$(ARENE)M(CO)_{3-x}(SiCl_3)_x$
$(M = Mn, Re, x = 2; M = Ru, x = 1)$
DERIVATIVES

by

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$M = Ru, x = 1$) DERIVATIVES

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ABSTRACT

Compounds of the type (arene)$M(CO)_{3-x}(SiCl_3)_x$ (M = Mn, Re, x = 1; M = Ru, x = 2) were synthesized by heating the corresponding $M(CO)_{6-x}(SiCl_3)_x$ complex with the appropriate arene. The complexes were characterized by ^1H and ^{13}C NMR, IR and mass spectroscopy, and C/H analysis. The (arene)$Re(CO)_2(SiCl_3)$ derivatives where arene = C_6H_6, MeC_6H_5, $Bu^tC_6H_5$, 1,4-$Me_2C_6H_4$, 1,4-$Pr^i{}_2C_6H_4$, 1,4-$Bu^t{}_2C_6H_4$, 1,3,5-$Me_3C_6H_3$, 1,2,3,4-$Me_4C_6H_2$, 1,2,4,5-$Me_4C_6H_2$, Me_6C_6, and Et_6C_6 were prepared at 240 °C in yields of 25 to 80%. The manganese compounds, (arene)$Mn(CO)_2(SiCl_3)$, where arene = C_6H_6, MeC_6H_5, $Bu^tC_6H_5$, 1,2-$Me_2C_6H_4$, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$, 1,4-$Bu^t{}_2C_6H_4$, and Et_6C_6 were prepared at 230 °C in yields of 20 to 60%. The (arene)$Ru(CO)(SiCl_3)_2$ compounds where arene = Et_6C_6 or 1,3,5-$Bu^t{}_3C_6H_3$ were prepared at 150 °C in 80% yields.

Some of the (arene)$M(CO)_{3-x}(SiCl_3)_x$ complexes were of interest in the study of restricted rotation about the arene-transition metal bond. They are related to complexes such as (1,4-$Bu^t{}_2C_6H_4$)$M(CO)(SiCl_3)_2$ (M = Ru, Os) which are rare examples of complexes that exhibit this type of restricted rotation. The complexes studied here included (1,4-$Bu^t{}_2C_6H_4$)$Mn(CO)_2(SiCl_3)$, (Et_6C_6)$Re(CO)_2(SiCl_3)$, (Et_6C_6)$Ru(CO)(SiCl_3)_2$, and (Et_6C_6)$Mn(CO)_2(SiCl_3)$. There was no evidence for restricted rotation of the arene ring about

the arene-manganese bond in the $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ complex even though the metal-arene distance is shorter than that in the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ compound.

The line-shape analysis of the variable temperature ^1H NMR spectra of the signals due to the aromatic CH protons of $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ provided the following parameters for the barrier to rotation about the arene-ruthenium axis: $\Delta H^{\ddagger} = 26 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -52 \pm 11$ J mol^{-1} K^{-1}, and $\Delta G^{\ddagger}_{298} = 41 \pm 5$ kJ mol^{-1}. Surprisingly, this barrier is lower than that in $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$.

The low temperature ^{13}C NMR spectra of the complex $(Et_6C_6)Re(CO)_2(SiCl_3)$ exhibited decoalescence phenomena below -20 °C. This phenomenon is interpreted as the slowing of ethyl group rotation rather than restricted rotation of the arene ring about the arene-transition metal axis.

The low temperature ^{13}C NMR studies of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex exhibited no decoalescence phenomenon, i.e., the signals remained sharp singlets, to -90 °C. This behaviour was attributed to the presence of the conformer with all the methyl groups distal to the $Ru(CO)(SiCl_3)_2$ fragment, along with free rotation of arene ring about the metal atom.

DEDICATION

TO GARFIELD FOR HANGING IN THERE!

QUOTATION

NE TE CONFINDANT ILLEGITIMI

(Don't let the bastards get you down)

ACKNOWLEDGEMENTS

I would like to thank Marcey Tracey and Dr. Anna Becalska, for their help in obtaining the low temperature NMR spectra for this study.

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A special thanks to my personal "chew dog", Mutley, for taking more abuse than one skinny, little Englishman deserves.

Last, but not least, I would like to extend my gratitude to my supervisor, Prof. R.K. Pomeroy, for his support and guidance throughout this project. Thanks for being there.

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INTRODUCTION

Complexes with an arene π-bonded to a transition metal were first prepared in 1919[1]. However, it was not until the mid-fifties that the exact nature of these complexes was ascertained.[2] Since that time virtually all transition metals have been shown to form complexes with an η^6-arene to metal bond.[3]

The first silicon-transition metal bond was synthesized in 1956.[4] Like arene-transition metal complexes, many compounds having silicon-transition metal bonds are now known.[5]

Pomeroy and co-workers [6,7] have prepared a number of complexes containing both an arene ligand and a silicon-transition metal bond. Numerous compounds of the type (arene)M(CO)$(SiCl_3)_2$ where M = Os or Ru were prepared by heating the aromatic hydrocarbon with the appropriate $M(CO)_4(SiCl_3)_2$ complex. Two compounds of the type (arene)$Re(CO)_2(SiCl_3)$ had also been prepared by a similar method. To further add to the series of arene-transition metal complexes containing a silicon-transition metal bond the preparation of derivatives of the type (arene)$M(CO)_2(SiCl_3)$ where M = Re or Mn have been carried out. The latter complexes would be the first manganese-arene complexes which also contain a manganese-silicon bond.

The (arene)M(CO)$(SiCl_3)_2$ complexes, (M = Ru, Os), are interesting since some of them exhibit restricted rotation of the arene ring about the transition metal.[6,7] The derivative $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ was one of the first compounds found to exhibit a barrier to rotation about the arene-transition metal bond which could be observed on the NMR time scale.[6] This barrier to rotation of an arene ring about the arene-transition metal axis has been of interest for some time.[8] It is usually small[9] but when special steric[10] or electronic[11] interactions are present in a complex the barrier can become large. This allows for slowed or even halted rotation of the aromatic ring about the arene-transition metal axis to be observed on the NMR time scale. Such is the case for the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ where steric interactions between the large trichlorosilyl ligands and the bulky t-butyl substituents of the arene ring, prevent the free rotation of the arene ring at low temperatures.

There are other compounds which are of interest in the study of the influence of steric interactions on the rotation of the arene ring around the arene-transition metal axis. The first of these compounds is $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$. In this complex the shorter manganese-arene distance would be expected to increase the steric interactions between the t-butyl and trichlorosilyl groups so as to increase the barrier to rotation about the arene-manganese bond compared to that in the rhenium analogue. Thus, whereas no barrier to rotation about the arene-rhenium bond was observed on the NMR time scale for the $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$[7] complex, a barrier to rotation about the arene-manganese bond might be observed for $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$.

Another arene-transition metal complex of interest was $(1,3,5\text{-}Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$. Surprisingly, preliminary results indicated there was a smaller barrier to rotation about the arene-ruthenium bond in this complex than in the corresponding $(1,4\text{-}Bu_2{}^tC_6H_4)Ru(CO)(SiCl_3)_2$ derivative.[7] More accurate values of the parameters to the barrier to rotation in the $(1,3,5\text{-}Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex would be helpful in the study of the detailed mechanism of the rotation of the arene ring about the arene-transition metal axis in these complexes.

Finally, three hexaethylbenzene complexes of the type $(Et_6C_6)M(CO)_x(SiCl_3)_{3-x}$ (M = Re, Mn, $x = 2$; M = Ru, $x = 1$) were prepared. These complexes are of interest in the study of the rotation of the hexaethylbenzene ligand about the hexaethylbenzene-transition metal bond. It was thought that the results of the low temperature NMR studies of the above complexes would be useful in helping to resolve the current controversy in the literature between McGlinchey and Mislow and their respective co-workers. This controversy involves the interpretation of the coalescence phenomenon observed in the NMR spectra of several $(Et_6C_6)ML_3$ complexes, most notably $(Et_6C_6)Cr(CO)_2(CS)$. McGlinchey[12] has interpreted the changes in the variable temperature NMR spectra of the compound as restricted rotation of the hexaethylbenzene ligand about the arene-transition metal bond. On the other hand, Mislow[13] believes that the phenomenon can be explained solely on the basis of halted ethyl group rotation on the hexaethylbenzene ligand itself.

McGlinchey has recently provided convincing NMR evidence for halted arene ring rotation about the $[Et_5(OAc)C_6]$-chromium bond in $[Et_5(OAc)C_6]Cr(CO)_3$.[14] The NMR studies of hexaethylbenzene-transition metal complexes prepared in this study, however, show no evidence for halted or even slowed arene rotation in molecules which are more sterically crowded than those studied by McGlinchey. Further investigation is needed to completely understand the factors involved in the rotation of hexaethylbenzene about the arene-transition metal bond.

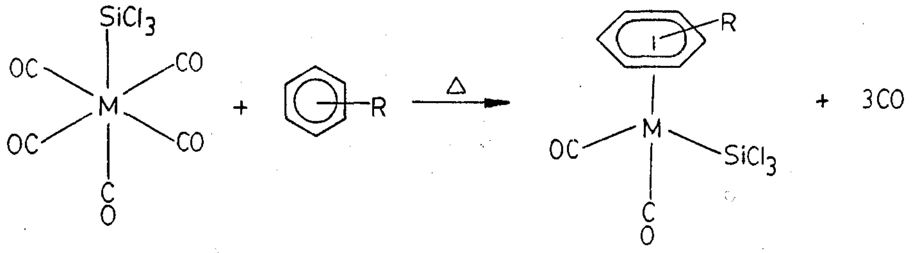
The NMR studies of the rotational barriers of the hexaethylbenzene-transition metal complexes, along with those the $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ and $(1,3,5\text{-}Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ compounds will also provide valuable data for the Ph.D. project of Mr. A. Ramos. He is carrying out the theoretical modeling of the barrier to rotation in arene-transition metal complexes.

RESULTS AND DISCUSSION

1. (Arene)Re$(CO)_2(SiCl_3)$ Complexes

All of the (arene)Re$(CO)_2(SiCl_3)$ complexes were prepared in 20-80% yield by heating $Re(CO)_5(SiCl_3)$ and the aromatic hydrocarbon at 240 °C for 12 h (260 °C and 24 h for hexamethyl- and hexaethylbenzene derivatives) in a sealed tube. The $Re(CO)_5(SiCl_3)$ complex was prepared from $Re_2(CO)_{10}$ and $HSiCl_3$ by the literature method.[15] The general reactions involved in the preparation of the (arene)Re$(CO)_2(SiCl_3)$ derivatives are shown in Equation 1.1 where M = Re. Liquid arenes were reacted neat, with the arene also serving as the solvent, whereas for the reactions that involved solid arenes heptane was added. This prevented the solid arenes from subliming to the cooler parts of the reaction vessel.

$$(OC)_5M{-}M(CO)_5 + HSiCl_3 \xrightarrow[\Delta]{CO} 2(OC)_5M(SiCl_3) + H_2$$



Equation 1.1 General reactions involved in the preparation of (arene)M$(CO)_2(SiCl_3)$ complexes (M = Re or Mn)

In some cases another product in addition to the desired product was produced in the preparation of the (arene)$Re(CO)_2(SiCl_3)$ complexes. The mass spectrum of one of these (arene)$Re(CO)_2(SiCl_3)$ other products, isolated from the reaction of benzene with $Re(CO)_5(SiCl_3)$, exhibited a parent ion peak at 668 m/e. This molecular weight indicated the presence of a binuclear rhenium compound and corresponded to a molecular ion having the composition $Re_2(Cl)_2(CO)_8$. The daughter ion pattern of this spectrum could also be assigned to the systematic fragmentation of $Re_2(Cl)_2(CO)_8$.

The infrared spectrum of the carbonyl region of these second products exhibited four bands. The positions of two of the bands (2024, 1915 cm^{-1} for both the benzene and hexamethylbenzene products) remain constant. The positions, relative intensities, and line widths of these two bands match almost exactly the infrared spectrum of the $[(\mu\text{-}Cl)_3Re_2(CO)_6]^-$ anion (ν(CO) 2024 and 1916 cm^{-1})[16] (see Figure 1.1).

The other two carbonyl stretches in the infrared spectra of the second products shifted position depending upon which arene was used in the reaction with $Re(CO)_5(SiCl_3)$. The band at higher wave number shifted from 2085 to 2063.5 cm^{-1} when $Re(CO)_5(SiCl_3)$ was reacted with benzene or hexamethylbenzene

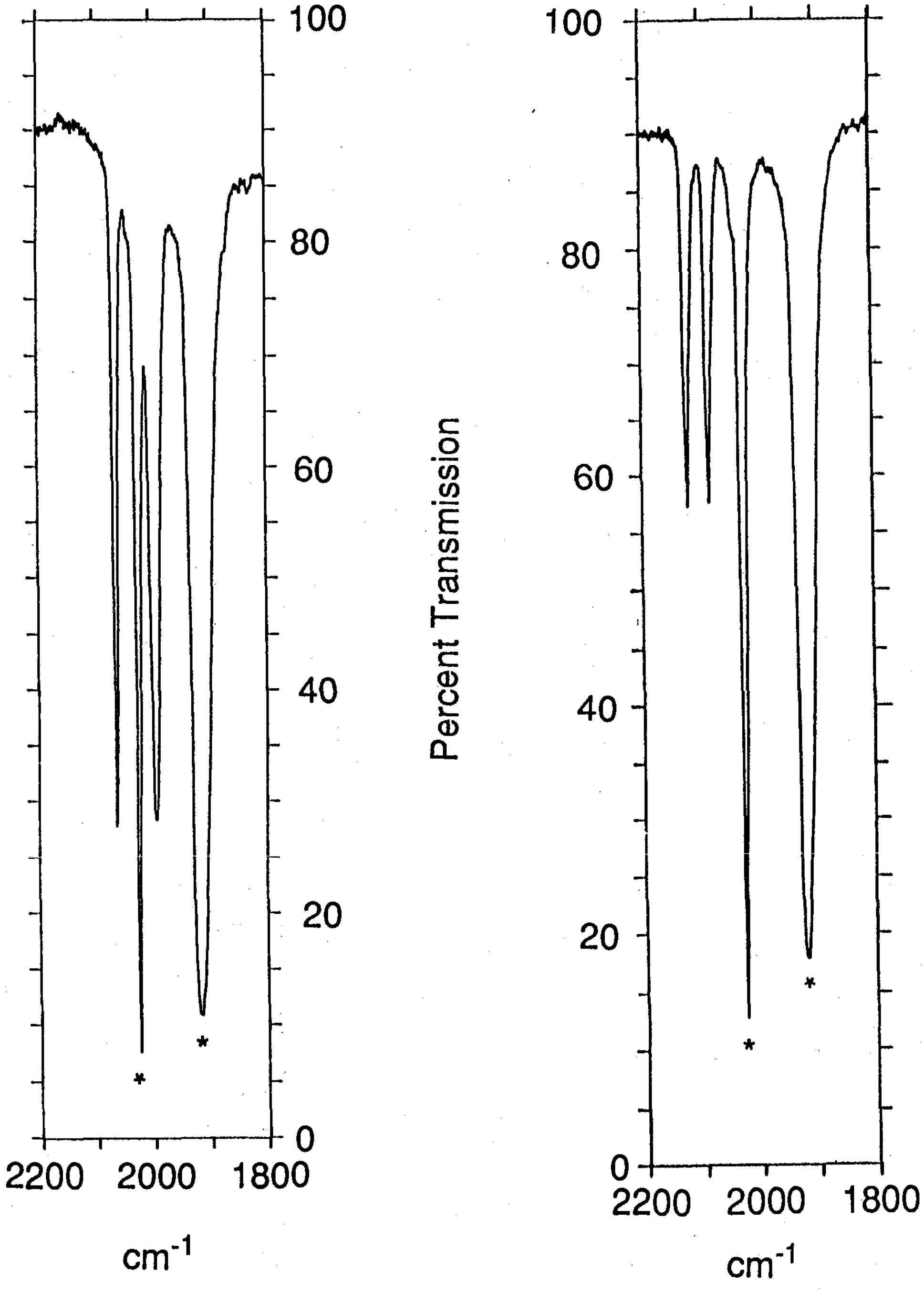


Figure 1.1 Infrared spectra of (left) [(arene)Re(CO)$_3$]$^+$ [(μ-Cl)$_3$Re(CO)$_6$]$^-$ ν(CO)*: 2024, 1915.5 cm^{-1}; (right) [(C$_5$Me$_5$)Ir(CO)$_2$(CH$_2$Cl)]$^+$ [(μ-Cl)(μ-Br)$_2$Re$_2$(CO)$_6$]$^-$ ν(CO)*: 2022, 1916 cm^{-1} (ref. 16)

respectively. The position of the lower band appears at 1993.5 cm^{-1} for the hexamethylbenzene reaction but cannot be observed in the benzene reaction product since it is obscured by the strong absorption band of the $[(\mu\text{-Cl})_3Re_2(CO)_6]^-$ at 2024 cm^{-1}. It is known that compounds of the type $[(arene)Re(CO)_3]^+$ PF_6^- show similar shifts in their infrared spectra: 2081, 2012 cm^{-1}, and 2072, 2001 cm^{-1} for $[(C_6H_6)Re(CO)_3]^+$ PF_6^- and $[(1,4\text{-}Me_2C_6H_4)Re(CO)_3]^+$ PF_6^-, respectively.[17] Therefore on the basis of the above infrared and mass spectral data the second product formed in the reaction of an arene with $Re(CO)_5(SiCl_3)$ was tentatively identified as $[(arene)Re(CO)_3]^+$ $[Re_2(\mu\text{-Cl})_3(CO)_6]^-$. The complex $[(C_6Me_6)Re(CO)_3]^+$ $[Re_2(\mu\text{-Cl})_3(CO)_6]^-$ has previously been prepared by Lewis[18] but no chemical characterization of this complex could be found. Further characterization of these products was not carried out since they were not relevant to this study.

