) and the solution stirred overnight. Following chromatography on a neutral-alumina column (10 × 1 cm) with hexane as eluant, complex **17** was isolated in 63.6% yield.

Photolysis of 2. (a) Irradiation of a hexane (10 mL) solution of **2** (10 mg, 0.024 mmol) under a nitrogen purge at 0 °C for 30 min in a Pyrex tube resulted in an IR spectrum (ν(CO), hexane) having strong absorptions at 2013 and 1922 cm^{-1} for $Cp^*Re(CO)_3$ and other absorptions at 1904 and 1912 cm^{-1} for *exo*-**14** and *endo*-**14** respectively, plus residual absorptions at 1961 and 1890 cm^{-1} for **2**. (b) Irradiation of **2** (10 mg, 0.024 mmol) in hexane was conducted at 0 °C in a quartz tube, under a purge of propene. The IR spectrum showed only two new ν(CO) bands at 1904 and 1912 cm^{-1} for *exo*-**14** and *endo*-**14**, respectively. (c) A hexane solution of **2** (10 mg, 0.024 mmol) was irradiated for 30 min under a CO purge at 0 °C in a Pyrex tube. The IR spectrum showed the formation of bands at 2013 and 1922 cm^{-1} for $Cp^*Re(CO)_3$. (d) Irradiation of a 10-mL hexane solution of **2** (10 mg, 0.024 mmol) in a Pyrex tube at 0 °C in the presence of added PMe_3 gave an IR (ν(CO)) spectrum with bands at 1923 and 1860 cm^{-1} for $Cp^*Re(CO)_2(PMe_3)$ and weaker ones at 1904 and 1912 cm^{-1} for *exo*-**14** and *endo*-**14**, respectively, plus residual absorptions at 1961 and 1890 cm^{-1} for the unreacted **2**. (e) Photolysis of **2** (5 mg, 0.012 mmol) in cyclohexane-d_{12} (0.7 mL) in a NMR tube for 30 min gave a ^1H NMR spectrum showing δ 5.75 (m, 1 H), 4.95 (d, 1 H, J = 16.5 Hz), and 4.87 (d, 1 H, J = 8.7 Hz) assignable to the three vinyl protons of propene, δ 1.65 (d, 3 H, J = 7.0 Hz) assignable to the methyl protons of propene, and resonances for *exo*-**14** and *endo*-**14**.

Photolysis of *exo*-14 and *endo*-14. (a) A mixture of **2** and **14** (endo and exo) (12 mg) in hexane (10 mL) was irradiated at 0 °C under 1 atm of CO and monitored by IR. The IR (ν(CO)) spectra showed that the bands of complex **14** (exo, endo) rapidly disappeared in 10 min followed more slowly by disappearance of those of **2** in 20 min. (b) Irradiation of *exo*/*endo*-**14** (7 mg, 0.018 mmol) in cyclohexane-d_{12} (0.7 mL) in a NMR tube for 30 min gave a ^1H NMR spectrum that exhibited the production of free propene [δ 5.75 (m, 1 H), 4.95 (d, 1 H), 4.87 (d, 1 H), 1.65 (d, 3 H)] and the formation of **2** as the major product accompanied by a significant amount of the starting material. The IR spectrum (ν(CO), hexane) clearly showed five bands at 1971 (w), 1930 (s), 1901 (s), 1877 (w), and 1714 (m) cm^{-1} assignable to the known[29] binuclear complex $Cp_2^*Re_2(CO)_5$ and other bands at 2013 and 1922 cm^{-1} (for $Cp^*Re(CO)_3$) and at 1961 at 1890 cm^{-1} (for **2**). The binuclear complex $Cp_2^*Re_2(CO)_5$ was further confirmed by MS (EI) (molecular ion peak at m/z 726 with an expected isotopic abundance pattern).

Irradiation of *endo*-14. A pure sample of *endo*-**14** (5 mg, 0.013 mmol) in hexane (3 mL) was irradiated for 5 min in a Pyrex tube at 0 °C or room temperature. The IR (ν(CO)) spectrum showed two strong absorptions at 1904 and 1912 cm^{-1} for *exo*-**14** and *endo*-**14**, respectively, with an intensity ratio of approximately 2:1, and other very weak bands from $Cp^*Re(CO)_3$ (2013 and 1922 cm^{-1}) and **2** (1961 and 1890 cm^{-1}). Removal of hexane and dissolution of the solid residue in C_6D_6 gave a ^1H NMR spectrum showing two hydride chemical shifts at δ −9.2 (exo) and −11.7 (endo) with an integral ratio of exo:endo ≈ 2.5:1.

Thermolysis of 14. (a) A benzene (10 mL) solution of *exo*/*endo*-**14** (10 mg, 0.026 mmol) was heated under nitrogen in an oil bath at 75–80 °C for 24 h. The IR (ν(CO)) showed absorptions at 1961 and 1890 cm^{-1} for **2**, 2013 and 1922 cm^{-1} for $Cp^*Re(CO)_3$, and five bands at 1971 (w), 1930 (s), 1901 (s), 1877 (w), and 1714 (m) cm^{-1} assignable[29] to $Cp_2^*Re_2(CO)_5$. Furthermore, the ^1H NMR spectrum showed resonances at δ −9.2 and −11.7 assignable to the hydrides of *exo*-**14** and *endo*-**14**, respectively, in a 0.28:1 ratio. (b) A hexane solution of *exo*/*endo*-**14** (12 mg, 0.031 mmol) and three drops of PMe_3 in a sealed tube was heated in an oil bath at 60–65 °C for 4 h. The IR spectrum did not show any change.

Thermal Conformational Conversion of *exo*-14 to *endo*-14. A pure sample of *exo*-**14** (7 mg, 0.018 mmol) and 0.7 mL of C_6D_6 were added to a NMR tube under N_2. The tube was flame-sealed, wrapped with aluminum foil, kept in a constant-temperature bath at different temperatures for varying periods of time, and checked by ^1H NMR spectroscopy at 400 MHz. The ratio of exo to endo was measured by integration of the Re–H resonances of each isomer.

Kinetics of the Conversion of *exo*-14 to *endo*-14. Four NMR samples each of a mixture of *exo*-**14** and *endo*-**14** (7 mg, 0.018 mmol) were prepared in C_6D_6 (0.7 mL) under nitrogen. Then, the four NMR sample tubes were wrapped with aluminum foil and kept at four different temperatures: 25, 30, 35, and 40 °C, respectively. The ratios of the Re–H resonances of *endo*-**14** and *exo*-**14** with time were monitored by 100-MHz ^1H NMR spectroscopy and were used to determine the rate constants k_1 at different temperatures.

Reduction of $Cp^*Re(CO)(Br)(\eta^3\text{-}C_3H_5)$ (17). A solution of *endo*-**17** (10 mg, 0.021 mmol) in about 10 mL of freshly distilled ether was stirred at room temperature. Five drops of lithium triethylborohydride were added dropwise to the ether solution, and stirring was continued for 2 h. The solution was dried under vacuum to give a white solid residue, which was washed with hexane (10 × 3 mL). The hexane washings were collected and filtered through a short Celite column (1 cm × 1 cm). Removal of hexane gave a white solid, which was identified by IR and ^1H NMR spectroscopy. IR (ν(CO)): 1912 (*endo*-**14**), 1904 cm^{-1} (*exo*-**14**). ^1H NMR (C_6D_6): δ −11.7, −9.2 ppm (Re–H of *endo*-**14** and *exo*-**14**, respectively) with an integral ratio of exo:endo ≈ 0.26.

Photolysis of $Cp^*Re(CO)_2(PMe_3)$ with Propene. Irradiation of $Cp^*Re(CO)_2(PMe_3)$ (30 mg, 0.066 mmol) in hexane (30 mL) at 0 °C with a propene purge for 30 min resulted in an IR spectrum having a strong absorption at 1845 cm^{-1} for $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (**12**), weaker bands for *exo*-**14** and *endo*-**14** (1904 and 1912 cm^{-1}) and **2** (1961 and 1890 cm^{-1}), and a weakest band for $Cp^*Re(CO)(H)(\eta^2\text{-}CH_2PMe_2)$ (1878 cm^{-1}). The hexane solution was filtered through a short Celite column and dried under vacuum. The residual solid was dissolved in C_6D_6 (0.7 mL), and the ^1H NMR spectrum showed a major hydride resonance at δ −9.23 (*exo*-**14**), a minor hydride resonance at δ −11.66 (*endo*-**14**), and a weak hydride resonance at δ −9.92 for $Cp^*Re(CO)(H)(CH_2PMe_2)$.

