Synthesis and X-ray Structure of the Rhenium Methyl Complex *trans*-Cp*Re(CO)$_2$(Me)I and a Study of the Products of Photolysis of the Rhenium Alkyl Methyl and Dimethyl Complexes Cp*Re(CO)$_2$(Me)R (R = Ph, *p*-Tolyl, Me) under CO

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Reaction of Cp*Re(CO)$_2$I$_2$ with methylcopper affords *cis*-Cp*Re(CO)$_2$(Me)I, which converts to the trans isomer on prolonged reaction or in the presence of neutral alumina. The X-ray structure of the trans isomer has been determined. The related chloro complexes Cp*Re(CO)$_2$(Me)Cl and Cp*Re(CO)$_2$(*p*-tolyl)Cl are formed in the photolyses of compounds **3** and **1** (below) in CCl$_4$. Photolysis of Cp*Re(CO)$_2$(Me)R (R = *p*-tolyl (**1**), Ph (**2**), Me (**3**)) in the presence of CO has been carried out in hydrocarbons, CCl$_4$, and benzene-*d*$_6$. In hydrocarbons, **1** and **2** produce Cp*Re(CO)$_3$, CH$_4$, and either toluene or benzene, respectively; **3** produces Cp*Re(CO)$_3$ and CH$_4$. In benzene-*d*$_6$ **1** gave CH$_3$D and toluene-4-*d*, and **3** gave mainly CH$_3$D. These results are consistent with a general scheme involving successive homolysis of the metal−methyl and metal−aryl bonds to give methyl and aryl radicals that abstract H or D from the solvent and carbonylation of the rhenium dicarbonyl fragment. Products known or expected to arise from further photolysis of Cp*Re(CO)$_3$ in benzene-*d*$_6$, such as Cp*$_2$Re$_2$(CO)$_3$, Cp*$_2$Re$_2$(CO)$_5$, and Cp*Re(CO)$_2$(η^2-C$_6$D$_6$), were also found. Photolysis of **1** in CCl$_4$ in the presence or absence of CO gave CH$_3$Cl and Cp*Re(CO)$_2$(*p*-tolyl)Cl, but no *p*-chlorotoluene, indicating the preferential homolysis of the Re−Me bond and the rapid scavenging of the subsequent radicals by the chlorinated solvent. Photolysis of the dimethyl complex **3** gave CH$_3$Cl and some evidence of a small amount of Cp*Re(CO)$_2$(Me)Cl, but the major rhenium product was Cp*Re(CO)$_2$Cl$_2$, consistent with the more facile homolysis of both Re−Me bonds in **3**. Production of small amounts of CH$_2$D$_2$ (in benzene-*d*$_6$) and CH$_4$ and CH$_2$Cl$_2$ (in CCl$_4$) are discussed in terms of a competing pathway. Notably, in none of these photolyses were there observed other than trace amounts of products such as *p*-xylene, which would be expected to be major products if reductive elimination were to occur.

Introduction

As part of a continuing investigation of the syntheses, structures, and reactions of (pentamethylcyclopentadienyl)rhenium half-sandwich complexes, we have recently turned our attention to the synthesis of examples with rhenium−alkyl or rhenium−aryl bonds. The stepwise substitution of the rhenium−iodide bonds in Cp*Re(CO)$_2$I$_2$ afforded the aryl iodo and aryl methyl complexes Cp*Re(CO)$_2$(Ar)I and Cp*Re(CO)$_2$(Ar)Me.[1] Alkylation of the dichloro complex Cp*Re(CO)$_2$Cl$_2$ by using an organocopper reagent provided the dialkyl complexes Cp*Re(CO)$_2$R$_2$ (R = Me, Et).[2] Photolysis of the dinitrogen complexes Cp*Re(CO)(L)(N$_2$) (L = organophosphine or phosphite) in chlorobenzene furnished the phenyl chloro complexes Cp*Re(CO)(L)(Ph)Cl.[3] In this paper we report two further developments of this chemistry.

First, we show that changing the halogen in Cp*Re(CO)$_2$X$_2$ from Cl to I allows the reaction with methylcopper to proceed only with monosubstitution, affording Cp*Re(CO)$_2$(Me)I. This is initially obtained as the cis isomer, which converts to the trans isomer on prolonged reaction or in the presence of neutral alumina. The X-ray structure of the trans isomer has been determined.

Second, we have investigated the results of photolyzing the aryl methyl and dimethyl complexes Cp*Re(CO)$_2$(Me)R (R = Ph, *p*-tolyl, Me) in solution in the presence of CO. The objective here was to extend the previous work of Hill[4] on the photochemistry of *cis*-

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(1) Klahn, A. H.; Toro, A.; Arenas, M.; Manriquez, V.; Wittke, O. *J. Organomet. Chem*. **1997**, *532*, 39.

(2) Klahn, A. H.; Manzur, C.; Toro, A.; Moore, M. *J. Organomet. Chem*. **1996**, *516*, 51.

(3) Leiva, C.; Sutton, D. *Organometallics* **1998**, *17*, 4568.

(4) Hill, R. H.; Palmer, B. J. *Organometallics* **1989**, *8*, 1651.

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$Cp^*Re(CO)_2Me_2$ in order to try to determine the primary photoreaction and the fate of the alkyl and aryl ligands in this process and to compare the results with those previously obtained by Goldberg and Bergman[5] using the cyclopentadienyl analogue $CpRe(CO)_2Me_2$. The products formed in hydrocarbon solvents under the conditions of our experiments are consistent with a general scheme involving metal−carbon bond homolysis to give aryl and methyl radicals that abstract H from the hydrocarbon solvent. The products from photolyses in CCl_4 indicate significant differences in the chemistry in this solvent, and the methyl chloro and aryl chloro complexes $Cp^*Re(CO)_2(Me)Cl$ and $Cp^*Re(CO)_2$(*p*-tolyl)-Cl have been characterized in these reactions. Notably, products that would be anticipated if reductive elimination were to occur were generally not observed for photolyses in either solvent.

Results

1. Synthesis and Characterization of *cis*- and *trans*-$Cp^*Re(CO)_2(Me)I$. The reaction of $Cp^*Re(CO)_2I_2$ with methylcopper in THF led to the loss of IR absorption bands for the diiodide complex and the formation of new absorptions at 2004 and 1939 cm^{-1} due to the initial formation of *cis*-$Cp^*Re(CO)_2(Me)I$. Upon completion of the reaction, column chromatography on silica gel allowed isolation of first the trans isomer and then the cis isomer. It was observed that increasing the reaction time before the workup increased the proportion of the trans isomer which was eventually recovered and that chromatography of the pure cis isomer on neutral alumina also led to isomerization, indicating that cis−trans isomerization occurs in solution and is promoted by contact with alumina.

The assignment of the geometry of the two isomers is based upon the observed relative intensity patterns for the two ν(CO) absorption bands in each case. For the trans isomer, the lower wavenumber band is the more intense, and this is consistent with similar relative intensities previously observed for related trans isomers of the type $Cp^*Re(CO)_2X_2$ or $Cp^*Re(CO)_2XY$. Examples are *trans*-$Cp^*Re(CO)_2(Ph)I$,[1] *trans*-$Cp^*Re(CO)_2R_2$ (R = Me, Et),[2] *trans*-$Cp^*Re(CO)_2I_2$,[6] *trans*-$Cp^*Re(CO)_2\{PO(OMe)_2\}I$,[7] and *trans*-$Cp^*Re(CO)_2(Et)Br$.[8] This assignment is further supported by the determination of the X-ray crystal structure and the observation of a single ^{13}C resonance for the chemically equivalent carbonyl ligands. Correspondingly, the cis isomer exhibits spectroscopic properties consistent with a cis geometry, such as a higher intensity for the higher wavenumber of the two ν(CO) absorptions and two carbonyl carbon resonances. Finally, the ν(CO) absorptions of this isomer occur at lower wavenumbers compared with that of the trans isomer, as has commonly been seen in similar cases.[2,6]

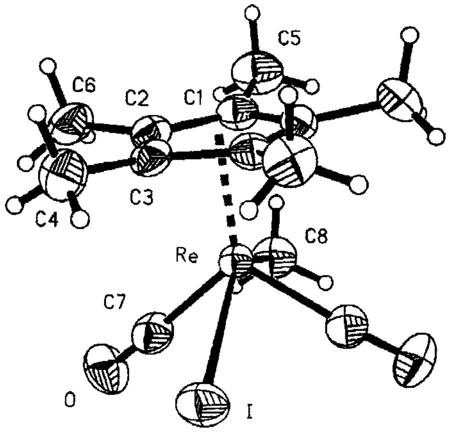

Figure 1. X-ray structure of *trans*-$Cp^*Re(CO)_2(Me)I$.