The $[(arene)Re(CO)_3]^+[Re_2(\mu\text{-Cl})_3(CO)_6]^-$ complexes could not be separated from the desired $(arene)Re(CO)_2(SiCl_3)$ complex by either recrystallization or sublimation (an exception was $[(benzene)Re(CO)_3]^+[Re_2(\mu\text{-Cl})_3(CO)_6]^-$ which preferentially crystallized from a methylene chloride-hexane solution). The formation of the undesired $[(arene)Re(CO)_3]^+$ $[Re_2(\mu\text{-Cl})_3(CO)_6]^-$ complexes was thought to be caused by the presence of trace amounts of oxygen in the starting reaction mixture. Indeed, reaction of hexamethylbenzene and $Re(CO)_5(SiCl_3)$ in heptane with added oxygen resulted in the exclusive production of the $[(Me_6C_6)Re(CO)_3]^+$ $[Re_2(\mu\text{-}Cl)_3(CO)_6]^-$ complex.

In order to produce the desired (arene)$Re(CO)_2(SiCl_3)$ complexes exclusively, strict precautions were needed to eliminate trace amounts of oxygen. These precautions included distillation and storage of the heptane and liquid arenes under nitrogen. The recrystallization of the solid arenes was also carried out under nitrogen. Even following these precautions reaction of hexamethyl- or hexaethylbenzene with $Re(CO)_5(SiCl_3)$ still produced small amounts of the $[(arene)Re(CO)_3]^+$ $[Re_2(\mu\text{-}Cl)_3(CO)_6]^-$ compounds. In these cases the desired (arene)$Re(CO)_2(SiCl_3)$ complex could be formed exclusively if the reaction mixtures were heated at 260 °C for 24 h. It is believed that the $[(arene)Re(CO)_3]^+[Re_2(\mu\text{-}Cl)_3(CO)_6]^-$ complexes decompose at this higher temperature.

Derivatives with benzene (C_6H_6), toluene (MeC_6H_5), t-butylbenzene ($Bu^tC_6H_5$), p-xylene ($1,4\text{-}Me_2C_6H_4$), mesitylene ($1,3,5\text{-}Me_3C_6H_3$), durene ($1,2,4,5\text{-}Me_4C_6H_2$), prehnitene ($1,2,3,4\text{-}Me_4C_6H_2$), p-di-isopropylbenzene ($1,4\text{-}Pr^i{}_2C_6H_4$), p-di-t-butylbenzene ($1,4\text{-}Bu^t{}_2C_6H_4$) and hexamethylbenzene (Me_6C_6) as arene ligands were synthesized. All the (arene)Re$(CO)_2(SiCl_3)$ complexes are colourless, air-sensitive solids which are insoluble in hexane, but are readily soluble in CH_2Cl_2. All derivatives were characterized by ^{1}H and ^{13}C NMR, IR, mass spectroscopy, and C/H analysis. See Tables 1.1-1.4.

The synthesis of the (arene)Re$(CO)_2(SiCl_3)$ derivatives where the arene was either chlorobenzene or tri-t-butylbenzene were attempted but were unsuccessful. The chlorobenzene was most probably inert to reaction under the general reaction conditions, while tri-t-butylbenzene may decompose at the temperatures needed for reaction with $Re(CO)_5(SiCl_3)$.

The reaction of $(MeC_6H_5)Re(CO)_2(SiCl_3)$ with hexamethylbenzene in heptane under the general reaction conditions produced $(Me_6C_6)Re(CO)_2(SiCl_3)$. Therefore, like the corresponding (arene)Ru(CO)$(GeCl_3)_2$ complexes (arene)Re$(CO)_2(SiCl_3)$ derivatives undergo arene exchange.[19]

The infrared spectra in the carbonyl region of the (arene)Re$(CO)_2(SiCl_3)$ derivatives consist of two bands. A sample infrared spectrum is shown in Figure 1.2. The positions of these bands characteristically shift to a lower wavenumber with increasing methyl substitution at the arene ring. The CO stretching frequencies in the

Table 1.1 Analytical Data for the (Arene)Re$(CO)_2(SiCl_3)$ Derivatives

	%C		%H	
Arene	calcd	found	calcd	found
C_6H_6	21.13	21.36	1.32	1.56
MeC_6H_5	23.06	23.22	1.72	1.74
$Bu^tC_6H_5$	28.21	28.02	2.76	2.79
1,4-$Me_2C_6H_4$	24.88	24.99	2.09	2.14
1,4-$Pr^i{}_2C_6H_4$	31.20	31.45	3.37	3.52
1,4-$Bu^t{}_2C_6H_4$[a]	33.89	33.90	3.91	3.89
1,3,5-$Me_3C_6H_3$[a]	26.59	26.61	2.43	2.27
1,2,3,4-$Me_4C_6H_2$	28.21	28.34	2.76	2.74
1,2,4,5-$Me_4C_6H_2$	28.21	28.27	2.76	2.81
Me_6C_6	31.20	31.34	3.37	3.32

a) previously prepared by R.K. Pomeroy

(arene)Re$(CO)_2(SiCl_3)$ complexes range from 1993.5 and 1941 cm^{-1} for (C_6H_6)Re$(CO)_2(SiCl_3)$ to 1968 and 1914.5 cm^{-1} for (Me_6C_6)Re$(CO)_2(SiCl_3)$ (see Table 1.2). The increase of electron density on the ring increases the metal to carbonyl backbonding. This increase of electron density in the π^* orbitals of the CO ligand causes a decrease in the CO bond order which results in a lower CO stretching frequency.[20]

Two tetramethyl substituted benzene compounds, durene (1,2,4,5-$Me_4C_6H_2$)-, and prehnitene (1,2,3,4-$Me_4C_6H_2$)-Re$(CO)_2(SiCl_3)$ exhibit a high frequency band at 1976 cm^{-1} in both cases. However, the low frequency band appears at 1928 cm^{-1} for prehnitene but shifts to 1922 cm^{-1} for durene. Therefore, not only the number of substituents but also the position of these substituents on the arene ring influence the absorption frequencies of the carbonyl bands.

The ^1H NMR spectra of the arene ligand in (arene)Re$(CO)_2(SiCl_3)$ complexes show the characteristic shielding of the aromatic protons. A sample ^1H NMR spectrum is shown in Figure 1.3. The signals of the ring protons (see Table 1.3) are shifted an average of 1.5 ppm upfield relative to the same signals in the free ligand . This upfield shift can be explained as a result of the perturbation of the ring current of the aromatic ring upon

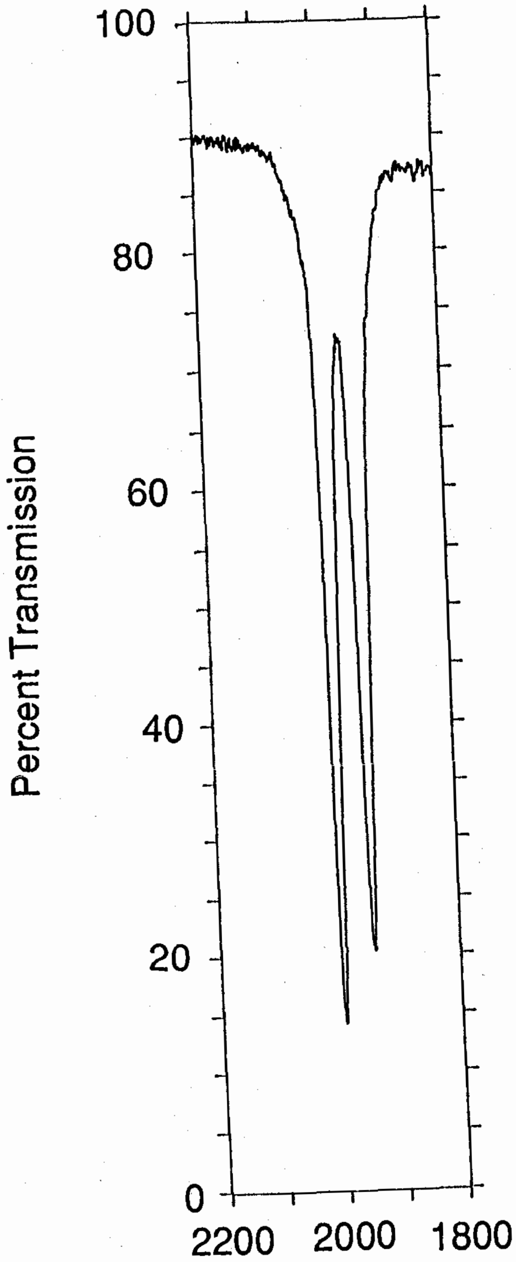


Figure 1.2 Infrared spectra of $(C_6H_6)Re(CO)_2(SiCl_3)$ in CH_2Cl_2 (ν(CO) 1993.5, 1941 cm^{-1})

Table 1.2 IR and Mass Spectral Data for the $(\text{Arene})\text{Re(CO)}_2(\text{SiCl}_3)$ Derivatives

Arene	ν(CO) cm^{-1} (CH_2Cl_2)	$(M^+)^b$
C_6H_6	1993.5, 1941	454
MeC_6H_5	1989, 1937.5	468
$Bu^tC_6H_5$	1988.5, 1934.5	510
1,4-$Me_2C_6H_4$	1986, 1937	482
1,4-$Pr^i{}_2C_6H_4$	1984, 1931	538
1,4-$Bu^t{}_2C_6H_4{}^a$	1983, 1928	566
1,3,5-$Me_3C_6H_3{}^a$	1981.5, 1928.5	496
1,2,4,5-$Me_4C_6H_2$	1976, 1922	510
1,2,3,4-$Me_4C_6H_2$	1976, 1928	510
Me_6C_6	1968, 1914.5	538

a) previously prepared by R.K. Pomeroy b) parent ion in each case.

complexation to a transition metal.[21] Alternatively this shift can be explained as a result of the magnetic anisotropy of the metal.[22] It is most likely that the upfield shift of the aromatic protons is a combination of both effects.

Chemical shifts of methyl, or methylene protons on carbons attached to the arene ring are shifted slightly downfield. In (arene)Re$(CO)_2(SiCl_3)$ complexes the signals due to these protons appear an average of 0.2 ppm downfield of the corresponding signals in the free ligand. The deshielding of these protons is believed to be a result of the anisotropy of the metal moiety.[23]

Chemical shifts of methyl groups further from the aromatic ring remain relatively unchanged from those in the free ligand. For example, the t-butyl protons in $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$ are shifted only 0.02 ppm downfield from the t-butyl protons in p-di-t-butylbenzene.

The $^{13}C\{^1H\}$ NMR spectra of the aromatic ligands in the (arene)Re$(CO)_2(SiCl_3)$ complexes show the characteristic shielding of the aromatic carbon atoms with respect to the free ligand. A typical ^{13}C NMR spectrum is shown in Figure 1.4. Unsubstituted aromatic carbons are shifted an average of 33 ppm upfield while substituted aromatic carbons are

Table 1.3 ^{1}H NMR Spectral Data for the (Arene)Re$(CO)_2(SiCl_3)$ Derivatives in $CDCl_3$

	ppm		
Arene	C_{ar}-H	C_{ar}-C-H	C_{ar}-C-C-H
C_6H_6	5.81		
MeC_6H_5	5.74(m)	2.54	
$Bu^tC_6H_5$	5.86(m)		1.35
1,4-$Me_2C_6H_4$	5.81	2.44	
1,4-$Pr^i{}_2C_6H_4$	5.81	2.72(h)[b]	1.25(d)[b]
1,4-$Bu^t{}_2C_6H_4$[a]	5.94		1.30
1,3,5-$Me_3C_6H_3$[a]	5.50	2.60	
1,2,3,4-$Me_4C_6H_2$	5.44	2.31,2.26	
1,2,4,5-$Me_4C_6H_2$	5.89	2.37	
Me_6C_6		2.48	

a) previously prepared by R.K. Pomeroy b) J = 7.0 Hz
m = multiplet d = doublet h = heptet

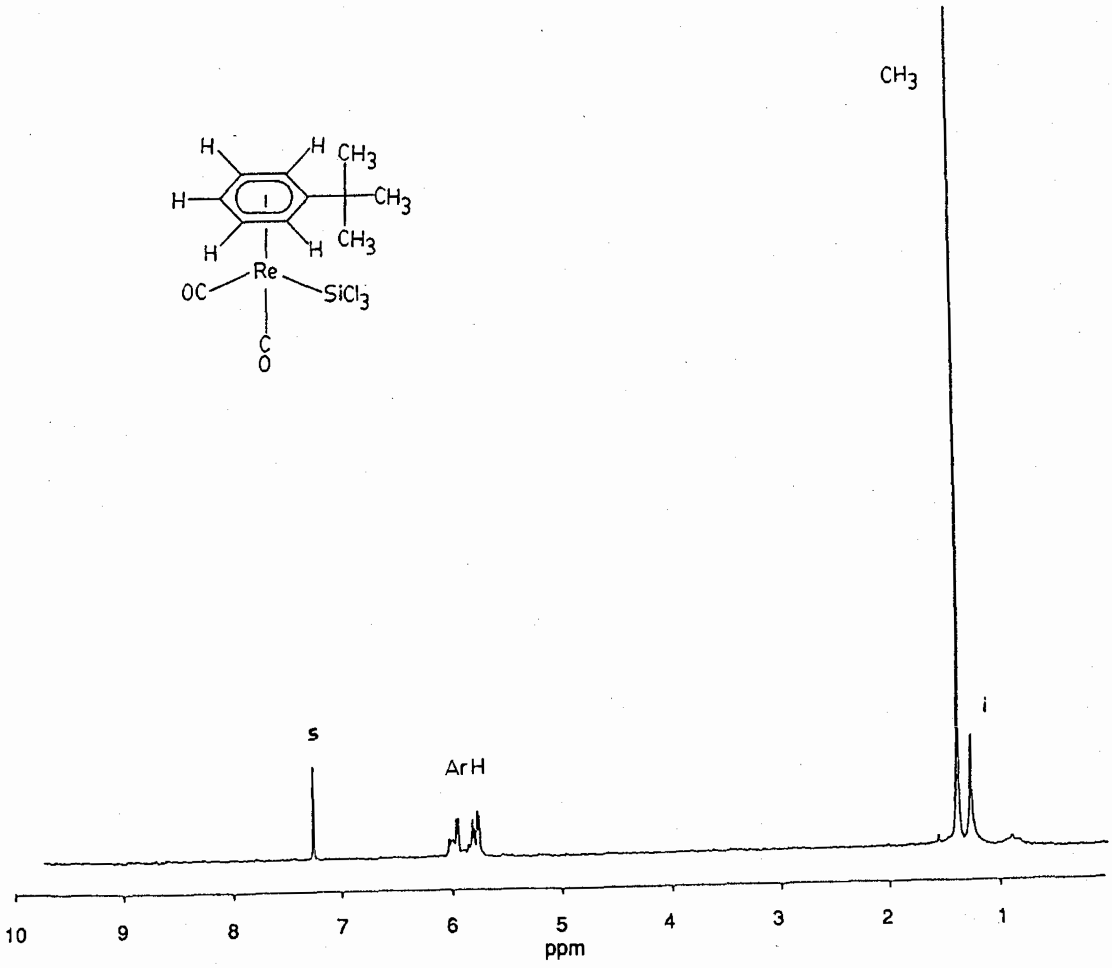


Figure 1.3 100 MHz ^{1}H NMR spectrum of $(Bu^tC_6H_5)Re(CO)_2(SiCl_3)$ in $CDCl_3$; s = solvent, i = hexane

shifted to a lesser degree, 24 ppm upfield. Methyl and methylene carbons attached to the ring are shifted up to 1 ppm in either direction while the chemical shifts of carbon atoms further from the aromatic ring remain virtually the same as those in the free aromatic hydrocarbon (see Table 1.4).