Photolysis of $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (12). Irradiation of a hexane (25 mL) solution of **12** (15 mg, 0.032 mmol) was continued for 40 min at 0 °C. A small amount of brown solid was formed, and the solution IR (ν(CO)) spectrum showed a strong absorption from the starting material **12** (1845 cm^{-1}), weaker bands for *exo*/*endo*-**14** (1904 and 1912 cm^{-1}) and **2** (1961 and 1890 cm^{-1}), and two weakest bands for $Cp^*Re(CO)_2(PMe_3)$ (1923 and 1860 cm^{-1}). Chromatography on an alumina column (7 × 1 cm) with hexane as an eluant gave unreacted **12** and a mixture of **2** and *exo*/*endo*-**14**.

Results and Discussion

(a) Alkene Complexes. (i) Synthesis. The (pentamethylcyclopentadienyl)rhenium alkene complexes of the general formula $Cp^*Re(CO)_2(\eta^2\text{-alkene})$ (alkene = ethene) (**1**), propene (**2**), 2-pentene (**3**), 1-octene (**4**), *cis*-2-octene (**5**), cyclohexene (**6**), 4-methylcyclohexene (**7**), cyclooctene (**8**), allene (**9**), 1,3-cyclohexadiene (**10**), and 1,4-cyclohexadiene (**11**)) and the trimethylphosphine propene complex $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (**12**) have been prepared by five different methods. (i) Irradiation of the

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[29] Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* 1982, 27.

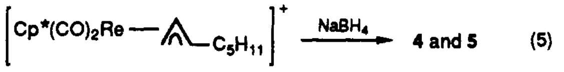
tricarbonyl complex $Cp^*Re(CO)_3$ and the corresponding alkene in hexane yielded complexes **1**–**4** and **6**–**8** and C–H activation products were also observed in most cases (eq 1). (ii) Irradiation of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ (or $Cp^*Re(CO)(PMe_3)(N_2)$) and the appropriate diene (or propene) in hexane gave complexes **10** and **11** (or the trimethylphosphine propene complex (**12**) (eqs 2 and 3). (iii) UV irradiation of $Cp^*Re(CO)_3$ in tetrahydrofuran (THF) yielded the THF complex, which was then reacted with allene at room temperature without further irradiation to give the η^2-allene complex **9** (eq 4). (iv) Nucleophilic addition of H^- or MeO^- to the η^3-allylalkane cationic complex produced the related η^2-alkene complexes **2a**, **4**, **5**, or **6a** (eq 5 or 6).

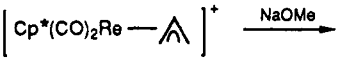
$$Cp^*Re(CO)_3 \xrightarrow{h\nu,\ \text{alkene}} Cp^*Re(CO)_2(\eta^2\text{-alkene}) \quad (1)$$

$$Cp^*Re(CO)_2(N_2) \xrightarrow{h\nu,\ \text{diene}} Cp^*Re(CO)_2(\eta^2\text{-diene}) \quad (2)$$

$$Cp^*Re(CO)(PMe_3)(N_2) \xrightarrow{h\nu,\ \text{propene}} \underset{\mathbf{12}}{Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)} \quad (3)$$

$$Cp^*Re(CO)_3 \xrightarrow{h\nu,\ \text{THF}} Cp^*Re(CO)_2(THF) \xrightarrow{CH_2{:}C{:}CH_2} \underset{\mathbf{9}}{Cp^*Re(CO)_2(\eta^2\text{-}C_3H_4)} \quad (4)$$





$$Cp^*Re(CO)_2(\eta^2\text{-}CH_2{=}CHCH_2OMe) \quad (6)$$

2a

The reaction with $Cp^*Re(CO)_2(THF)$ (eq 4) offers the mildest procedure for the synthesis of an alkene complex from the alkene, and we have used this method for the allene complex **9** because of the instability of allene on irradiation. However, in general the direct irradiation method has been employed (eq 1) so that results may be compared with earlier work where this was used successfully for a variety of dicarbonyl(alkene)manganese complexes with C_5H_5, C_5H_4Me, or C_5Me_5 coligands.[5,7,20] The diene complexes **10** and **11** were synthesized by irradiation of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ with the respective diene (eq 2) since the shorter irradiation times available with the more photolabile dinitrogen ligand[30] minimized photodecomposition of the diene. Interestingly, the η^2-diene complex **10** and the η^4-1,3-cyclohexadiene complex **13** were both isolated from the photochemical reaction of $Cp^*Re(CO)_3$ with cyclohexene in hexane. The complex $Cp^*Re(CO)(PMe_3)$(propene) (**12**) was synthesized by the photolysis of $Cp^*Re(CO)(PMe_3)(N_2)$ in hexane in the presence of propene (eq 3). Both the η^2-1-octene (**4**) and the η^2-*cis*-2-octene complex **5** were produced by the nucleophilic reaction of the η^3-octenyl cationic complex with sodium borohydride (eq 5).

In general, the reactions were monitored by IR spectroscopy and were stopped when the IR bands of the desired product reached maximum intensity. In all the cases (except in the case of complex **12**, which was chromatographed on silica gel (60 G)), the pure alkene complex was separated from the mixture with residual $Cp^*Re(CO)_3$ by chromatography on an alumina column. The new η^2-alkene rhenium complexes **1**–**12** were obtained as white microcrystalline solids that are stable in a pure state. The η^4-1,3-cyclohexadiene complex **13** was unstable and decomposed slowly during several hours.

A comparison of the photolytic reactions of ethene with $Cp^*Re(CO)_3$ and $Cp^*Re(CO)_2(N_2)$ showed that the dinitrogen complex was much more efficient. The IR spectrum indicated complete conversion to the ethene complex **1** (with also a little of the tricarbonyl) after 20 min of photolysis of $Cp^*Re(CO)_2(N_2)$ with ethene, whereas there was less than 50% conversion of $Cp^*Re(CO)_3$ to the ethene complex in this time (and indeed it took more than 1 h for the IR absorptions of **1** to become more intense than those of the tricarbonyl). No evidence of any further product was obtained. Bergman has reported the formation of a vinyl hydrido complex in the low-temperature photochemical reaction of ethene with the related rhenium complex $CpRe(PMe_3)_3$.[31] We observed no formation of a corresponding vinyl hydrido complex $Cp^*Re(CO)_2(H)(CHCH_3)$[32] at room temperature and did not investigate lower temperatures.

In the case of propene, further products were formed in addition to the propene complex **2**, and the ν(CO) absorptions at 1904 and 1912 cm^{-1} of these products intensified relative to the ν(CO) absorptions at 1890 and 1961 cm^{-1} for **2** as irradiation was continued. These additional products are the exo and endo isomers of the allylhydrido complex $Cp^*Re(CO)(H)(\eta^3\text{-}C_3H_5)$ (**14**), resulting from C–H activation of the allylic C–H bond of the coordinated propene in **2** with the loss of one CO group,[25] and are discussed below. A mixture of *cis*- and *trans*-2-pentene resulted in rhenium complexes *cis*-**3** and *trans*-**3** that were not separable by column chromatography but were identified to be present in a ca. 1:1.7 ratio by ^1H NMR spectroscopy. A further product was the 2-penten-1-yl hydrido complex $Cp^*Re(CO)(H)(\eta^3\text{-}C_5H_9)$ (**15**) and its isomers. Similarly, irradiation of 1-octene resulted in both the 1-octene complex **4** and a single isomer of the 2-octene-1-yl hydrido complex $Cp^*Re(CO)(H)(\eta^3\text{-}C_8H_{15})$ (**16**). Complex **4** was independently synthesized along with the *cis*-2-octene isomer **5** by the nucleophilic attack of $NaBH_4$ on the cationic 2-octen-1-yl complex $[Cp^*Re(CO)_2(\eta^3\text{-}C_8H_{15})][BF_4]$ (eq 5).

Irradiation of cyclohexene and $Cp^*Re(CO)_3$ produced two products in addition to the cyclohexene complex **6**, but NMR spectroscopy showed that neither of these contained hydride and therefore could not be a cyclohexenyl hydrido complex. These products instead were characterized fully by IR, NMR, and mass spectroscopy as the η^2-1,3-cyclohexadiene complex **10** and the η^4-1,3-cyclohexadiene carbonyl complex $Cp^*Re(CO)(\eta^4\text{-}C_6H_8)$ (**13**). Thus, in the case of this cyclic alkene, the results indicate that the cyclohexene complex **6** undergoes a dehydrogenation reaction on irradiation possibly through the participation of an unobserved cyclohexenyl hydrido complex.

The 1,3-cyclohexadiene (**10**) and 1,4-cyclohexadiene (**11**) complexes were synthesized quickly and in good yield by photolysis of the dinitrogen complex $Cp^*Re(CO)_2(N_2)$ in the presence of the diene. For chromatography, a neutral-alumina column was used, and this is especially important for isolation of **11**, as this complex easily isomerized to **10** on an acidic alumina column or in the presence of

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[30] Klahn-Oliva, A. H.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107. Aramini, J. M.; Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *J. Organomet. Chem.* **1990**, *385*, 73.