Table 1. Selected Bond Lengths and Interbond Angles for $Cp^*Re(CO)_2(Me)I$

(a) Bond Lengths (Å)			
Re(l)−I(l)	2.800(1)	Re(l)−C(l)	2.326(9)
Re(l)−C(2)	2.309(6)	Re(l)−C(3)	2.298(6)
Re(l)−C(7)	1.939(6)	Re(l)−C(8)	2.267(9)
C(l)−C(2)	1.412(8)	C(l)−C(5)	1.504(13)
C(2)−C(3)	1.419(8)	C(2)−C(6)	1.509(8)
C(3)−C(4)	1.488(8)	C(1)−C(7)	1.127(7)
(b) Interbond Angles (deg)			
I(l)−Re(l)−C(7)	79.5(2)	I(l)−Re(l)−C(8)	136.5(3)
C(7)−Re(l)−C(8)	74.5(2)	C(7)−Re(l)−C(7A)	104.8(4)
C(2)−C(l)−C(5)	125.0(4)	C(2)−C(l)−C(2A)	109.6(9)
C(l)−C(2)−C(3)	108.3(6)	C(l)−C(2)−C(6)	126.7(6)
C(3)−C(2)−C(6)	124.7(6)	C(2)−C(3)−C(4)	127.4(6)
C(2)−C(3)−C(3A)	107.0(4)	C(4)−C(3)−C(3A)	125.2(4)
Re(l)−C(7)−O(1)	176.1(6)		

The X-ray structure of *trans*-$Cp^*Re(CO)_2(Me)I$ (Figure 1) confirms the geometry of the isomer and is an addition to the list of structure determinations of related cyclopentadienylrhenium alkyl or aryl complexes. These include *trans*-$Cp^*Re(CO)_2(Ph)I$,[1] *trans*-$Cp^*Re(CO)_2Et_2$,[2] *trans*-$CpRe(CO)_2(CH_2Ph)H$,[9] and *trans*-$CpRe(CO)_2(COMe)Me$.[5] Selected bond lengths and angles are presented in Table 1. The Re−C(Me) bond (2.267(9) Å) is, as expected, longer than the Re−C(Ph) bond (2.191(6) Å) in the corresponding phenyl complex *trans*-$Cp^*Re(CO)_2(Ph)I$.[1] It compares well with corresponding rhenium−alkyl bonds in *trans*-$CpRe(CO)_2(COMe)Me$[5] (2.245(4) Å), *trans*-$CpRe(CO)_2(CH_2Ph)H$[9] (2.29(1) Å), and *trans*-$Cp^*Re(CO)_2Et_2$[2] (2.262(10) Å). The interbond angle subtended by the two CO groups at Re (105°) is also close to the angle in similar trans complexes.[1,2,5−7,9]

2. Photolysis of $Cp^*Re(CO)_2(Me)R$ (R = Ph, *p*-Tolyl, Me) under CO. a. Characterization of the Products. The photolysis ($\lambda \geq 275$ nm) of degassed cyclohexane solutions of *trans*-$Cp^*Re(CO)_2Me$(*p*-tolyl) (**1**) in a Pyrex vessel at room temperature under 1 atm of CO for 20 min led to the decrease of ν(CO) IR bands for the starting complex at 2002 and 1927 cm^{-1} and the production of $Cp^*Re(CO)_3$ (ν(CO) 2012 and 1921 cm^{-1}). The ^1H NMR spectrum of the sample after irradiation showed, in the aromatic region, the presence of some starting material and a new set of resonances assigned to free toluene. The organometallic and organic components from the photolysis of **1** in cyclohexane were separated by vacuum transfer and were analyzed independently.

The GC spectrum of the organic fraction showed a peak with a retention time (RT) of 2.11 min, and the

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(5) (a) Goldberg, K. I.; Bergman, R. G. *Organometallics* **1987**, *6*, 430. (b) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.

(6) Einstein, F. W. B.; Klahn, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

(7) Klahn, A. H.; Leiva, C.; Mossert, K.; Sutton, D. *J. Organomet. Chem.* **1994**, *469*, 69.

(8) Nunn, C. M.; Cowley, A. H.; Lee, S. W.; Richmond, M. G. *Inorg. Chem.* **1990**, *29*, 2105.

(9) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

corresponding GC/MS spectrum gave peaks at *m*/*z* 92 (M^+, 37) and 91 ($M^+ - H$, 100). A toluene sample in cyclohexane showed a similar RT and fragmentation pattern. No evidence of 1,4-dimethylbenzene (*p*-xylene) was observed. The ^{1}H NMR spectrum of the organometallic component in benzene-d_6 showed a resonance at δ 1.72 assigned to Cp*Re(CO)$_3$ and resonances due to residual starting material. The IR spectrum in hexane showed ν(CO) bands corresponding to the starting material and the tricarbonyl complex.[10]

The photolysis was repeated under the same conditions, but this time the gas-phase product was analyzed by GC/MS. This showed a peak with a RT of 2.71 min with *m*/*z* 16 (M^+, 100), 15 ($M^+ - H$, 80), 14 ($M^+ - 2H$, 25) as the sole product. Methane and CO samples were analyzed independently (the latter to check the possible presence of CH_4 in the CO used; none was found), to provide data on the retention time and the fragmentation pattern of the parent ion under our experimental conditions. The CH_4 showed a RT of 2.71 min with *m*/*z* 16 (M^+, 100), 15 ($M^+ - H$, 76), 14 ($M^+ - 2H$, 28). The gas-phase product was therefore identified as methane. No evidence of ethane or acetone was observed.

Photolysis for 20 min of a degassed pentane solution of *trans*-Cp*Re(CO)$_2$(Me)Ph (**2**) in a Pyrex vessel at room temperature under 1 atm of CO also led to loss of ν(CO) IR bands at 2002 and 1927 cm^{-1} for the starting material and the formation of Cp*Re(CO)$_3$. The organometallic and organic components were separated and analyzed as above. The GC spectrum of the organic phase showed a peak with a RT of 1.32 min, and the GC/MS showed peaks at *m*/*z* 78 (M^+, 100) and 77 ($M^+ - H$, 30). A benzene sample in pentane showed a similar RT and fragmentation pattern. The organometallic component showed the presence of complex **2** and Cp*Re(CO)$_3$. Photolysis of **2** was then carried out in cyclohexane at room temperature for 20 min. Methane was the only product observed in the GC/MS of the headspace gas. A new ^{1}H NMR resonance observed at δ 7.20 was assigned as free benzene. No evidence of toluene was observed in either the ^{1}H NMR spectrum or GC/MS.

Photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**3**) under 1 atm of CO in cyclohexane at room temperature for 20 min gave Cp*Re(CO)$_3$ and methane as the only products. No evidence of the formation of ethane, acetone, or 2,3-butanedione was obtained.