Although the origin of the changes in the ^{13}C chemical shifts for arene complexes compared to those of the free ligand is somewhat uncertain,[24] the shielding of the aromatic carbon atoms is usually explained by the decrease in π-bonding character of the arene ring upon complexation to a transition metal moiety.[25] An alternate explanation involves the effect of an electron-rich metal in close proximity to the carbon atoms of the ring.[26] This effect has been used to explain the large upfield shifts observed in the ^{1}H NMR spectra of transition metal hydrides.[27]

As expected the signal due to the carbonyls in the (arene)$Re(CO)_2(SiCl_3)$ complexes are weak when compared to the carbon signals of the organic ligand. This is a result of both the long T_1 of the carbonyl carbons as well as these carbons having no NOE.[24] The carbonyl carbons are also broad due to coupling to the quadrupolar rhenium nuclei.[24] The signals of the carbonyls in (arene)$Re(CO)_2(SiCl_3)$ complexes shift from 191.9 ppm for

$(C_6H_6)Re(CO)_2(SiCl_3)$ to 196.7 ppm for $(Me_6C_6)Re(CO)_2(SiCl_3)$. This slight shielding of the carbonyls is thought to be the result of increased substitution of the arene ligand. This shift is opposite to what might be expected from simple shielding arguments (i.e., an increase of electron density at the carbonyl carbon should cause an upfield shift). This is commonly observed for organometallic complexes and has been rationalized as resulting from changes to the ΔE parameter in the paramagnetic term of chemical shift.[24]

Table 1.4 $^{13}C\{^1H\}$ NMR Spectral Data For (Arene)Re(CO)$_2$(SiCl$_3$) Complexes in CD_2Cl_2 in ppm

Arene	C_{ar}-H	C_{ar}-C	C_{ar}-C	C_{ar}-C-C	CO
C_6H_6	92.8				191.9
MeC_6H_5	90.1,92.7[b] 94.7[c]	111.0	20.5		192.9
$Bu^tC_6H_5$	90.6,92.8[b] 93.4[c]	125.8	34.9	31.2	193.1
1,4-$Me_2C_6H_4$	94.4	108.4	19.8		193.9
1,4-$Pr^i{}_2C_6H_4$	91.9	125.6	32.5	23.7	194.4
1,4-$Bu^t{}_2C_6H_4$[a]	90.5	125.6	34.7	31.2	194.4
1,3,5-$Me_3C_6H_3$[a]	91.8	113.3	20.3		194.6
1,2,3,4-$Me_4C_6H_2$	95.2	108.5[d],109.0[e]	16.3[f] 19.9[g]		195.3
1,2,4,5-$Me_4C_6H_2$	98.5	108.2	18.2		195.4
Me_6C_6		108.3	17.3		196.7

a) previously prepared by R.K. Pomeroy b) C_2 or C_3 c) C_4 d) C_1 and C_4
e) C_2 and C_3 f) C_1, and C_4, g) C_2, and C_3,

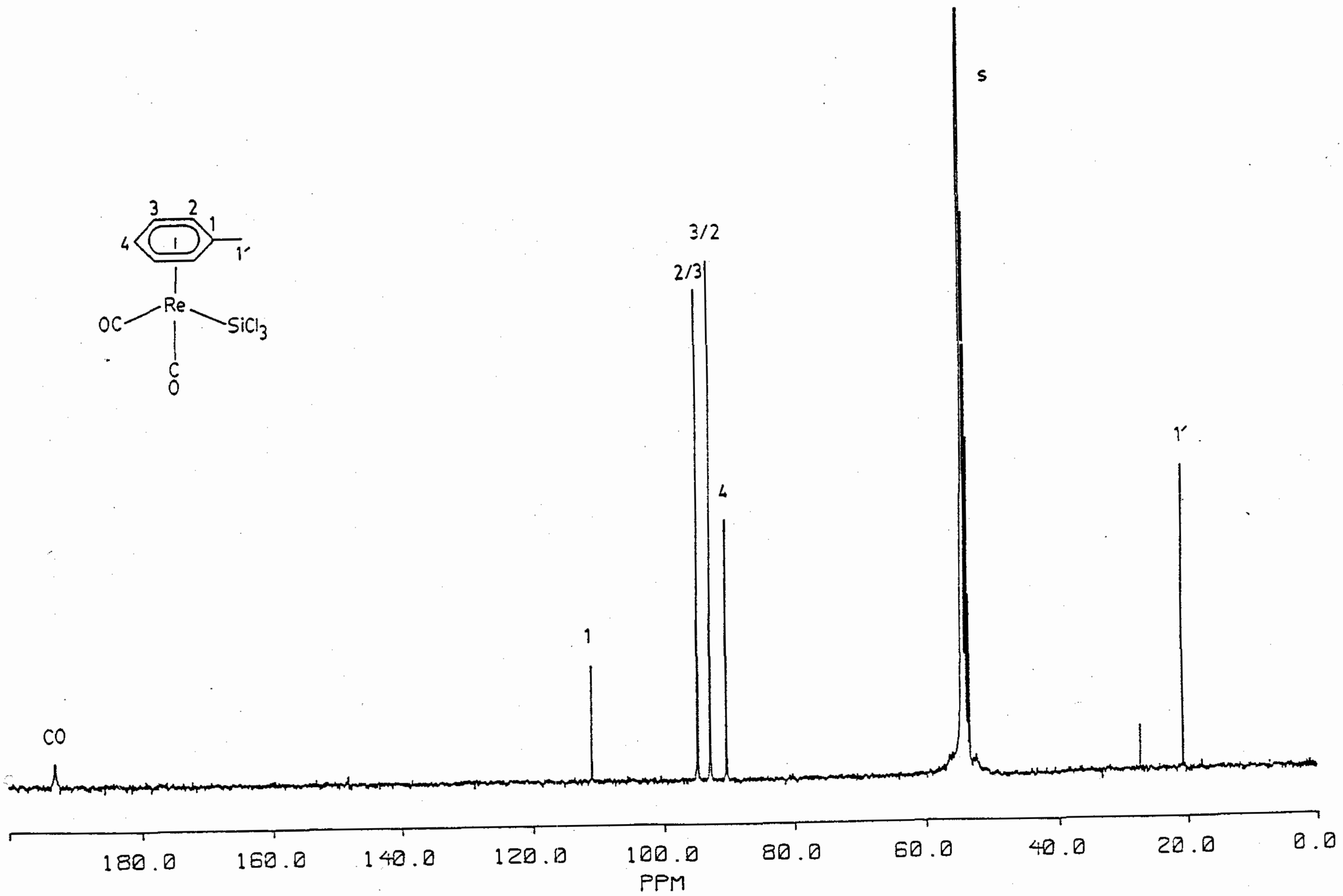


Figure 1.4 100.6 MHz $^{13}C\{^1H\}$ NMR spectrum of $(MeC_6H_5)Re(CO)_2(SiCl_3)$ in CH_2Cl_2/CD_2Cl_2; s=solvent

2. Synthesis of (Arene)Mn$(CO)_2$$(SiCl_3)$

Several complications arose in the preparation of the (arene)Mn$(CO)_2$$(SiCl_3)$ complexes. These reactions were plagued by nonreproducible reaction rates, drastic variations in yield, and at times total consumption of the Mn$(CO)_5$$(SiCl_3)$ with no trace of product formation. These observations are consistent with a radical process[28] for the reaction of Mn$(CO)_5$$(SiCl_3)$ with aromatic hydrocarbons which is being affected by the presence of minor impurities in the starting materials.

In most cases, good yields of the desired (arene)Mn$(CO)_2$$(SiCl_3)$ complexes could be obtained if all starting materials were rigorously purified. The purification procedure involved sublimation of the Mn$(CO)_5$$(SiCl_3)$; solid arenes were recrystallized under nitrogen and then sublimed; liquid arenes were refluxed under nitrogen and over potassium and distilled (under nitrogen) before use. In the reaction of solid arenes, i.e., di-t-butylbenzene or hexaethylbenzene, with Mn$(CO)_5$$(SiCl_3)$ the added precaution of preparing the reaction mixtures in a dry box was taken. However, even following all these precautions, the yields of the $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2$$(SiCl_3)$ and (Et_6C_6)Mn$(CO)_2$$(SiCl_3)$ complexes showed large variations.

With the precautions outlined above, all the (arene)Mn(CO)$_2$(SiCl$_3$) derivatives were synthesized in 20-70% yield by heating Mn(CO)$_5$(SiCl$_3$)[15] with the aromatic hydrocarbon at 230 °C for 12 h. The reaction scheme for the preparation of the (arene)Mn(CO)$_2$(SiCl$_3$) complexes is given in Equation 1.1 where M = Mn. As with the (arene)Re(CO)$_2$(SiCl$_3$) complexes, in reactions with liquid arenes the arene served as the solvent, whereas reactions with solid arenes required the addition of heptane to prevent the solid arenes from subliming to the cooler parts of the reaction vessel.

The derivatives of (arene)Mn(CO)$_2$(SiCl$_3$) with benzene (C_6H_6), toluene (MeC_6H_5), p-xylene (1,4-$Me_2C_6H_4$), o-xylene (1,2-MeC_6H_4), mesitylene (1,3,5-$Me_3C_6H_3$), t-butylbenzene ($Bu^tC_6H_5$) and p-di-t-butylbenzene (1,4-$Bu^t{}_2C_6H_4$) as arene ligands were synthesized. All the (arene)Mn(CO)$_2$(SiCl$_3$) complexes were yellow, air-sensitive solids which were soluble in CH_2Cl_2. Unlike the (arene)Re(CO)$_2$(SiCl$_3$) derivatives, the (arene)Mn(CO)$_2$(SiCl$_3$) complexes were soluble in hexane and could also be sublimed (>80 °C, <0.02 mm of Hg). These two characteristics most likely result from the smaller dipole moment of the arene-manganese bond as compared to that of the arene-rhenium bond. All derivatives were characterized by ^{1}H and ^{13}C NMR, IR, mass spectroscopy, and C/H analysis. See Tables 2.1-2.4.

Table 2.1 Analytical Data for the (Arene)Mn$(CO)_2(SiCl_3)$ Derivatives

	%C		%H	
Arene	calcd	found	calcd	found
C_6H_6	29.70	29.94	1.87	2.10
MeC_6H_5	32.03	32.11	2.39	3.37
$Bu^tC_6H_5$	37.97	38.16	3.72	3.73
1,2-$Me_2C_6H_4$	34.16	34.25	2.87	2.90
1,4-$Me_2C_6H_4$	34.16	34.40	2.87	3.02
1,4-$Bu^t{}_2C_6H_4$	44.10	43.64	5.09	4.81
1,3,5-$Me_3C_6H_3$	36.14	36.00	3.31	3.18

Since the (arene)Mn$(CO)_2(SiCl_3)$ complexes were soluble in hexane it was thought that different conformations of the carbonyls with respect to the arene ligand might be detected in their infrared spectra. Examples of these different conformations are depicted in Figure 2.1. The half width of the carbonyl absorptions for the (1,4-$Bu^t{}_2C_6H_4$)Mn$(CO)_2(SiCl_3)$ derivative were compared with those of the (C_6H_6)Mn$(CO)_2(SiCl_3)$ complex but no detectable broadening of the bands was observed. Different conformations of the carbonyl groups could not be observed in the infrared spectra of the (arene)Re$(CO)_2(SiCl_3)$ complexes even if they were present. This is because the CO absorptions of complexes in CH_2Cl_2 are broadened and make the detection of conformational isomers impossible.

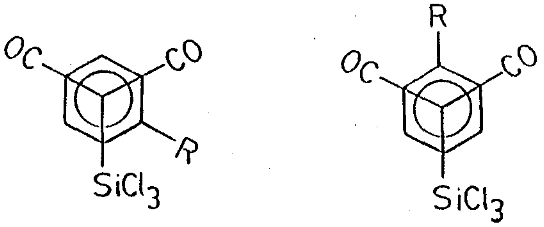
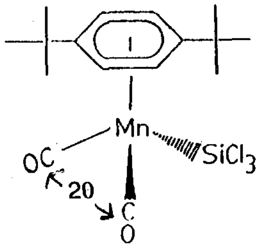


Figure 2.1 Possible conformations of the $(CO)_2Mn(SiCl)_3$ moiety with respect to a substituted aromatic ring.

Since the total dipole vector of a vibrational mode can be taken to be the sum of the individual vectors arising from the CO oscillations, and the intensities of the oscillations are proportional to the squares of the dipole vectors, there is a relationship between the intensities of the CO absorption bands and the angles between the CO bond directions. For two CO groups the ratio of the intensities of the symmetric and antisymmetric bands is given by the relationship $I_{sym}/I_{asym} = \{2r \cos(\theta)\}/\{2r \sin(\theta)\} = \cot(\theta)$.[29] Where I_{sym} and I_{asym} are the absorbances of the symmetric and antisymmetric stretches respectively. Therefore, the relative angle between two carbonyls ,2θ, can be calculated by the formula $2\theta = 2(\mathrm{arccotan}\, I_{sym}/I_{asym})^{1/2}$. For the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ the angle 2θ was determined to be 83 ° (see Figure 2.2). It was hoped to compare this angle with the C-M-C bond angle found in the solid state. Unfortunately an X-ray quality crystal of $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ could not be grown.



$$I_{symm}/I_{asymm} = \cot^2\theta$$

Figure 2.2 C-Mn-C angle in $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$

The infrared spectra of the carbonyl region of the (arene)$Mn(CO)_2(SiCl_3)$, like those of the (arene)$Re(CO)_2(SiCl_3)$ derivatives, show two strong absorptions bands. The CO absorption bands in the (arene)$Mn(CO)_2(SiCl_3)$ complexes also shift to lower wavenumber with increasing alkyl substitution of the arene ligand. Frequencies of the absorption bands in the (arene)$Mn(CO)_2(SiCl_3)$ complexes range from 1989.5 and 1945.5 cm^{-1} for $(C_6H_6)Mn(CO)_2(SiCl_3)$ to 1978.5 and 1931.5 cm^{-1} for $(1,3,5\text{-Me}_3C_6H_3)Mn(CO)_2(SiCl_3)$ (see Table 2.2). As with the (arene)$Re(CO)_2(SiCl_3)$ complexes, the position of the substituents affects the carbonyl absorption frequencies. This is demonstrated by the complexes $(1,2\text{-Me}_2C_6H_4)Mn(CO)_2(SiCl_3)$ and $(1,4\text{-Me}_2C_6H_4)Mn(CO)_2(SiCl_3)$ which exhibit carbonyl absorptions at 1983, 1936.5 and 1981.5, 1935 cm^{-1} respectively. A typical infrared spectrum of an (arene)$Mn(CO)_2(SiCl_3)$ derivative is shown in Figure 2.3. This figure is also an example of how bands are sharpened and their positions shifted upon going from a polar to a nonpolar solvent.

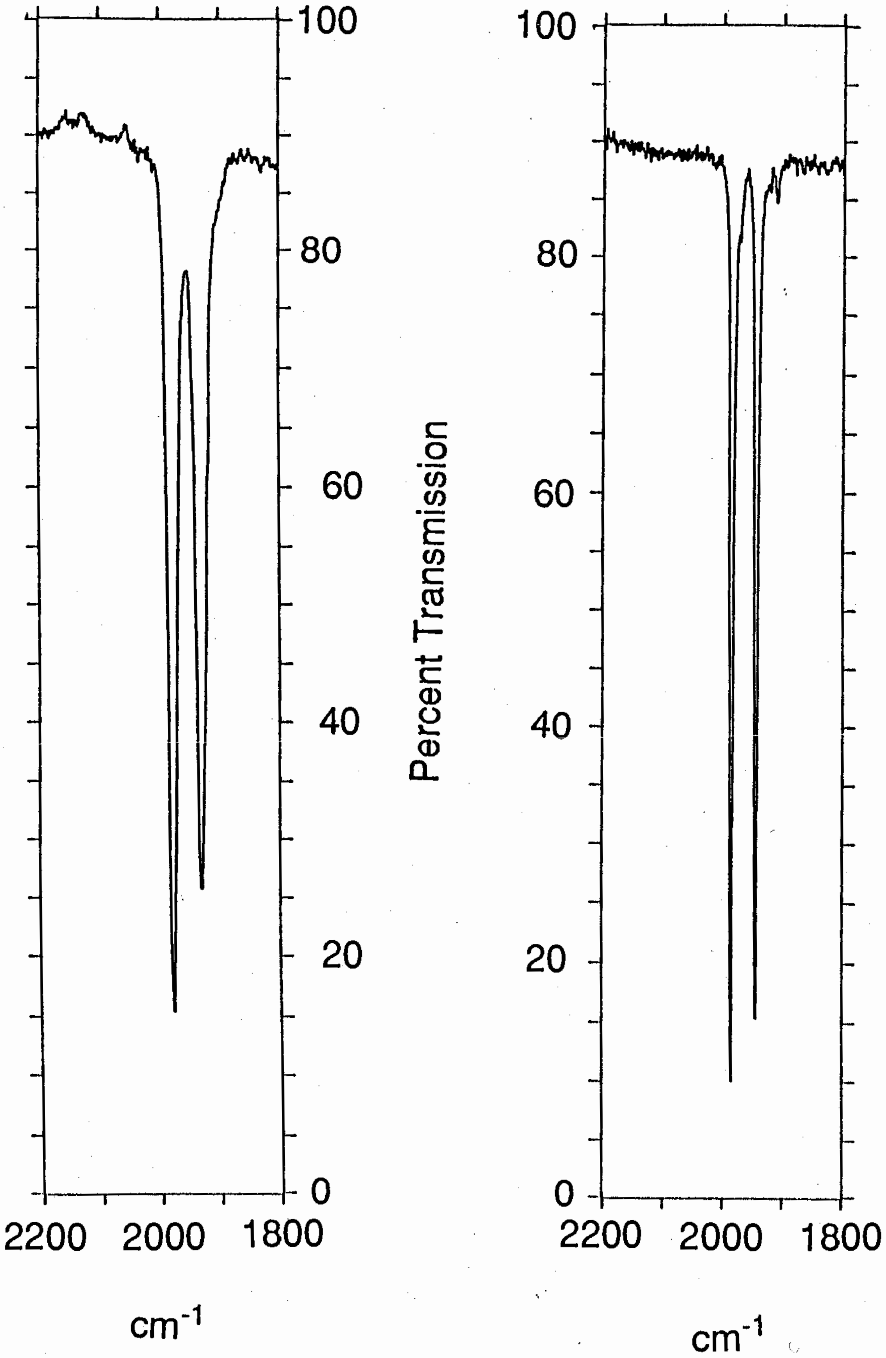


Figure 2.3 Infrared spectra of $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ in (left) CH_2Cl_2 (ν(CO) 1977.5, 1930 cm^{-1}) and (right) hexane (ν(CO) 1984.5, 1943.5 cm^{-1}).

