

Transition Metal Alkylidene Complexes Via the Ring-Opening of Cyclopropenes

Thesis by
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for Julie and my family

IT is not the critic who counts, not the man who points out how the strong man stumbled, or where the doer of deeds could have done them better. The credit belongs to the man who is actually in the arena; whose face is marred by dust and sweat and blood; who strives valiantly, who errs and comes short again and again; who knows the great enthusiasms, the great devotions, and spend himself in a worthy cause; who, at the best, knows in the end the triumph of high achievement; and who, at the worst, at least fails while daring greatly, so that his place shall never be with those cold and timid souls who know neither victory nor defeat.

- Theodore Roosevelt

Abstract

The first chapter details the preparation and structural characterization of a rhenium (VII) oxo-vinylalkylidene complex and discusses its activity in olefin metathesis reactions. A substitution reaction affords the rhenium (V) oxo-trisalkoxide precursor, a species that surprisingly adopts a facial arrangement of three very bulky alkoxide ligands in its crystal structure. This complex reacts with 3,3-diphenylcyclopropene in a non-coordinating solvent to yield a mixture of two rhenium alkylidene isomers. Over time one species predominates and is isolated. An X-ray diffraction study of the isolated complex and ^1H NMR studies of the isomerization process are described. Reactivity studies indicate that the isolated product demonstrates very limited olefin metathesis activity. However, the addition of Lewis acid cocatalysts to the rhenium alkylidene complex generates a much more active catalyst system, in particular, for the metathesis of cis-2-pentene. No propagating alkylidene species are observed during the metathesis reaction.

The second chapter describes the synthesis and characterization of a dicyclopropene compound from which the preparation of ROMP diinitiators is reasoned to be possible. The starting material-1,4-di(1-phenylvinyl)benzene-is readily prepared *via* a Grignard reaction and subsequent dehydration. A series of three steps analogous to those of the 3,3-diphenylcyclopropene synthesis yield the desired product-1,4-di(1-phenylcycloprop-2-enyl)benzene. Alternate pathways to the product also are proposed and the investigations are detailed. In particular, a biphasic cyclopropanation reaction using either bromoform or chloroform as a carbene source affords the respective dicyclopropane intermediates. Ultimately the syntheses of bis(metal alkylidene) complexes from reactions of this dicyclopropene with various transition metal precursors have implications for the formation of polymers which propagate in two directions and for the preparation of triblock copolymers.

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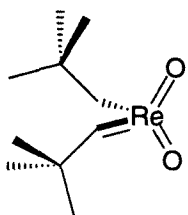
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Chapter 1

Synthesis, Structure and Reactivity of a Rhenium Oxo-Vinylalkylidene Complex

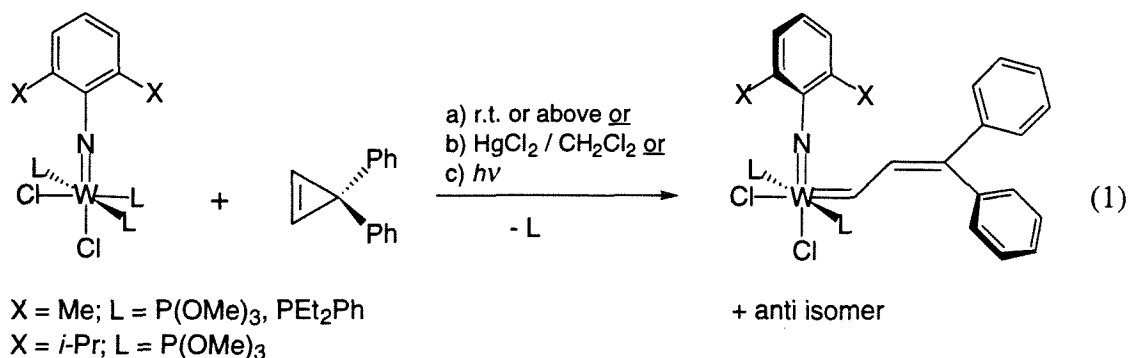
Introduction

Many olefin metathesis catalysts are based on rhenium oxides, usually supported on alumina.^{1,2} In these heterogeneous systems, rhenium oxo-alkylidene species that may form under the reaction conditions are plausible sites of catalytic activity. However, examples of isolable rhenium oxo-alkylidene complexes are very rare.³ Only one, $\text{ReO}_2(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)$ (*vide infra*), has been structurally characterized^{3a} and none



of these has demonstrated olefin metathesis activity. The primary interest in the synthesis of homogeneous rhenium metathesis catalysts stems from the large amount of data accumulated for classical metathesis systems, which demonstrate that rhenium is more tolerant of functional groups than molybdenum or tungsten.² Furthermore, such catalysts could be modified and studied more readily than the heterogeneous system.

Recent work has shown that cyclopropenes react with a wide variety of metal precursors to give vinylalkylidene complexes as products,⁴ some of which are active metathesis catalysts.^{4b-d,f} In particular, several tungsten(VI) imido-vinylalkylidene complexes^{4b,c} have been prepared from 3,3-diphenylcyclopropene and appropriate tungsten(IV) imido precursors, which have labile phosphite or phosphine ligands (eq 1).

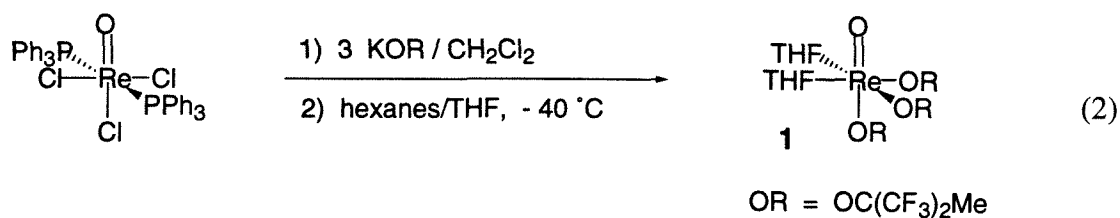


We reasoned that if a rhenium(V) oxo complex with labile ligands could be prepared, this complex—an isolobal analog of these tungsten(IV) imido species—might react with cyclopropenes to give rhenium(VII) oxo-vinylalkylidene complexes.

Herein we report the preparation, structural characterization, and reactivity of a rhenium(VII) oxo-vinylalkylidene complex. In particular, this compound is active for olefin metathesis in the presence of Lewis acid cocatalysts. The synthesis and structure of a precursor rhenium(V) oxo complex also is detailed.