To test for the possible photodissociation of CO from the aryl methyl or dimethyl complexes, an *n*-hexane solution of *trans*-Cp*Re(CO)$_2$MeR (R = Ph (**2**), Me (**3**)) in a Pyrex vessel was photolyzed for 25 min at room temperature in the presence of a large excess of PPh$_3$. Gas chromatographic analysis of the product mixture indicated the production of methane in both cases, and for **2** the GC/MS of the organic sample showed the production of benzene. The IR spectrum of the organometallic material only showed new ν(CO) frequencies at 1913 and 1865 cm^{-1}, identified as those of Cp*Re(CO)$_2$PPh$_3$.[11] There was no indication of the formation of Cp*Re(CO)(PPh$_3$)(Ph)Me or Cp*Re(CO)(PPh$_3$)Me$_2$.

b. Isotopic Labeling Studies. Isotopic labeling experiments were done in order to elucidate the hydrogen source in the production of toluene, benzene, and methane in the photolysis of **1**−**3**. First, the photolysis of *trans*-Cp*Re(CO)$_2$(Me)(*p*-tolyl) (**1**) in degassed benzene-d_6 in a sealed NMR tube under CO (1 atm) was monitored by ^{1}H NMR spectroscopy. After ~20 min of irradiation there was a decrease in intensity of the resonances for the starting material and production of resonances due to toluene-4-*d* and Cp*Re(CO)$_3$.

After ~45 min photolysis, the ^{1}H NMR spectrum showed the complete disappearance of the starting material, a decrease in intensity of the resonance due to Cp*Re(CO)$_3$, and new resonances in the Cp* region assigned to Cp*$_2$Re$_2$(CO)$_5$ and Cp*$_2$Re$_2$(CO)$_3$ by comparison of the ^{1}H NMR and IR spectra with those reported previously.[12] A resonance at δ 1.59 was tentatively assigned to Cp*Re(CO)$_2$(η^2-C$_6$D$_6$), by comparison with the ^{1}H NMR and IR spectra of the known compound Cp*Re(CO)$_2$(η^2-C$_6$H$_6$).[12a] Subsequent GC/MS analysis of the organic fraction showed a major product with RT 3.19 min which gave peaks at *m*/*z* 93 (M^+, 64) and 92 ($M^+ - H$, 100), identified as $C_6H_4DCH_3$. There was also a peak at *m*/*z* 97 (M^+, 23), which was identified as $C_6D_5CH_3$. The pattern for $C_6H_4DCH_3$ was similar to that observed for a synthesized sample of toluene-4-*d* (see below). There was also a trace amount of a material giving a peak with RT 5.95 having *m*/*z* 106 (M^+, 50) and 91 ($M^+ - CH_3$, 100), identified as 1,4-dimethylbenzene (*p*-xylene).

The same experiment was carried out for *trans*-Cp*Re(CO)$_2$(Me)Ph (**2**) and *trans*-Cp*Re(CO)$_2$Me$_2$ (**3**) under conditions similar to those above. The ^{1}H NMR spectra in benzene-d_6 after 25 min of photolysis again showed the formation of Cp*Re(CO)$_3$, Cp*$_2$Re$_2$(CO)$_5$, Cp*$_2$Re$_2$(CO)$_3$, and Cp*Re(CO)$_2$(η^2-C$_6$D$_6$), as observed above in the reaction of **1** in benzene-d_6. The GC/MS of the organic fraction after photolysis of **2** showed a peak with RT 3.23 min having *m*/*z* 97 (M^+, 100), which was identified as $C_6D_5CH_3$ (Figure 2), and a small unassigned peak having RT 6.54 min with *m*/*z* 107.

These experiments were repeated under the same conditions in a Pyrex vessel, and this time the gas phase and the organic material were analyzed by GC and GC/MS. After **1** was irradiated in benzene-d_6 under CO (1 atm) for 20 min, the GC/MS of the gas phase showed a peak with RT 2.72 min having *m*/*z* 17 (relative intensity 53), 16 (100), and 15 (40). From a comparison with the spectra of the pure compounds, this spectrum was deduced to be that of a mixture of 68% CH_4 and 32% CH_3D. The highest *m*/*z* value of 17 corresponds to M^+ of CH_3D. However, the peak at *m*/*z* 16 in the sample is the most intense. The GC and GC/MS of the organic fraction showed the presence of $C_6H_4DCH_3$ as the major product and a trace of $C_6D_5CH_3$. A sample of toluene-4-*d* for comparison showed a peak in the GC/MS with a RT of 3.45 min having *m*/*z* 93 (M^+, 65), 92 ($M^+ - H$, 100), and 91 ($M^+ - 2H$ or $M^+ - D$, 25). Thus, this showed the same fragments as observed for toluene but a parent peak of 1 mass unit greater, as expected.

Following the photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**3**) in benzene-d_6 under 1 atm of CO the GC/MS of the gas

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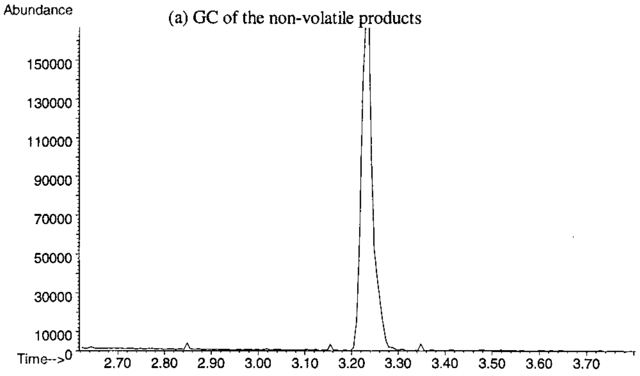
(10) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5810.

(11) Angelici, R. J.; Facchin, G.; Singh, M. M. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 275.

(12) (a) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576. (b) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.


(a) GC of the non-volatile products

(b) RT 3.23 min $C_6D_5CH_3$

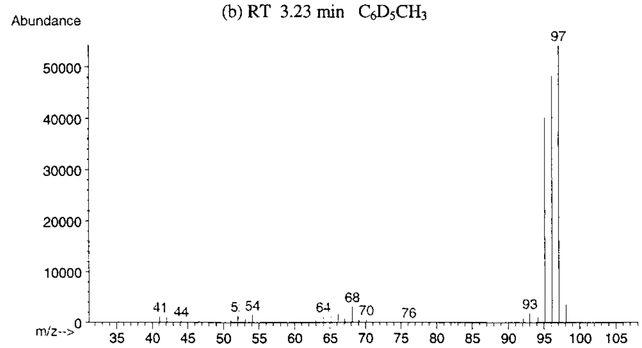


Figure 2. GC/MS results for the organic fraction following the photolysis of **2** in benzene-d_6: (a) GC trace; (b) GC/MS for peak with RT = 3.23 min, indicating $C_6D_5CH_3$.

phase showed a product with a RT of 2.05 min having *m*/*z* 18 (relative intensity 66), 17 (32) 16 (100), 15 (39), and 14 (35). This was deduced to be a mixture of CH_4, CH_3D, and CH_2D_2. The highest *m*/*z* value of 18 corresponds to M^+ for CH_2D_2. However, the peak at *m*/*z* 16 is the most intense. Methane-d_2 was synthesized for a comparison, and the mass spectrum showed that M^+ at *m*/*z* 18 is the most intense peak, there is a less intense peak at *m*/*z* 17 for $M^+ - H$, and the *m*/*z* 16 peak is weak (indicating preferential loss of H over D). The relative ratios of the different constituents in the gas mixture were calculated to be CH_4:CH_3D:CH_2D_2 = 73:8:32. The mechanism proposed for their formation will be discussed below.

c. Photolysis of *trans*-Cp*Re(CO)$_2$(Me)R (R = *p*-Tolyl (1), Me (3)) in CCl$_4$. When the photolysis of *trans*-Cp*Re(CO)$_2$(Me)(*p*-tolyl) (**1**) under CO at room temperature for 20 min was carried out in CCl_4, **1** disappeared and the products observed were Cp*Re(CO)$_2$(*p*-tolyl)Cl and CH_3Cl. The ^1H NMR spectrum of **1** before irradiation showed resonances at δ 0.76 (3H), 1.75 (15H), and 2.39 (3H) assigned to Re–Me, Cp*, and the tolyl ligand, respectively, and tolyl ring proton resonances at δ 6.87 (2H) and 7.52 (2H). The spectrum after irradiation showed new resonances at δ 1.78 (15H) and 2.37 (3H), 6.93 (d, 2H), and 7.51 (d, 2H) assigned respectively to the Cp* and tolyl ligands in the product. The IR spectrum showed two new bands at ν(CO) 2039 and 1962 cm^{-1} (Figure 3).[13,14] The IR and ^1H NMR spectra of the product after chromatography were in agreement with those observed for the crude material. The EIMS gave a weak parent peak at *m*/*z* 504, a fragment at *m*/*z* 476, and a base peak at *m*/*z* 446. The isotopic pattern was consistent with the presence of one chlorine atom. All the spectroscopic data indicated that the product was Cp*Re(CO)$_2$(*p*-tolyl)Cl, which was synthesized by a similar procedure in the absence of CO for comparison (see Experimental Section).