Table 2.2 IR and Mass Spectral Data for the (Arene)Mn$(CO)_2(SiCl_3)$ Derivatives

Arene	$\nu(CO)cm^{-1}$ in CH_2Cl_2	M^{+a}
C_6H_6	1989.5, 1945.5	322
MeC_6H_5	1985.5, 1939.5	338
$Bu^tC_6H_5$	1983, 1938.5	378
1,2-$Me_2C_6H_4$	1981.5, 1935	350
1,4-$Me_2C_6H_4$	1983, 1936.5	350
1,4-$Bu^t{}_2C_6H_4$	1977.5, 1930	490
1,3,5-$Me_3C_6H_3$	1978.5, 1931.5	364

a) Parent ion in each case

A comparison of the positions of the carbonyl absorptions in (arene)Mn$(CO)_2(SiCl_3)$ with those of the corresponding (arene)Re$(CO)_2(SiCl_3)$ complexes shows an incongruent shift of band positions. The symmetric stretch appears at a lower frequency in the (arene)Mn$(CO)_2(SiCl_3)$ derivatives compared to those of the corresponding (arene)Re$(CO)_2(SiCl_3)$ complex, while the asymmetric stretch shifts to a higher frequency in the (arene)Mn$(CO)_2(SiCl_3)$ compounds. An example of this is seen in the following complexes: $(C_6H_6)Mn(CO)_2(SiCl_3)$ (ν(CO) 1989.5, 1945.5 cm^{-1}) and $(C_6H_6)Re(CO)_2(SiCl_3)$ (ν(CO) 1993.5, 1941 cm^{-1}). These opposing shifts of differing CO absorption bands are often seen in transition metal complexes upon exchanging a first row with a third row transition element.[30]

The ^1H NMR spectra of the (arene)$Mn(CO)_2(SiCl_3)$ complexes are similar to those of the corresponding (arene)$Re(CO)_2(SiCl_3)$ compounds. The aromatic protons in the (arene)$Mn(CO)_2(SiCl_3)$ derivatives are shifted 1.6 ppm upfield relative to those of the free arene (see Table 2.3). This shift is slightly larger (0.1 ppm) than the shielding effect observed in the (arene)$Re(CO)_2(SiCl_3)$ complexes. The manganese atom may therefore cause more of a perturbation of the ring current effect than the corresponding rhenium atom.[21] Also the closer proximity of the $Mn(CO)_2(SiCl_3)$ unit to the arene ring may increase the anisotropic effect.[22]

Unlike the arene shifts in the (arene)$Re(CO)_2(SiCl_3)$ complexes the other signals in the ^1H NMR spectra of the (arene)$Mn(CO)_2(SiCl_3)$ complexes remain virtually unchanged with respect to those of the uncomplexed arene. It is probable that these protons are beyond the anisotropic deshielding zone of the metal moiety.[26] A sample ^1H NMR spectrum is shown in Figure 2.4.

The ^{13}C NMR spectra of the aromatic ligands of the

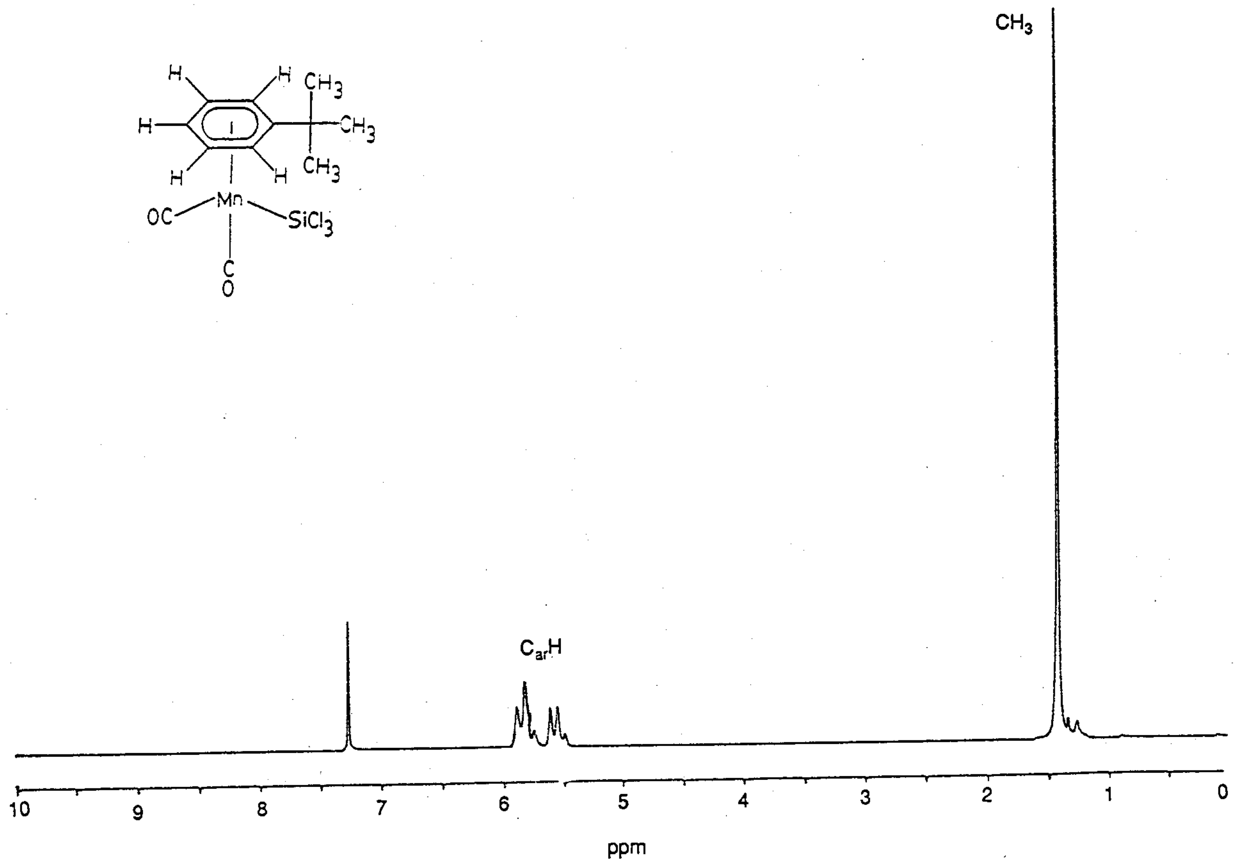


Figure 2.4 100 MHz ^{1}H NMR spectrum of $(Bu^tC_6H_5)Mn(CO)_2(SiCl_3)$ in $CDCl_3$; s = solvent

Table 2.3 ^1H NMR Spectral Data for the $(Arene)Mn(CO)_2(SiCl_3)$ Derivatives

$CDCl_3$ (ppm)

Arene	C_{ar}-H	C_{ar}-C-H	C_{ar}-C-C-H
C_6H_6	5.72		
MeC_6H_5	5.61(m)	2.31	
$Bu^tC_6H_5$	5.65(m)		1.39
$1,2-Me_2C_6H_4$	5.59(m)	2.30	
$1,4-Me_2C_6H_4$			
$1,4-Bu^t{}_2C_6H_4$			
$1,3,5-Me_3C_6H_3$			

m = multiplet

$(arene)Mn(CO)_2(SiCl_3)$ derivatives show the characteristic upfield shift of the aromatic carbons when compared with the free ligand (see Table 2.4). Unsubstituted aromatic carbons are shifted an average of 32 ppm upfield while substituted aromatic carbons are shifted an average of 26 ppm. The signals due to carbons directly attached to the ring, as well as those farther from the ring are shifted up to 1 ppm in either direction. These small shifts are thought to be the result of solvent effects. A typical ^{13}C NMR spectrum of an $(arene)Mn(CO)_2(SiCl_3)$ compound is shown in Figure 2.5.

The carbonyl signals appear at a lower field in the $(arene)Mn(CO)_2(SiCl_3)$ complexes than in the rhenium analogues. This is typical of organometallic compounds on shifting from a first to a third row element.[31] Like the (arene)Re$(CO)_2(SiCl_3)$ derivatives, a slight downfield shift is observed in the (arene)Mn$(CO)_2(SiCl_3)$ complexes upon increasing the alkyl substitution of the arene ring. These range from 220.3 ppm for the $(C_6H_6)Mn(CO)_2(SiCl_3)$ complex to 222.3 ppm for the $(1,3,5\text{-}Me_3C_6H_3)Mn(CO)_2(SiCl_3)$ derivative.

Table 2.4 $^{13}C\{^1H\}$ NMR Spectral Data for the (Arene)$Mn(CO)_2(SiCl_3)$ Derivatives in CH_2Cl_2/CD_2Cl_2 (ppm)

Arene	$\mathbf{C}_{ar}$-H	$\mathbf{C}_{ar}$-C	C_{ar}-$\mathbf{C}$	C_{ar}-C-$\mathbf{C}$	**CO**
C_6H_6	95.3				220.3
MeC_6H_5	95.2,92.7^a 97.3^b	111.6	20.7		221.0
$Bu^tC_6H_5$	94.4,93.8^a 96.4^b	125.3	34.9	31.1	221.4
1,2-$Me_2C_6H_4$	97.4^c 95.1^d	109.9	19.0		221.7
1,4-$Me_2C_6H_4$	97.0	108.2	19.8		221.9
1,4-$Bu^t{}_2C_6H_4$					
1,3,5-$Me_3C_6H_3$	94.6	112.6	20.5		222.3

a) C_2/C_3 b) C_4 c) C_3 and C_6 d) C_4 and C_5

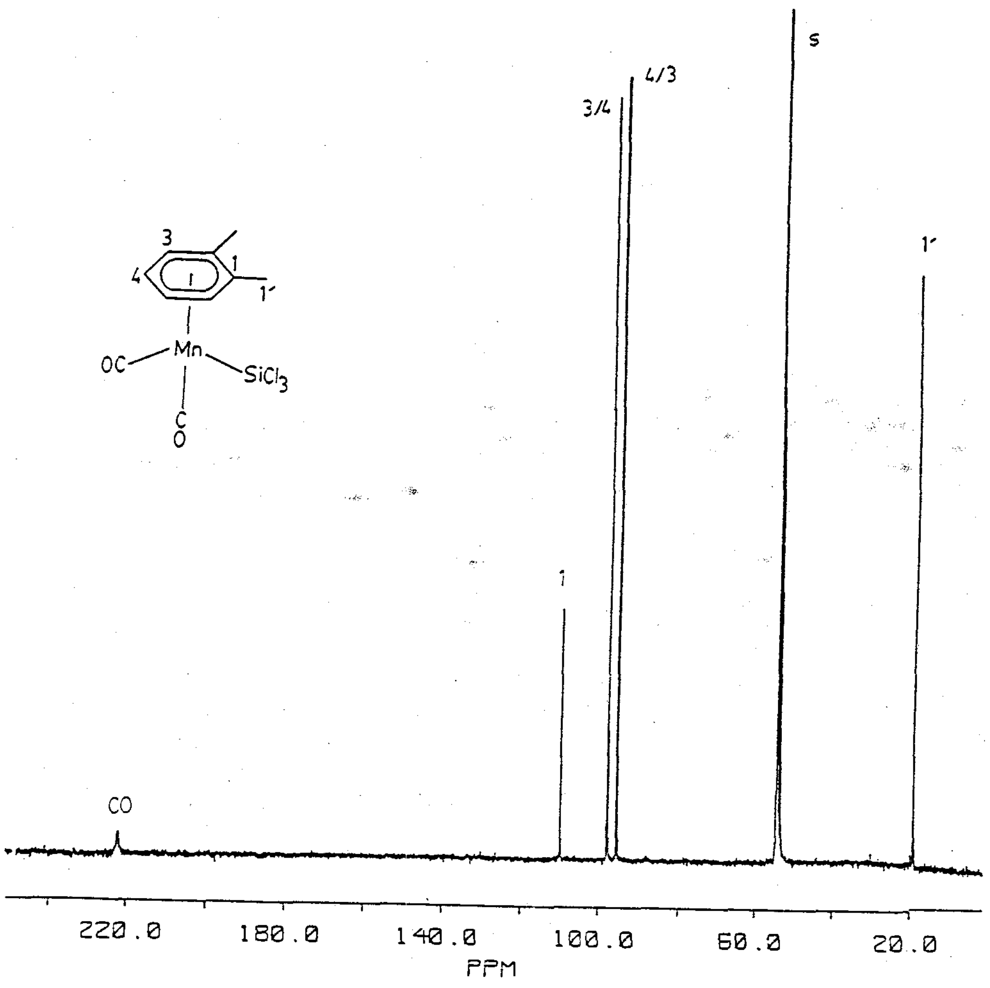
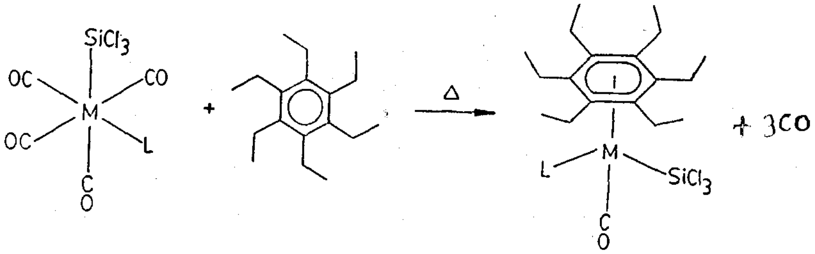


Figure 2.5 100.6 MHz $^{13}C\{^1H\}$ NMR spectrum of $(1,2\text{-}Me_2C_6H_4)Mn(CO)_2(SiCl_3)$ in CH_2Cl_2; s=solvent

3. $(Et_6C_6)M(CO)(SiCl_3)(L)$ M = Mn, Re, L = CO; M = Ru, L = $SiCl_3$

The new compound $(Et_6C_6)Ru(CO)(SiCl_3)_2$ was synthesized from the cis-$Ru(CO)_4(SiCl_3)_2$[32] complex following the literature method for other derivatives of the type (arene)$Ru(CO)(SiCl_3)_2$.[6] The $(Et_6C_6)Mn(CO)_2(SiCl_3)$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ derivatives were prepared from the corresponding $Mn(CO)_5(SiCl_3)$ and $Re(CO)_5(SiCl_3)$ complexes by the general procedures outlined in Sections 1 and 2. Attempts to prepare $(Et_6C_6)Os(CO)(SiCl_3)_2$ by heating a solution of hexaethylbenzene and cis-$Os(CO)_4(SiCl_3)_2$[32] at 220 °C was unsuccessful. This failure was most likely due to the instability of the $(Et_6C_6)Os(CO)(SiCl_3)_2$ complex at this temperature. The general equation for the preparation of the $(Et_6C_6)M(CO)(SiCl_3)(L)$ complexes is shown in Equation 3.1.



Equation 3.1 General equation for the preparation of the $(Et_6C_6)M(CO)(SiCl_3)L$ M = Mn, Re, L = CO; M = Ru, L = $SiCl_3$ Derivatives

The physical characteristics of the $(Et_6C_6)Mn(CO)_2(SiCl_3)$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ complexes were the same as those of the related (arene)$M(CO)_2(SiCl_3)$

derivatives. The $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex was a white, relatively air stable, crystalline solid which was soluble in CH_2Cl_2 but not in hexane. All complexes were characterized by ^1H and ^{13}C NMR, IR, mass spectroscopy and C/H analysis. See Tables 3.1-3.4. X-ray crystal structure determinations were carried out for the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ complexes. An X-ray quality crystal of the $(Et_6C_6)Mn(CO)_2(SiCl_3)$ complex could not be grown and therefore a crystal structure could not be obtained.