Results and Discussion

Synthesis of *fac*-ReO[OC(CF₃)₂Me]₃(THF)₂. The reaction of ReOCl₃(PPh₃)₂ with 3 equiv of KOC(CF₃)₂Me in dichloromethane, followed by recrystallization from hexanes/THF (20:1) gives air-sensitive blue crystals of ReO[OC(CF₃)₂CH₃]₃(THF)₂ (**1**) in 35% yield (eq 2).⁵ This low yield can be accounted in part by the additional recrystallization procedure needed to separate pure **1** from the triphenylphosphine byproduct. The ¹H NMR data for **1** in CD₂Cl₂ are consistent with a dynamic structure at room temperature where the THF and hexafluoro-*tert*-butoxide ligands rapidly equilibrate on the NMR timescale. Only one methyl resonance (δ 1.71) and two broadened methylene resonances (δ 3.99 and 1.97), ascribable to the alkoxide and THF ligands, respectively, are observed.



The structure of **1** as determined by X-ray crystallography is shown in Figure 1, and relevant bond distances and angles are listed in Table 1. A roughly octahedral

arrangement of ligands is observed with the three bulky alkoxide ligands occupying one face of the distorted octahedron. The coordination sphere in **1** is quite crowded, as indicated by the long Re-O bond to one of the THF ligands [Re-O(6) = 2.236 Å] and by distortion from octahedral symmetry [O(1)-Re(1)-O(2) = 162°]. The Re=O bond distance (1.681 Å) is normal.⁶ To the best of our knowledge, **1** is the only known, structurally characterized example of a rhenium(V) oxo *tris*-alkoxide complex.

Table 1. Select Bond Distances and Angles for *fac*-ReO[OC(CF₃)₂CH₃]₃(THF)₂ (**1**)

Distances (Å)			
Re-O(1)	1.681 (4)	Re-O(4)	1.964 (4)
Re-O(2)	1.943 (4)	Re-O(5)	2.180 (4)
Re-O(3)	1.956 (4)	Re-O(6)	2.236 (4)
Angles (deg)			
O(1)-Re-O(2)	161.8 (2)	O(3)-Re-O(4)	87.2 (2)
O(1)-Re-O(3)	101.2 (2)	O(4)-Re-O(5)	85.6 (2)
O(1)-Re-O(4)	98.7 (2)	O(5)-Re-O(6)	87.4 (2)
O(1)-Re-O(5)	84.7 (2)	O(3)-Re-O(6)	99.3 (2)
O(1)-Re-O(6)	84.9 (2)	Re-O(2)-C(21)	152.3 (4)
O(2)-Re-O(3)	93.4 (2)	Re-O(3)-C(31)	135.6 (4)
O(2)-Re-O(4)	92.8 (2)	Re-O(4)-C(41)	133.9 (4)

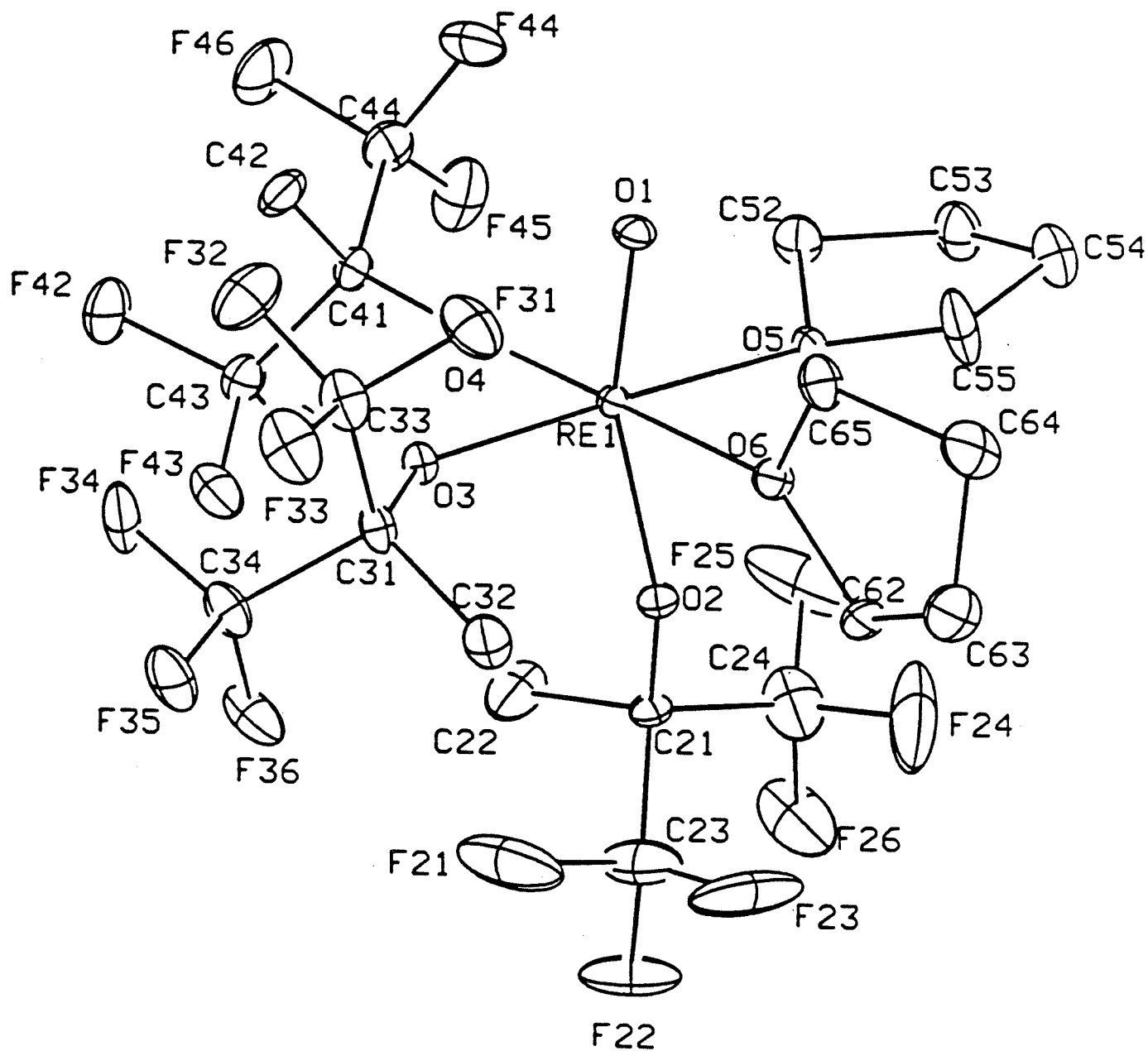
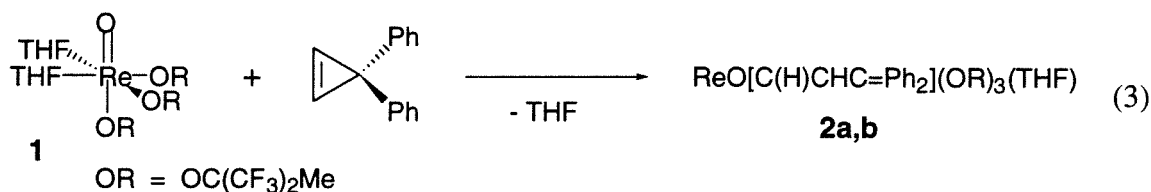


Figure 1. ORTEP drawing of *fac*-ReO[OC(CF₃)₂CH₃]₃(THF)₂ (1).