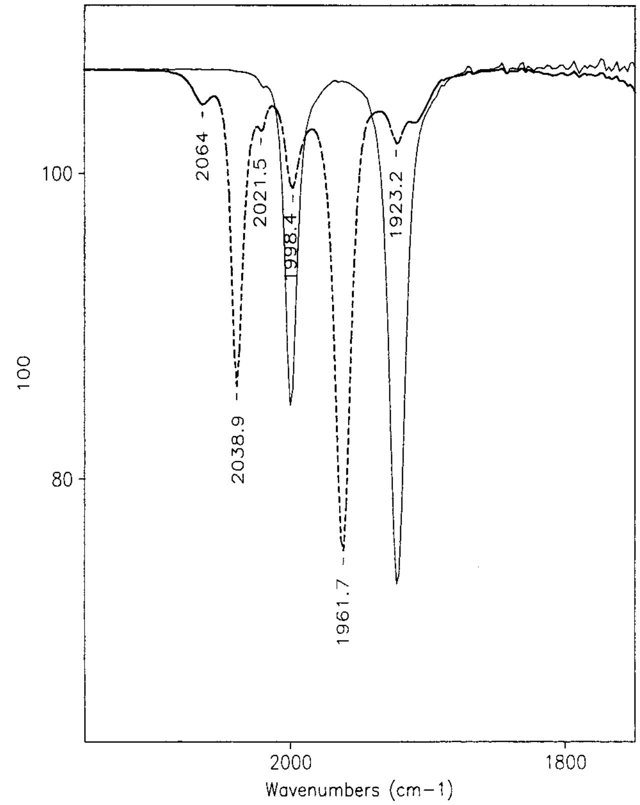


Figure 3. IR spectra before and after photolysis of **1** in CCl_4: (solid line) spectrum of **1**; (dotted line) spectrum after photolysis for 10 min.

The GC/MS of the headspace gas (Figure 4) showed a peak at RT 8.12 min having *m*/*z* 50 (M^+, 100) (Figure 4c) and a peak at RT 12.65 min having *m*/*z* 117 ($M^+ -$ Cl, 100). These were identified as CH_3Cl and CCl_4 solvent, respectively, by a comparison with the retention times and fragmentation patterns observed for authentic samples. The spectrum also revealed traces of CH_4 present in the sample (RT 2.73 min with *m*/*z* 16 (M^+, 100)) (Figure 4b), the formation of which will be discussed below. The photolysis was repeated in the absence of CO, and the same products (CH_3Cl, CH_4 (trace), and Cp*Re(CO)$_2$(*p*-tolyl)Cl) were observed in the GC/MS and IR spectra. The sample was photolyzed an additional 30 min, and no evidence of decomposition or any new products was observed.

Photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**3**) in CCl_4 under CO at room temperature for 10 min led to the loss of ν(CO) IR absorption bands from the starting material (1993 and 1915 cm^{-1}) and the formation of four new bands in the carbonyl region at 2064, 2031, 1997, and 1958 cm^{-1} (Figure 5). The more intense bands at 2064 and 1997 cm^{-1} were assigned to *trans*-Cp*Re(CO)$_2$Cl$_2$.[14] The two weaker bands at 2031 and 1958 cm^{-1} were

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[13] The IR spectrum in CCl_4 also shows absorptions at 2064 and 1998 cm^{-1} assigned to the presence of a small amount of *trans*-Cp*Re(CO)$_2$Cl$_2$.[14]

[14] Klahn-Oliva, A. H.; Ph.D. Thesis, Simon Fraser University, 1986; p 143. Characterizing data are as follows. *trans*-Cp*Re(CO)$_2$Cl$_2$: IR (CH_2Cl_2) ν_{CO} 2059, 1986 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.89. *cis*-Cp*Re(CO)$_2$Cl$_2$: IR (CH_2Cl_2) ν_{CO} 2037, 1959 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98.

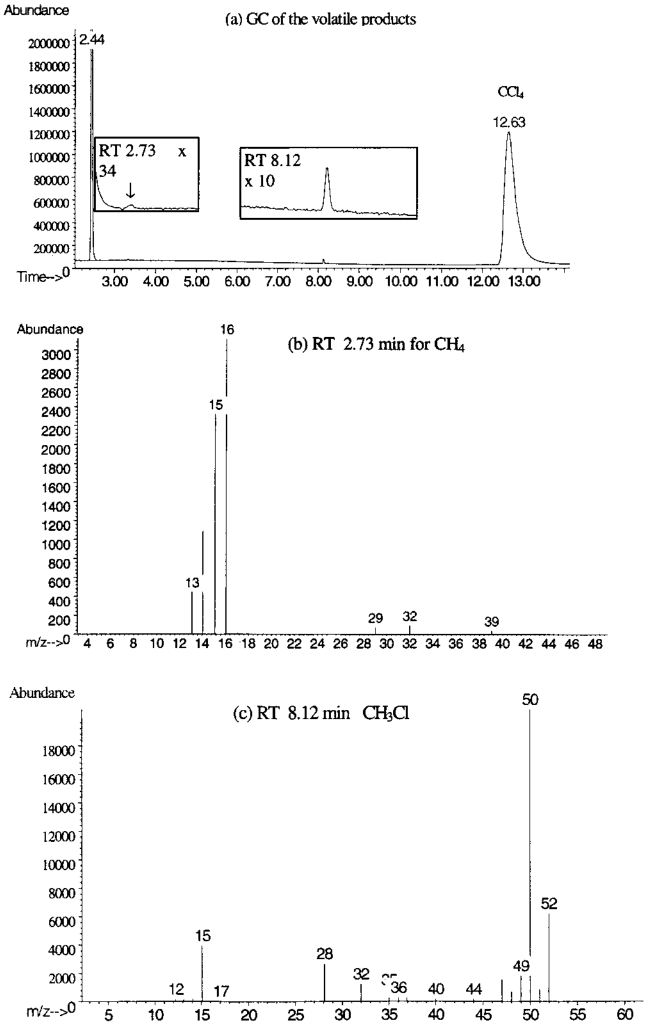

Figure 4. CG/MS results for the volatile products from the reaction of **1** in CCl_4: (a) GC trace; (b) CG/MS for peak with RT = 2.73 min, indicating CH_4; (c) CG/MS for peak with RT = 8.12 min, indicating CH_3Cl.

tentatively assigned to $Cp^*Re(CO)_2(Me)Cl$. The GC/MS of the gas phase showed a peak (RT 7.66 min) with *m*/*z* 50 (M^+, 100), which was identified as CH_3Cl. This was the major product. The spectrum also showed evidence of the formation of CH_4 (RT 2.64 min, *m*/*z* 16 (M^+, 100)) and CH_2Cl_2 (RT 9.94 min, *m*/*z* 84 (M^+, 100)) as minor products.