[31] (a) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (b) Bergman, R. G.; Wenzel, T. T. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

[32] Although we know of no (η^1-vinyl)rhenium complex of the type $(C_5Me_5)Re(CO)_2(H)(\eta^1\text{-}CHCH_2)$, a closely related bromo vinyl compound $(C_5Me_5)Re(CO)_2(Br)(CHCHBr)$ has been reported in ref 10b.

Table I. Analytical, Infrared, and Mass Spectral Data for Alkene and Allyl Complexes 1–17

			MS, m/z		analysis[b]	
complex	L	IR(hexane)[a] ν(CO), cm^{-1}	M$^+$	base	% C	% H
		$Cp^*Re(CO)_2L$				
1	ethene	1964 (vs), 1894 (vs)	406	348	41.92 (41.50)	4.98 (4.69)
2	propene	1961 (vs), 1890 (vs)	420	348	42.80 (42.94)	4.84 (5.05)
2a	3-methoxypropene	1964 (vs), 1893 (vs)	450	348	43.10 (42.75)	5.11 (5.16)
3	2-pentene	1955 (vs), 1884 (vs)	448	348	45.58 (45.62)	5.77 (5.63)
4	1-octene	1960 (vs), 1888 (vs)	490	378	49.08 (49.06)	6.51 (6.38)
5	*cis*-2-octene	1955 (vs), 1883 (vs)	490	348	49.27 (49.06)	6.08 (6.38)
6	cyclohexene	1952 (vs), 1881 (vs)	460	348	46.90 (47.04)	5.68 (5.48)
6a	3-methoxycyclohexene	1954 (vs), 1883 (vs)	490	400	46.80 (46.61)	5.51 (5.56)
7	4-methylcyclohexene	1952 (vs), 1881 (vs)	474	378	48.11 (48.18)	5.90 (5.75)
8	cyclooctene	1955 (vs), 1885 (vs)	488	378	49.15 (49.26)	6.00 (5.99)
9	allene	1978 (vs), 1910 (vs)	418	360	43.01 (43.15)	4.80 (4.59)
10	η^2-1,3-cyclohexadiene	1960 (vs), 1891 (vs)	458	400	47.40 (47.25)	5.07 (5.07)
11	η^2-1,4-cyclohexadiene	1957 (vs), 1886 (vs)	458	348	47.50 (47.25)	5.05 (5.07)
		$Cp^*Re(CO)(PMe_3)L$				
12	propene	1846 (s)	468	426	43.58 (43.67)	6.46 (6.48)
		$Cp^*Re(CO)L$				
13	η^4-1,3-cyclohexadiene	1891 (s)	430	400	*c*	
		$Cp^*Re(CO)(H)(L)$				
exo-14	η^3-C_3H_5	1904 (s)	392	360	43.48 (42.95)	5.26 (5.41)
endo-14	η^3-C_3H_5	1912 (s)	392	360	43.55 (42.95)	5.27 (5.41)
15[d]	η^3-C_5H_9	1891 (s)	420	386	46.18 (45.80)	5.80 (6.01)
exo-16	η^3-C_8H_{15}	1899 (s)	462	428	49.54 (49.43)	6.91 (6.77)
		$Cp^*Re(CO)(Br)(L)$				
endo-17	η^3-C_3H_5	1962 (s)	470[e]	400[e]	35.96 (35.74)	4.10 (4.29)

[a] Abbreviations: s = strong, vs = very strong. [b] Calculated values in parentheses. [c] Not analyzed. [d] Mixture of isomers (see text). [e] For ^{187}Re and ^{79}Br isotopes.

acid. A solution of the η^2-cyclohexadiene complex **10** in hexane containing cyclohexadiene when irradiated for 30 min at 0 °C resulted in an IR absorption at 1891 cm^{-1}, which is assigned to **13**, in addition to residual absorptions from **10**. However the ν(CO) absorptions of **10** were still more intense than those of **13** even after 90 min of irradiation. Complex **13** appeared not to be very stable in solution, even under an atmosphere of N_2 in the freezer.

From the irradiation of 4-methylcyclohexene, the η^2-4-methylcyclohexene complex **7** was obtained but the solution also showed a ν(CO) absorption at 1890 cm^{-1} for an additional product that unfortunately was no longer evident following chromatography. As the absorption is close to the ν(CO) band for **13** and one of the bands for **10**, it is possible that this represents the formation of a corresponding diene dehydrogenation product such as $Cp^*Re(CO)_2(\eta^2$-$C_7H_{10})$ or $Cp^*Re(CO)(\eta^4$-$C_7H_{10})$. When pure **7** was irradiated in hexane for 10 min, the IR spectrum showed the new ν(CO) band at 1890 cm^{-1}, with intensity similar to the bands of **7**. However within 2 days this absorption disappeared (sample in hexane solution under N_2 at room temperature) and the unstable compound has not been identified.

The photolysis of $Cp^*Re(CO)_3$ with cyclooctene in hexane was inefficient. After 90 min, the IR spectrum showed that the ν(CO) absorptions of the tricarbonyl were still more intense than those of the cyclooctene complex **8** (ν(CO) 1955 and 1885 cm^{-1}). The yield was only about 14%. A possible reason is that the flexible and bulky cyclooctene does not easily attack the rhenium atom, because of the steric effect of the Cp* methyls, and easily redissociates during the photolysis. There was no evidence for the formation of either cyclooctenyl hydrido or cyclooctadiene complexes in this case. The known[29] binuclear complex $Cp^*_2Re_2(CO)_5$ was also isolated, suggesting that the rates of capture of the unsaturated fragment $Cp^*Re(CO)_2$ by the alkene or by $Cp^*Re(CO)_3$ are competitive. In a separate experiment irradiation of the pure cyclooctene complex **8** in a quartz or Pyrex tube for only 15 min resulted in loss of **8** and formation of $Cp^*_2Re_2(CO)_5$.

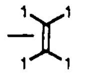
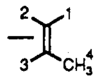
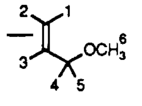
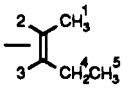
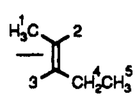
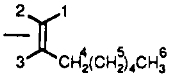
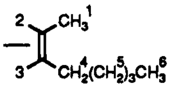
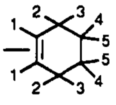
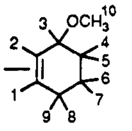
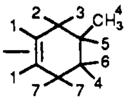
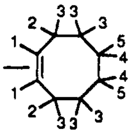
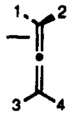
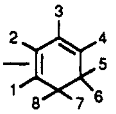
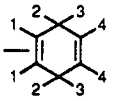
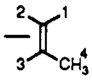
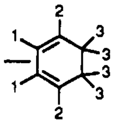
The allene complex **9** was formed in good yield by bubbling allene through a vigorously stirred solution of $Cp^*Re(CO)_2(THF)$ in THF, and it is stable in a pure state.

The trimethylphosphine complex **12** was obtained by irradiation of a solution of $Cp^*Re(CO)(PMe_3)(N_2)$ in hexane with a propene purge. However, the synthesis was not clean; other products obtained in small amounts following chromatography on silica gel were $Cp^*Re(CO)_2(PMe_3)$, the propene complex **2**, and the allyl hydrido complexes *exo*- and *endo*-**14**.

The new rhenium alkene complexes **1**–**13** were fully characterized by analysis (except **13**) and spectroscopy (Tables I–III). They are mostly air-stable as solids or when dissolved in nonpolar organic solvents. In general, the alkene ligand in these complexes is not readily displaced by other ligands. A similar feature was noted for the corresponding $CpRe(CO)_2$(alkene) complexes.[17] For example, there was no reaction of **2** with CO or PMe_3 in the dark and the alkene was not displaced from **2**, **4**, or **7** by pressurizing with N_2. The IR spectra show the expected one or two ν(CO) absorptions, and these show the expected trends to lower wavenumber as the number of alkyl substituents increases. The ν(CO) absorptions for the cyclic alkenes are at lower wavenumber than for the comparable acyclic alkenes. The ν(CO) absorptions of the dicarbonyl diene complexes **10** and **11** are higher than those of the cyclohexene complex **6**, suggesting that the dienes are stronger acceptors. Furthermore, the different ν(CO) absorptions of the two diene complexes **10** and **11** suggest that conjugated 1,3-cyclohexadiene is a better acceptor than the nonconjugated 1,4-cyclohexadiene. Finally, the ν(CO) absorptions of the allene complex **9** are the highest, an indication that the strongest d–π back-bond occurs between rhenium and allene.