Preparation of *syn,mer*-ReO[C(H)CH=CPh₂][OC(CF₃)₂Me]₃(THF). Compound **1** and 3,3-diphenylcyclopropene undergo a rapid reaction in C₆D₆ at room temperature to give a blood-red solution containing a mixture of two vinylalkylidene complexes (eq 3). The two products are distinguishable by ¹H NMR spectroscopy, as characterized by pairs of downfield doublets [¹H (C₆D₆) **2a**: δ12.66, 9.49 (*J* = 13 Hz); **2b**: δ12.31, 9.33 (*J* = 11 Hz)] ascribable to the H_α and H_β resonances, respectively, of the vinylalkylidene ligands.⁷ After 20 h at room temperature a complete isomerization of **2a** to **2b** has occurred and **2b** can be isolated cleanly on a preparative scale in 87% yield. Elemental analysis, ¹H and ¹³C NMR data of **2b** are consistent with the stoichiometry ReO[C(H)CH=CPh₂][OC(CF₃)₂Me]₃(THF). Also a meridional geometry of the alkoxide ligands is reflected in the ¹H NMR data, in which two methyl resonances (δ 1.50 and 1.41) in a 1:2 ratio are observed. NMR solutions of **2b** are generally stable for 24 h at room temperature before significant decomposition is observed.



Orange-brown crystals of **2b** were obtained by recrystallization from a saturated hexanes solution, and the structure of a single crystal was determined by an X-ray diffraction study (Figure 2, Table 2). The complex is a distorted octahedron with meridional alkoxide ligands. The oxo and alkylidene ligands are *cis* and coplanar, an arrangement which avoids competition between these π -bonded ligands for the same set of Re 3d orbitals. In particular, the vinyl substituent on the alkylidene moiety is oriented toward the oxo ligand (*syn* form). The Re=O (1.674 Å) and Re=C_α (1.917 Å) bond distances are normal.^{3b,6} Also the coordinated THF lies *trans* to the alkylidene ligand and this bond is weak, as shown by the long Re-O(5) bond distance (2.315 Å). Other

significant features include the shorter Re-O(2) bond distance (1.909 Å) and the wider Re-O(2)-C(21) bond angle (170.0°) of the alkoxide trans to the oxo group relative to those of the other two alkoxides. These observations are indicative of an increase in the bond order of this particular rhenium-alkoxide bond. Also this alkoxide ligand does not deviate from the ideal octahedral geometry [O(2)-Re-C(1) = 90.9°] relative to the alkylidene moiety, whereas the mutually trans alkoxides bend away [O(3)-Re-C(1) = 102.4° and O(4)-Re-C(1) = 99.3°] from the alkylidene.

Table 2. Select Bond Distances and Angles for *syn,mer*-
ReO[C(H)CH=CPh₂][OC(CF₃)₂CH₃]₃(THF) (**2b**)

Distances (Å)			
Re-O(1)	1.674 (7)	Re-O(5)	2.315 (7)
Re-O(2)	1.909 (6)	Re-C(1)	1.917 (10)
Re-O(3)	1.968 (7)	C(1)-C(2)	1.430 (13)
Re-O(4)	1.986 (7)	C(2)-C(3)	1.378 (13)
Angles (deg)			
O(1)-Re-O(2)	174.4 (4)	O(3)-Re-O(5)	79.7 (3)
O(1)-Re-O(3)	93.7 (3)	O(3)-Re-C(1)	102.4 (3)
O(1)-Re-O(4)	93.3 (3)	O(4)-Re-O(5)	78.3 (3)
O(1)-Re-O(5)	86.7 (3)	O(4)-Re-C(1)	99.3 (3)
O(1)-Re-C(1)	94.7 (4)	Re-O(2)-C(21)	170.0 (7)
O(2)-Re-O(3)	85.7 (3)	Re-O(3)-C(31)	136.3 (6)
O(2)-Re-O(4)	85.2 (3)	Re-O(4)-C(41)	136.7 (6)
O(2)-Re-C(1)	90.9 (4)	Re-C(1)-C(2)	128.5 (7)
O(3)-Re-O(4)	156.5 (3)	C(1)-C(2)-C(3)	121.6 (9)