The photolysis was repeated and was followed by ^1H NMR spectroscopy in CCl_4. The spectrum after 5 min of photolysis showed resonances at δ 1.93 (s, 15H, Cp*) and at δ 0.82 (s, 3H, Me), which were tentatively assigned to $Cp^*Re(CO)_2(Me)Cl$. The spectrum also showed a broad resonance at δ 5.15, which was identified as CH_2Cl_2; no evidence of $Cp^*Re(CO)_3$ was observed. The ^1H NMR spectrum taken after 22 min of photolysis showed a Cp* signal corresponding to *trans*-$Cp^*Re(CO)_2Cl_2$ at δ 2.00 and a weak Cp* signal at δ 2.21, indicating traces of the cis isomer. The reaction was repeated to try to isolate the rhenium products. The IR spectrum after 10 min of photolysis showed the carbonyl bands associated with the unreacted starting material **3** and *trans*-$Cp^*Re(CO)_2Cl_2$ and a small amount of the tentatively assigned $Cp^*Re(CO)_2(Me)Cl$. A yellow-orange solid obtained following chromatography showed a ^1H NMR spectrum (in $CDCl_3$) with a strong resonance at δ 1.88 assigned[14] to *trans*-$Cp^*Re(CO)_2Cl_2$ (the major product) and resonances assigned to $Cp^*Re(CO)_2(Me)Cl$ at δ 0.74 (3H) and 1.80 (15H). The IR, NMR, and mass spectra of a similar product isolated from the irradiation of **3** in CCl_4 under N_2 confirmed the assignment (see Experimental Section).

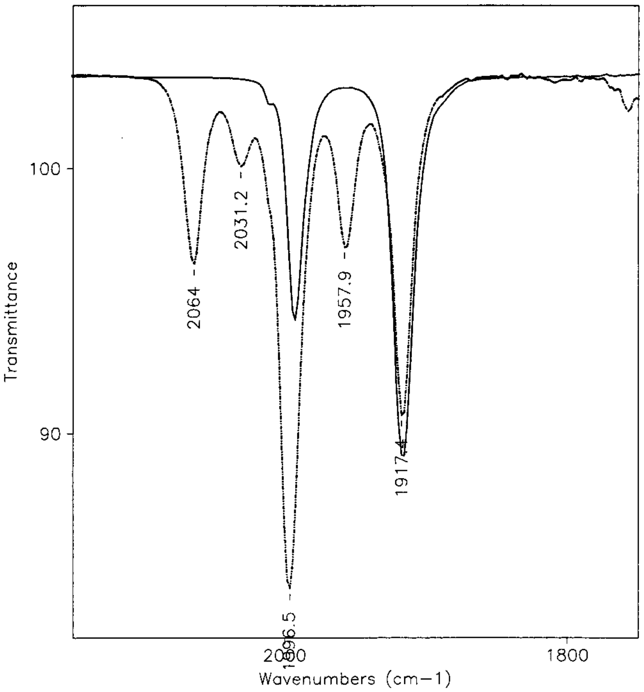

Figure 5. IR spectra before and after photolysis of **3** in CCl_4 (solid line) spectrum of **3**; (dotted line) spectrum after photolysis for 10 min.

Discussion

In previous work, Hill and Palmer studied the photochemistry of *cis*-$Cp^*Re(CO)_2Me_2$ in methylcyclohexene and found that room-temperature photolysis led to the production of *trans*-$Cp^*Re(CO)_2Me_2$ and $Cp^*Re(CO)_3$.[4] At low temperatures, however, the cis−trans isomerization was the only detectable reaction. This isomerization was determined to proceed by photochemical CO loss to give the unsaturated complex $Cp^*Re(CO)Me_2$ followed by recombination with CO. The production of the tricarbonyl species at ambient temperature was presumed to arise from a reaction of the photogenerated unsaturated species with starting complex. This preliminary study was primarily focused on the cis−trans isomerization, and other products associated with the formation of $Cp^*Re(CO)_3$ were not investigated. It was, however, recognized that the low-temperature experiments conducted in a glass may not be representative of reactions at room temperature in solution. This is because bond homolysis may be rapidly followed by recombination in the low-temperature glass, so that no net reaction is observed,[15] whereas homolytic cleavage of the metal−methyl bonds could be an important process under the latter conditions. In this study, by carrying out the ambient-temperature photolysis of the trans isomer (**3**) mainly under CO, we have sought to capture the primary rhenium photoproduct, identify the

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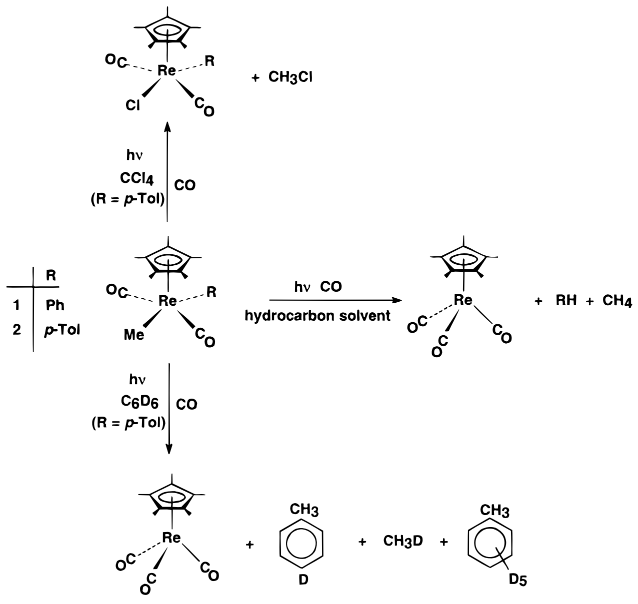
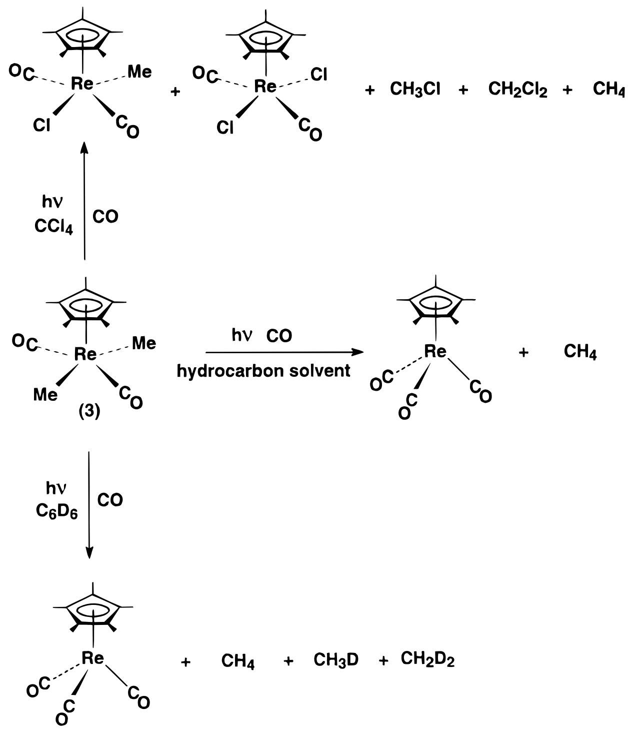
[15] Van Leeuwen, P. W. N. M.; van der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169.

Scheme 1



Scheme 2



fate of the methyl groups, and so determine the details of the photoreaction under these conditions. Furthermore, we have sought to compare the results for the dimethyl compound with two examples of similar aryl methyl complexes. What then emerges is that under these conditions CO loss is unimportant, whereas rhenium–methyl and rhenium–aryl bond homolyses constitute the dominant photoreactions.

Photolysis of *trans*-Cp*Re(CO)$_2$(Me)(*p*-tolyl) (**1**) under CO in cyclohexane produced Cp*Re(CO)$_3$, toluene, and methane. Similarly, photolysis of the phenyl methyl complex **2** in pentane gave the tricarbonyl species, benzene, and methane (Scheme 1). A mechanism consistent with these products is successive homolytic cleavage of the rhenium–methyl and rhenium–aryl bonds to give methyl and aryl radicals followed by hydrogen abstraction from the solvent. In agreement with this hypothesis, photolysis of **1** under CO in benzene-d_6 provided the monodeuterated products toluene-4-*d* and methane-*d* (Scheme 1). In addition, however, a small amount of toluene-d_5 was observed. We consider that this most likely arises from a radical aromatic substitution involving the CH$_3$ radical with the solvent C$_6$D$_6$, as has been proposed by others.[16] Another possible explanation for this product could be oxidative addition of C$_6$D$_6$ to a methylrhenium intermediate followed by reductive elimination of C$_6$D$_5$CH$_3$. This does not seem likely, for several reasons. It would involve a rhenium(IV) or -(V) oxidation level and require loss of a CO ligand in order to provide a vacant site for the activation of the solvent. However, when **1** was photolyzed in the presence of a large excess of PPh$_3$, we did not observe any evidence for the formation of the (triphenylphosphine)rhenium complex Cp*Re(CO)(PPh$_3$)(Me)Ph, suggesting that overall photochemical loss of CO from **1** does not readily occur. This is not necessarily in conflict with the previous evidence for CO dissociation in the case of *cis*- and *trans*-Cp*Re(CO)$_2$Me$_2$ in low-temperature glasses,[4] since as mentioned above metal–carbon bond homolysis may not be observable in a low-temperature glass due to rapid back-reaction but may be overwhelmingly faster than CO dissociation in solution at ambient temperature.

