Ring-Methyl Activation in Pentamethylcyclopentadienyl Complexes. 5.[1] Syntheses and Structures of Tetramethylfulvene Complexes of Ruthenium(II)

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As previously reported, [{(η^5-C_5Me_5)$RuCl_2$}$_2$], **1a**, is oxygenated to the μ-oxo complex, [{(η^5-C_5Me_5)$RuCl_2$}$_2$O], **2a** (Angelici, R. J.; et al *Organometallics* **1992**, *11*, 2303). It is now shown that **2a** spontaneously decomposes in chloroform solution by activation of a methyl C−H bond, to give the dinuclear tetramethylfulvene (TMF) complex [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], **3a**, and water. The structure of **3a** in the solid state (established by an X-ray structure determination) showed two crystallographically different but structurally similar centrosymmetric dinuclear molecules, each having a TMF η^6-bonded to ruthenium(II). Each metal atom is approximately octahedrally coordinated by the η^6-$C_5Me_4CH_2$ and by three chlorides, two of which bridge to the other ruthenium and one of which is terminal. The chloride bridges are broken on reaction with ligands L to give [(η^6-$C_5Me_4CH_2$)$RuCl_2$(L)], **4a** (L = py), or **5a** (L = Me_2SO). All the complexes **2**−**5** are diamagnetic. NMR spectra of solutions of **3a** show the presence of several structural isomers; these do not interconvert rapidly on the NMR time scale below 70 °C. The adducts **4a** and **5a** also show an unexpected rigidity; thus, **4a** shows two noninterconverting isomers (rotamers). One is symmetric (*trans*), and the other unsymmetric (*cis*). The bonding is interpreted in terms of a η^4,η^2-TMF to Ru(II) rather than the alternative η^5,η^1-TMF to Ru(IV), by analysis of the details of the crystal structure determination of **3a** and the ^1J(C−H) of the exocyclic =CH_2 in the ^{13}C NMR spectrum. Reasons for the observed geometries are proposed. The mechanism for the O_2-induced C−H activation is discussed.

Introduction

We,[3] as well as other researchers,[4] have recently discovered new routes for the functionalization of pentamethylcyclopentadienyl complexes by C−H activation. One aim of our work is to introduce a functionality X, as η^5-$C_5Me_4CH_2X$, which will act as a *hand* to grasp, orient, and rigidly hold potential reactants to the metal in such a way that highly stereospecific reactions are promoted.

C−H activation of ring methyls has been found to occur under the influence of strong bases[5] or thermally.[6] We recently reported in preliminary communications that the oxygen-promoted cleavage of a C−H takes place with conspicuous facility in η^5-$C_5Me_5Ru^{III}$ complexes under ambient conditions.[7,8] We now present full details of the C−H cleavage in [{(η^5-C_5Me_5)$RuCl_2$}$_2$], **1a**,[9] which leads to the η^6-tetramethylfulvene (TMF) complex [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], **3a**, via the intermediate μ-oxo complexes, [{(η^5-C_5Me_5)$RuCl_2$}$_2$O], **2a**.[10] The Ru(II) TMF complexes exhibit interesting reactivity patterns leading to new chemistry, aspects of which are reported in this paper.

Results and Discussion

(i) Conversion of [{(η^5-C_5Me_5)RuX_2}$_2$], 1 (a, X = Cl; b, X = Br) into [{(η^6-$C_5Me_4CH_2$)RuX_2}$_2$], 3. The

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(pentamethylcyclopentadienyl)ruthenium(III) complex **1a**[9] reacts readily with oxygen in a remarkable series of reactions. The first identifiable product appears to be the (μ-oxo)ruthenium(IV) complex [{(η^5-C_5Me_5)-$RuCl_2$}$_2$O], **2a**, which was recently structurally characterized by Angelici and his co-workers.[10] We have successfully repeated the synthesis of **2a** and find that it can be made in crystalline form, in the presence of dibenzothiophene, below 0 °C, as described (eq 1). At ambient temperature in $CDCl_3$ solution **2a** rapidly rearranges under anerobic conditions to give the tetramethylfulvene complex and water (Scheme 1); complex **3a** could be crystallized from the chloroform solution. The solid was stable for only a few hours at ambient temperature and decomposed quite rapidly in solution. It was readily soluble in chloroform and dichloromethane, slightly soluble in tetrahydrofuran, acetone, or toluene, and insoluble in diethyl ether or hexane.

The conversion of **1a** into **3a** occurred directly and essentially quantitatively when the (pentamethylcyclopentadienyl)ruthenium complex **1a** was stirred in chloroform under oxygen (30 min/1 atm/20 °C); 0.5 equiv of O_2 was consumed within a few minutes for every dimer of **1a**, after which oxygen uptake ceased (Figure 1).

A sample of crystalline μ-oxo complex **2a** was made and dissolved in $CDCl_3$ under argon with complete exclusion of air; the change in the ^{1}H NMR spectrum with time was monitored (Figure 2). Initially the solution was characterized by a singlet at δ 1.78 due to **2a**.[10] After 2 min (25 °C), a complex ^{1}H NMR pattern characteristic of **3a** (and indicating the presence of ca. 10%) was visible, and water (δ 1.55) was detected. After 10 min, most of complex **2a** (ca. 90%) had decomposed to **3a** and the water signal grew in intensity. After 60 min, complex **2a** could no longer be detected; the overall reaction proceeded according to eq 2.

We may conclude that the conversion of **1a** into **3a** is a two-step process (eqs 1 and 2).

$$[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2] + {}^1/_2O_2 \rightarrow \underset{\textbf{1a}}{} \qquad [\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2O] \quad (1)$$
$$\textbf{2a}$$

$$[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2O] \rightarrow \underset{\textbf{2a}}{} \qquad [\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2] + H_2O \quad (2)$$
$$\textbf{3a}$$

The oxidation of [{(η^5-C_5Me_5)$RuCl_2$}$_2$], **1a**, could also be carried out in the presence of an alcohol. In this case the conversion into **3a** still occurred in high yield, but in addition the alcohol was transformed into an aldehyde or a ketone. Thus acetaldehyde (formed with a turnover of 1.5 equiv per ruthenium) was detected in the reaction of **1a** with oxygen in the presence of ethanol, and acetone (turnover 2) was detected in the presence of 2-propanol.