(ii) ^{1}H NMR Spectra of Alkene Complexes. ^{1}H NMR data (Table II) gave additional confirmatory evi-

Table II. ^{1}H Chemical Shifts and Coupling Constants for Compounds 1–13

complex	alkene ligand	δ, ppm, and J, Hz[a,b]	
1		1.68 (s, 4)	H(1)
		1.60 (s, 15)	Cp*
2		2.16 (dd, 1, $J_{1,2}$ = 1.7, $J_{1,3}$ = 12.1)	H(1)
		1.35 (dd, 1, $J_{2,3}$ = 9.8)	H(2)
		1.97 (m, 1)	H(3)
		2.05 (d, 3, $J_{3,4}$ = 5.7)	H(4)
		1.61 (s, 15)	Cp*
2a		2.08 (dd, 1, $J_{1,3}$ = 10.5, $J_{1,2}$ – 2.7, $J_{1,5}$ = 0.7)	H(1)[d]
		1.36 (br d, 1, $J_{2,4}$ = 8.2, $J_{2,5}$ = 1.2)	H(2)
		2.05 (m, 1)	H(3)
		2.97 (t, 1, $J_{4,5}$ = 10.5, $J_{3,4}$ = 10.5)	H(4)
		4.30 (dd, 1, $J_{3,5}$ = 3.5)	H(5)
		3.25 (s, 3)	H(6)
		1.52 (s, 15)	Cp*
3[c]		1.83 (d, 3, $J_{1,2}$ = 6.1)	H(1)
		2.52 (m, 1)	H(2)
		2.32 (m, 1)	H(3)
		1.60 (m, 2)	H(4)
		1.18 (t, 3, $J_{4,5}$ = 7.3)	H(5)
		1.64 (s, 15)	Cp*
3[c]		2.06 (d, 3, $J_{1,2}$ = 2)	H(1)
		2.21 (m, 1) or 2.14 (m, 1)	H(2)
		2.14 (m, 1) or 2.21 (m, 1)	H(3)
		1.86 (m, 2)	H(4)
		1.23 (t, 3, $J_{4,5}$ = 7.3)	H(5)
		1.70 (s, 15)	Cp*
4		2.47 (m, 1)	H(1)
		2.19 (d, 1, $J_{2,3}$ = 10.5)	H(2)
		2.01 (m, 1)	H(3)
		1.61 (m, 2)	H(4)
		1.35–1.40 (br m, 8)	H(5)
		0.95 (br t, 3, $J_{5,6}$ = 6.9)	H(6)
		1.65 (s, 15)	Cp*
5		1.87 (d, 3, $J_{1,2}$ = 6)	H(1)[d]
		2.52 (m, 1, $J_{2,3}$ = 9.8)	H(2)
		2.40 (m, 1)	H(3)
		1.53–1.61 (m, 2)	H(4)
		1.37–1.45 (m, 6)	H(5)
		1.00 (br t, 3, $J_{5,6}$ = 6)	H(6)
		1.72 (s, 15)	Cp*
6		2.42 (dd, 2, $J_{1,2}$ = 2, $J_{1,3}$ = 3)	H(1)[d]
		2.85 (m, 2)	H(2)
		2.91 (m, 2)	H(3)
		1.57 (m, 2)	H(4)
		1.45 (m, 2)	H(5)
		1.61 (s, 15)	Cp*
6a		2.39 (m, 1, $J_{1,8}$ or $J_{1,9}$ = 3.5)	H(1)[d]
		2.45 (d, 1, $J_{1,2}$ = 9.3, $J_{2,3}$ = 4.8)	H(2)
		4.56 (t, 1, $J_{3,4}$ = 7.4, $J_{3,5}$ = 6.3)	H(3)
		1.44 (m, 2)	H(4,7)
		2.01 (m, 1, $J_{4,5}$ = 12.8, $J_{5,6}$ = 7.5, $J_{5,7}$ = 2.5)	H(5)
		1.27 (m, 1, $J_{6,7}$ = 12.8, $J_{4,6}$ = 2.5)	H(6)
		2.81 (m, 2)	H(8,9)
		3.42 (s, 3)	H(10)
		1.61 (s, 15)	Cp*
7		2.50 (m, 2)	H(1)
		2.39 (m, 1)	H(2)
		2.64 (m, 1)	H(3)
		0.98 (d, 2, $J_{4,5}$ = 6.6)	H(4)
		1.46–1.52 (m, 1)	H(5)
		1.10–1.32 (m, 2)	H(6)
		2.90 (m, 2)	H(7)
		1.62 (s, 15)	Cp*
8		1.98 (d, 2, $J_{1,2}$ = 9)	H(1)
		2.70 (d, 2, $J_{2,3}$ = 13.5)	H(2)
		1.70–1.78 (m, 6)	H(3)
		1.49–1.56 (m, 2)	H(4)
		1.37–1.44 (m, 2)	H(5)
		1.65 (s, 15)	Cp*
9		1.48 (br s, 2)	H(1,2)[d,e]
		5.60 (t, 1, $J_{1(2),3}$ = 2.7)	H(3)
		6.67 (t, 1, $J_{1(2),4}$ = 2.7)	H(4)
		1.61 (s, 15)	Cp*
10		2.31 (m, 1, $J_{1,2}$ = 9)	H(1)[d]
		2.40 (m, 1, $J_{2,3}$ = 5.5, $J_{2,4}$ = 1)	H(2)
		6.52 (m, 1, $J_{3,4}$ = 10, $J_{3,5(6)}$ = 1.5)	H(3)
		5.52 (m, 1, $J_{4,5(6)}$ = 5.5)	H(4)
		1.82 (m, 2, $J_{5(6),7}$ = 5, $J_{5(6),8}$ = 7)	H(5,6)
		2.70 (m, 1, $J_{7,8}$ = 14)	H(7)
		2.87 (m, 1)	H(8)
		1.60 (s, 15)	Cp*
11		2.34 (br s, 2)	H(1)
		3.17 (d, 2, $J_{2,3}$ = 16.8)	H(2)
		3.44 (d, 2)	H(3)
		5.74 (br s, 2)	H(4)
		1.61 (s, 15)	Cp*
12		1.78–1.85 (br m, 1)	H(1)
		0.60 (dt, 1, $J_{2,3}$ = 8.8 J_{PH} = 3)	H(2)
		1.16–1.31 (m, 1)	H(3)
		2.24 (dd, 3, $J_{3,4}$ = 6, $J_{1,4}$ or $J_{2,4}$ = 1)	H(4)
		1.31 (d, 9, J_{PH} = 8.5)	PMe_3
		1.69 (s, 15)	Cp*
13		3.22 (m, 2)	H(1)
		2.95 (m, 2)	H(2)
		1.30–1.44 (m, 4)	H(3)
		1.51 (s, 15)	Cp*

[a] Items in parentheses are reported as multiplicity, number of protons, coupling constants. Abbreviations: br = broad, d = doublet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, s = singlet, t = triplet. [b] All samples were measured in C_6D_6 at 400 MHz. [c] Compounds **3** cis and trans were present together in the sample (ratio: cis/trans = 1/1.7). [d] Alkene proton assignments determined by decoupling experiments. [e] Alkene proton assignments determined by NOE experiments.

dence of the formulation of **1**–**13** as the proposed new rhenium alkene complexes.

The room-temperature 400-MHz ^{1}H NMR spectrum of the ethene complex **1** exhibits only a single resonance for the four ethene protons at δ 1.68 ppm, indicating a rapid rotation of the ethene ligand at this temperature. The propene complex **2** exhibits individual resonances for the protons H(1), H(2), and H(3) and the methyl proton H(4). The multiplet at δ 1.97 with coupling to each olefinic proton and three methyl protons was reasonably assigned to H(3). The doublet of doublets at δ 2.16 with a larger coupling ($J_{1,3}$ = 12.1 Hz) was assigned to H(1) trans to H(3), and the doublet of doublets at δ 1.35 with a smaller coupling ($J_{2,3}$ = 9.8 Hz) was assigned to H(2) cis to H(3) on the basis that trans-olefinic coupling constants are usually larger than cis ones. (Usually J_{cis} = 6–12 Hz, J_{trans} = 12–18 Hz.) It is not possible to distinguish whether the propene is static or rotating in this complex from the ^{1}H NMR spectrum.