No evidence of the reductive-elimination products *p*-xylene and toluene was observed in the photolysis of **1** or **2** in cyclohexane, but when the photolysis of **1** was carried out in benzene-d_6, traces of *p*-xylene were detected. One explanation for this is a degree of recombination of CH$_3^\bullet$ with CH$_3$C$_6$H$_5^\bullet$ in the benzene solvent cage. Nevertheless, carbon–carbon bond formation by reductive elimination from the photoexcited rhenium aryl methyl complexes does not appear to be an important pathway.

Further evidence for homolytic cleavage of the metal–methyl bond in these aryl methyl complexes is the formation of CH$_3$Cl in the photolysis of **1** in CCl$_4$ under CO. However, it is significant that we did not also observe the correspondingly trapped aryl radical as CH$_3$C$_6$H$_4$Cl. Furthermore, the products differed in several ways from those observed for photolyses in hydrocarbon solvents (Scheme 1). No Cp*Re(CO)$_3$ was detected, but instead the formation of the aryl chloro complex Cp*Re(CO)$_2$(*p*-tolyl)Cl was indicated. These results suggest that homolysis of the Re–methyl bond is much faster than that of the Re–aryl bond (in accord with the expectation that the Re–methyl bond is weaker) and that the radicals so formed (CH$_3$ and Cp*Re(CO)$_2$(*p*-tolyl)) rapidly abstract Cl from CCl$_4$. The solvent dependence of the product distribution in each case reflects the relative ease of Cl abstraction from the chlorinated solvent compared with H from the hydrocarbon solvent. Noticeably, in CCl$_4$ the same products were obtained in the presence or absence of added CO and did not include Cp*Re(CO)$_3$, indicating also that the rate of successive homolysis of the Re–CH$_3$ *and* Re–aryl bonds necessary to furnish the Cp*Re(CO)$_2$ fragment required for CO uptake to give Cp*Re(CO)$_3$ is

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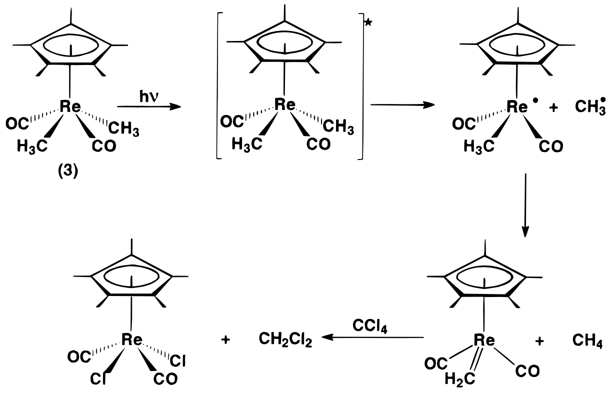
[16] Rausch, M. D.; Boon, W. H.; Mintz, E. A. *J. Organomet. Chem.* **1978**, *160*, 81.

Scheme 3



prohibitively slow compared with the abstraction of Cl by the primary photoproducts indicated above.

Turning now to the simpler dimethyl complex, the photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**3**) under CO in cyclohexane formed CH$_4$ and Cp*Re(CO)$_3$ as the only products (Scheme 2). Again, no evidence of reductive-elimination products such as ethane and acetone was observed. These products are consistent with the primary photoprocess being successive homolysis of the Re$-$methyl bonds to give Cp*Re(CO)$_2$ and $CH_3^{\bullet}$ that abstracts hydrogen from the solvent. However, further investigation on the photolysis of **3** carried out in benzene-d_6 showed that methane, methane-d, methane-d_2, and Cp*Re(CO)$_3$ were all formed. The methane-d must result from deuterium abstraction from the solvent by CH$_3$, in agreement with the postulated mechanism. The formation of undeuterated methane may result from a methyl group abstracting hydrogen from the other methyl group that remains coordinated to the metal center. The concurrent formation of CH$_2$D$_2$ is consistent with such a mechanism, where it may be envisaged that in the presence of CO the rhenium methylene intermediate Cp*Re(CO)$_2$CH$_2$ reacts further with the deuterated solvent or dissociates a transient methylene which does so (Scheme 3).

Another possible explanation for the formation of methane is an intramolecular α-hydrogen transfer, which would also form the same rhenium methylene intermediate. This mechanism has been proposed to occur for manganese, cobalt, and tungsten alkyl complexes.[17] Our results, however, suggest that the dominant photoprocess in the case of **3** is homolytic cleavage of the methyl$-$rhenium bonds.

The photolysis of **3** under CO in CCl$_4$ produced CH$_3$Cl, as expected if Re$-$CH$_3$ homolysis occurs. A product with IR ν(CO) bands, mass spectrum, and ^{1}H NMR resonances consistent with the formulation *trans*-Cp*Re(CO)$_2$(Me)Cl was formed in moderate yield, but the major rhenium product was *trans*-Cp*Re(CO)$_2$Cl$_2$ (Scheme 2). Notably, no Cp*Re(CO)$_3$ was formed from photolysis in this solvent. These results suggest that the initial rhenium photolysis product Cp*Re(CO)$_2$Me is rapidly scavenged by the chlorinated solvent to give Cp*Re(CO)$_2$(Me)Cl. The Cp*Re(CO)$_2$Cl$_2$ formed could arise from loss of the second methyl from either of the above to leave the Cp*Re(CO)$_2$ or Cp*Re(CO)$_2$Cl fragments that are also scavenged by the solvent. The positions and intensity ratios of the ν(CO) absorption bands and the positions of the Me and Cp* resonances of *trans*-Cp*Re(CO)$_2$(Me)Cl are similar to those observed for *trans*-Cp*Re(CO)$_2$(Me)I, whose structure has been determined in this work, and thus support the assignment of trans stereochemistry.

The formation of also some methane and dichloromethane from the photolysis of **3** in CCl$_4$ can be accounted for in much the same way as the formation of CH$_4$ and CH$_2$D$_2$ in the reaction with benzene-d_6, as discussed above and shown in Scheme 3. The production of Cp*Re(CO)$_2$(η^2-C$_6$D$_6$), Cp*$_2$Re$_2$(CO)$_5$, and Cp*$_2$Re$_2$(CO)$_3$ complexes from the photolysis of **1**$-$**3** in benzene-d_6 is not unexpected, since these are known photoproducts of the photolysis of Cp*Re(CO)$_3$.[12]

While in the photolyses reported here the overwhelming evidence is for homolysis of the rhenium$-$methyl and $-$aryl bonds, in previous studies of the photochemistry of metal$-$methyl and metal$-$aryl complexes, evidence supporting either bond homolysis or reductive elimination has been obtained, depending on the particular case.[18] The photolysis of diphenylbis(cyclopentadienyl)titanium[16,19] and -zirconium[20] complexes yielded benzene and biphenyl, and it was shown that the biphenyl arises both from reductive elimination *and* (along with benzene) by homolysis followed by attack of a radical-like species on the solvent.[16]