Table 3.1 Analytical Data for the $(Et_6C_6)M(CO)(SiCl_3)L$
M = Mn, Re, L = CO; M = Ru, L = $SiCl_3$ Derivatives

M	%C		%H	
	calcd	found	calcd	found
Mn	48.84	48.94	6.15	6.09
Re	38.55	38.40	4.85	4.87
Ru	35.41	35.57	4.69	4.71

The infrared spectra in carbonyl region of the $(Et_6C_6)Re(CO)_2(SiCl_3)$ and $(Et_6C_6)Mn(CO)_2(SiCl_3)$ complexes (see Table 3.2) are similar to the other (arene)$Re(CO)_2(SiCl_3)$ and (arene)$Mn(CO)_2(SiCl_3)$ derivatives discussed previously. The infrared spectrum of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ is shown in Figure 3.1

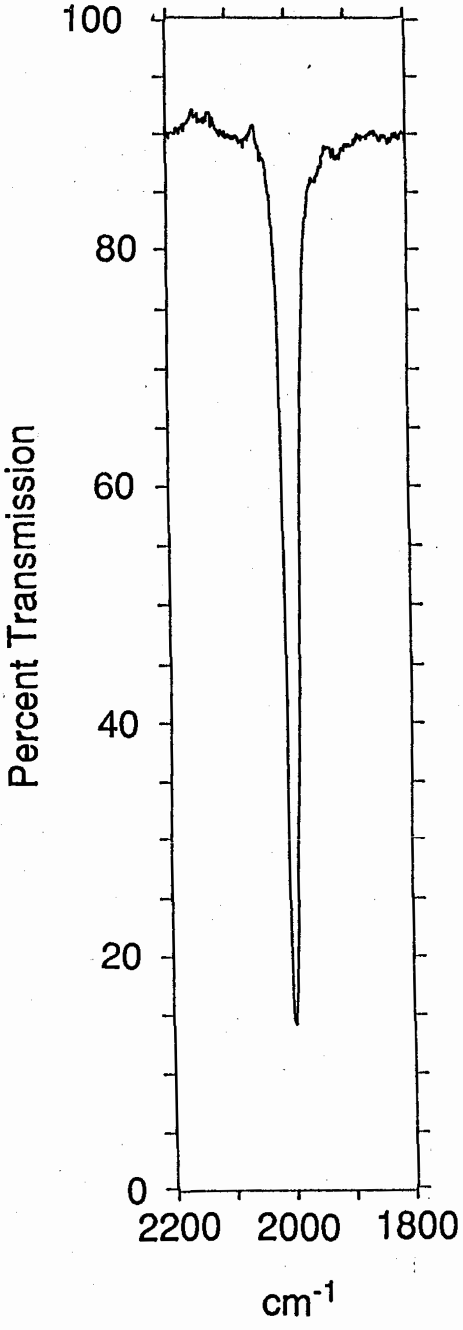


Figure 3.1 Infrared spectrum of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ in CH_2Cl_2 (ν(CO) 1996 cm^{-1})

Table 3.2 IR and Mass Spectral Data for the $(Et_6C_6)M(CO)(SiCl_3)L$ $M = Mn, Re, L = CO; M = Ru, L = SiCl_3$ Derivatives

M	ν(CO) $cm^{-1\,a}$	$(M^+)^b$
Mn	1965 1916	490
Re	1970 1916	624
Ru	1996	646

a) in CH_2Cl_2 b) parent ion in each case

The ^1H NMR spectral data of the $(Et_6C_6)M(CO)(SiCl_3)L$ complexes are reported in Table 3.3. All spectra consist of a quartet due to the methylene hydrogens and a triplet for the methyl hydrogens (see Figure 3.2). In all cases the resonances of the methyl protons are shifted an average of 0.2 ppm downfield from the corresponding signals of the free arene. However, the signal due to the methylene hydrogens is shifted 0.2 ppm downfield in the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex whereas in the $(Et_6C_6)Re(CO)_2(SiCl_3)$ and $(Et_6C_6)Mn(CO)_2(SiCl_3)$ derivatives, the signals due to these protons remain virtually unshifted from those of the uncomplexed ligand. This may be due the $Ru(CO)(SiCl_3)_2$ moiety having a larger anisotropic effect on the methylene protons[22] or it may reflect the presence of predominantly one conformation of the hexaethylbenzene ligand in the

$(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex.

^{13}C NMR spectral data for the $(Et_6C_6)M(CO)(SiCl_3)L$ derivatives are reported in Table 3.4. All the carbon resonances exhibit shifts which are characteristic for arenes complexed to transition metal moieties. The ^{13}C NMR spectra of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ is shown in Figure 3.3. The aromatic carbons in the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex appear at a lower field than those of the corresponding $(Et_6C_6)Mn(CO)_2(SiCl_3)$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ complexes. This is most likely due to less electron density being transferred from the d orbitals of the $Ru(CO)(SiCl_3)_2$ fragment to the π^* orbitals of the hexaethylbenzene ligand due to the greater electron withdrawing ability of $SiCl_3$ group compared to CO. The carbonyl stretching frequency of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ when compared to frequencies of the carbonyl stretches in the $(Et_6C_6)Mn(CO)_2(SiCl_3)$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ complexes is consistent with less electron density on the ruthenium atom than on the manganese or rhenium atoms (see Table 3.3). The resonances of the methylene and methyl carbons are deshielded by up to 1.4 ppm by the various metal moieties. A reasonable explanation for the variations in these shifts cannot be established without further NMR studies.

Table 3.3 ^{1}H NMR Spectral Data for the $(Et_6C_6)M(CO)(SiCl_3)L$ (M = Mn, Re, L = CO; M = Ru, L = $SiCl_3$) Derivatives[a]

M	CH_2	CH_3
Mn	2.70	1.32
Re	2.67	1.34
Ru	2.89	1.36

a) J = 8.0 Hz in all cases

Table 3.4 ^{13}C NMR Spectral Data for the $(Et_6C_6)M(CO)(SiCl_3)L$ (M = Mn, Re, L = CO; M = Ru, L = $SiCl_3$) Derivatives [a]

M	C_{ar}	CH_2	CH_3	CO
Mn	114.3	23.1	16.5	224.2
Re	114.9	22.9	18.0	196.5
Ru	124.1	23.7	16.4	197.8

a) Et_6C_6 in CD_2Cl_2: 15.5 (CH_3), 21.6 (CH_2), 137.2 (C_{ar})

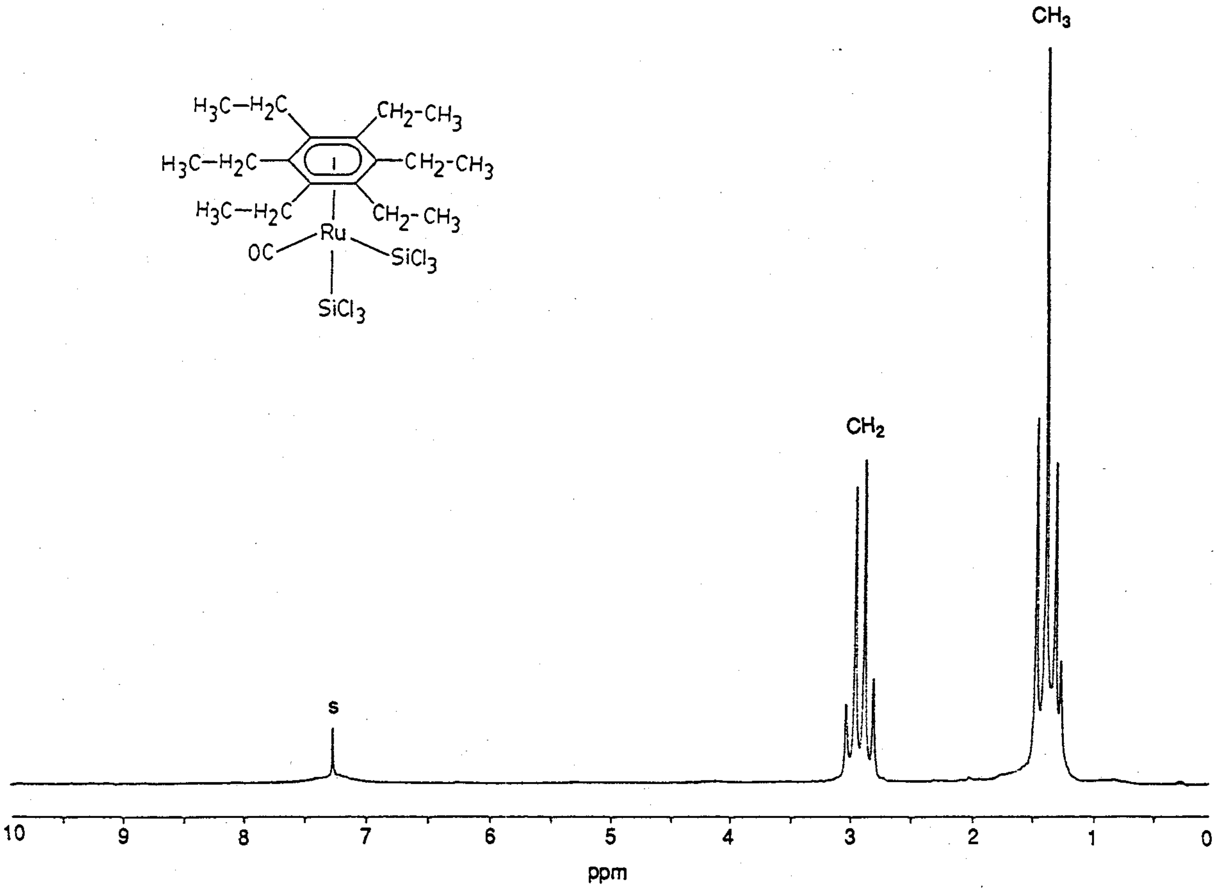


Figure 3.2 100 MHz ^1H NMR spectrum of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ in $CDCl_3$; s = solvent

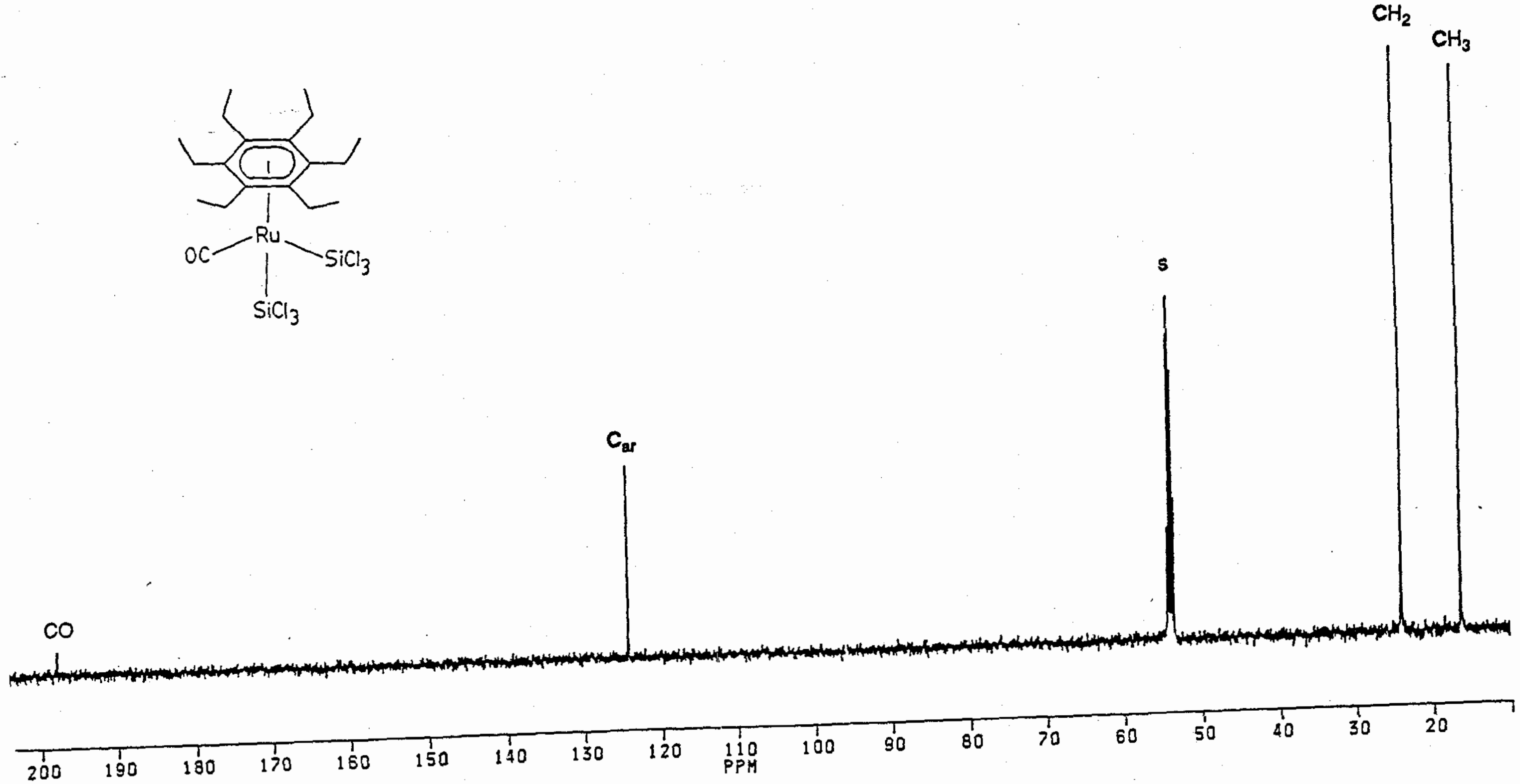


Figure 3.3 126 MHz $^{13}C\{^1H\}$ NMR spectrum of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ in CD_2Cl_2

Crystals of the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex suitable for X-ray crystal structure determination[33] were grown from toluene. The crystal structure of this complex obtained at -80 °C is shown in Figure 3.4. Selected bond lengths and bond angles are reported in Tables 3.5 and 3.6.

Upon examination of the crystal structure of $(Et_6C_6)Re(CO)_2(SiCl_3)$ (Figure 3.4) it can be seen that the $Re(CO)_2(SiCl_3)$ fragment adopts a "piano stool" arrangement with respect to the coordinated hexaethylbenzene ligand. The metal fragment assumes an almost eclipsed conformation with respect to the arene carbons as was also observed for the $(C_6H_6)Ru(CO)(GeCl_3)_2$ complex[34] which is also symmetrically substituted at the arene ring. The hexaethylbenzene ligand itself adopts a conformation with two methyl groups proximal to the metal moiety (C52 and C12) while four methyl groups are distal. This conformation is but one of four energetically favored conformations of the hexaethylbenzene ligand when complexed to an ML_3 moiety[13c] (see Figure 3.5). The conformers in Figure 3.5 are arranged in order of the most favorable to the least favorable conformation of the hexaethylbenzene ligand in sterically crowded $(Et_6C_6)ML_3$ complexes. This particular conformation of the hexaethylbenzene ligand (conformer 3 in Figure 3.5) has been reported for other $(Et_6C_6)ML_3$ complexes.[12a, 13d] (Conformers 1[13a-c], 2[13a,c,d], and 4[13a,b,12b] have also been observed in

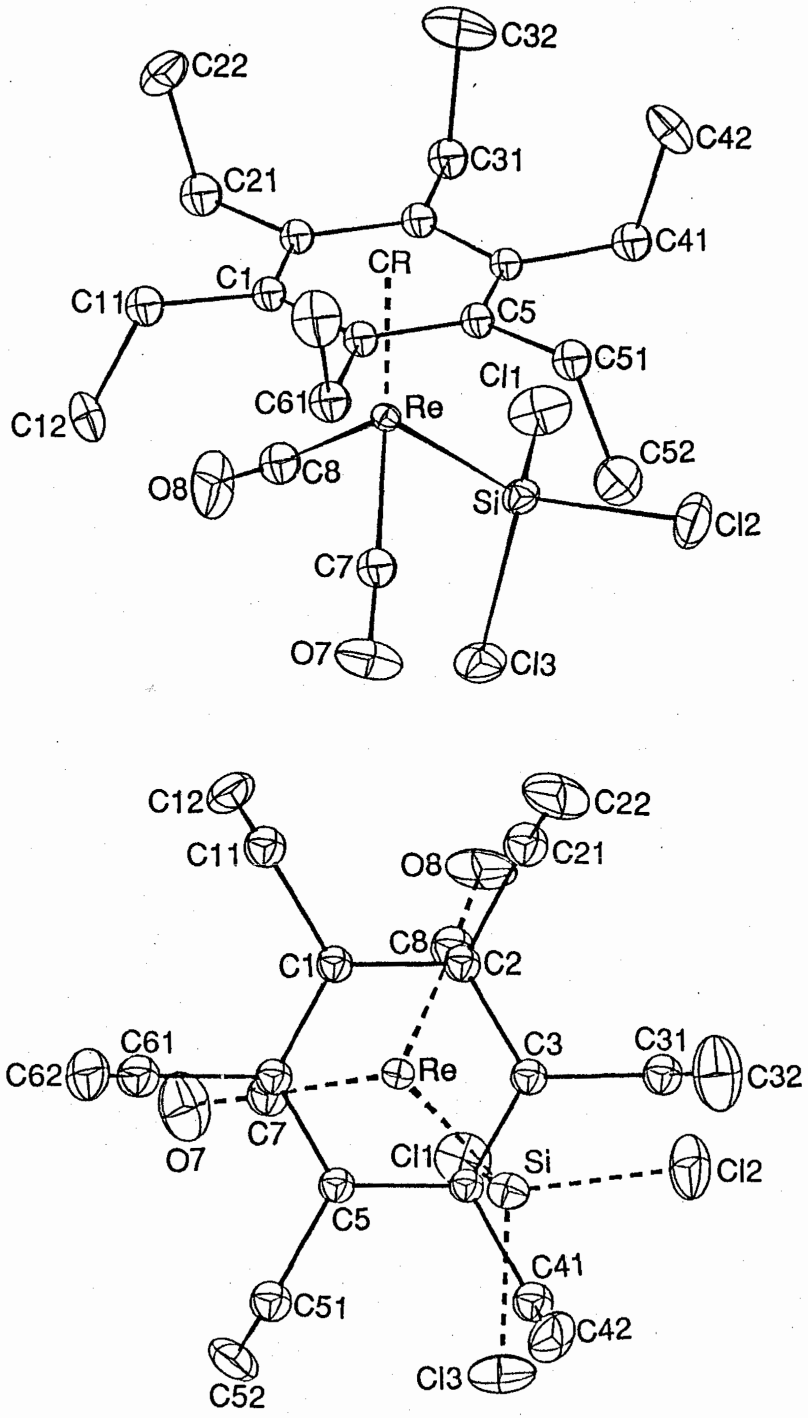


Figure 3.4 X-ray crystal structure of $(Et_6C_6)Re(CO)_2(SiCl_3)$: top (bottom) view approximately parallel (perpendicular) to the plane of the benzene ring.