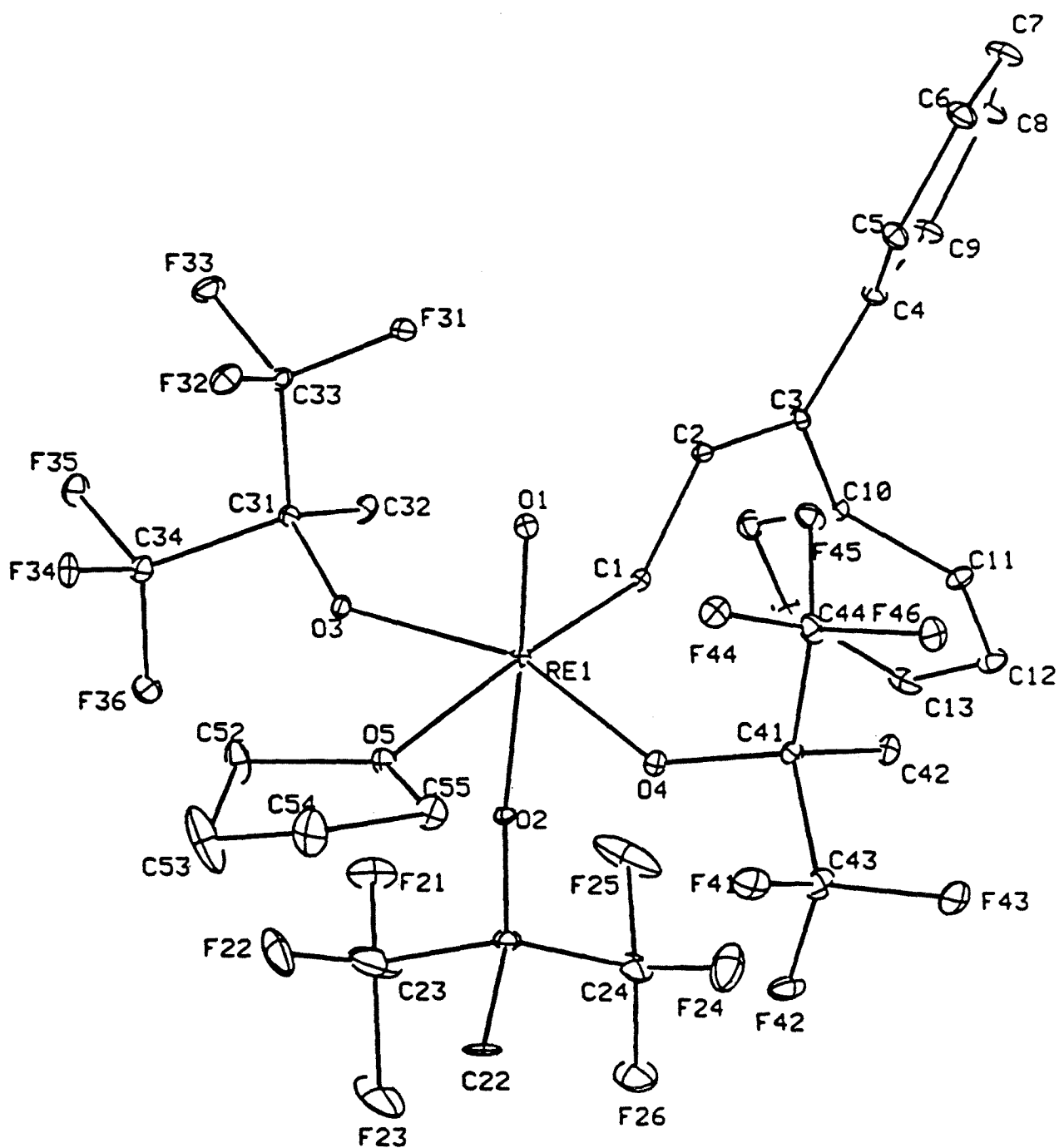
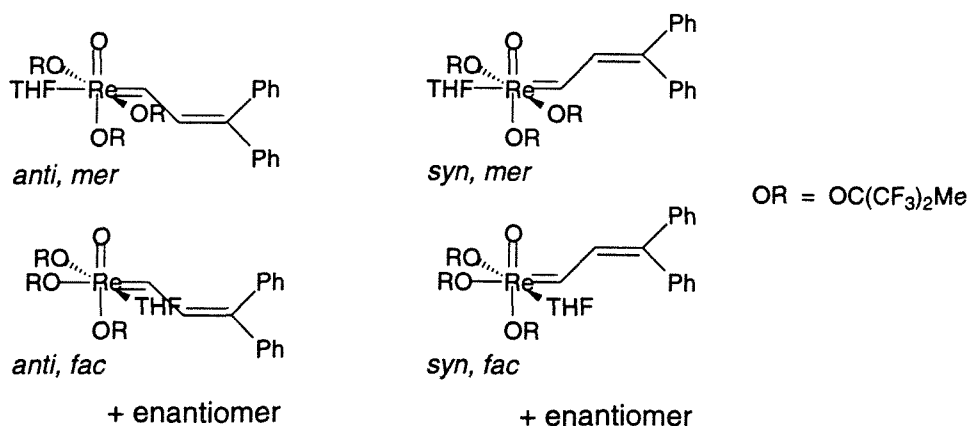


Figure 2. ORTEP drawing of *syn,mer*-ReO[C(H)=CHCPh₂][OC(CF₃)₂CH₃]₃(THF) (2b).

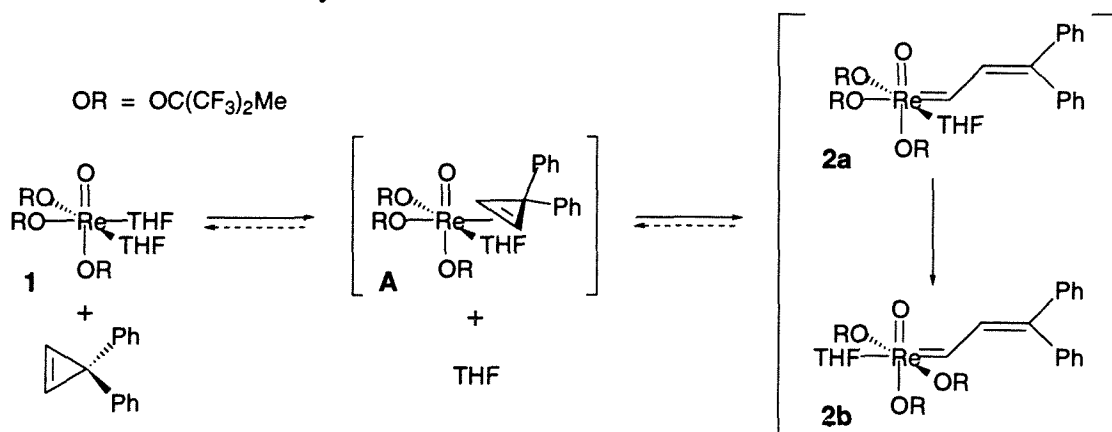
Isomerization. Figure 3 depicts four possible isomers of the stoichiometry $\text{ReO}[\text{C}(\text{H})\text{CH}=\text{CPh}_2][\text{OC}(\text{CF}_3)_2\text{Me}]_3(\text{THF})$ assuming that the oxo and alkylidene ligands are *cis* and coplanar. These result from a combination of either a facial or meridional arrangement of alkoxide ligands and either a *syn* or *anti* orientation of the alkylidene ligand relative to the oxo group. The isolated product **2b** is the "*syn, mer*" isomer, while the other product **2a** is believed to be the "*syn, fac*" isomer based on the following observations: 1) The isomerization of **2a** to **2b** occurs readily at room temperature ($t_{1/2} = 2$ h). Full details can be found in the Experimental Section. 2) The rate of the isomerization is *retarded* by added THF.⁸ A *fac* to *mer* isomerization could account for this observation, especially if the process occurs *via* a pentacoordinate intermediate resulting from initial THF dissociation. In contrast, the interconversion of *anti* and *syn* alkylidenes seems unlikely to involve a dissociative process, one that would account for the rate dependence on THF concentration. For complexes of the type $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR})_2$, rotation about the metal-carbon double bond to give a mixture of *anti* and *syn* alkylidenes is extremely slow (10^{-10} s^{-1}) at room temperature; and addition of THF does not alter the rate of interconversion.^{3b} Therefore, it seems reasonable to identify compound **2a** as the *syn, fac* isomer based on these arguments.

Figure 3. Isomers of the Stoichiometry $\text{ReO}[\text{C}(\text{H})\text{CH}=\text{CPh}_2][\text{OC}(\text{CF}_3)_2\text{Me}]_3(\text{THF})$.