Metal$-$methyl bond homolysis has been observed in the photolysis of CpCo(PPh$_3$)Me$_2$ or [Me$_2$Co(bpy)$_2$]ClO$_4$ in toluene or benzene, where methane was a major product.[21] Similar results have been reported for the photolysis of Cp$_2$TiMe$_2$ and Cp$_2$ZrMe$_2$, where again methane was a major product.[15,22] In each of these cases, the source of abstracted hydrogen was identified to be the solvent. However, there is also the possibility of a cyclopentadienyl ligand providing the hydrogen source.[16,20] On the other hand, photochemical reductive elimination of methyl groups to give ethane has also been observed in a few specific cases.[21,23]

While the only previous photochemical study of Cp*Re(CO)$_2$Me$_2$ has been that of Hill and Palmer mentioned above,[4] the cyclopentadienyl analogue CpRe(CO)$_2$Me$_2$ was studied by Goldberg and Bergman under photochemical and thermal conditions.[5] They found that irradiation of CpRe(CO)$_2$Me$_2$ under 20 atm of CO gave a clean conversion to 2,3-butanedione, CpRe(CO)$_3$, and a trace of acetone but no evidence of ethane or methane was observed. They proposed that homolysis of rhenium$-$methyl bonds occurs in this reaction and that the methyl radicals undergo carbonylation followed by combination of the acetyl radicals to yield the 2,3-butanedione. Upon photolysis of CpRe(CO)$_2$Me$_2$ in CCl$_4$,

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(17) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Part I, Chapter 7, p 285. (b) Cross, R. J. In *The Chemistry of the Metal$-$Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 599.

(18) For reviews of organometallic photochemistry see: (a) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249. (b) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(19) Peng, W.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1978**, *26*, 231.

(20) Tung, H.-S.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1981**, *52*, 197.

(21) (a) Becalska, A.; Hill, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4346. (b) Fukuzumi, S.; Ishikawa, K.; Tanaka, T. *Organometallics* **1987**, *6*, 358.

(22) Samuel, E. *J. Organomet. Chem.* **1980**, *198*, C65 and references therein.

(23) Hill, R. H.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1472.

acetyl chloride, CH_3Cl, and $CpRe(CO)_3$, and a trace of acetone were obtained. When the reaction was carried out with a better radical trap ($CBrCl_3$), the only products observed were CH_3Br and $CpRe(CO)_2(Me)Br$.[5] In our experiments, we did not observe any CO incorporation into the organic products at 1 atm of CO, but we did not carry out photolyses with higher CO pressures.

Conclusion

The complexes *cis*- and *trans*-$Cp^*Re(CO)_2(Me)I$ have been synthesized, and the crystal structure of the trans isomer has been determined. The photochemistry of *trans*-$Cp^*Re(CO)_2Me_2$ in solution at room temperature is found to differ from that previously reported in a glass at low temperature and involves homolysis of the rhenium−methyl bonds. The methyl radicals then react with the hydrocarbon or chlorinated solvent to give CH_4 or CH_3Cl. The corresponding methyl phenyl or methyl *p*-tolyl complexes are found to undergo homolysis of the Re−methyl bond faster than that of the Re−aryl bond so that photolysis in CCl_4 results in the ability to observe the aryl chloro complexes $Cp^*Re(CO)_2(Ph)Cl$ and $Cp^*Re(CO)_2$(*p*-tolyl)Cl.

Experimental Section

General Methods. All manipulations were performed under nitrogen by using standard Schlenk or vacuum line techniques unless stated otherwise. The complexes *trans*-$Cp^*Re(CO)_2MeR$ (R = *p*-tolyl, Ph, Me) were prepared by the published procedures.[1,2] All solvents were freshly distilled under nitrogen. Pentane, cyclohexane, and hexane were distilled from sodium wire, diethyl ether was distilled from sodium and benzophenone, and CCl_4 was dried over P_4O_{10} and distilled from 4A sieves. All reagents were obtained from Aldrich except where mentioned. The CO was purchased from Linde, D_2 was purchased from Matheson, and D_2O (99.9%) was purchased from Isotec Inc. IR spectra were recorded on a Bomem Michelson-120 spectrophotometer. The samples were run in solution in a CaF_2 cell. ^1H NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.13 MHz. The ^1H NMR spectra in nondeuterated solvents were carried out using a standard suppression program from the Bruker pulse program library. Gas chromatographic analyses were performed by using a Hewlett-Packard 5880A instrument equipped with a flame ionization detector and a fused-silica DB-1 coated column (15 m × 0.25 mm i.d.; 0.25 mm film). Mass spectra and CG/mass spectra were obtained on Hewlett-Packard 5985B or G1800A GC/MS instruments equipped with a DB-1 fused-silica column (30 m × 0.25 mm i.d.; 0.25 mm film) or a GSQ column (30 m × 0.53 mm i.d.) (J & W Scientific) with a 100 μL sampling loop at variable pressure, operating at 70 eV for electron impact (EI). Because of different instrumental conditions (e.g., column length) quoted retention times for GC and/or GC/MS runs on different samples are not necessarily comparable, except where indicated. The masses are reported for ^{35}Cl and ^{187}Re isotopes where present. Photochemical reactions were carried out under CO (1 atm) at room temperature with a water-jacketed 200 W Hanovia medium-pressure mercury lamp as the UV source. The irradiation was conducted in a Pyrex tube, which was placed adjacent to the lamp, or in sealed 5 mm NMR tubes.

Preparation of *cis*- and *trans*-$Cp^*Re(CO)_2(Me)I$. To a suspension of yellow MeCu in 10 mL of THF (prepared from 200 mg (0.9 mmol) of $CuBr{\cdot}SMe_2$ (Aldrich) and 1.2 mL (1.9 mmol) of MeLi (Aldrich, 1.4 M in diethyl ether) at −23 °C) was added 150 mg (0.24 mmol) of solid $Cp^*Re(CO)_2I_2$. The resulting mixture was stirred at −23 °C for 40 min and then warmed to room temperature and stirred for an additional 40 min. At this point the IR spectrum in THF showed the complete disappearance of the diiodo complex and strong absorption bands at 2004 and 1939 cm^{-1}. The reaction mixture was then concentrated under vacuum to about one-third of its initial volume and 2 drops of water were added to destroy the excess MeCu. Filtration through Celite and evaporation of the solvent to dryness yielded an orange solid. In column chromatography on silica gel 60 (prepared in hexane), a mixture of hexane/CH_2Cl_2 (4:1) moved an orange-yellow band of *trans*-$Cp^*Re(CO)_2(Me)I$, from which a yellow solid was obtained. Further elution with hexane/CH_2Cl_2 (1:1) moved a red band of the cis isomer.

Data for *trans*-$Cp^*Re(CO)_2(Me)I$ are as follows. Mp: decomposed over 185 °C. IR (CH_2Cl_2): ν_{CO} 2010 (s), 1937 (vs) cm^{-1}. IR (hexane): ν_{CO} 2018 (s), 1954 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.79 (s, 3H, Me) and 1.97 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −26.90 (Me), 10.40 (C_5*Me_5*), 99.80 (*C_5*Me_5), and 193.98 (CO). EIMS (*m/z*): 520 (M^+), 505 ($M^+ - Me$), 492 ($M^+ - CO$). Anal. Found: C, 30.02; H, 3.35. Calcd for $C_{13}H_{18}O_2IRe$: C, 30.00; H, 3.46.

Data for *cis*-$Cp^*Re(CO)_2(Me)I$ are as follows. Red crystals. Mp: decomposed over 185 °C. IR (CH_2Cl_2): ν_{CO} 2041 (vs), 1966 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (s, 3H, Me) and 2.00 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −18.20 (Me), 10.19 (C_5*Me_5*), 101.24 (*C_5*Me_5), and 204.06 and 207.96 (CO). EIMS (*m/z*): 520 (M^+), 505 ($M^+ - Me$), 492 ($M^+ - CO$). Anal. Found: C, 30.04; H, 3.34. Calcd for $C_{13}H_{18}O_2IRe$: C, 30.00; H, 3.46.