The assignments for the remaining alkene complexes were determined by standard decoupling or NOE experiments. The protons of the η^4-cyclohexadiene complex **13** were assigned by comparison with previously reported values for similar compounds CpIr(η^4-cyclohexadiene),[33]

Table III. Principal Fragments in the Mass Spectra of Alkene and Allyl Complexes 1–17

complex	m/z [assignment]^a
1	406 [M^+], 378 [$M^+ - C_2H_4$ (or CO)], 376 [$M^+ - C_2H_4$ (or CO) $- 2H$], 348^b [$M^+ - C_2H_4 - CO - 2H$ (or $M^+ - 2CO - 2H$)]
2	420 [M^+], 390 [$M^+ - CO - 2H$], 378 [$M^+ - C_3H_6$], 376 [$M^+ - C_3H_6 - 2H$], 362 [$M^+ - 2CO - 2H$], 360 [$M^+ - 2CO - 4H$], 348^b [$M^+ - CO - C_3H_6 - 2H$]
2a	450 [M^+], 394 [$M^+ - 2CO$], 392 [$M^+ - 2CO - 2H$], 390 [$M^+ - 2CO - 4H$], 378 [$M^+ - C_3H_5OMe$], 376 [$M^+ - C_3H_5OMe - 2H$], 362 [$M^+ - 3CO - 4H$], 350 (weak) [$M^+ - CO - C_3H_5OMe$], 348^b [$M^+ - CO - C_3H_5OMe - 2H$]
3	448 [M^+], 418 (weak) [$M^+ - CO - 2H$], 390 [$M^+ - 2CO - 2H$], 388 [$M^+ - 2CO - 4H$], 378 [$M^+ - C_5H_{10}$], 376 [$M^+ - C_5H_{10} - 2H$], 348^b [$M^+ - CO - C_5H_{10} - 2H$]
4	490 [M^+], 460 [$M^+ - CO - 2H$], 430 [$M^+ - 2CO - 4H$], 428 [$M^+ - 2CO - 6H$], 378^b [$M^+ - C_8H_{16}$], 376 [$M^+ - C_8H_{16} - 2H$], 348 [$M^+ - CO - C_8H_{16} - 2H$]
5	490 [M^+], 460 [$M^+ - CO - 2H$], 430 [$M^+ - 2CO - 4H$], 428 [$M^+ - 2CO - 6H$], 378 [$M^+ - C_8H_{16}$], 376 [$M^+ - C_8H_{16} - 2H$], 348^b]$M^+ - CO - C_8H_{16} - 2H$]
6	460 [M^+], 430 [$M^+ - CO - 2H$], 400 [$M^+ - 2CO - 4H$], 378 [$M^+ - C_6H_{10}$], 348^b [$M^+ - C_6H_{10} - 2H$]
6a	490 [M^+], 458 [$M^+ - CO - 4H$], 430 [$M^+ - 2CO - 4H$], 400^b [c], 378 (weak) [$M^+ - C_6H_9OMe$], 348 [$M^+ - CO - C_6H_9OMe - 2H$]
7	474 [M^+], 444 [$M^+ - CO - 2H$], 414 [$M^+ - 2CO - 4H$], 399 [$M^+ - 2CO - CH_3 - 4H$], 378^b [$M^+ - C_7H_{12}$], 376 [$M^+ - C_7H_{12} - 2H$], 348 [$M^+ - CO - C_7H_{12} - 2H$]
8	488 [M^+], 458 [$M^+ - CO - 2H$], 428 [$M^+ - 2CO - 4H$], 426 [$M^+ - 2CO - 6H$], 378^b [$M^+ - C_8H_{14}$], 376 [$M^+ - C_8H_{14} - 2H$], 348 [$M^+ - CO - C_8H_{14} - 2H$]
9	418 [M^+], 390 [$M^+ - CO$], 378 (weak) [$M^+ - C_3H_4$], 376 [$M^+ - C_3H_4 - 2H$], 360^b [$M^+ - 2CO - 2H$], 358 [$M^+ - 2CO - 4H$], 348 [$M^+ - CO - C_3H_4 - 2H$]
10	458 [M^+], 430 [$M^+ - CO$], 400^b [$M^+ - 2CO - 2H$], 378 (weak) [$M^+ - C_6H_8$], 376 [$M^+ - C_6H_8 - 2H$], 348 [$M^+ - CO - C_6H_8 - 2H$]
11	458 [M^+], 430 [$M^+ - CO$], 400 [$M^+ - 2CO - 2H$], 378 (weak) [$M^+ - C_6H_8$], 376 [$M^+ - C_6H_8 - 2H$], 348^b [$M^+ - CO - C_6H_8 - 2H$]
12	468 [M^+], 438 (weak) [$M^+ - CO - 2H$], 426^b [$M^+ - C_3H_6$], 394 [$M^+ - CO - C_3H_6 - 4H$], 392 [$M^+ - PMe_3$], 364 [$M^+ - PMe_3 - CO$]
13	430 [M^+], 400^b [$M^+ - CO - 2H$], 350 (weak) [$M^+ - C_6H_8$], 348 [$M^+ - C_6H_8 - 2H$]
14	392 [M^+], 390 [$M^+ - 2H$], 362 [$M^+ - CO - 2H$], 360^b [$M^+ - CO - 4H$], 358 [$M^+ - CO - 6H$]
15	420 [M^+], 418 [$M^+ - 2H$], 390 [$M^+ - CO - 2H$], 388 [$M^+ - CO - 4H$], 386^b [$M^+ - CO - 6H$]
16	462 [M^+], 460 [$M^+ - 2H$], 432 [$M^+ - CO - 2H$], 430 [$M^+ - CO - 4H$], 428^b [$M^+ - CO - 6H$]
17	470 [M^+], 442 [$M^+ - CO$], 400^b [$M - CO - C_3H_5 - H$]
$Cp^*Re(CO)(PMe_3)(N_2)$	454 [M^+], 426^b [$M^+ - N_2$ (or $M^+ - CO$)], 396 [$M^+ - N_2 - CO - 2H$], 394 [$M^+ - N_2 - CO - 4H$], 378 [$M^+ - PMe_3$], 366 [$M^+ - N_2 - CO - C_2H_6 - 2H$], 364 [$M^+ - N_2 - CO - C_2H_6 - 4H$]
$Cp^*Re(CO)_2(PMe_3)$	454^b [M^+], 426 [$M^+ - CO$], 396 [$M^+ - 2CO - 2H$], 394 [$M^+ - 2CO - 4H$], 378 [$M^+ - PMe_3$], 366 [$M^+ - 2CO - C_2H_6 - 2H$], 364 [$M^+ - 2CO - C_2H_6 - 4H$]

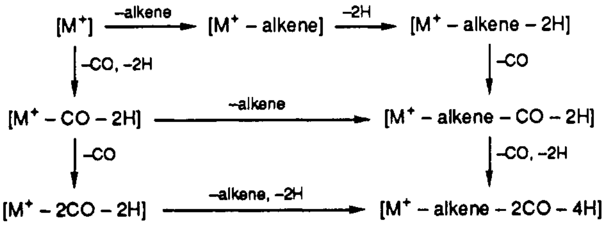
^{a} Masses are quoted for the ^{187}Re isotope. ^{b} Base peak. ^{c} This mass corresponds to [$Cp^*Re(\eta^6\text{-}C_6H_6)$]$^+$; see text.

CpRh(η^4-cyclohexadiene),[34] and CpCo(η^4-cyclohexadiene),[35] where in general the chemical shifts of inner η^4-diene protons are observed downfield relative to the outer η^4-diene protons.

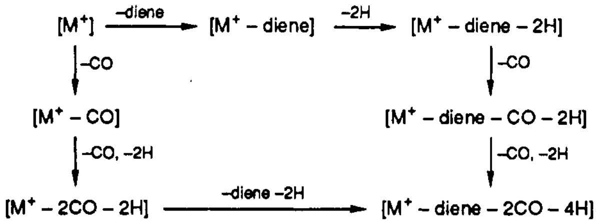
The η^2-allene ligand is known to rotate about the metal–allene axis in, for example, complexes of iron, rhodium, and platinum.[36,37] We therefore investigated whether similar rotation was occurring in complex **9** by recording the variable-temperature ^{1}H NMR spectrum from 273 to 183 K, in toluene-d_8. Such rotation would explain why H(1) and H(2) appear equivalent at 22 °C and produce a broad signal, while H(3) and H(4) are inequivalent. The resonances for H(3) and H(4) were unaffected, but as the temperature was lowered from 273 K, the broad resonance at δ 1.48 for H(1)/H(2) collapsed into the baseline, and then below 213 K two peaks at δ 2.02 and 0.93 ppm on either side of this appeared. These began to sharpen at 183 K, but at this temperature the limiting sharp spectrum had not yet been reached.

The barrier to rotation at the coalescence temperature 223 K was estimated to be $\Delta G^{\ddagger}_{223} = 9.6 \pm 0.2$ kcal mol^{-1} and is in the range of allene rotational barriers (7–13 kcal mol^{-1}) observed for a number of neutral or cationic metal–allene complexes of platinum, rhodium, or iron.[36,37] A second process available to allene complexes is the transfer of the metal from one double bond to the other by a series of 90° rotation–translations.[36] We observed magnetization transfer from H(1)/H(2) to H(3) and H(4) and vice versa at 90 °C in the ^{1}H NMR spectra of **9**, consistent with such a process occurring with a higher activation barrier than for the simple allene rotation.