Characterization of [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], 3a. Microanalysis data were consistent with the formulation $[(C_5Me_4CH_2)RuCl_2]_n$. A solution of the complex in acetone was essentially nonconducting ($\Lambda_m = 0.55\ \Omega^{-1}$ cm^2 mol^{-1}), showing that it was not ionic.[11] The FAB

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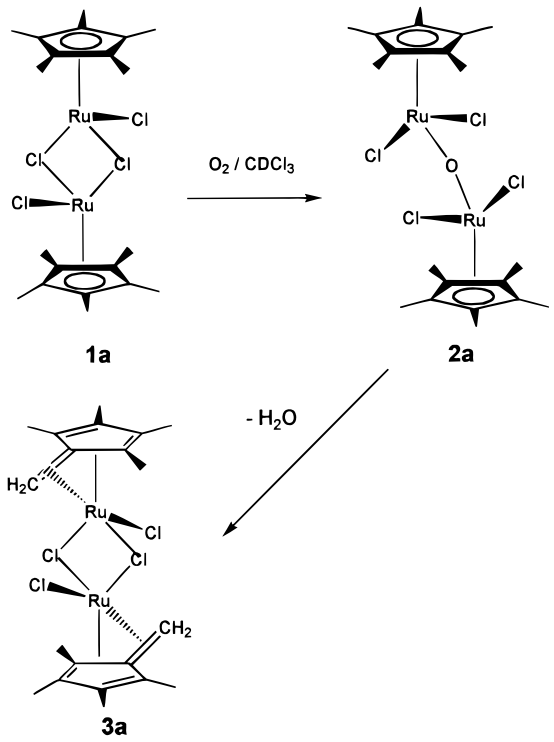
Scheme 1. Conversion of [{(η^5-C_5Me_5)$RuCl_2$}$_2$], 1a, into [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], 3a, via [{$C_5Me_5RuCl_2$}$_2$O], 2a



mass spectrum showed the parent molecular ion at *m/e* 612, the expected value for [{($C_5Me_4CH_2$)$RuCl_2$}$_2$]$^+$, while the osmometric molecular weight in chloroform solution was found to be 700, not inconsistent with the 612 expected for a dimer, $n = 2$. The IR spectrum of **3a** showed very weak broad bands (1616 and 1635 cm^{-1}), consistent with the presence of a coordinated exocyclic TMF C=CH_2 double bond.

As the ^{1}H and ^{13}C NMR spectra of **3a** were very complex and showed the presence of several isomers, the structure was determined by X-ray crystallography. Single crystals were grown from a chloroform−hexane solution in the presence of dibenzothiophene (as stabilizer); even so they were only stable in the mother liquid below −20 °C, and the crystal structure was determined at −123 °C. X-ray analysis[7] of these crystals showed the presence of two crystallographically different but structurally similar centrosymmetric dinuclear molecules [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], one of which is shown in Figure 3. Each dimer was associated with three chloroform molecules of solvation, but dibenzothiophene had not been incorporated into the crystal and was not found. The coordination about each Ru(II) was approximately octahedral, three sites being taken up by an η^6-TMF ligand, one of which was the exocyclic C=CH_2 [Ru−CH_2, 2.268(4), 2.271(4), and C=CH_2, 1.401(6), 1.398(6) Å]. The remaining three sites were taken up by one terminal chloride, approximately *trans* to =CH_2 ($\angle CH_2$−Ru−Cl, 170.60(11), 171.02(11)°; Ru−Cl, 2.4037(11), 2.4097(11) Å), and two bridging chlorides (Ru−Cl, 2.4679(13), 2.4657(11), and 2.4680(13), 2.4591(11) Å), each approximately *trans* to one of the endocyclic double bonds. The metal atoms are 3.663 Å apart, and nonbonded, consistent with diamagnetic Ru(II), d^6. The angles at ruthenium are $\angle$Cl(br)−Ru−Cl(br) 82.53(4) and Cl(br)−Ru−Cl(ter) 86.96(4), 86.85(4),

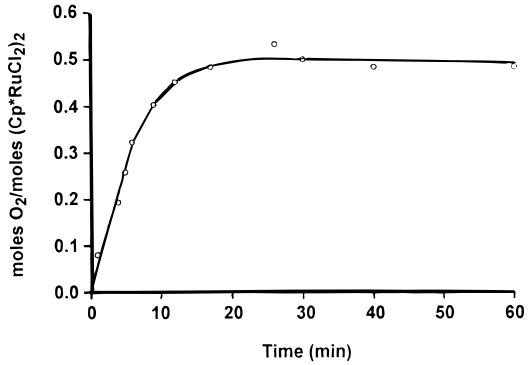


Figure 1. Measurement of the uptake of oxygen during the conversion of $[\{C_5Me_5RuCl_2\}_2]$, **1a**, into $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a**, in $CHCl_3$.

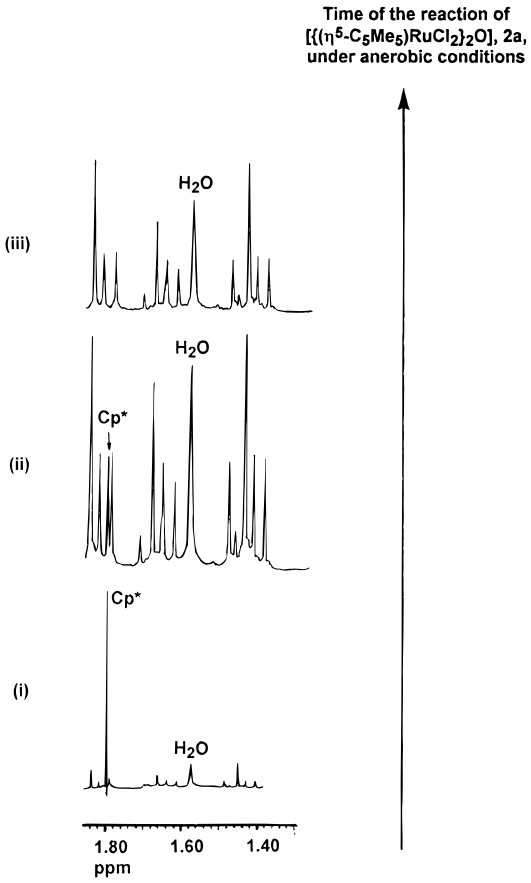


Figure 2. Methyl region of the ^1H NMR spectrum ($CDCl_3$ solution) during the conversion of $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2O]$, **2a** (Cp* = C_5Me_5, δ 1.79), under anaerobic conditions, into $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a**, and water ($\delta$ 1.58): (i) after 2 min of reaction; (ii) after 10 min; (iii) after 60 min.