Crystal Structure Determination. Dark orange crystals of *trans*-$Cp^*Re(CO)_2(Me)I$ suitable for X-ray crystallography were obtained from CH_2Cl_2/hexane (1:1) at −20 °C. A dark orange polyhedral-shaped crystal of dimensions ca. 0.16 × 0.14 × 0.08 mm was mounted on a glass fiber and used for crystallographic measurements. The intensity data were collected at 298 K on a Siemens R3/V diffractometer using graphite-monochromated Mo Kα radiation in the $2\theta/\theta$ scan mode with 2 standard reflections monitored every 100 reflections. A total of 1419 unique reflections were collected, of which 1215 were considered as observed with $I > 2\sigma(I)$. Lattice parameters and their esds were derived from the setting angles of 25 reflections with $5° \le 2\theta \le 40°$. The structure was solved by direct phase determination. The positional and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares cycles. The hydrogen atom positions were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic *U* values. The programs used to solve and refine the structure were SHELXS-97 and SHELXL-97, respectively. Final agreement factors were $R = 0.035$, $R_w = 0.061$, and $S = 0.978$, on the basis of all data. Final $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 0.74$, and $\Delta\rho_{min} = -0.97$ e Å^{-3} on the final difference Fourier map. The atomic scattering factors were taken from the SHELXL-97 program. Selected interatomic distances and bond angles are included in Table 1. All other data are provided as Supporting Information.

Gas Chromatography and GC/MS Control. Authentic samples of benzene, toluene, *o*-, *m*-, and *p*-xylene (dimethylbenzene), acetone, chlorobenzene, *p*-chlorotoluene, and biacetyl in solution were examined by GC and GC/MS to establish retention times and mass spectral patterns. These runs were repeated for the different solvents used in the photolysis experiments. Similarly, gas analysis was carried out for CO, N_2, CH_4, CH_3Cl, CH_2Cl_2, CCl_4, benzene-*d_6*, cyclohexane, and hexane.

Room-Temperature Photolysis. All the experiments were conducted in a similar manner. Therefore, a typical procedure will be described. A solution of *trans*-$Cp^*Re(CO)_2Me$(*p*-tolyl) (**1**) (20 mg, 0.041 mmol) in cyclohexane (5 mL) was transferred to a Pyrex Carius tube (fitted with a Teflon valve) and subjected to three freeze−pump−thaw cycles. The vessel was then filled with CO (1 atm) and sealed. The solution was irradiated for approximately 20 min in a water bath at room temperature. After photolysis the crude sample was analyzed by IR and ^{1}H NMR spectroscopy, gas chromatography (GC), and GC/MS.

Synthesis of Toluene-4-*d*. A solution of *p*-tolylmagnesium bromide was prepared by standard methods.[24] A 2 mL sample was transferred under N_2 into a Schlenk tube in a cold water bath, and D_2O was slowly added dropwise until no further reaction was observed. The product was extracted with hexane (2 × 2 mL). The GC showed a peak with RT 4.44 min. The GC/MS showed a peak with RT 3.45 having *m*/*z* 93 (M^+, 65), 92 ($M^+ - H$, 100), and 91 ($M^+ - 2H$ or $M^+ - D$, 25). A toluene sample was run under the same experimental conditions to aid in the identification. The GC showed a peak with RT 4.47 min. The GC/MS showed a peak with RT 3.45 having *m*/*z* 92 (M^+, 55) and 91 ($M^+ - H$, 100).

Synthesis of Methane-*d*. Methylmagnesium bromide was prepared by a standard method.[24] A 6 mL sample was transferred under N_2 into a Schlenk tube in a cold water bath and subjected to three freeze−pump−thaw cycles, and D_2O (99.9%) was slowly added by syringe until no further reaction was observed. The mass spectrum was run by taking a headspace sample in a gas syringe and injecting the sample into the GC/MS. The GC/MS showed a peak with RT 1.37 having *m*/*z* 17 (M^+, 100), 16 ($M^+ - H$, 61) and 15 ($M^+ - 2H$ or $M^+ - D$, 22).[25]

Synthesis of Methane-*d*$_2$.[26] Raney nickel was prepared by a standard method[27] and was washed several times with D_2O to remove any ethanol present. A D_2O solution of 1,3-dithiane was added to the Raney nickel under N_2 at room temperature. The mixture was subjected to three cycles of freeze−pump−thaw and was slowly warmed to room temperature. D_2 gas was bubbled into the closed system for 3 min. The mass spectrum was run by taking a headspace sample in a gas syringe and injecting into the GC/MS. The GC/MS showed a peak with a RT 1.40 with *m*/*z* 18 (M^+, 100), 17 ($M^+ - H$, 28) and 16 ($M^+ - 2H$ or $M^+ - D$, 3).[25]

Characterization of Cp*Re(CO)$_2$(*p*-tolyl)Cl. A solution of Cp*Re(CO)$_2$Me(*p*-tolyl) (**1**; 25 mg, 0.05 mmol) in 3 mL of freshly distilled CCl_4 was degassed twice by freeze−pump−thaw and then irradiated for 15 min at room temperature. During the photolysis, a slow flux of N_2 was maintained. The IR spectrum after the photolysis indicated the disappearance of the methyl tolyl complex **1**. The solvent was removed, and the residue was dissolved in ca. 2 mL of hexane and the solution transferred to an air-free neutral alumina column prepared in hexane. The complex was eluted with a hexane/ether mixture (5:1). A yellow band was collected, and the solvent was removed under vacuum to give a yellow-orange powder. IR (hexane): ν_{CO} 2041, 1966 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 15H, Cp*), 2.28 (s, 3H, Me), 6.92 (d, 2H, C_6H_4Me, $J_{H-H} = 8.0$ Hz), 7.50 (d, 2H, C_6H_4Me, $J_{H-H} = 8.0$ Hz). EIMS (*m*/*z*): 504 (M^+), 476 ($M^+ - CO$), 446 ($M^+ - 2CO - 2H$).

Characterization of Cp*Re(CO)$_2$(Me)Cl. A solution of Cp*Re(CO)$_2$Me$_2$ (**3**; 20 mg, 0.05 mmol) in 3 mL of freshly distilled CCl_4 was degassed by two freeze−pump−thaw cycles and then irradiated for 10 min at room temperature. During the photolysis a slow flux of N_2 was maintained. The IR spectrum after the photolysis exhibited carbonyl bands associated with the starting material **3**, Cp*Re(CO)$_2$Cl$_2$, and Cp*Re(CO)$_2$(Me)Cl. The solvent was removed, and the residual solid was dissolved in ca. 2 mL of hexane and the solution transferred to an air-free neutral alumina column prepared in hexane. The starting material **3** was eluted with hexane, and a yellow band was eluted with a hexane/diethyl ether mixture (5:1). The solvent was removed under vacuum, and a yellow-orange powder was obtained. The IR spectrum of the yellow-orange product in hexane showed two different species. One species was identified as *trans*-Cp*Re(CO)$_2$Cl$_2$ as the major product. IR (hexane): ν_{CO} 2066, 2000 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.88 (s, Cp*). EIMS (12 eV; *m*/*z*): 448 (M^+), 420 ($M^+ - CO$), 392 ($M^+ - 2CO$). The minor species present was identified as Cp*Re(CO)$_2$(Me)Cl. IR (hexane): ν_{CO} 2033, 1960 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.74 (s, 3H, Me), 1.80 (s, 15H, Cp*). EIMS (12 eV; *m*/*z*): 428 (M^+), 400 ($M^+ - CO$), 372 ($M^+ - 2CO$).

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Supporting Information Available: Tables of crystallographic data and collection conditions, coordinates and displacement coefficients for the non-hydrogen atoms, all bond lengths and interbond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for Cp*Re(CO)$_2$(Me)I (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[24] Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Practical Organic Chemistry*, 5th ed.; Longman Scientific & Technical: New York, 1989; p 531.

[25] For a discussion of the mass spectra of deuterium-substituted methanes see: (a) Evans, M. W.; Bauer, N.; Beach, J. Y. *J. Chem. Phys.* **1946**, *14*, 701. (b) Stevenson, D. P.; Wagner, C. D. *J. Chem. Phys.* **1951**, *19*, 11.

[26] Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989; p 29.

[27] Reference 24, p 450.