Table 3.5 Selected Bond Lengths[a] for $(Et_6C_6)Re(CO)_2(SiCl_3)$

atoms[b]	
Re-Si(1)	2.377(3)
Re-C(7)	1.89(1)
Re-C(8)	1.94(2)
Re-C(R)	1.866
C(7)-O(1)	1.16(2)
C(8)-O(2)	1.13(2)
Si(1)-Cl(1)	2.100(4)
Si(1)-Cl(2)	2.091(4)
Si(1)-Cl(3)	2.084(4)
C(1)-C(2)	1.43(2)
C(2)-C(3)	1.47(2)
C(3)-C(4)	1.42(2)
C(4)-C(5)	1.45(2)
C(5)-C(6)	1.41(2)
C(6)-C(1)	1.44(2)
C(1)-C(11)	1.53(2)
C(2)-C(21)	1.52(2)
C(3)-C(31)	1.52(2)
C(4)-C(41)	1.52(2)
C(5)-C(51)	1.52(2)
C(6)-C(61)	1.52(2)
C(11)-C(12)	1.54(2)
C(21)-C(22)	1.50(2)
C(31)-C(32)	1.52(2)
C(41)-C(42)	1.53(2)
C(51)-C(52)	1.52(2)
C(61)-C(62)	1.54(2)

a) in angstroms b) numbering as in Figure 3.4

Table 3.6 Selected Bond Angles[a] for $(Et_6C_6)Re(CO)_2(SiCl_3)$

atoms[b]	
Si(1)-Re-C(7)	85.9(3)
Si(1)-Re-C(8)	80.5(3)
Si(1)-Re-C(R)	130.2
C(7)-Re-C(8)	88.3(5)
C(7)-Re-C(R)	128.1
C(8)-Re-C(R)	128.0
Re-C(7)-O(1)	177.7(9)
Re-C(8)-O(2)	174.5(9)
Re-Si(1)-Cl(1)	113.9(2)
Re-Si(1)-Cl(2)	117.1(2)
Re-Si(1)-Cl(3)	121.2(2)
Cl(1)-Si(1)-Cl(2)	101.3(2)
Cl(1)-Si(1)-Cl(3)	100.3(2)
Cl(2)-Si(1)-Cl(3)	99.9(2)
C(1)-C(2)-C(3)	119.9(8)
C(2)-C(3)-C(4)	118.9(8)
C(3)-C(4)-C(5)	120.7(9)
C(4)-C(5)-C(6)	119.6(9)
C(5)-C(6)-C(1)	121.0(9)
C(6)-C(1)-C(2)	119.6(9)
C(2)-C(1)-C(11)	120.4(8)
C(3)-C(2)-C(21)	120.6(8)
C(4)-C(3)-C(31)	121.4(9)
C(5)-C(4)-C(41)	118.9(8)
C(6)-C(5)-C(51)	120.1(9)
C(1)-C(6)-C(61)	119.0(9)
C(6)-C(1)-C(11)	120.0(8)
C(1)-C(2)-C(21)	119.5(8)
C(2)-C(3)-C(31)	119.7(8)
C(3)-C(4)-C(41)	120.1(9)
C(4)-C(5)-C(51)	120.3(9)
C(5)-C(6)-C(61)	119.8(9)
C(1)-C(11)-C(12)	114.5(8)
C(2)-C(21)-C(22)	113.8(9)
C(3)-C(31)-C(32)	113.2(9)
C(4)-C(41)-C(42)	110.4(8)
C(5)-C(51)-C(52)	116.6(9)
C(6)-C(61)-C(62)	112.9(9)

a) in degrees b) numbering as in Figure 3.4

the solid state of various $(Et_6C_6)ML_3$ complexes).

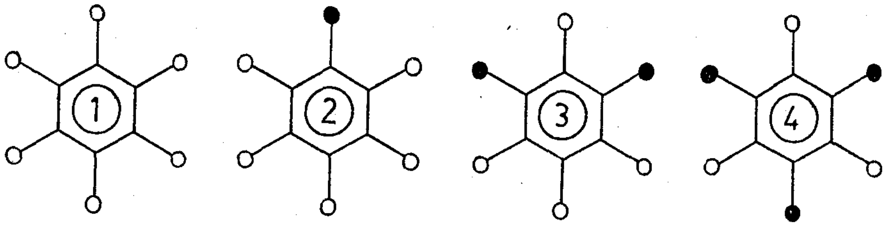


Figure 3.5 The four favored stereoisomers of Et_6C_6 for $(Et_6C_6)ML_3$ complexes. The metal atom is above the plane of the paper. The filled (open) circles represent proximal (distal) methyl groups projecting towards (away from) the observer.

The trichlorosilyl ligand eclipses one of the distal methyls while a CO ligand is found between the two proximal methyls. The position of the trichlorosilyl group and the carbonyls is the conformation that minimizes the non-bonding interactions between the ligands on the metal and the substituents on the arene ring.

The structural parameters of the hexaethylbenzene ligand in the crystal structure of $(Et_6C_6)Re(CO)_2(SiCl_3)$ do not differ, within the bounds of their standard deviations, from those of other Et_6C_6-transition metal complexes. No alternation of C_{ar}-C_{ar} bond lengths is observed. The average values of the arene C_{ar}-C_{ar} distances, the C_{ar}-C_{ar}-C_{ar} bond angles and the C_{ar}-CH_2-CH_3 bond angles are 1.44(2) Å, 120.0(9)° and 113.5(9)°, respectively. These values compare well with those of the $(Et_6C_6)Cr(CO)_3$ complex (1.424(6) Å, 120.0(3)°, and 113.8(3)°, respectively).[12b] All other bond lengths and bond angles of the hexaethylbenzene ligand of the complex $(Et_6C_6)Re(CO)_2(SiCl_3)$ are within the bounds of those considered as normal for η^6-arene-transition metal complexes.

The Re-CR (CR = centroid of the arene ring) distance of the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex is 1.866 Å. This distance is in good agreement with Re-CR distance of 1.855 Å found in the complex $[(1,3,5\text{-}Me_3C_6H_3)Re(CO)_3]^+[AlBr_4]^-$.[36] The average Re-CO bond distance (1.92(2) Å), average Re-C-O bond angle (176.1(9)°), and C-O bond distance (1.14(2) Å) are also in good agreement with those found in the complex $[(1,3,5\text{-}Me_3C_6H_3)Re(CO)_3]^+[AlBr_4]^-$ (1.89(2) Å, 178(2)°, and 1.15(2) Å respectively).[36] The CO-Re-CO bond angle was determined from the infrared spectrum to be 83° (see Section 2). This value is somewhat lower than that determined for the crystal of 88.3(5)°. However, due to the accuracy of the measurement in solution, as well as the packing forces in the crystal, these two values are still in reasonable agreement.

The Re-Si distance in the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex is 2.377(3) Å. This value is equal within experimental error to that of 2.380(8) Å found in the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$.[37] The dimensions of the $SiCl_3$

group in the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex are similar to those of the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ (see below).[38]

A crystal structure of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex at -50 °C was determined. (The crystal used in this study was also grown from toluene.) The structure is shown in Figure 3.6. Selected bond lengths and bond angles are reported in Tables 3.7 and 3.8.

The crystal structure of the complex $(Et_6C_6)Ru(CO)(SiCl_3)_2$ revealed that the unit cell consists of two independent molecules with different conformations (A and B) of the arene ring in exactly equal proportions. It is not unusual for the hexaethylbenzene ligand to adopt two different conformations in the same unit cell.[13a,c,d] Due to the almost isoenergetic nature of the various conformations of the hexaethylbenzene ligand in $(Et_6C_6)ML_3$ complexes (Figure 3.6) steric effects as well as subtle crystal packing forces can influence the conformational preferences of the hexaethylbenzene ligand in the solid state. Thus, various conformations of the Et_6C_6 ligand have been observed in different crystal structures in varying proportions.

In conformer A all six methyl groups are distal whereas in conformer B four methyl groups are distal while two are proximal. Conformers A and B also differ in that the metal moiety in conformer A eclipses the aromatic carbons while in conformer B the metal moiety is slightly staggered. In conformer B one of the trichlorosilyl groups is eclipsed by the distal C2 carbons (i.e., C2, C21, C22) while it is flanked by the proximal C1 and C3 atoms.

Outside of the conformational differences of the hexaethylbenzene ligand, the structural parameters of conformations A and B do not differ from one another or from other Et_6C_6-transition metal complexes within the bounds of their standard deviations. There is no alternation of the C_{ar}-C_{ar} bonds; the average C_{ar}-C_{ar} bond distances for A and B are 1.422(9) Å and 1.424(9) Å, respectively. The average C_{ar}-C_{ar}-C_{ar} and C_{ar}-CH_2-CH_3 bond angles for A (B) are 119.8(6)° (119.3(6)°) and 114.2(6)° (114.7(6)°) respectively. The C11-C12 bond distance of 1.39(2) Å in conformer B is somewhat smaller than the average (1.52(1) Å) due to disorder in the crystal. All other bond lengths and bond angles of the Et_6C_6 ligand in the conformers of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex are within normal boundaries. The Ru-CR distance in conformers A and B of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex are 1.871 and 1.892 Å, respectively. This distance is in good agreement with Ru-CR distance of 1.876 Å found in the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$. It is, however, significantly

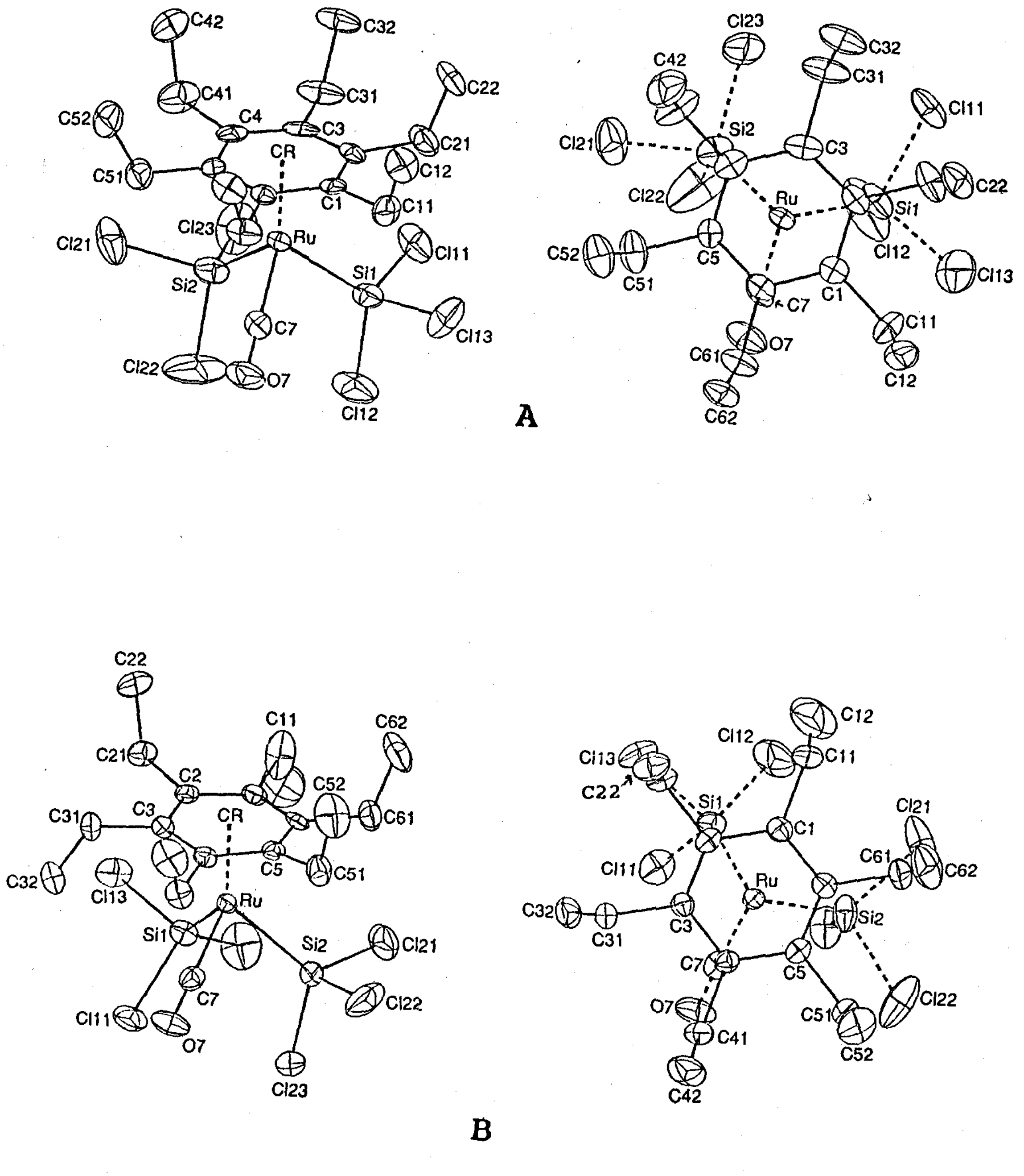


Figure 3.6 X-ray structure of $(Et_6C_6)Ru(CO)(SiCl_3)_2$: Conformer A (top); B(bottom). Left (right), view approximately parallel (perpendicular) to the plane of the benzene ring.

Table 3.7 Selected Bond Lengths[a] for $(Et_6C_6)Ru(CO)(SiCl_3)_2$

atoms[b]	A	B
Ru-Si(1)	2.349(2)	2.325(2)
Ru-Si(2)	2.340(2)	2.323(2)
Ru-C(R)	1.871	1.892
Ru-C(7)	1.839(8)	1.832(8)
C(7)-O(1)	1.149(8)	1.155(8)
Si(1)-Cl(11)	2.069(3)	2.082(3)
Si(1)-Cl(12)	2.060(3)	2.062(3)
Si(1)-Cl(13)	2.078(3)	2.073(3)
Si(2)-Cl(21)	2.078(3)	2.069(3)
Si(2)-Cl(22)	2.056(3)	2.080(3)
Si(2)-Cl(23)	2.056(3)	2.069(3)
C(1)-C(2)	1.424(9)	1.441(9)
C(2)-C(3)	1.43(1)	1.395(9)
C(3)-C(4)	1.43(1)	1.427(9)
C(4)-C(5)	1.42(1)	1.435(9)
C(5)-C(6)	1.422(9)	1.416(9)
C(6)-C(1)	1.420(9)	1.420(9)
C(1)-C(11)	1.518(9)	1.53(1)
C(2)-C(21)	1.51(1)	1.514(9)
C(3)-C(31)	1.53(1)	1.534(9)
C(4)-C(41)	1.52(1)	1.522(9)
C(5)-C(51)	1.53(1)	1.520(9)
C(6)-C(61)	1.517(9)	1.528(9)
C(11)-C(12)	1.51(1)	1.39(2)
C(21)-C(22)	1.51(1)	1.52(1)
C(31)-C(32)	1.51(1)	1.53(1)
C(41)-C(42)	1.51(1)	1.52(1)
C(51)-C(52)	1.49(1)	1.52(1)
C(61)-C(62)	1.51(1)	1.52(1)

a) in angstroms b) numbering as in Figure 3.6

Table 3.8 Selected Bond Angles[a] for $(Et_6C_6)Ru(CO)(SiCl_3)_2$

atoms[b]	A	B
Si(1)-Ru-Si(2)	88.29(8)	86.17(8)
Si(1)-Ru-C(7)	84.8(2)	85.5(2)
Si(2)-Ru-C(7)	85.0(2)	82.4(2)
Si(1)-Ru-C(R)	126.8	131.0
Si(2)-Ru-C(R)	128	128.7
C-Ru-C(R)	129.2	126.8
Ru-C(7)-O(1)	175.9	175.1(6)
Ru-Si(1)-Cl(11)	116.6(1)	116.0(1)
Ru-Si(1)-Cl(12)	120.7(1)	120.6(1)
Ru-Si(1)-Cl(13)	113.2(1)	116.9(1)
Ru-Si(2)-Cl(21)	115.1(1)	119.4(1)
Ru-Si(2)-Cl(22)	119.5(1)	111.8(1)
Ru-Si(2)-Cl(23)	116.2(1)	118.4(1)
Cl(11)-Si(1)-Cl(12)	101.8(1)	102.0(1)
Cl(11)-Si(1)-Cl(13)	101.8(1)	98.1(1)
Cl(12)-Si(1)-Cl(13)	99.9(1)	99.7(1)
Cl(21)-Si(2)-Cl(22)	97.1(2)	101.5(1)
Cl(21)-Si(2)-Cl(23)	101.1(1)	102.7(1)
Cl(22)-Si(2)-Cl(23)	104.8(2)	100.2(1)
C(1)-C(2)-C(3)	119.4(6)	120.1(6)
C(2)-C(3)-C(4)	119.6(6)	120.6(6)
C(3)-C(4)-C(5)	120.0(6)	119.1(6)
C(4)-C(5)-C(6)	120.0(6)	120.0(6)
C(5)-C(6)-C(1)	120.2(6)	118.9(6)
C(6)-C(1)-C(2)	120.2(6)	119.3(6)
C(2)-C(1)-C(11)	119.6(6)	119.5(6)
C(3)-C(2)-C(21)	119.8(6)	119.1(6)
C(4)-C(3)-C(31)	119.8(7)	119.1(6)
C(5)-C(4)-C(41)	119.8(7)	120.6(6)
C(6)-C(5)-C(51)	119.9(6)	120.1(6)
C(1)-C(6)-C(61)	119.4(6)	118.9(6)
C(6)-C(1)-C(11)	120.3(6)	120.0(6)
C(1)-C(2)-C(21)	120.7(6)	119.1(6)
C(2)-C(3)-C(31)	120.1(7)	120.1(6)
C(3)-C(4)-C(41)	120.2(7)	120.3(6)
C(4)-C(5)-C(51)	120.1(6)	119.7(6)
C(5)-C(6)-C(61)	120.3(6)	121.0(6)
C(1)-C(11)-C(12)	114.5(6)	117.7(9)
C(2)-C(21)-C(22)	113.6(6)	111.4(6)
C(3)-C(31)-C(32)	116.1(6)	114.6(6)
C(4)-C(41)-C(42)	111.8(7)	116.3(6)
C(5)-C(51)-C(52)	117.2(7)	112.4(7)
C(6)-C(61)-C(62)	114.9(6)	112.8(6)

a) in degrees b)numbering as in Figure 3.6

longer than 1.806 Å found for the $(C_6H_6)Ru(CO)(GeCl_3)_2$[34] complex and it may reflect the greater steric interactions in the Et_6C_6 and $Bu^t{}_2C_6H_4$ complexes compared to the C_6H_6 compound. In conformer A (B) the Ru-CO bond distance is 1.839(8) Å (1.832(8) Å); the Ru-C-O bond angle 175.9(6)° (175.1(6)); and C-O bond distance 1.149(8) Å (1.155(8) Å). These values are in good agreement with those of the $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$[38] which are 1.843(5) Å, 177.1(5)°, and 1.141(7)°, respectively. The average Ru-Si distance in A (B) is 2.344(2)Å (2.324(2)Å) which is comparable to the Ru-Si distance of 2.339(1) Å in the $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex.[38] As with the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex the dimensions of the $SiCl_3$ group in the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ derivative are similar to those of the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$.