A reaction pathway consistent with these observations for the formation of isomers **2a** and **2b** is proposed in Scheme 1, in which **2a** is presumed to be the *syn, fac* isomer. The first step in the reaction probably involves a dissociative ligand exchange to give an intermediate olefin complex **A**. Though no olefin complexes are observed in the reaction mixture, these species are plausible intermediates based on previous results with related systems.^{4a-c,9,10} The olefin complex may exist as a single intermediate (depicted as **A**) or as a mixture of *fac* and *mer* isomers if either of the following apply: 1) The rate of isomerization of intermediate **A** is comparable or faster than to the rate of vinylalkylidene formation; or 2) both isomers are formed in the first step from a fluxional pentacoordinate species. Intermediate olefin complex(es) then may rearrange to give vinylalkylidene complex(es). Isomer **2a** which predominates initially in the reaction mixture is observed to undergo facile rearrangement to isomer **2b** as the reaction proceeds.¹¹ However, it is not known whether the *mer* vinylalkylidene complex **2b** is formed exclusively from the rearrangement of **2a**, presumably the *fac* form, or whether it also is accessed directly by rearrangement of a *mer* olefin complex.

Scheme 1. Formation of Rhenium Vinylalkylidene Isomers and Proposed Isomerization Pathway



Reactivity of 2b and Lewis Acid Cocatalyzed Olefin Metathesis. Although **2b** is air-sensitive, it is tolerant of various functionalities. In the presence of acetone or benzaldehyde, **2b** does not undergo a Wittig-type reaction at room temperature to produce the corresponding olefins.¹² Compound **2b** does not react readily with internal and terminal olefins.^{13,14} Presumably, the alkylidene and olefin are not oriented properly for olefin metathesis. Based on the rapid exchange of THF in **2b** with free THF, the coordination site occupied by the THF ligand is available for an olefin to bind. However, this site is located trans to the alkylidene ligand. Thus, some rearrangement of the ligand environment would be required before the mutually trans alkylidene ligand and coordinated olefin can interact. Analogous behavior was reported by Schrock and coworkers for related rhenium monoimido alkylidene complexes.¹⁵ In particular, the complexes with a meridional arrangement of phenoxide ligands were not active for olefin metathesis, which also was attributed in part to the location of the available binding site for olefins trans to the alkylidene.

However, the addition of various Lewis acids to **2b** generates moderately active metathesis catalysts. In particular, a 1:1 mixture of GaBr₃ and **2b** can metathesize 100 equiv of *cis*-2-pentene at the rate of ~ 6.7 turnovers min⁻¹ at room temperature (Table 3). The addition of AlCl₃, GaCl₃, and B(C₆F₅)₃ to **2b** also can induce modest metathesis activity, whereas the addition of AlBr₃ only results in slight enhancement of activity.

Table 3. Lewis Acid Cocatalyzed Metathesis of *cis*-2-pentene

<u>Lewis Acid</u>	<u>Equiv</u>	<u>Time (h)^a</u>
GaBr ₃	1.0 ^b	0.8
GaBr ₃	0.4	7.2
GaCl ₃	0.4	9.1
AlBr ₃	0.5	3.5
AlCl ₃	0.5	3.5 ^c
B(C ₆ F ₅) ₃	1.0	12.2

^a Time at which equilibrium mix of 2-butenes, 2-pentenenes and 3-hexenes was achieved.

^b Turnover frequency (TOF) = 6.7 min⁻¹. ^c Observe only 40% conversion of pentene.

The manner by which the Lewis acids activate the metal center in **2b** is not well-defined, although various suggestions have been made for the role of Lewis acids in other olefin metathesis systems. In some cases, the Lewis acid is believed to remove an anionic ligand to afford a highly active cationic catalyst¹⁶ or to promote substitution of the anionic ligands with halides to generate a more active metal halide complex.¹⁵ Alternatively the Lewis acid can bind directly to the oxo ligand, an interaction which is thought to decrease the activation energy for the decomposition of the metallacycle intermediate¹⁷ or to promote electrophilic attack of the alkylidene ligand on the olefin.^{18,19} Most likely, the sterically encumbered Lewis acid $B(C_6F_5)_3$ can activate **2b** only by binding to the oxo ligand.

Attempts to observe propagating alkylidene species in the Lewis acid-cocatalyzed metathesis of olefins were unsuccessful. In a typical experiment, the Lewis acid (0.5 equiv of $GaBr_3$) was added to a solution of **2b** (8 mg) and an olefin (10 equiv of 1-hexene) in C_6D_6 . No new downfield resonances, ascribable to propagating metal alkylidene species, were observed in the 1H NMR studies over a period of several hours. However, resonances of the parent alkylidene and a new vinylalkylidene species [1H (C_6D_6): δ 13.20 (d, $Re=CH$, $J = 11$ Hz) and 9.35 (d, $CH=CPh_2$, $J = 11$ Hz)] were observed in a 1:1 ratio after 20 min at room temperature. Here the Lewis acid appears to have formed either an adduct, a metal halide or cationic complex with compound **2b**, an observation that is consistent with a shift of the vinylalkylidene resonances and with formation of a 1:1 mixture of vinylalkylidene species upon adding 0.5 equiv of $GaBr_3$. The new vinylalkylidene then decomposed within one hour, while the parent vinylalkylidene resonances disappeared more slowly. These observations are general for the Lewis acids used herein, even in the absence of olefins. However, the addition of $B(C_6F_5)_3$ to **2b** yielded a relatively stable, new alkylidene species which persisted in solution for 12 h before significant decomposition was observed.

Conclusions

In summary, a rhenium(VII) oxo-vinylalkylidene complex **2b** can be prepared from 3,3-diphenylcyclopropene and a suitable rhenium(V) oxo precursor. The synthesis of **2b** is an extension of the cyclopropene chemistry, that has resulted in the preparation of active catalysts for olefin metathesis based on tungsten vinylalkylidene^{4b} and ruthenium vinylcarbene^{4f} complexes. Compound **2b** does not react readily with acyclic olefins, which may result from the location of the available coordination site for olefins. However, active olefin metathesis catalysts are generated upon addition of suitable Lewis acids to **2b**. The metathesis of functionalized and cyclic olefins and the modification of the ligand environment in this rhenium system have not been fully investigated.

Experimental

General Considerations. All manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk techniques with a double manifold vacuum line or a Vacuum Atmospheres drybox. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4-Å molecular sieves. Hexane(s) was stirred over concentrated H₂SO₄, dried over MgSO₄ and CaH₂, and distilled from sodium benzophenone ketyl solubilized with tetraglyme. Dichloromethane and dichloromethane-*d*₂ (Cambridge Isotopes) were distilled from CaH₂ and degassed by several freeze/pump/thaw cycles. Benzene-*d*₆ and THF-*d*₈ (Cambridge Isotopes) were vacuum-transferred from sodium benzophenone ketyl.