86.15(4), and 87.40(3)°, while those at the bridging chloride, ∠Ru−Cl(br)−Ru′, are 97.47(4)°. The C_5 ring is planar, with the attached methyls bent away from the metal, but the methylenic $=CH_2$ is bent toward the Ru by ca. 0.94 Å from the C_5 plane.

The structure of **3a** is similar to that found for other η^6-TMF complexes, including $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)ZrPh]$,[12] $[(\eta^6\text{-}C_5Me_4CH_2)M(\eta^5\text{-}C_5Me_5)]^+$ (M = Ru or Os),[13] $[(\eta^6\text{-}C_5Me_4CH_2)Ru(\eta^4\text{-}C_8H_{12})]$,[14] and $[(\eta^6\text{-}C_5Me_4CH_2)Re(\eta^1\text{-}C_6F_5)(CO)_2]$,[15] which all have similar M−CH_2 and >C=CH_2 bond lengths. In $[(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)ZrPh]$ the TMF is in a highly unsymmetrical environment and shows four separate methyl and two separate (and coupled) CH_2 signals in the ^1H NMR spectra, arising from the magnetically inequivalent methyls and the CH_2 hydrogens; the ^{13}C NMR spectra also show inequivalent methyls.[12] By comparison, complex $[(\eta^6\text{-}C_5Me_4CH_2)Ru(\eta^4\text{-}C_8H_{12})]$ shows symmetrical ^1H NMR spectra with two methyls and one signal for the exocyclic $=CH_2$; this is consistent with the X-ray structure which shows the cyclooctadiene double bonds to be approximately parallel to the endocyclic TMF double bonds.[14] The X-ray structure of $[(\eta^6\text{-}C_5Me_4CH_2)Re(\eta^1\text{-}C_6F_5)(CO)_2]$ also shows the TMF bonded symmetrically, with the C_6F_5 trans to the $=CH_2$.[15]

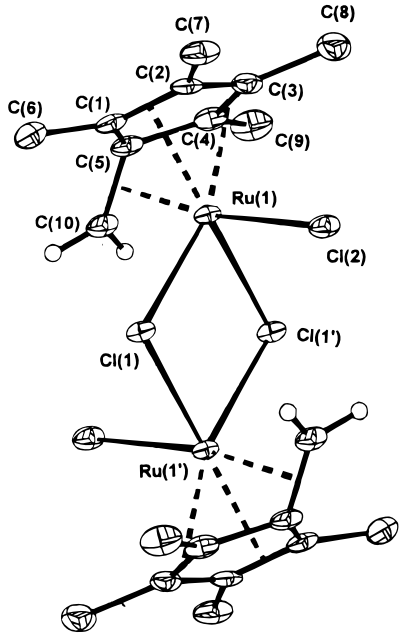


Figure 3. Structure of $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a**, from the X-ray study.[7]

The ^1H NMR spectrum of **3a** in $CDCl_3$ solution (Figure 4) showed the presence of at least four types of tetramethylfulvene ligands, arising from isomerism. The most prevalent set of resonances showed two signals for the methyl groups (δ 1.46, 1.89) and one signal for the two equivalent hydrogens on the methylene (δ 5.96) and indicated the presence of a plane of symmetry through the liganded TMF. This must be due to the isomer found in the crystal structure determination which is present to the extent of ca. 40% in solution. The three others each showed two inequivalent CH_2 protons and four signals for the four ring methyls and, hence, were in very asymmetric environments. The ^{13}C NMR spectrum in $CDCl_3$ was also very complex and showed four signals for methylene carbons in the range δ 70−85 and more than 10 signals for methyl carbons around δ 10, as well as the ring carbons at around δ 100.

The form of the spectra obtained was solvent-dependent, indicating the existence of equilibria between the

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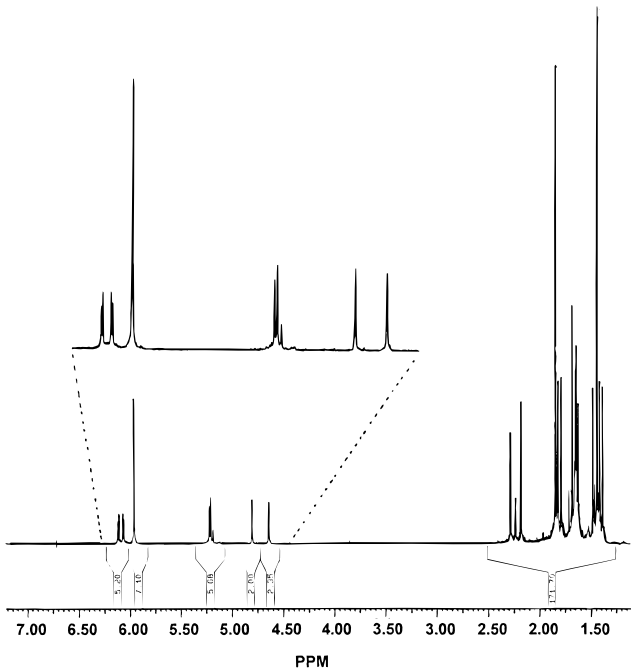


Figure 4. Details of the ^{1}H NMR spectrum (especially the methylene region) of [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], **3a**, in $CDCl_3$ solution.