4. NMR Studies of Selected Arene-Transition Metal Complexes

4.1 $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$

The large barrier to rotation about the arene-ruthenium bond observed in the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex was attributed to steric interactions between the bulky t-butyl substituents of the aromatic ring and the large trichlorosilyl groups attached to the ruthenium atom.[7] These steric interactions in the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ and related complexes, prevent the arene ring from tilting to allow one t-butyl group to easily pass over a trichlorosilyl ligand. This interaction is depicted in Figure 4.1.1.

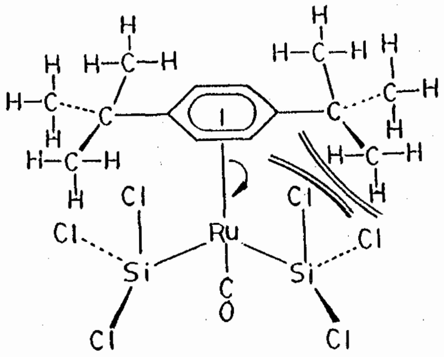


Figure 4.1.1 Steric interaction between the t-butyl and trichlorosilyl groups of the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex upon rotation.

The barrier to rotation is large enough in the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex that the rotation of the arene ring about the ruthenium arene bond can be stopped on the ^1H and ^{13}C NMR time scales at -60 °C. The aromatic region of the ^1H NMR exhibits a pseudo AB pattern while the signals in the aromatic region of the $^{13}C\{^1H\}$ NMR are all doubled. These NMR patterns are consistent with the structural conformation shown in A of Figure 4.1.2. However, in the solid state the $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex has the structure depicted in B of Figure 4.1.2.[38] This structure should give rise to six signals of equal intensity in the aromatic region of the ^{13}C NMR spectrum. As well, the aromatic region of the ^1H NMR should consist of three signals with relative intensities of 1:1:2 (the signals with relative intensities of 1 should be doublets). Therefore, the ^{13}C NMR spectrum of the complex in solution can be rationalized on the assumption that in solution at low temperature the arene ring rocks back and forth as shown in Figure 4.1.2.

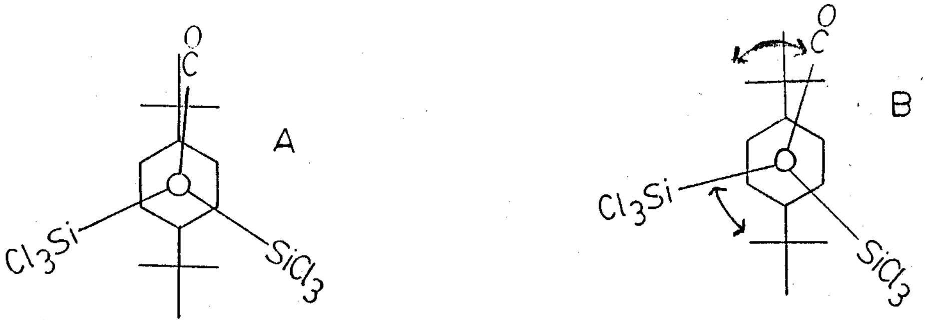


Figure 4.1.2 Conformation of the complex $(1,4\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$, (A) in solution at low temperature and (B) in the solid state.

The rotation of the arene ring about the arene-rhenium bond in the corresponding $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$

complex could not be stopped on the NMR time scale.[7] Even at -120 °C the ^1H NMR spectrum showed no evidence of restricted rotation. The free rotation of the arene ligand in the $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$ complex can be explained by the ability of one t-butyl substituent of the aromatic ring being able to tilt down between the CO groups while simultaneously lifting the other t-butyl group over the trichlorosilyl ligand.

The distance between an arene ligand and a first row transition metal element is generally about 0.1 Å shorter than the corresponding distance for the third row member of the chemical group.[39] The closer proximity of the arene ligand to the metal fragment in $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ compared to that in $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$ should therefore increase the steric interactions between the t-butyl and the trichlorosilyl groups. It was hoped that this increase in steric interactions would be large enough to allow a barrier to rotation about the manganese-arene bond in the $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ complex to be detected on the NMR time scale. If arene rotation about the metal atom in the $(1,4\text{-}Bu^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ complex could be stopped the most likely conformation of the molecule (based on steric interactions) would be that which is depicted in Figure 4.1.3. (This conformation was found in the solid state for the $(1,4\text{-}Bu^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$[38]

complex.) The aromatic region of the ^1H NMR would consist of a pseudo AB pattern while the aromatic region of the ^{13}C NMR would consist of two signals (A and B) due to the unsubstituted carbons and one signal for the substituted carbons.

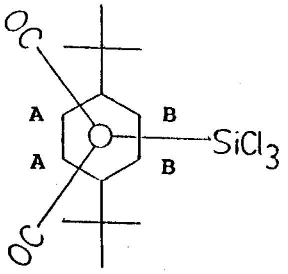


Figure 4.1.3 Predicted conformation of the $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ in solution at low temperature.

The variable temperature ^1H NMR spectra of the complex $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ was studied to -90 °C but no evidence of slowed rotation of the arene ring about the arene-manganese bond was observed. NMR spectra at lower temperatures could not be obtained. Although the $(1,4\text{-Bu}^t{}_2C_6H_4)Mn(CO)_2(SiCl_3)$ complex likely has a higher barrier to rotation about the arene-metal axis than the corresponding $(1,4\text{-Bu}^t{}_2C_6H_4)Re(CO)_2(SiCl_3)$ complex, this barrier is still not large enough to be detected on the NMR time scale.

4.2 $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$

Line shape analysis of the low temperature NMR spectra of the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex determined the barrier to rotation about the arene-ruthenium bond, $\Delta G^{\ddagger}_{298}$, to be 54 ± 4 kJ mol^{-1}.[7] It was thought that the barrier to rotation in the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ derivative would be even larger due to increased steric interactions. At -95 °C the aromatic region of the ^1H NMR spectra of the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex exhibited two broad signals in a 2:1 ratio. This is consistent with the structure shown in Figure 4.2.1. Due to the low solubility of the complex a complete line shape analysis was not performed but from the ^1H NMR data the barrier to rotation in the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ derivative could be estimated to be 35 kJ mol^{-1}.[7] Surprisingly, this value is much smaller than the value of $\Delta G^{\ddagger}_{298}$ determined for the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ complex.

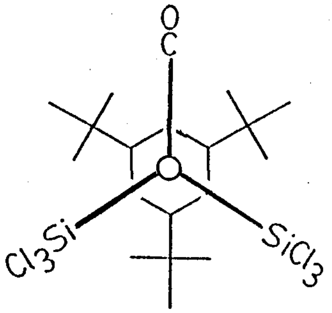


Figure 4.2.1 Predicted conformation of the complex $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ in solution at low temperature.

The lower barrier to rotation about the arene-ruthenium axis in the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex was attributed to the ability of one of the t-butyl substituents of the aromatic ring being able to tilt down over the CO ligand which simultaneously lifts the other t-butyl substituents over the trichlorosilyl groups.[7] This type of tilting in the $(1,4\text{-Bu}^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ derivative (depicted in Figure 4.2.2) does not result in a lowering of the steric interactions because of the geometry of the arene ring. This is consistent with the study of the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Cr(CO)_2(PPh_3)$ complex where no barrier to rotation about the arene-chromium bond could be observed on the NMR time scale in solution to -60 °C.[40]

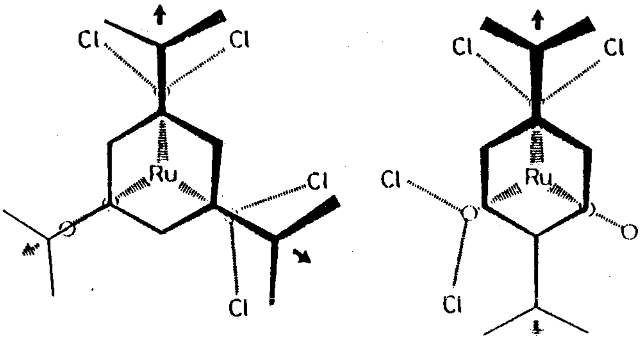


Figure 4.2.2 Schematic representation of the ring tilting in the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex.

As part of this study the variable temperature ^1H NMR spectra of the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex were studied to -124 °C. A complete line shape analysis of the aromatic region was performed. Visual fitting of the simulated spectra, produced by DNMR3,[41] to the real spectra provided rate constants. Real and simulated ^1H NMR spectra of the aromatic region of the $(1,3,5\text{-Bu}^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex are shown in Figure 4.2.3. Application of the Eyring equation (assuming a transmission coefficient of 1) and a least squares plot of the data, yielded the following parameters for the barrier to rotation about the arene-ruthenium bond in the $(1,3,5\text{-}Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex: $\Delta H^{\ddagger} = 26 \pm 2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -52 \pm 11$ J mol^{-1} K^{-1} and $\Delta G^{\ddagger}_{298} = 41 \pm 5$ kJ mol^{-1}.[42]

A decoalescence phenomenon was also observed for the methyl resonances of the t-butyl groups of the $(1,3,5\text{-}Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex. However, due to the small chemical shift differences between the two signals these were not fully resolved and were therefore not useful for line shape analysis.

4.3 $(Et_6C_6)M(L)_3$ Complexes

There is a controversy in the literature that concerns the static and dynamic properties of hexaethylbenzene when it is bound as a ligand in $(Et_6C_6)ML_3$ complexes, especially as in the $(Et_6C_6)Cr(CO)_2(CS)$ complex.[12,13] The variable temperature $^{13}C\{^1H\}$ NMR of the $(Et_6C_6)Cr(CO)_2(CS)$ exhibits one signal for the aromatic carbons, and the CH_2 and the CH_3 carbons of the ethyl groups at room temperature. These singlets are due to the rapid interconversion of the ethyl groups as well as rapid rotation of the arene ring about the arene-chromium axis. The aromatic and ethyl resonances each

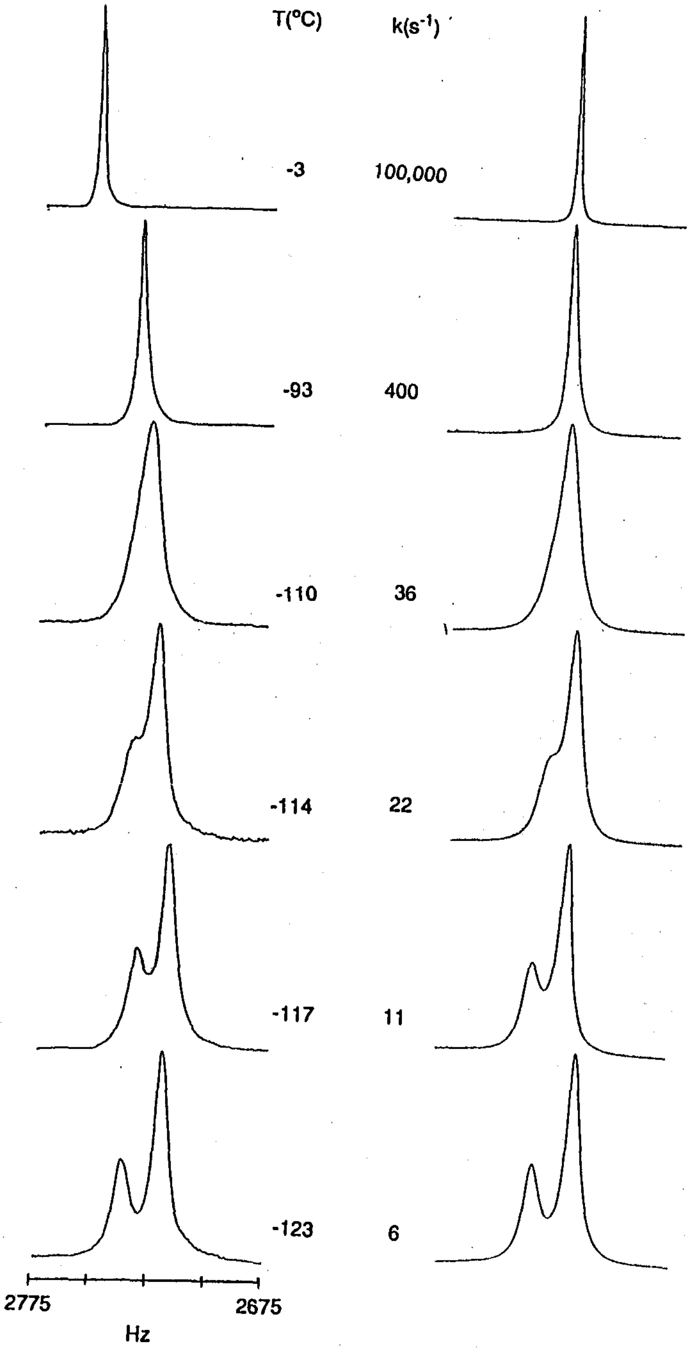


Figure 4.2.3 Variable temperature ^{1}H NMR spectra of the aromatic region of the $(1,3,5\text{-}Bu^t_3C_6H_3)Ru(CO)(SiCl_3)_2$ complex; (left) experimental, (right) simulated.

resolve into four signals of relative intensities 1:2:2:1 at low temperature in the ^{13}C NMR spectrum. Several other $(Et_6C_6)ML_3$ complexes also exhibit this phenomena.[13d]

It has been shown that the complex $(Et_6C_6)Cr(CO)_2(CS)$ adopts the conformation depicted in Figure 4.3.1. in the crystal state.[12b] In this conformation three of the methyl groups are distal and three proximal with respect to the $Cr(CO)_2(CS)$ unit. McGlinchey and co-workers believe that this three-distal conformation (conformer 3, Figure 3.2) is the one that is present at low temperature in solution and is responsible for the 1:2:2:1 pattern of signals observed in the aromatic and ethyl regions of the ^{13}C NMR. To arrive at this pattern one has to invoke halted rotation about the arene-chromium axis as well as halted ethyl group rotation in the $(Et_6C_6)Cr(CO)_2(CS)$ complex (as shown in Figure 4.3.1).

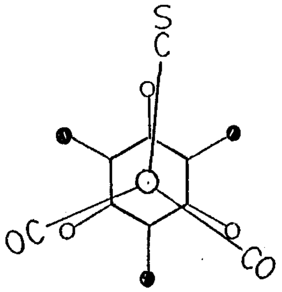


Figure 4.3.1. Conformation of the $(Et_6C_6)Cr(CO)_2(CS)$ complex in the solid state.

On the other hand, Mislow and co-workers explain the decoalescence to be the result of only halted ethyl group rotation, but the conformation of the compound in solution at low temperature is that depicted in Figure 4.3.2. This conformation of the $(Et_6C_6)Cr(CO)_2(CS)$ complex also results in the 1:2:2:1 pattern in the aromatic and ethyl regions of the ^{13}C NMR spectrum without the need to invoke halted arene rotation about the arene-chromium axis.

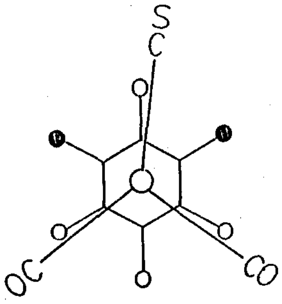


Figure 4.3.2 Mislow's predicted conformation of the complex $(Et_6C_6)Cr(CO)_2(CS)$ in solution at low temperature.