1-Hexene and *cis*-2-pentene (Aldrich) were degassed by several freeze/pump/thaw cycles, dried by passing through a column of activated alumina, and stored in the drybox. AlBr₃, AlCl₃, GaBr₃, and GaCl₃ (Strem) were sublimed prior to use. KOC(CF₃)₂Me was prepared from hexafluoro-2-methylisopropanol (PCR) and potassium hydride in diethyl ether. B(C₆F₅)₃ was prepared from boron trichloride and pentafluorophenyl lithium in diethyl ether. ReOCl₃(PPh₃)₂²⁰ and 3,3-diphenylcyclopropene²¹ were prepared by literature methods.

NMR spectra were recorded on a General Electric QE-300 Plus (¹H, 300.10 MHz; ¹³C, 75.49 MHz) spectrometer. Chemical shifts are reported relative to residual protons in deuterated solvents (CDHCl₂, δ 5.32; C₆D₅H, δ 7.15). All coupling constants are reported in Hz. Elemental analyses were performed by Oneida Research Service of Whitesboro, NY.

fac-ReO[OC(CF₃)₂Me]₃(THF)₂ (1). KOC(CF₃)₂Me (3.26 g, 14.8 mmol) was added to a stirred suspension of yellow Re(O)Cl₃(PPh₃)₂ (4.00 g, 4.80 mmol) in dichloromethane (20 ml). A dark violet solution formed after 5 min and was stirred at

room temperature for 1 h. The solvent was removed in vacuo, and the residue was extracted in hexanes (4 x 10 ml). The combined extracts were filtered through a sintered glass frit and then concentrated to dryness. The resulting violet microcrystalline solid was recrystallized, often more than once, from a minimum volume of hexanes/THF (20:1) at -40°C to give 1.51 g (35%) of analytically pure blue crystals: ^1H NMR (CD_2Cl_2) δ 3.99 (br, 4, THF: H_α), 1.97 (br, 4, THF: H_β), 1.71 (s, 9, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 123.77 (CF_3 , $J_{\text{CF}} = 289$), 94.92 ($\text{OCMe}(\text{CF}_3)_2$, $J_{\text{CF}} = 29$), 73.88 (THF: C_α), 25.19 (THF: C_β), 16.56 (CH_3). Anal. Calcd for $\text{C}_{20}\text{H}_{25}\text{F}_{18}\text{O}_6\text{Re}$: C, 27.00; H, 2.83. Found: C, 27.37; H, 2.79.

syn,mer- $\text{ReO}[\text{C}(\text{H})\text{CH}=\text{CPh}_2][\text{OC}(\text{CF}_3)_2\text{Me}]_3(\text{THF})$ (**2b**). 3,3-Diphenylcyclopropene (0.325 g, 1.69 mmol) was added to a solution of **1** (1.50 g, 1.69 mmol) in dichloromethane (20 ml). A blood-red solution formed immediately and was stirred at room temperature for 20 h. The solvents were removed in vacuo to afford a quantitative yield of a red-brown microcrystalline solid. The product was recrystallized from a minimum amount of dichloromethane at -40°C to give 1.48 g (two crops, 87%) of isomerically pure orange-brown crystals: ^1H NMR (CD_2Cl_2) δ 12.15 (d, 1, $\text{Re}=\text{CH}$, $J = 11$), 9.13 (d, 1, $\text{CH}=\text{CPh}_2$, $J = 11$), 7.57-7.08 (m, 10, H_{aryl}), 4.04 (br, 4, THF: H_α), 1.93 (br, 4, THF: H_β), 1.50 and 1.41 (CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 280.13 ($\text{Re}=\text{CH}$, $J_{\text{CH}} = 147$), 163.15 ($\text{CH}=\text{CPh}_2$), 136.03, 134.08, 133.22, 132.60, 131.50, 130.24, 128.85, 128.56, 128.19 and 127.75 (C_{aryl}), 125.00 and 123.05 (CF_3 , $J_{\text{CF}} = 289$), 81.86 and 81.44 ($\text{OC}(\text{CF}_3)_2\text{Me}$), 70.06 (THF: C_α), 25.61 (THF: C_β), 15.66 (CH_3). Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{F}_{18}\text{O}_5\text{Re}$: C, 36.87; H, 2.89. Found: C, 37.07; H, 2.50.

Isomerization of Vinylalkylidene Complexes 2a,b. In this ^1H NMR study, 3,3-diphenylcyclopropene (1 equiv) was added to a solution of **1** (10 mg) and mesitylene (2 μl) in C_6D_6 , which immediately became blood-red in color. The reaction was monitored

at regular intervals, every 20 min for the first 4 h and then every 2 h thereafter. A mixture of two vinylalkylidene complexes [**2a**: δ 12.66 (d, 1, Re=CH, $J = 13$), 9.49 (d, 1, CH=CPh₂, $J = 13$); **2b**: δ 12.31 (d, 1, Re=CH, $J = 11$), 9.33 (d, 1, CH=CPh₂, $J = 11$)] were observed in a 4:1 ratio after 5 min, and no cyclopropene resonances were detected. The latter pair of doublets (**2b**) grew in at the expense of the former (**2a**), and the rate was determined from two half-lives. After 20 h there was a 1:25 mixture of products **2a** and **2b**, and the reaction had gone to 95% completion relative to the internal standard.

Lewis Acid Cocatalyzed Metathesis of *cis*-2-pentene. *Cis*-2-pentene (80 μ l, 100 equiv) and the Lewis acid were added to a solution of **2b** (7.5 mg) and mesitylene (2 μ l) in C₆D₆ (0.4 ml) in a resealable NMR tube. Upon addition of the Lewis acid, the solution was observed to undergo a color change from blood-red to dark brown within seconds. ¹H NMR spectra of the reaction mixture were acquired at regular intervals. Relative concentrations of *cis*-2-pentene and a mixture of 2-butenes and *trans*-2-pentene were measured by integrations of the β -methyl resonances against the internal standard. The turnover frequency was calculated at 40% conversion of *cis*-2-pentene. (The rate was established within the detection limits of NMR spectroscopy.) The results obtained by this method have proven to be consistent with those obtained by gas chromatography.²²

X-ray Diffraction Study of *fac*-ReO[OC(CF₃)₂Me]₃(THF)₂ (1**).** Single crystals of **1** suitable for an X-ray diffraction study were grown from hexanes/THF at -40 °C. All data sets were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and the ω scan method. The unit-cell parameters were obtained from the angular settings of 25 reflections. Crystal data and specific data collection parameters are listed in Table I. The 6891 raw intensity data were adjusted for a 4% decrease in intensity and a 13.2% variation in azimuthal scan. The data

were corrected for absorption and for Lorentz and polarization effects. The transmission factors ranged from 0.24 to 0.26. All calculations were performed on a VAX/IBM cluster system using a local program set. The structure was solved by automated Patterson analysis (PHASE) and refined by standard least-squares and Fourier techniques. The asymmetric unit consists of one molecule in general position. The scattering factors for neutral atoms were used in the refinement, including anomalous dispersion terms for Re.²³ All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were assigned idealized locations. The final residuals for **1** are listed in Table I. The largest peak in the final difference Fourier map had an electron density of 0.88 e Å⁻³ (background). The final positional parameters are given in the supplementary material.