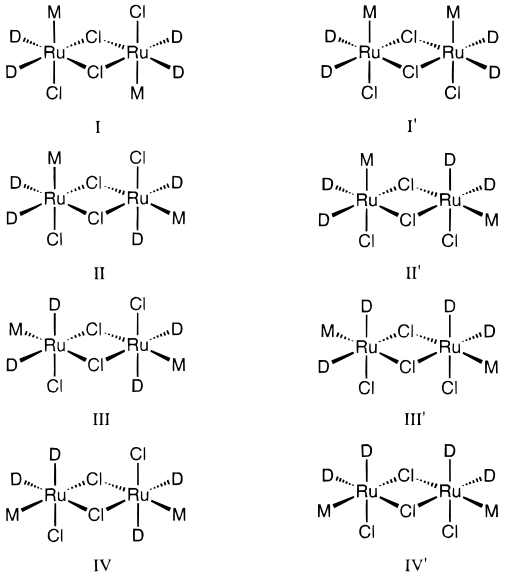


Figure 5. Representation of the various isomers expected for the dinuclear **3a**. (D−D−M stands for one tetramethylfulvene ligand, where D−D represents the C_5Me_4 ring double bonds and M is the methylene group.)

various isomeric forms.[16] For example, by contrast with the four methylene groups seen in $CDCl_3$, the ^{1}H NMR spectrum in deuterated toluene showed signals of *six* exocyclic methylene groups. If we assume that all the isomers are dinuclear, then quite a number of different possibilities exist; these are sketched in Figure 5 as four pairs, clipped together by Cl bridges in two different ways, where D D M (D, ring double bond; M, exocyclic methylene) represents one TMF spanning three fac sites of an octahedron, the other three being taken up by chlorides. Isomer I is that found in the crystal structure determination, where the dimer is centrosymmetric and where the coordinated tetramethylfulvene ligand has a plane of symmetry along the C═CH_2 perpendicular to the ring plane, and that which shows the resonances at δ 1.46, 1.69 (2 × s, Me), 5.96 (s, 2H, CH_2). The dimeric isomer I′ has a plane of symmetry through the bridging chlorides and perpendicular to the Ru−Ru vector and should also show a similar NMR spectrum. The other isomers (II, II′, etc) are of lower symmetry, which is reflected in more complex NMR spectra.

The ^{1}H NMR spectrum of **3a** did not vary significantly with temperature from −80 °C to +50 °C, above that temperature in C_6D_6 or C_7D_8 some reversible changes were detectable, but unfortunately decomposition set in there. It is however clear that there is an absence of fast dynamic intra- or intermolecular processes for the isomers. This points to the existence of a highly rigid and inert coordination about the metal atom in each case.

By comparison to the chloride, the diamagnetic (pentamethylcyclopentadienyl)ruthenium(III) bromide [{(η^5-C_5Me_5)$RuBr_2$}$_2$], **1b**, is significantly less reactive toward the oxygen-induced C−H cleavage. Thus very little reaction occurred on stirring a chloroform solution of **1b** in air over 24 h at ambient temperature. However, when the solution was refluxed, the tetramethylfulvene bromide complex [{(η^6-$C_5Me_4CH_2$)$RuBr_2$}$_2$], **3b**, was formed in 85% yield. The ^{1}H NMR spectrum was very similar to that of **1a** and showed the presence of the isomers in very similar ratios. The lower reactivity of the bromide **1b** by comparison with the chloride **1a** may indicate that cleavage of the Ru−halide bond is an essential part of the rate-determining step, since the heavier and softer halide is expected to form the stronger bond to Ru.

Adducts [(η^6-$C_5Me_4CH_2$)$RuCl_2$(L)] (4a, L = py; 5a, L = Me_2SO). Complex [{(η^6-$C_5Me_4CH_2$)$RuCl_2$}$_2$], **3a**, reacted with pyridine to give the adduct [(η^6-$C_5Me_4CH_2$)-$RuCl_2$(py)], **4a** (eq 3).

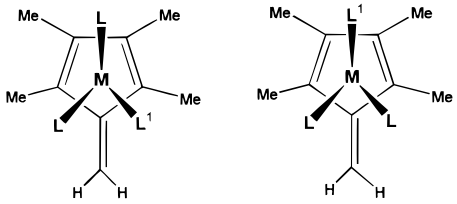
$$[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2] + 2L \rightarrow \underset{\textbf{3a}}{} \quad 2[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(L)] \quad (3)$$

4a, L = py
5a, L = Me_2SO

The ^{1}H NMR spectrum showed that two isomers of a 1:1 adduct, **4a**, were formed. Resonances at δ 1.20, 1.70, 1.95, and 1.98 for the methyls and at δ 4.42 and 5.10 for the methylene protons, assigned to the TMF ligand in an asymmetric environment, are due to isomer **A**. Resonances due to a TMF in a symmetrical environment (isomer **B**) were observed at δ 1.41 and 1.66 for the methyls and 5.46 for the methylenes; the ratio of the two isomers **A**:**B** was ca. 5:1. The ^{13}C NMR spectrum also showed the presence of an asymmetric TMF ligand in the isomer **A** and a symmetric TMF ligand in the isomer **B**. It is suggested that the isomers are rotamers, as shown in Scheme 2. The coupled ^{13}C−^{1}H spectrum of the methylene carbons showed a triplet (^1J(C−H) 167.0 Hz; δ 83.3) and a double doublet (δ 78.0, ^1J(C−H) 167.6 and 167.7 Hz) arising from the symmetric and

(16) The NMR spectrum of a single crystal of complex [(η^6-C_5Me_4-CH_2)Re(η^1-C_6F_5)$(CO)_2$], **6**, also shows the presence of two isomers, one (ca. 90% in toluene) being symmetric while the other, minor, is unsymmetric.[15] The major isomer is that found in the X-ray structure determination, and the authors suggest that the minor isomer forms from this on dissolution. No interconversion between the two on the NMR time scale was noted.