Scheme I. Mass Spectrum Fragmentation Scheme for Acyclic and Cyclic Alkene Complexes 2–8 (Alternative Pathways Omitted for Clarity)



Scheme II. Mass Spectrum Fragmentation Scheme for Dicarbonyl η^2-Diene Complexes 9–11 (Alternative Pathways Omitted for Clarity)



(iii) Mass Spectra of Alkene Complexes. The mass spectra of **1–13** (Table III) show interesting variations

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Table IV. ^{1}H NMR Data for Allyl Complexes 14–17

(a) chemical shift, δ[a]

complex	Cp*	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)
exo-14	1.69	2.11	1.89	1.76	2.57	2.42	−9.23
endo-14	1.77	2.67	0.25	0.65	3.26	4.01	−11.65
exo-16	1.71	2.25	2.34	2.56		3.65	−8.94
endo-17	1.87	2.98	1.05	1.80	3.15	4.59	*a*

(b) coupling constants,[b] Hz

complex	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{1,5}$	$J_{1,6}$	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
exo-14	2.3 (1.7)	(0.5)	(2.1)	6.7 (7.1)	2.5 (2.5)	(0.6)	(0.6)	9.5 (10.0)	0.0 (0.2)	2.3 (2.5)	10.2 (10.5)	0.0 (0.3)	7.2 (7.1)	2.0 (2.0)	0.0 (0.9)
endo-14	1.5 (1.9)	(0.5)	(2.1)	5.5 (5.6)	2.5 (2.9)	(0.5)	(0.5)	8.4 (8.3)	0.0 (0.6)	1.0 (0.4)	9.3 (8.8)	0.0 (0.6)	5.5 (5.8)	2.8 (3.2)	1.0 (1.0)
exo-16	2.7 (2.6)	(0.6)	(0.0)[c]	6.8 (7.0)	(2.6)	(0.5)	(0.0)[c]	10.0 (10.0)	(0.5)	7.2[c] (*d*)	9.8 (9.7)	(0.0)	1.5[c] (1.5)[c]	(0.3)	(1.0)
endo-17	1.5			6.9				7.1		1.5	9.4		5.9		

[a] This atom is Br in *endo*-17. [b] Computer simulated values in parentheses. [c] The coupling constant listed is to the 4-methenyl hydrogens in the 1-octenyl group. [d] Values of 7.2 and 6.5 Hz were calculated for the two 4-methenyl hydrogens, which had a *gem* coupling of 10.0 Hz.

depending on the nature of the alkene and ancillary ligands. The interpretation of the principal fragmentation for these complexes is shown in Schemes I and II.

In summary, we observe evidence for parallel fragmentation processes; first loss of either CO or alkene, accompanied by loss of 2H from Cp* (more rapid when CO is lost first) and then loss of alkene or CO, respectively. It is notable that loss of even a second CO group can occur without release of the alkene moiety. The loss of 2H from Cp* during fragmentation has been well documented in Cp*–rhenium complexes, for example in the fragmentation of Cp*Re(CO)$_3$.[38]

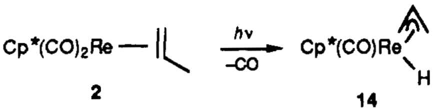
In view of the fact that stable cationic allyl complexes such as [Cp*Re(CO)$_2$(η^3-C$_3$H$_5$)]$^+$ and substituted allyl analogues are easily made by hydride abstraction from the alkene complex,[28] it is interesting to note that, in the fragmentation of the propene (or other alkene) complex radical cation (M$^+$), the loss of a single H atom from the alkene is never observed, even though it would result in the production of these species.

Further details of the interpretation of the mass spectra are provided as supplementary material.

(b) Allyl Hydrido Complexes. (i) Synthesis and Characterization. The photolysis of Cp*Re(CO)$_3$ in the presence of propene, 2-pentene, or 1-octene was observed to produce, in addition to the alkene complex, further products identified in each case as one or more allyl hydrido complexes 14–16 (Table I). The amounts of these products increased relative to the amount of the alkene complex (determined from ν(CO) absorption intensities) as photolysis continued. The principal results for different alkenes may be summarized as follows. In the case of propene, two isomers of the allylhydridorhenium complex 14 were observed by IR spectroscopy and were successfully isolated by chromatography, as isomerization occurs only slowly in solution at room temperature.

In the case of 2-pentene, five isomers of the pentenylhydridorhenium complex 15 were detected by ^{1}H NMR spectroscopy, even though the IR spectrum showed only one ν(CO) absorption at 1891 cm^{-1}. The principal isomer is assigned the *exo*-2-penten-1-yl structure shown as **15a**; the others are undetermined. In the photochemical reaction of 1-octene, only one isomer of the corresponding 2-octen-1-ylhydridorhenium complex 16 was observed and isolated; it is assigned the exo structure shown.

Photolysis of the pure propene complex 2 in hexane under a propene purge also resulted in the allyl hydrido complex 14. On this basis it is proposed that these allyl hydrido complexes result from intramolecular C–H activation of an allylic C–H bond following photochemical CO loss from the precursor alkene complex, as indicated for propene complex 2 in eq 7.



2 14 (7)

Irradiation of the propene complex 2 in quartz under a purge of N$_2$ gave only a low yield of the allyl hydrido complex 14, suggesting that photodissociation of propene from 2 is a competing reaction. In agreement, NMR monitoring of the photolysis of 2 in a sealed tube in C$_6$D$_{12}$ produced signals for both the allyl hydrido complex 14 and free propene. Therefore a purge of propene is necessary to obtain a reasonable yield of 14 from 2.

For the allyl hydrido complex 14, two ν(CO) absorptions were observed in the IR spectrum, at 1904 and 1912 cm^{-1}. Subsequently, two isomers were separated, crystallized, and fully characterized. X-ray structure determinations showed them to be the exo and endo isomers (ν(CO) 1904 and 1912 cm^{-1} respectively), differing in the "down" or "up" orientation of the allyl group in the half-sandwich complex.[25a] The allyl hydrido complex 14 is remarkably stable. No reaction was observed with PMe$_3$ over 4 h at 60–65 °C in an attempt to either substitute the CO group by PMe$_3$ or reductively eliminate propene. Thermolysis of 14 in benzene at 75–80 °C for 24 h resulted in decomposition to 2, Cp*Re(CO)$_3$, and Cp*$_2$Re$_2$(CO)$_5$, but much of 14 survived (see section iii, below).

(ii) ^{1}H NMR Spectra of Allyl Hydrido Complexes. The solution ^{1}H NMR spectra of *exo*-14 and *endo*-14 are completely in agreement with the solid-state structures determined by X-ray crystallography. The assignments are given in Table IV. The position of the hydride resonance for the exo isomer in the ^{1}H NMR spectrum (δ −9.23) is shifted downfield, compared with that of the endo isomer (δ −11.65), by over 2 ppm. In the other examples of allyl hydrido compounds 15 and 16 synthesized from 2-pentene and 2-octene, the hydride resonances fall close to either of these values, and we have tentatively used this correlation to assign exo or endo configurations to these complexes, in the absence of crystal structures (see below).

As has been pointed out recently,[39] there have been some difficulties and discrepancies in assigning chemical shifts and coupling constants for η^3-allyl ligands in situations where all five protons are inequivalent.[40-42] Assigning the resonance of the central proton is straightforward because

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of its coupling to the four neighboring protons. However, the assignment of the correct resonances for each of the two anti protons and each of the two syn protons is less trivial. In the case of Pt(II) complexes, the anticipated magnitudes of homonuclear (H,H) and heteronuclear (H,Pt and H,P) couplings together with the assumption that anti protons are generally to higher field than syn protons, have been the basis for recent detailed assignments.[39] In the tungsten compound CpW(NO)I(η^3-C_3H_5), where the crystal structure shows that the allyl group is asymmetrically bonded in a σ–π form, the assignments were made on the basis of the homonuclear coupling constants.[43] For example, it is expected that the trans coupling constant $J_{H_cH_a}$ in the "olefinic" fragment would be larger than the vicinal coupling J_{H_c,H_a} in the "saturated" fragment.[39]

In this study, we have sought additional evidence from NOE enhancements, selective decoupling, and computer simulation[44] in order to provide convincing assignments for all five inequivalent allylic protons in each isomer, especially in relation to the position of the hydride ligand. Details are provided as supplementary material.

In no NOE experiment was there any evidence for magnetization transfer to the resonances of the endo isomer when resonances of the exo isomer were irradiated (or vice versa) in a mixture of isomers at 20 °C. But, as will be pointed out below, slow thermal conversion of *exo*-14 to *endo*-14 is observed, and the reverse photochemically, but at rates too slow for observable magnetization transfer at the temperature employed here.