X-ray Diffraction Study of *syn,mer*-ReO[C(H)CH=CPh₂][OC(CF₃)₂Me]₃(THF)

(**2b**). Single crystals of **2b** were obtained from a saturated hexanes solution cooled to -40°C. Crystal data and specific data collection parameters are listed in Table I. The 6707 raw intensity data were adjusted for a 5% decrease in intensity and a 14.4% variation in azimuthal scan. The data were corrected for absorption and for Lorentz and polarization effects. The transmission factors ranged from 0.29 to 0.34. The structure was solved and refined as for **1**, and hydrogen atoms were idealized with $d(\text{C-H}) = 0.95$ Å. The final residuals for **2b** are listed in Table I. The fluorine atoms on C(23) and C(24) showed high thermal motion and oscillation in the refinement. Attempts to model half-atom disorder were unsuccessful. The largest peak in the final difference Fourier map had an electron density of 2.36 e Å⁻³ (near Re). The final positional parameters are given in the supplementary material.

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- (8) When 50 equiv of THF-*d*₈ were added after 1 min to the freshly prepared mixture of vinylalkylidene species **2a** and **2b** in a NMR tube, a significant decrease in the rate of isomerization ($t_{1/2} = 18$ h) was observed.
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(11) The isomerization of **2a** to **2b** is written as an irreversible process based on the observation that conversion of pure **2b** to **2a** could not be promoted photochemically nor thermally.

(12) Based on ^1H NMR experiments with an internal standard, **2b** is unreactive toward acetone, acetonitrile, benzaldehyde, and ethyl acetate. For example, 10 equiv of benzaldehyde were combined with **2b** (10 mg) in C_6D_6 and monitored over a period of 24 h at 25 °C. No significant change was measured in the composition of the mixture nor concentration of the components relative to an internal standard.

(13) Only very slow metathesis of olefins is observed. For example, **2b** (8 mg) in C_6D_6 will metathesize 100 equiv of *cis*-2-pentene to equilibrium in 31 h. NMR studies of the reaction mixture also indicate that only the parent vinylalkylidene complex **2b** is present throughout the reaction. Only partial decomposition of **2b** is observed during the reaction, as ~60% of the original alkylidene resonance remains after 31 h relative to an internal standard. No propagating alkylidene species are detected. The identity of the true catalyst is unknown and may be a more reactive propagating alkylidene species resulting from slow initiation, a decomposition product of the parent vinylalkylidene, or a trace impurity. In addition ^{19}F NMR data from the study of a freshly prepared sample of **2b** in benzene- d_6 are consistent with the presence of $\text{HOC}(\text{CF}_3)_2\text{Me}$, a byproduct of the hydrolysis of either **1** or **2b**.

(14) Compound **2b** does react with cyclic olefins, e. g. norbornene, albeit not in a well-defined manner, to afford high molecular weight polymers. Investigation of the metathetical activity of **2b** with cyclic olefins continues and will be reported at a later time.

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Chapter 2

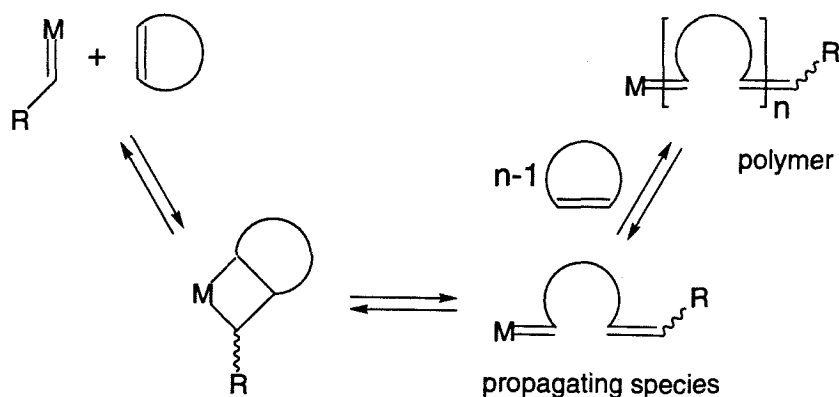
Preparation of a Di(cyclopropenyl)benzene Compound As a Precursor to ROMP Diinitiators

Introduction

Ring-Opening Metathesis Polymerization (ROMP) refers to the synthesis of unsaturated polymers specifically from cyclic olefins.¹ This process requires certain transition metal catalysts and affords polymers with the same degree of unsaturation as the monomers incorporated (Scheme 1). ROMP differs notably from other olefin polymerizations, such as Ziegler-Natta systems² which polymerize *acyclic* as well as cyclic olefins through the double bond and generate polymers more highly saturated than the monomers.

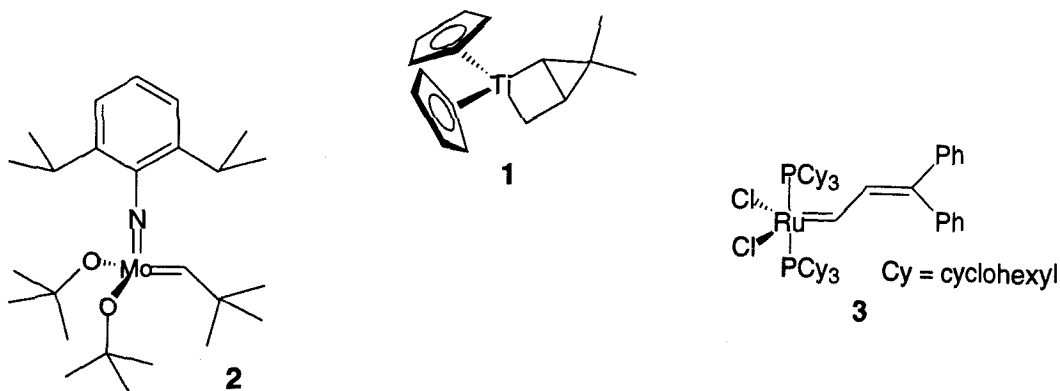
The mechanism of ROMP is well-established.³ Transition metal alkylidene and metalla-cyclobutane species are key intermediates in ROMP and other olefin metathesis reactions. The reaction involves the cycloaddition of the (cyclic) olefin and metal alkylidene to give a metallacyclobutane intermediate (Scheme 1). The metallacycle may then undergo productive or degenerate cleavage of the ring structure. Productive cleavage yields new carbon-carbon and carbon-metal double bonds. In the case of a cycloalkene, the olefin bond is incorporated into the growing polymer chain. Most strained cycloalkenes are readily polymerized because relief of ring strain favors productive cleavage and thus incorporation of the monomer. Cycloalkenes having little or no ring strain tend to be relatively unreactive but can be polymerized under ideal equilibrium conditions. The

Scheme 1. Ring-Opening Metathesis Polymerization (ROMP)



resulting alkylidene then reacts with the cyclic monomer in another iteration of the cycle and thus propagates the polymer chain.