Scheme 2. Unsymmetric (A) and Symmetric (B) Isomers of $[(\eta^6\text{-}C_5Me_4CH_2)ML_2L^1]$



4a, M = Ru, L = Cl, L^1 = py
5a, M = Ru, L = Cl, L^1 = Me_2SO
6, M = Re, L = CO, L^1 = C_6F_5

the asymmetric TMF ligands, **B** and **A**, respectively. There was no significant change in **A:B** ratio when the reaction temperature was varied from −80 to +40 °C or when the ratio of reactants was varied from Ru:py = 1:1 to 1:3; complex **4a**, with the same isomer ratio, was also obtained on reaction of pyridine with $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(Me_2SO)]$. By contrast to these spectra which indicated very static systems, the spectra of the coordinated pyridines were normal and were consistent with the expected rotation about the N−Ru axis.

Complex $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a**, was also shown by ^{1}H NMR spectroscopy to react with 4-methylpyridine, 4-*tert*-butylpyridine, and isoquinoline, giving similar mixtures of isomers.

Reaction of both **1a**,**b** with air in the presence of dimethyl sulfoxide (Me_2SO) gave the (tetramethylfulvene)ruthenium(II) dimethyl sulfoxide halide complexes, **5a**,**b** (eq 4). In this case however, both the chloro and the bromo complexes **1a**,**b** reacted under ambient conditions.

$$\underset{\mathbf{1}}{[\{(\eta^5\text{-}C_5Me_5)RuX_2\}_2]} + {}^1/_2O_2 + 2Me_2SO \rightarrow [(\eta^6\text{-}C_5Me_4CH_2)RuX_2(Me_2SO)] + H_2O \quad (4)$$

5a, X = Cl
5b, X = Br

Complex **3a** also reacted with dimethyl sulfoxide to give **5a**; monitoring the reaction by ^{1}H NMR spectroscopy showed that it was completed immediately on mixing to give **5a** as the sole product.

By contrast to the pyridine analogs, **5a**,**b** were single isomers. The ^{1}H and ^{13}C NMR spectra of complex **5a** showed that both the methylene protons, the methyls of the TMF, and the methyls of the dimethyl sulfoxide ligand were all inequivalent. The chemical shifts of the >C═CH_2 (^{1}H NMR δ 4.90, 4.98, ^{13}C NMR, δ 114.6, 83.2) are in very similar positions to the isomers of **3a**, indicating that the tetramethylfulvene ligand is still η^6-coordinated. Again, neither **5a** nor **5b** show dynamic behavior or exchange with free Me_2SO on the NMR time scale under ambient conditions and appear to be stereochemically rigid. Thus, if the methylene group is *cis* to the dimethyl sulfoxide ligand, the methyl and methylene protons of the tetramethylfulvene ligand and the methyl groups of the dimethyl sulfoxide ligand will be diastereotopic, resulting in the observed inequivalence in the NMR spectra. These adducts are thus equivalent to the more prevalent unsymmetric, isomer **A** of the pyridine adduct **4a**.

The structure of the (pentamethylcyclopentadienyl)-ruthenium(II) dimethyl sulfoxide complex $[(\eta^5\text{-}C_5Me_5)RuCl(Me_2SO)_2]$, obtained from $[\{(\eta^5\text{-}C_5Me_5)RuCl\}_4]$ and dimethyl sulfoxide in the absence of oxygen, was determined by X-ray diffraction and was shown to have the dimethyl sulfoxide ligand S-coordinated to the ruthenium metal.[17] We suggest that the dimethyl sulfoxide is also coordinated through sulfur in **5a**: ν(SO) bands at 1030 and 1106 cm^{-1} are consistent with this.

The complex **3a** also reacts readily with carbon monoxide to give $[(\eta^5\text{-}C_5Me_4CH_2Cl)Ru(CO)_2(Cl)]$, the chemistry of which has already been discussed.[1]

Structural Considerations for the TMF Complexes. The most surprising features of the TMF complexes, both of **3a**, which has been fully characterized by an X-ray structural determination,[18] and of the various adducts, such as the pyridine and dimethyl sulfoxide complexes, $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(L)]$, **4a**, and **5a**, are (i) that isomers, which are effectively rotamers (Scheme 2), exist, (ii) that they do not interconvert on the ^{1}H NMR time scale up to ca. 50 °C, and (iii) that there is no detectable exchange between free L and coordinated L on the ^{1}H NMR time scale. Similarly, the various isomers of complex **3a** showed sharp ^{1}H NMR signals up to ca. +70 °C; at higher temperatures there was some broadening indicating that some interchange processes were becoming rapid on the NMR timescale, but these could not be quantified owing to the onset of irreversible decomposition. For both **4a** and **5a** NMR data show that the most stable rotamer is the unsymmetrical one. Complexes of π-bonded unsaturated ligands normally show rather low barriers to axial rotation.

Not only is the coordination rather rigid but the metal center, Ru(II), d^6, seems to be substantially more inert than isostructural and isoelectronic complexes such as the (arene)ruthenium(II) halides or the (pentamethylcyclopentadienyl)rhodium complexes (Rh(III), d^6).[19]

It seems likely that this conformational rigidity is due to the presence of the coordinated *exo*-methylene, which has the effect of "fixing" the ligands on the other side of the metal. Whether the bonding of fulvene complexes is best represented as η^5, η^1 to M^{n+2} [which would be Ru(IV) here] or η^4, η^2 to M^n [Ru(II) here] has been discussed by several authors.[12,13,20] The first representation describes a σ-bond from the metal to the *exo*-CH_2 and a more normal cyclopentadienyl bonding, while the second implies that the fulvene bonds as a neutral triene.

On the basis of organic analogies, it has been suggested that if the one-bond coupling between the methylenic carbon and the attached hydrogens, ^1J(C−H), is less than ca. 145 Hz, the methylenic carbon is sp^3 hybridized and the binding is formally η^5, η^1, while a ^1J(C−H) of more than ca. 150 Hz implies the methylenic carbon is sp^2 hybridized and the binding is formally η^4, η^2; that is, the TMF binds as a triene. The value of ^1J(C−H) of 167−168 Hz seen for both the rotamers of the pyridine adduct, **4a**, suggests that the latter situ-

(17) Wang, M. H.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 127.