Neither of these explanations can be discarded as unreasonable. However, without special steric or electronic interactions to impede the rotation of the arene ring about the arene-chromium axis in the $(Et_6C_6)Cr(CO)_2(CS)$ complex, Mislow's interpretation at this time seems more plausible. For the complex $(Et_5(OAc)C_6)Cr(CO)_3$ McGlinchey and co-workers have, however, shown convincing evidence for halted rotation of the arene ring. This complex has the same conformation of the arene ring as the $(Et_6C_6)Cr(CO)_2(CS)$ derivative in the solid state except that one of the proximal methyl groups is replaced by a proximal acetyl group. It was shown that the carbonyl resonances of the $Cr(CO)_3$ unit split into two signals of relative intensities 2:1 in solution at -100 °C and in the CPMAS solid state spectrum at -30 °C.[14] This result is consistent with halted rotation of the arene ring.

4.3.1 $(Et_6C_6)Re(CO)_2(SiCl_3)$

The conformation of the arene ring in $(Et_6C_6)Re(CO)_2(SiCl_3)$ in the solid state as found by X-ray crystallography (see Section 3) is depicted in Figure 4.3.1.1. As with the $(Et_6C_6)Cr(CO)_2(CS)$ complex, the ^{13}C NMR spectrum of $(Et_6C_6)Re(CO)_2(SiCl_3)$ at room temperature is expected to show one signal in the aromatic, methylene, and methyl regions due to the rapid rotation of the ethyl groups and rapid rotation of the arene ligand about the metal atom. If the rotation of the ethyl groups is halted the singlets should resolve into four signals with relative intensities of 1:2:2:1. If halted arene rotation about the metal atom is also invoked and the compound retains the conformation observed in the crystal structure, the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex should exhibit six signals of equal intensity in the aromatic, methylene, and methyl regions. Unlike the $(Et_6C_6)Cr(CO)_2(CS)$ complex, if the conformation of $(Et_6C_6)Re(CO)_2(SiCl_3)$ is the same in solution at low temperature as that found in the solid state the carbonyl signal should resolve into two signals of equal intensity.

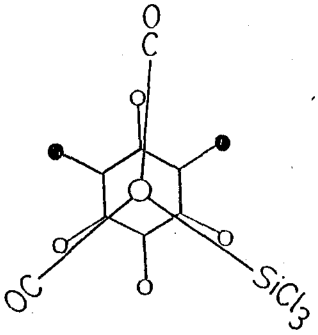


Figure 4.3.1.1 Conformation of the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex in the solid state.

The variable temperature ^{13}C NMR spectrum of the $(Et_6C_6)Re(CO)_2(SiCl_3)$ complex below -23 °C exhibits decoalescence phenomenon in the aromatic, methylene and methyl regions (See Figure 4.3.1.2). Solubility problems prevented the ^{13}C NMR spectra from being obtained at lower temperatures than -97 °C. The possible further resolution of these peaks could therefore not be observed. Since a limiting low temperature spectrum of $(Et_6C_6)Re(CO)_2(SiCl_3)$ could not be obtained a detailed line shape analysis could be not performed. The only interpretation which can be put forward to explain the observed decoalescence phenomenon is that it appears to be caused by the slowing of the ethyl group rotation. If slowed arene rotation were involved the carbonyl signal would also be affected. As can be seen in Figure 4.3.1.2 the carbonyl signal remains unchanged which implies that there is still free rotation of the arene ligand.

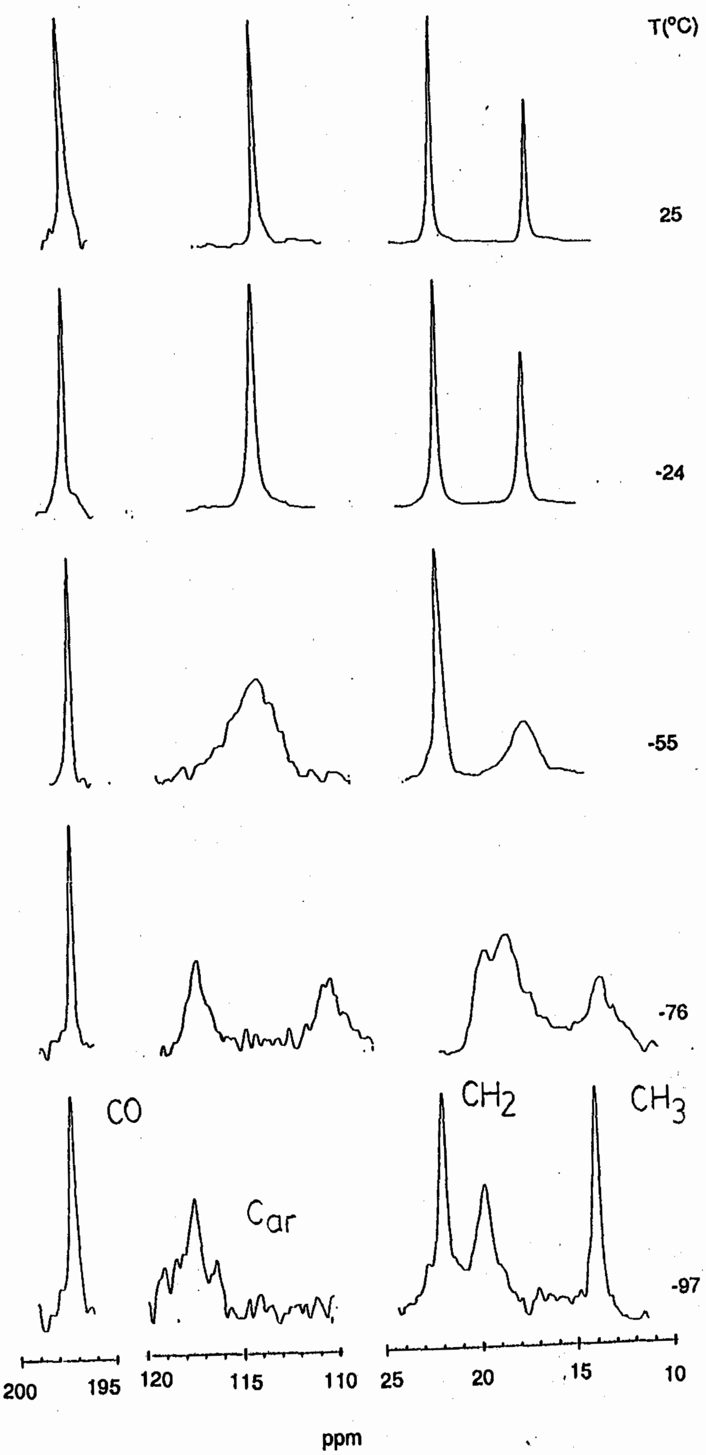


Figure 4.3.1.2 Variable temperature 100.6 MHz ^{13}C NMR spectra of the complex $(Et_6C_6)Re(CO)_2(SiCl_3)$. Spectra from left to right include the carbonyl, aromatic, and ethyl regions.

4.3.2 $(Et_6C_6)Ru(CO)(SiCl_3)_2$

The complex $(Et_6C_6)Ru(CO)(SiCl_3)_2$ was found to have two different conformations in the solid state. These conformations are depicted in Figure 4.3.2.1. At room temperature $(Et_6C_6)Ru(CO)(SiCl_3)_2$ should exhibit one signal for the aromatic, methylene, and methyl regions (due to the rapid interconversion of the ethyl groups of the hexaethylbenzene ligand combined with the rapid rotation of the arene ring about the ruthenium atom). With the added restriction of halted ethyl group rotation the aromatic, methylene and methyl regions of the ^{13}C NMR spectrum of conformer B would resolve into four signals with relative intensities of 1:2:2:1, while those of conformer A would remain a singlet. Thus, if both conformers are present in solution each region of the ^{13}C NMR would consist of five signals. If halted arene rotation also occurred, and if the same conformations that are observed in the crystal state are present in solution at low temperature, then conformer A would show four signals of relative intensities 1:2:2:1 for each of the aromatic, methylene, and methyl resonances, while conformer B would resolve into 6 signals of equal intensity. Therefore, if both conformations of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex are in solution at low temperature and both halted ethyl group and arene rotation occurs the ^{13}C NMR spectrum should consist of ten signals in each of the aromatic, methyl, and methylene regions. (The carbonyl region should consist of two signals.)

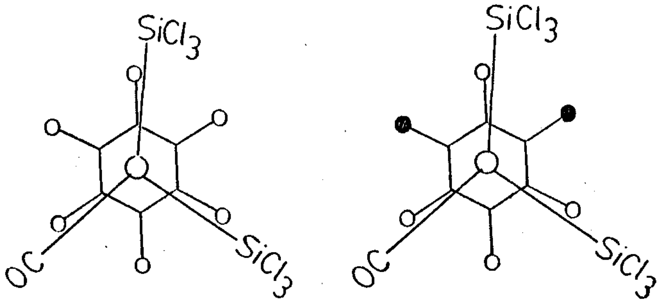


Figure 4.3.2.1 Representations of the two conformers of the complex $(Et_6C_6)Ru(CO)(SiCl_3)_2$ found in the crystal state. (Left) conformer A, (right) conformer B.

The variable temperature ^{13}C and ^{1}H NMR studies of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex were carried out by Professor McGlinchey at McMaster University. The line broadening due to temperature effects made the ^{1}H NMR spectra useless for detection of any decoalescence phenomena. The variable temperature ^{13}C NMR spectrum exhibited singlets for the aromatic, methylene, and methyl regions down to -90 °C. The signals in the spectrum at -90 °C were, however, broad which indicated the onset of decoalescence. Unfortunately, solubility problems prevented the study of the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex at lower temperatures.

The results of the variable temperature ^{13}C NMR study of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ implies that the only conformer of the complex present to any significant extent in solution at low temperature is conformer A. Recall that $(Et_6C_6)Re(CO)_2(SiCl_3)$ began to show restricted ethyl group rotation in solution between -20 and -55°C. It would be expected that if any other conformer except A is present to a significant extent then restricted rotation of ethyl groups in $(Et_6C_6)Ru(CO)(SiCl_3)_2$ would occur at temperatures at least comparable to those observed for $(Et_6C_6)Re(CO)_2(SiCl_3)$. The results are also consistent with free rotation of the arene ring about the arene-ruthenium axis.

These results are in agreement with those observed for $(Et_6C_6)Cr(CO)_2(PPh_3)$ complex [13c] which does not exhibit any decoalescence in the low temperature ^{13}C NMR spectra whereas the $(Et_6C_6)Cr(CO)_3$ complexes do and in $(Et_6C_6)Cr(CO)_2(PPh_3)$ as well as $(Et_6C_6)Ru(CO)(SiCl_3)_2$ the non bonding interactions are thought to prevent the conformers of the hexaethylbenzene ligand, other than the six distal conformer, from being populated to a significant extent. As stated previously, this may also account for the small chemical shift differences of the methyl signals in the $(Et_6C_6)Ru(CO)(SiCl_3)_2$ complex relative to those of the free ligand.

4.3.3 $(Et_6C_6)Mn(CO)_2(SiCl_3)$

Low temperature ^{13}C NMR spectra of $(Et_6C_6)Mn(CO)_2(SiCl_3)$

have not yet been obtained. The manganese complex is, however, expected to exhibit similar behavior as that found for $(Et_6C_6)Re(CO)_2(SiCl_3)$.

EXPERIMENTAL

All manipulations of compounds were carried out under nitrogen with use of Schlenk techniques. Hexane, benzene, toluene, t-butylbenzene, o- and p-xylene, mesitylene, p-di-i-propylbenzene, and prehnitene were refluxed over potassium, distilled, and stored over 4A molecular sieves under nitrogen until use. Chlorobenzene and methylene chloride were treated similarly except phosphorus pentoxide and calcium hydride, respectively, were used as drying agents. Olefin-free heptane was prepared by washing reagent grade heptane with conc. H_2SO_4/HNO_3 1:1, followed by 5% $NaHCO_3$, drying with $MgSO_4$, distilling from potassium, and treatment as the other solvents and liquid arenes. The solvents used for the NMR studies, $CDCl_3$, CD_2Cl_2, and $CHFCl_2$, were used as they were received from the supplier. A literature method was used to prepare $CDFCl_2$.[43] The solid arenes (p-di-t-butylbenzene, durene, hexamethyl- and hexaethylbenzene) were recrystallized from hexane and sublimed before use.

The starting materials $Re(CO)_5(SiCl_3)$,[15] $Mn(CO)_5(SiCl_3)$,[15] $Ru(CO)_4(SiCl_3)_2$,[32] and $Os(CO)_4(SiCl_3)_2$[32] were prepared from their respective metal carbonyls by published methods and sublimed before use. The complexes $(Bu^t{}_3C_6H_3)Ru(CO)(SiCl_3)_2$ and $(Et_6C_6)Ru(CO)(SiCl_3)_2$ were synthesized by published methods.[7]

Infrared spectra were recorded with a Perkin-Elmer 983 spectrometer; the internal calibration of the instrument was checked periodically against the known absorption frequencies of gaseous CO. Electron-impact mass spectra were obtained on a Hewlett Packard 5985 GC-MS system with an ionization voltage of 70 eV. The pattern of the envelope of ions of the parent peak for each compound matched that simulated by computer for the species involved. Microanalyses were performed by Mr. M. Yang of the Microanalytical Laboratory of Simon Fraser University.

Routine ^1H NMR spectra were recorded for $CDCl_3$ solutions with a 100-MHz Bruker spectrometer. All other NMR spectra were recorded with a Bruker 400-MHz spectrometer. Routine ^{13}C NMR spectra were obtained for compounds in CD_2Cl_2/CH_2Cl_2 (1:4) solutions and represent overnight accumulation of transients. The variable temperature ^{13}C NMR spectra were obtained for complexes in CD_2Cl_2/CH_2Cl_2 (1:4) solutions. A solution of the compound in $CD_2Cl_2/CHFCl_2$ (1:4) was used for ^{13}C NMR spectra below -100 °C. The variable temperature ^1H NMR spectra were recorded on $CD_2Cl_2/CDFCl_2$ (1:4) solutions of the complexes.

X-ray crystal structures of $(Et_6C_6)Ru(CO)(SiCl_3)_2$ and $(Et_6C_6)Re(CO)_2(SiCl_3)$ were determined by Mr. A. Ramos of the Chemistry Department of Simon Fraser University using an

Enraf-Nonius CAD4F diffractometer.

General Preparation of the (arene)Re(CO)$_2$(SiCl$_3$) Complexes.

A Carius tube was charged a stir bar, Re(CO)$_5$(SiCl$_3$) (100 mg, 0.217 mmol), and either 10 mL of liquid arene or, 1 mL of olefin-free heptane and 1 g of solid arene. The solutions were degassed by three consecutive freeze-pump-thaw-freeze cycles; the reaction mixture was then heated at 240 °C for 12 h. (For the reaction of benzene with Re(CO)$_5$(SiCl$_3$) a temperature of 230 °C and a reaction time of 24 h was used.) After this time the reaction mixture was cooled and treated in the following ways:

Reaction mixtures that involved liquid arenes were filtered through Celite and any remaining compound taken up in methylene chloride (2 x 10 mL). The liquids were combined and evaporated until about 10 mL remained whereupon hexane (10 mL) was added. This solution was kept at -20 °C for 12 h at which time the supernatant was decanted, the crystals that remained were washed with hexane (2 x 10 mL), and dried under vacuum.

For reactions that involved solid arenes, the reaction mixtures were extracted with hexane (3 x 10 mL), the residue that remained was dissolved in methylene chloride (3 x 10 mL), and filtered through Celite. The solution was then treated in the same manner as for reactions that involved liquid arenes.

The crude crystals obtained from the above procedures were recrystallized from methylene chloride and hexane. The crystals can be decolourized by adding charcoal to the hot methylene chloride solution of the crude material.

General Preparation of the (arene)$Mn(CO)_2(SiCl_3)$ Complexes

A Carius tube was charged with a stir bar, $Mn(CO)_5(SiCl_3)$ (100 mg, 0.304 mmol), and either 10 mL of liquid arene or, 1 mL of olefin-free heptane and 1 g of solid arene. The mixture was degassed by three successive freeze-pump-thaw-freeze cycles and then heated at 230 °C for 12 h (24 h for benzene). The reaction mixture was cooled and treated in one of the following ways:

For reactions that involved liquid arenes, the reaction mixtures were evaporated to dryness on the vacuum line and the residue extracted with methylene chloride (3 x 10 mL) and filtered through Celite. The methylene chloride was evaporated and the residue dissolved in a minimum of hot hexane. The solution was cooled and stored at -20 °C for 12 h. The supernatant was carefully decanted, and the crystals dried under vacuum.

For the reactions that involved solid arenes the reaction mixtures were extracted with methylene chloride (3 x 10 mL), filtered through Celite, and the methylene chloride removed on the vacuum line. The arene was sublimed from the reaction mixture at elevated temperatures (< 0.02 mm of Hg) and the remaining solid treated in the same manner as described above.

Analytically pure samples were prepared by a second, careful recrystallization from hexane.

Preparation of $(Me_6C_6)Re(CO)_2(SiCl_3)$ from $(MeC_6H_5)Re(CO)_2(SiCl_3)$.

A Carius tube was charged with a stir bar, $(MeC_6H_5)Re(CO)_2(SiCl_3)$ (20 mg), hexamethylbenzene (0.2 g), and 1 mL of olefin-free heptane. The reaction mixture was heated at 240 °C for 12 h. The solution was cooled and extracted with hexane (3 x 5 mL), and the remaining residue dissolved in methylene chloride (5 mL). The product was identified as $(Me_6C_6)Re(CO)_2(SiCl_3)$ by its infrared spectrum in the carbonyl region.

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