The coupling constants (Table IV) compare reasonably with literature values, though in only relatively few cases[39,43] have the smaller couplings been noted (for example between inequivalent syn protons H(2) and H(3) or inequivalent anti protons H(1) and H(4)).

For both *exo*-14 and *endo*-14 the anti protons H(2) and H(3) have δ values smaller than the syn protons H(1) and H(4). This is a frequently (but not universally) observed correlation for η^3-allyl compounds whether or not the termini are equivalent or inequivalent.[39–43,45–47] Note, however, that for the unsymmetrical σ–π allyl group in CpW(NO)I(η^3-C_3H_5)[43] and the molybdenum compound[48] both syn and anti protons of one terminus (the allylic protons) resonate at low δ, well separated from the vinylic protons at higher δ values. Also in accord with precedent are the observed greater couplings of the central proton H(5) to the anti protons H(1) and H(4) than to the syn protons H(2) and H(3). The essentially true η^3 π-allyl nature of the group in 14 is indicated by the fact that the H_c–H_a couplings for the H_a protons of the two termini do not differ markedly in either *exo*-14 (where the termini are bound with similar distances) or *endo*-14 (where a small asymmetry is observed in these distances).[25a] Again this contrasts with the situation for the σ–π allyl group in CpW(NO)(I)(η^3-C_3H_5), as mentioned earlier.[43]

Interestingly, when the positions of the syn and anti protons of *exo*-14 are compared with those of *endo*-14, it is found that, for the symmetrically bound η^3-allyl ligand in the exo isomer, the syn protons H(1) and H(4) (δ 2.11 and 2.57) are only slightly downfield from the anti protons H(2) and H(3) (δ 1.89 and 1.76). However, in the endo isomer the separation is much greater, and the syn protons (H(1) and H(4)) lie even further downfield (δ 2.67 and 3.26) and the anti protons (H(2) and H(3)) are shifted upfield of the exo positions (δ 0.25 and 0.65). This effect may be due to differential shielding by the Cp* group: in the endo isomer H(2) and H(3) most closely approach the Cp* methyls and experience a strong shielding; similarly, in the exo isomer H(5) most closely approaches the Cp* methyls, and accordingly, this resonance is shifted dramatically upfield (δ 2.42) compared with the position (δ 4.01) in the endo isomer. Similarly, in the exo isomer the syn protons H(2) and H(3) are shifted upfield moderately by comparison with the endo isomer.[49] The first of these results contrasts with results for Cp complexes, where generally it is found that δ_{anti}(exo) is less than δ_{anti}(endo).[43,45–47]

Table V. Data for the Ratio of Exo:Endo Isomers for 14 at Increasing Temperatures

final ratio exo:endo at time *t*	35.7	32.3	15.4	6.94	1.36	0.328	0.274
temp, °C	−12	−2.5	3	7	17.5	27.5	32
t, days	21	21	14	14	14	14	7

The main isomer formed in the case of 2-pentene with δ −9.32 for Re–H is tentatively assigned the structure *exo*-**15a** on the basis that the 2-pentene contains more trans than cis isomer (1.7:1) and that C–H activation of the less hindered methyl terminus is stereochemically and statistically more likely than the methylene. However, as the isomers decomposed on attempted separation, no supporting ^{1}H NMR evidence is available. The structures for the other components are undetermined. The ^{1}H NMR spectrum of 16 was successfully assigned by decoupling and computer simulation. It shows the hydride at δ −8.94 as expected for an exo isomer and the chemical shifts and coupling constants (Table IV) are close to those *exo*-14 compared with *endo*-14. Application of NOE and decoupling procedures allowed unambiguous assignment of the allyl protons for the bromo complex Cp*Re(CO)(Br)(η^3-C_3H_5) (17) and showed this to be the endo isomer (Table IV).

(iii) Isomerization of 14. As the temperature of a mixture of *exo*-14 and *endo*-14 in benzene-d_6 is raised, the ratio of endo:exo increases in favor of the endo isomer, as indicated by the relative intensities of the hydride resonances in the ^{1}H NMR spectrum (Table V). This is not reversible on decreasing the temperature. The rates of exo–endo conversion were measured at four different temperatures, and assuming first order kinetics, gave values for the rate constants $k = (9.21 \pm 0.65) \times 10^{-5}$ min^{-1} (298 K), $(19.33 \pm 0.55) \times 10^{-5}$ min^{-1} (303 K), $(51.45 \pm 4.00) \times 10^{-5}$ min^{-1} (308 K), and $(94.95 \pm 10.41) \times 10^{-5}$ min^{-1} (313 K), from which an activation energy $E_a = 28.9 \pm 3.2$ kcal mol^{-1} was calculated. This value may be compared with similar activation parameters $\Delta G^{\ddagger}$ of 28.9 and 31.4 kcal mol^{-1} obtained by Gibson[47] for the thermal isomerization of *endo*-CpRu(CO)(η^3-C_3H_5) and *endo*-CpRu(CO)(η^3-C_4H_7), respectively, where endo–exo conversion occurs.

It is notable that, for the bromo complex Cp*Re(CO)(Br)(η^3-C_3H_5) (17), it is the endo isomer only that is formed and, for Cp*Re(CO)(H)(η^3-C_3H_5) (14), the endo isomer is the thermally stable one. It was of interest to

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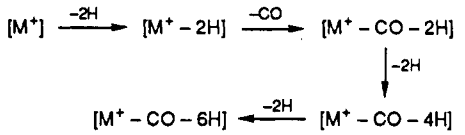
(49) A similar result has been obtained for the exo and endo isomers of the η^3-allyl cationic complex [Cp*Re(CO)$_2$(η^3-C_3H_5)][BF$_4$]. The H_a protons of the endo isomer are upfield from the H_a protons of the exo isomer, whereas H_c(exo) is upfield from H_c(endo). For the syn protons, H_s(exo) is upfield from H_s(endo); see ref 28.

Scheme III. Mass Spectrum Fragmentation Scheme for $Cp^*Re(CO)(H)(\pi^3\text{-}C_3H_5)$ (14) and Complexes 15–16



synthesize 14 from *endo*-17 by reaction with $LiHBEt_3$; even in this nonphotochemical synthesis a mixture of *exo*- and *endo*-14 was produced. Recently, a comparable Cp* ruthenium complex with a similar $Cp^*ML_2(\eta^3\text{-}C_3H_5)$ piano-stool structure has been described, i.e., $Cp^*RuBr_2(\eta^3\text{-}C_3H_5)$. It also has the endo structure in the solid state and in solution.[50]

The UV irradiation of a pure sample of *endo*-14 in hexane in a Pyrex tube for 5 min resulted in an approximate 2:1 mixture of exo:endo (determined from the ν(CO) intensities) and a small amount of decomposition to produce $Cp^*Re(CO)_3$ and $Cp^*Re(CO)_2(\eta^2\text{-}C_3H_6)$ (2). Thus the thermal exo–endo isomerization is reversed by UV irradiation (eq 8). The production of 2 also suggests that

$$exo\text{-}14 \underset{h\nu}{\overset{\Delta}{\rightleftharpoons}} endo\text{-}14 \qquad (8)$$

irradiation may induce hydrogen migration to the η^3-allyl group to reform the propene ligand to give the unsaturated species "$Cp^*Re(CO)(\eta^3\text{-}C_3H_6)$" that captures CO evolved in general decomposition. This is supported by the result of a 30-min irradiation of a mixture of *endo*- and *exo*-14 in cyclohexane-d_{12}, where the formation of 2 was observed, along with free propene (from the UV dissociation of 2; see earlier), $Cp^*Re(CO)_3$, and $Cp^*_2Re_2(CO)_5$. In addition, upon photolysis of a mixture of 2 and 14 under an atmosphere of CO, it was observed that the IR absorptions of 14 decreased rapidly, and those of 2 more slowly, suggesting that the propene complex 2 was being reformed by CO addition to 14.

The thermolysis of a mixture of *exo*- and *endo*-14 for 24 h at 75–80 °C under N_2 in benzene also led to the formation of the propene complex 2 together with $Cp^*Re(CO)_3$ and $Cp^*_2Re_2(CO)_5$, again an indication that hydrogen migration to the η^3-allyl group is occurring. It might be anticipated that the formation of the unsaturated species "$Cp^*Re(CO)(\eta^2\text{-}C_3H_6)$" by such a recombination could result in either capture or C–H activation of benzene to give either a benzene π-complex[51] or a phenylhydrido derivative,[30,31] but there was no evidence for formation of these species.