(18) It may also be noted that the structure we have found for **3a** is similiar to that of the "high-spin" form (with no Ru−Ru interaction) of complex **1a**, $[\{\eta^5\text{-}C_5Me_5RuCl_2\}_2]$;[9] however the bond lengths and angles are sufficiently different to make it clear that the two are not identical and, therefore, that **3a** is not a contaminant of **1a**.

(19) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1.

(20) See, for example: Cloke, F. G. N.; Day, J. P.; Green, J. C.; Morley, C. P.; Swain, A. C. *J. Chem. Soc., Dalton Trans.* **1991**, 789.

ation is present here. Similar bonding patterns have been proposed for η^6-TMF in $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_5Me_4CH_2)]^+$ [13] and $[(\eta^6\text{-}C_5Me_4CH_2)Re(\eta^1\text{-}C_6F_5)(CO)_2]$.[15]

The η^4, η^2 representation is also in agreement with the X-ray structure found for **3a**. Thus, for example, the length of the C−C bond from the ring to the exocyclic CH_2 (1.398(6), 1.401(6) Å) is consistent with that expected for a coordinated double bond.[21] As a further comparison, it is close to that for an aromatic C−C bond (1.395 Å) and significantly shorter than that expected for a single bond (e.g. 1.53 Å in toluene). The Ru−CH_2 distances found for **3a** (2.268(4) and 2.271(4) Å) are also significantly longer than those reported for Ru(II)−Me, 2.169 and 2.165 Å in $[(C_5H_5)Ru(Ph_2PCHMeCH_2PPh_2)\text{-}Me]$ and $[(C_5H_4\text{-neomenthyl})Ru(PPh_3)(CO)Me]$, respectively.[22]

We suggest that it may also be significant that the X-ray structure shows the *terminal* (and more electronegative) chloride in **3a** to be *trans* to the *exo*-CH_2 (∠Cl(terminal)−Ru−CH_2 170.60(11), 171.02(11)°); NMR indicates this isomer is also the most prevalent in solution. Assuming an analogous requirement in the adducts **4a** and **5a** for the CH_2 to be *trans* to a terminal Cl, then the geometry of the tripodal $RuCl_2L$ fragment will be fixed with respect to the TMF, corresponding to the unsymmetrical arrangement **A** discussed above, with the projection of Ru−L at an angle of ca. 60° to the C═CH_2. The reason for this arrangement is that since they are *trans* to each other the same metal orbitals will bind both the C═CH_2 and the Cl(terminal) synergically and stabilize them. This may be represented by electron density being fed from the more electron-rich C═C double bond into the Ru−Cl σ-bond and from the Ru−Cl π- into the Ru−olefin π*-interaction.

A similar explanation can be offered for the rhenium complex $[(\eta^6\text{-}C_5Me_4CH_2)Re(\eta^1\text{-}C_6F_5)(CO)_2]$, **6**, where the X-ray structure shows a *trans* arrangement of the *exo*-CH_2 and the C_6F_5 that is reflected in the NMR spectra, which indicate a symmetric TMF (represented as of type **B**). The C_6F_5, as the most electronegative substituent attached to the rhenium, would be expected to be *trans* to the TMF C═CH_2 on the above arguments. Interestingly, the NMR spectra also show the presence of another, minor, isomer with an asymmetric TMF ligand, and we presume that this has the structure **A** (M = Re, a = C_6F_5, b = CO) with *cis* carbonyls; presumably, here, as in **4a**, and in the isomeric forms of **3a** the alternative conformations are only slightly less stable.

Oxygen-Induced C−H activation: Mechanistic Considerations. There are many precedents for metal-promoted C−H activation involving O_2;[23] in quite a number of cases methyls on π-bonded ligands are activated by oxygen and transformed into ═CH_2 substituents, which are then bonded to the metal.[24]

These reactions are generally deemed to proceed via primary electron transfer from the metal complex to O_2 (eq 5).

$$\text{CpFe(arene)} + O_2/-100\ °C \rightarrow \text{CpFe(arene)}^+O_2^- \quad (5)$$

Thus Astruc reported that $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Me_6)]$ reacted with oxygen in pentane at 25 °C to give $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_6Me_5CH_2)]$ and water (H_2O) (eq 6) but when the same reaction was carried out at −78 °C the products were $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_6Me_5CH_2)]$ and hydrogen peroxide (H_2O_2) (eq 7).[4]

$$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Me_6)] + {}^1/_4O_2 \rightarrow [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_6Me_5CH_2)] + {}^1/_2H_2O \quad (6)$$

$$[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6Me_6)] + {}^1/_2O_2 \rightarrow [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_6Me_5CH_2)] + {}^1/_2H_2O_2 \quad (7)$$

A benzylic hydrogen on the arene will be removed as a proton by the superoxide anion ($O_2^{-\bullet}$) giving H_2O_2 via the $HO_2^\bullet$ radical; if there is no benzylic hydrogen, the superoxide anion as a nucleophile attacks at another site, for example, a benzene. Other reactions seem to follow similar paths.

The C−H activations involved in the formation of **3a** and **5a** from $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2]$ both required air. No hydrogen peroxide was detected (by starch iodide paper) either at 25 or at −78 °C; only water was formed.

Thus the reaction we see, in which the μ-oxo−Ru(IV) complex **2a** is converted into the TMF Ru(II) complex without any additional oxidants, is unusual.[25] It is also interesting that oxidation of the bromo analogue, **1b**, proceeded more easily in the presence of the ligand dimethyl sulfoxide (giving **5b**) than in its absence, when **3b** is the product. This suggests that the nucleophilicity of the metal center toward O_2 is enhanced by the presence of a ligand.

Experimental Section

Reactions were carried out using standard Schlenk line techniques; solvents and reagents were purified and dried by standard methods. Microanalyses were performed by the Sheffield University Microanalysis Service. IR spectra were recorded as KBr disks on a Perkin-Elmer PE1710 FTIR spectrometer; ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM250, AC250, or WH400 instruments using the solvent or tetramethylsilane as an internal standard.

Preparation of $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2]_2$, 3a, and of $[(\eta^6\text{-}C_5Me_4CH_2)RuBr_2]_2$, 3b. Complex $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2]$, **1a** (0.10 g, 0.16 mmol), was dissolved in chloroform (15 mL), and

(21) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.
(22) Consiglio, G.; Morandini, F.; Ciani, G.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 333. Lindsay, C.; Cesarotti, E.; Adams, H.; Bailey, N. A.; White, C. *Organometallics* **1990**, *9*, 2594.
(23) Simandi, L. I. *Catalytic Activation of Dioxygen by Metal Complexes*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.
(24) For example, see references cited by: Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. Hoard, D. W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 612.

(25) Although we have no evidence for it, another possibility needs to be considered: that a trace amount of oxygen is present (despite our best precautions) which initiates a catalytic cycle, eq 8−12. Step (8) would be the initiation, forming the superoxo ion and the Ru(v) cation from **2a**; **2a** and a new superoxide complex of Ru(IV) form in step (9), which loses H in steps (10) and (11) to give the TMF species, which then dimerizes to **3a** in step (12).

$$[\{\eta^5\text{-}C_5Me_5RuCl_2\}_2O] + O_2 \rightarrow [\{\eta^5\text{-}C_5Me_5RuCl_2\}_2O]^+O_2^- \quad (8)$$

$$[\{\eta^5\text{-}C_5Me_5RuCl_2\}_2O]^+O_2^- \rightarrow [\eta^5\text{-}C_5Me_5Ru(Cl)_2(O)] + [\eta^5\text{-}C_5Me_5RuCl_2]^+O_2^- \quad (9)$$

$$[\eta^5\text{-}C_5Me_5RuCl_2]^+O_2^- \rightarrow [\eta^6\text{-}C_5Me_4CH_2RuCl_2] + HO_2^\bullet \quad (10)$$

$$HO_2^\bullet + [\eta^5\text{-}C_5Me_5Ru(Cl)_2(O)] \rightarrow [\eta^6\text{-}C_5Me_4CH_2RuCl_2] + H_2O + O_2 \quad (11)$$

$$2[\eta^6\text{-}C_5Me_4CH_2RuCl_2] \rightarrow [\{\eta^6\text{-}C_5Me_4CH_2RuCl_2\}_2] \quad (12)$$

Since the O_2 which initiates in step (8) is recovered in step (11), the cycle only requires a trace of oxygen.

the mixture was stirred in air (0.5 h, 20 °C). The solution was concentrated to 5 mL, and dropwise addition of diethyl ether gave the orange-red solid $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a** (0.098 g; 99%). Anal. Calcd for $C_{20}H_{28}Cl_4Ru_2$: C, 40.3; H, 5.0; Cl, 23.0; mol wt 612. Found: C, 40.1; H, 4.9; Cl, 22.9; mol wt 700 (osmometry in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ CH_2 region, 4.65, 5.24 (2 × s, 2H), 4.80, 5.20 (2 × s, 2H), 5.96[26] (s, 2H), 6.05, 6.12 (2 × d, 2H, *J* 2 Hz); Me region, 2.29, 2.24, 2.18, 1.85,[26] 1.83, 1.81, 1.71, 1.69, 1.68, 1.67, 1.52, 1.50, 1.47, 1.45, 1.44,[26] 1.43 (see also Figure 4; temperature-invariant from −80 to +50 °C). ^{13}C NMR ($CDCl_3$): δ CH_2 region, 81.1, 81.6, 87.1, and 87.85. ^{1}H NMR (C_7D_8): CH_2 region, δ 4.25, 5.03 (2 × s, 2H), 4.27, 4.90 (2 × s, 2H), 4.45, 4.98 (2 × s, 2H), 6.01,[26] (s, 2H), 6.05 (s, 2H), 6.05, 6.12 (2 × d, 2H, *J* 2 Hz). Oxygen uptake was measured (at 1 atm and 20 °C) by dropping complex **1a** (1 mmol) into a flask (containing chloroform solvent and equipped with a magnetic stirrer) which had been flushed out with oxygen and was connected to a manometer.

The bromo analog, $[\{(\eta^6\text{-}C_5Me_4CH_2)RuBr_2\}_2]$, **3b**, was prepared (85% yield) from $[\{(\eta^5\text{-}C_5Me_5)RuBr_2\}_2]$, **1b**, in refluxing chloroform in the presence of air. Anal. Calcd for $C_{20}H_{28}Br_4Ru_2$: C, 30.6; H, 3.6; Br, 40.4. Found: C. 30.4; H, 3.7; Br, 40.5. ^{1}H NMR ($CDCl_3$): δ CH_2, 6.20, 6.24 (2 × d, 2H, *J* 2 Hz), 6.06,[26] (s, 2H), 4.73, 5.29 (2 × s, 2H), 4.54, 5.26 (2 × s, 2H), 4.52, 5.30 (2 × s, 2H), CH_3, 2.38. 2.33, 2.29, 1.93,[26] 1.90, 1.88, 1.87, 1.78, 1.75, 1.72, 1.70, 1.68, 1.66, 1.57, 1.55, 1.53, 1.45,[26] 1.43, 1.41.

X-ray Structure Determination of $[(\eta^6\text{-}C_6Me_4CH_2)RuCl_2]_2$, 3a. Crystals of **3a** were grown from chloroform−hexane (in the presence of dibenzothiophene as stabilizer). Crystal data: $[\{C_{10}H_{14}RuCl_2\}_2\cdot 3CHCl_3]$, M_r 970.47; monoclinic, $P2_1/c$, a = 16.574(5) Å, b = 16.555(6) Å, c = 13.409(4) Å, β = 106.03(1)°; V = 3536(2) Å^3, Z = 4, D_c = 1.823 g cm^{-3}, F(000) 1912, T = 150 K. Intensity data were collected on a FAST area detector; 11 340 data were measured, giving 5609 unique reflections. The structure was solved by Patterson methods and refined on 5601 F_o^2 values using full-matrix least squares. The final R factors were 0.041 and 0.031, respectively, for all 5609 and 4168 observed [$I > 2\sigma(I)$] data and 394 parameters. Full details including tables of bond lengths and angles, thermal parameters, and F_o/F_c are available as Supporting Information to ref 7 or by application to the Cambridge Crystallographic Data Centre.