(iv) Mass Spectra of Allyl Hydrido Complexes. The EI mass spectra of the allyl hydrido complexes 14–16 and the allyl bromo complex 17 are listed in Table III, and the fragmentation pathways for 14–16 are shown in Scheme III. The most notable feature of the hydride complexes 14–16 is that the observed isotopic patterns for M^+ do not correspond to the calculated patterns. Here, the hydride complexes differ from the alkene complexes discussed earlier and from the bromo complex 17, all of which exhibit patterns for M^+ close to the computed ones. The anomalies therefore appear to be related to the presence of the hydride ligand in 14–16. Taking the allyl hydrido complex 14 as an illustration, the observed M^+ pattern can be fitted by a superposition of the patterns for M^+ and $M^+ - 2H$ in a ratio of approximately 0.45:1. The patterns for complexes 15 and 16 can be similarly ascribed to superposition of M^+ and $M^+ - 2H$. The facile loss of 2H from the parent is not observed for the bromide 17 and therefore one of the hydrogens lost is presumed to be the hydride ligand. The other is most likely to arise from a Cp* ring methyl group.[38,52]

Most noticeable is the absence of fragmentation by loss of the allyl group or alkene in any of these hydride complexes, whereas it was noted that loss of alkene occurs readily in the mass spectra of the alkene complexes. This suggests that hydrogen migration to the allyl group to form the alkene complex does not occur in the fragmentation of M^+. Other features of these mass spectra are included as supplementary material.

(v) Mechanism of Formation of Allyl Hydrido Complexes. Although it is not possible to identify with certainty the mechanism by which the propene complex 2 transforms to the allyl hydrido complex 14 on photolysis (and similarly for the related formation of 15 and 16), we tentatively suggest that CO loss occurs on photolysis to give the unsaturated 16-electron species "$Cp^*Re(CO)(\eta^2\text{-}C_3H_6)$". This is followed by intramolecular C–H activation of an allylic C–H bond. An allylic C–H bond is one of the weakest (87 kcal mol^{-1}). We did think that we might be able to probe the formation of the 16-electron species by performing the photolysis of 2 in the presence of PMe_3, anticipating that the unsaturated species would capture PMe_3 to form $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (12), a compound synthesized previously from $Cp^*Re(CO)(PMe_3)(N_2)$ and propene and having a characteristically low value for ν(CO), 1846 cm^{-1}. No formation of 12 resulted, as determined by IR spectroscopy and isolation of the products. These were instead *exo*- and *endo*-14 and $Cp^*Re(CO)_2(PMe_3)$.[53] However, this result does not necessarily invalidate the formation of the 16-electron intermediate "$Cp^*Re(CO)(\eta^2\text{-}C_3H_6)$". It may be that the intramolecular C–H activation is much faster than capture of PMe_3. Preliminary photolysis of 2 in a glass at 77 K supports this, as we failed to observe any IR absorption for the putative unsaturated species; only those bands of 14 were produced.[54] A second possibility is that $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ may itself be photolabile. To test this, we irradiated $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (12) in hexane but observed it still to be substantially present after 40 min of irradiation in a quartz tube (see below).

The photolysis of $Cp^*Re(CO)_2(PMe_3)$ and $Cp^*Re(CO)(PMe_3)(N_2)$ in the presence of several hydrocarbons had been reported previously[30,31] but did not include alkenes. The observed products were consistent with photodissociation of a CO group to give the intermediate $Cp^*Re(CO)(PMe_3)$, and some of the hydrocarbons underwent C–H oxidative additions to this intermediate. We therefore carried out irradiations of $Cp^*Re(CO)_2(PMe_3)$ and $Cp^*Re(CO)(PMe_3)(N_2)$ in hexane with a propene purge. Loss of CO and N_2, respectively, and addition of propene occurred to give $Cp^*Re(CO)(PMe_3)(\eta^2\text{-}C_3H_6)$ (12) as the major product. The photodissociation of N_2 from $Cp^*Re(CO)(PMe_3)(N_2)$ is more efficient than that of CO from $Cp^*Re(CO)_2(PMe_3)$, making this a reasonable preparative route to 12, as lesser amounts of side products result. These side products are $Cp^*Re(CO)(H)(\eta^2\text{-}CH_2PMe_2)$ (expected to result from internal C–H oxidative addition in the intermediate $Cp^*Re(CO)(PMe_3)$[30,31]) and

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[53] $Cp^*Re(CO)_2(PMe_3)$ is expected to result from the competing photodissociation of propene from 2 (in the absence of added propene in this experiment) and capture of PMe_3.

[54] Hill, R. H.; Zhuang, J.-M.; Sutton, D. Unpublished work.

complexes 2 and 14 (which could result from either competitive PMe_3 dissociation from $Cp^*Re(CO)_2(PMe_3)$ or PMe_3 loss from 12 during photolysis). No product of C–H oxidative addition of propene to the intermediate $Cp^*Re(CO)(PMe_3)$ was observed.

While complex 12 seems to be reasonably stable under irradiation (above), minor amounts of the same products are formed in the irradiation of 12 alone, as are formed when $Cp^*Re(CO)(PMe_3)(L)$ (L = CO, N_2) are irradiated in the presence of propene. Interestingly, we saw no NMR evidence for the new allyl hydrido complex $Cp^*Re(PMe_3)(H)(\eta^3\text{-}C_3H_5)$ that might arise from CO loss from 12 followed by propene activation, in parallel with the results for 2.

Conclusions

The photolysis of $(C_5Me_5)Re(CO)_3$ in the presence of a variety of alkenes is similar to previously reported photolyses of the manganese complexes $(C_5H_5)Mn(CO)_3$, $(C_5H_4Me)Mn(CO)_3$, and $(C_5Me_5)Mn(CO)_3$[5,7,20] in providing analogous rhenium alkene complexes of the type $(C_5Me_5)Re(CO)_2(\eta^2\text{-alkene})$. However, a major difference is that on continued photolysis of the rhenium alkene complexes, intramolecular C–H activation occurs. The propene complex 2 has been studied in most detail, and the exo and endo isomers of the product allyl hydrido complex 14 have been fully characterized. Continued photolysis of the cyclohexene complex 6 yielded evidence for dehydrogenation products. These results further establish that organometallic compounds of rhenium are capable of entering into carbon–hydrogen activation reactions,[30,31,55] and work in this area is continuing.

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Supplementary Material Available: Textual details of the mass spectra of complexes 1–17 and the assignment of the ^1H NMR spectra of *exo*-14 and *endo*-14 and mass spectra for complexes 1–17 (8 pages). Ordering information is given on any current masthead page.

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Ketene Reactivity of *trans*-Bis(tricyclohexylphosphine)(η^1-formylketenyl)hydridoplatinum(II). Crystal and Molecular Structure of the Aniline Derivative. 17[1]

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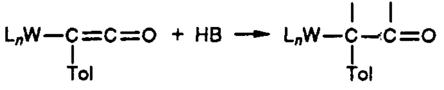
The (η^1-formylketenyl)platinum(II) complex $(PCy_3)_2Pt(H)(\eta^1\text{-}C(CHO)CO)$ reacts with primary aliphatic or aromatic amines, yielding the addition products $(PCy_3)_2Pt(H)C[(CHOH)(C(O)NHR)]$. The crystal structure of the aniline derivative has been determined. The crystals are monoclinic, $P2_1/c$, with a = 20.883 (12), b = 12.017 (6), c = 18.490 (8) Å, β = 108.00 (6)°, Z = 4. The amine adds to the C=O bond of the ketenyl group forming a planar ligand orthogonal to the coordination plane of Pt.

Introduction

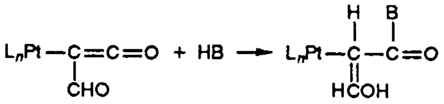
Recently there has been widespread interest in synthesis and reactivity studies on η^1-ketenyl complexes as synthons in addition reactions in organic chemistry. A simple synthetic route to obtain these complexes proceeds via insertion of carbon suboxide, C_3O_2, into metallic hydride bonds.[2] In the course of our systematic research on the reactivity of C_3O_2 we have obtained *trans*-$L_2Pt(H)(\eta^1\text{-}C(CHO)CO)$ by reacting C_3O_2 with *trans*-L_2PtH_2, with L = PCy_3, P*i*-Pr_3.[3]

Scheme I



$$L_nW{-}\underset{\text{Tol}}{C}{=}C{=}O + HB \longrightarrow L_nW{-}\overset{\text{H}}{\underset{\text{Tol}}{C}}{-}\overset{\text{B}}{C}{=}O$$

Scheme II



$$L_nPt{-}\underset{\text{CHO}}{C}{=}C{=}O + HB \longrightarrow L_nPt{-}\overset{\text{H}}{\underset{\text{HCOH}}{C}}{-}\overset{\text{B}}{C}{=}O$$

A full appreciation of the value of these compounds requires understanding of their structures, preferred conformations and mechanisms of reaction.[4] Actually, η^1-

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(2) Hillhouse, G. L. *J. Am. Chem. Soc.* 1985, *107*, 7772.

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