Reaction of $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2]$ with O_2 in the Presence of Ethanol or 2-Propanol. Complex $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2]$ (0.020 g, 0.033 mmol) was dissolved in the $CDCl_3$ (0.7 mL); ethanol (0.030 mL, 0.5 mmol) was added. The solution was stirred in air (5 min, 20 °C) and left standing in a NMR tube (2 h, 20 °C). The ^{1}H NMR spectrum showed that acetaldehyde (turnover, 1.5) and $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a** (100%), were formed. A similar experiment using 2-propanol in place of ethanol gave acetone (turnover, 2) and $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **1a** (100%), by ^{1}H NMR.

(26) These are assigned to the symmetrical isomer, e.g., (Figure 5).

Preparation of $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(Me_2SO)]$, 5a, and of $[(\eta^6\text{-}C_5Me_4CH_2)RuBr_2(Me_2SO)]$, 5b. Complex $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCl_2\}_2]$, **3a** (0.10 g, 0.16 mmol), was dissolved in chloroform (10 mL), and dimethyl sulfoxide (0.03 mL, 0.32 mmol) was added. The solution was stirred in air (0.5 h, 20 °C), the solvent was removed *in vacuo*, and the residue was crystallized from CH_2Cl_2−diethyl ether. The orange-red crystals of $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(Me_2SO)]$, **5a**, were obtained (0.10 g, 82%). It was also prepared directly from complex **1a** and dimethyl sulfoxide in chloroform solution in the presence of air (20 °C, 2 h; 90%). Anal. Calcd for $C_{12}H_{20}Cl_2ORuS$: C, 37.6; H, 5.2; Cl, 18.3. Found: C, 37.6; H, 5.3; Cl, 18.7. ^{1}H NMR ($CDCl_3$, δ): 1.69 (s, 3H, C_5Me_4), 1.72 (s, 3H, C_5Me_4), 1.86 (s, 3H, C_5Me_4), 1.91 (s, 3H, C_5Me_4), 3.08 (s, 3H, Me_2SO), 3.22 (s, 3H, Me_2SO), 4.90 (d, 1H, =CH_2, *J* 1 Hz), 4.98 (d, 1H, =CH_2, *J* 1 Hz). ^{13}C NMR ($CDCl_3$, δ): 8.8, 9.1, 10.1, 10.2 ($C_5\mathit{Me}_4$), 43.8, 45.9 (Me_2SO), 83.8 (=CH_2), 97.4, 100.0, 101.8, 104.4 (C_4Me_4), 114.9 (C=CH_2). IR (KBr): ν(SO) 1106 cm^{-1}. $[(\eta^6\text{-}C_5Me_4CH_2)RuBr_2(Me_2SO)]$, **5b**, was prepared analogously from **1b** ($CHCl_3$, Me_2SO, 80 °C, 1 h, 89%) or from **3b** ($CHCl_3$, Me_2SO, 25 °C, 24 h, 79%). Anal. Calcd for $C_{12}H_{20}Br_2ORuS$: C, 30.5; H, 4.25; Cl, 33.7. Found: C, 30.9; H, 4.65; Cl, 33.9. ^{1}H NMR ($CDCl_3$, δ): 1.74 (s, 3H, C_5Me_4), 1.85 (s, 3H, C_5Me_4), 1.92 (s, 3H, C_5Me_4), 2.06 (s, 3H, C_5Me_4), 3.23 (s, 3H, Me_2SO), 3.51 (s, 3H, Me_2SO), 5.02, 5.25 (2 × d, 1H, =CH_2).

Preparation of $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(NC_5H_5)]$, 4a. Complex $[\{(\eta^6\text{-}C_5Me_4CH_2)RuCL_2\}_2]$, **3** (0.05 g, 0.08 mmol), and pyridine (0.08 mL, 1 mmol) were reacted in chloroform (10 mL) to give after workup $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(NC_5H_5)]$, **4a**, as a brown solid. Yield: 0.05 g (79%). Anal. Calcd for $C_{15}H_{19}Cl_2NRu$: C, 46.8; H, 5.0; Cl, 18.4. Found: C, 46.7; H, 5.3; Cl, 19.3. ^{1}H NMR ($CDCl_3$, δ): *unsymmetric*, 1.20 (s, 3H C_5Me_4), 1.70 (s, 3H, C_5Me_4), 1.95 (s, 3H C_5Me_4), 1.98 (s, 3H C_5Me_4), 4.40 (s, 1H, =CH_2), 5.10 (s, 1H, =CH_2), 7.30 (m, 2H, NC_5H_5), 7.68 (m, 1H, NC_5H_5), 8.78 (d, 2H, NC_5H_5); *symmetric*, 1.41 (s, 6H C_5Me_4), 1.66 (s, 6H C_5Me_4), 5.46 (s, 2H, =CH_2), 7.40 (m, 2H, NC_5H_5), 7.86 (m, 1H, NC_5H_5), 8.86 (d, 2H, NC_5H_5). ^{13}C NMR ($CDCl_3$, δ): *unsymmetric*, 7.6, 8.3, 9.1, 9.9 ($C_5\mathit{Me}_4$), 77.6 (=CH_2), 95.7, 98.0, 98.5, 100.6 (C_4Me_4), 105.1 (C=CH_2), 124.8, 137.4, 155.0 (NC_5H_5); *symmetric*, 8.2, 9.3 ($C_5\mathit{Me}_4$), 80.2 (=CH_2), 95.6, 97.3, 102.7 (C_5Me_4), 125.8, 138.3, 159.9 (NC_5H_5); *unsymmetric:symmetric* = ca. 5:1.

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