Numerous examples of metallacyclobutanes and metal alkylidenes that are well-defined ROMP catalysts have been isolated and characterized over the past two decades.⁴ The titanacyclobutane **1**,⁵ prepared from 3,3-dimethylcyclopropene and a protected titanium methylidene, is an early example of a metathesis catalyst and, specifically, an initiator for the polymerization of norbornene. Under reaction conditions this metallacycle cleaves thermally to generate a reactive alkylidene which, in turn, is trapped by excess norbornene to form a new titanacycle. A newer generation of these homogeneous catalysts, which exhibit improved activity and tolerance of organic functionalities, have been developed with later transition metals, such as tungsten,⁶ molybdenum,⁷ rhenium⁸ and ruthenium.⁹ In particular, the molybdenum imido alkylidene complex **2**^{7b} and more recently the ruthenium vinylcarbene complex **3**^{9a} have been widely utilized as ROMP initiators. The latter, a relatively stable complex, has been especially attractive due to its remarkable tolerance of most polar functional groups—even protic media—and its relaxed handling requirements.



One of the more desirable qualities of a ROMP initiator is the ability to produce a living polymer.¹⁰ A polymer chain is said to be *living* when chain-terminating and chain-transfer events occur very slowly relative to propagation and all monomer units add irreversibly. Furthermore, when the rate of initiation is greater than or approximately equal to the rate of

propagation, polymers with a very narrow distribution of molecular weights can be prepared.¹¹ The preparation of low-dispersity polymers offers the best opportunity to control the bulk properties of such materials.

Previous studies¹²⁻¹⁴ also have shown that living ROMP systems are an important means of preparing well-defined block copolymers with low-dispersity segments. Metathesis catalysts have been used to generate block copolymers by several methods similar to those of living anionic and group-transfer polymerizations.^{15,16} The most straightforward synthesis involves the sequential addition of a different monomer to the living terminus of a homopolymer.¹² Block copolymers also are prepared by converting the living terminus into an initiator for a different polymerization process^{10,13} and by coupling the reactive end-groups of two different homopolymers.¹⁴ Extensions of these methods have been applied to the syntheses of multiblock copolymers *via* ROMP. ABA-type triblock copolymers can be prepared by adding monomer A to the living B terminus of an AB diblock copolymer. For example, a well-defined ABA triblock of *exo*-dicyclopentadiene and norbornene^{12a} (Fig 1) has been prepared by sequential addition of these monomers to the titanium catalyst **1**. This process requires three discrete polymerization steps wherein all of one monomer must be incorporated before the other monomer is added.

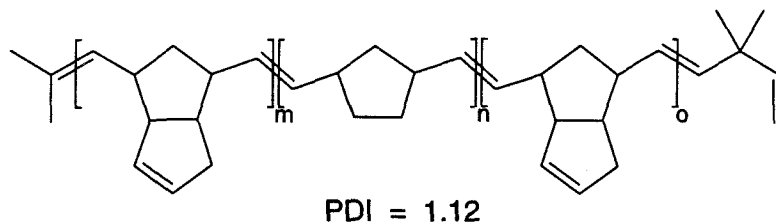
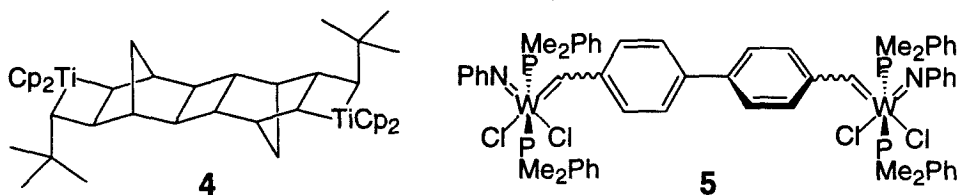


Figure 1.

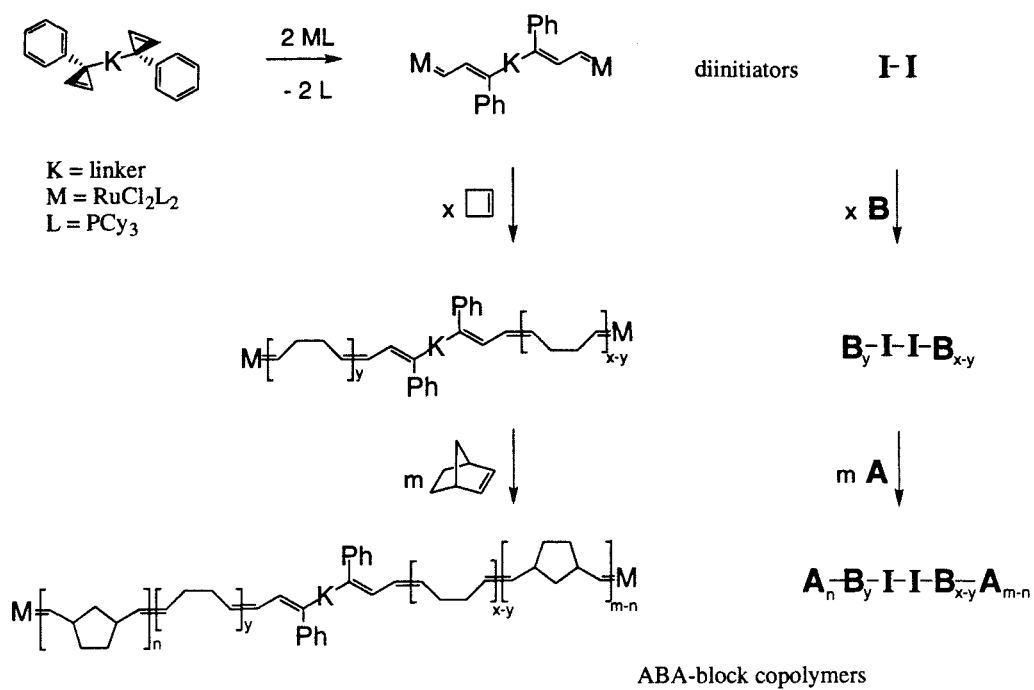
Alternatively ABA triblock copolymers can be prepared more efficiently with a difunctional initiator—one which polymerizes both A and B monomers in a living manner—by using fewer monomer additions.¹⁷ By initiating monomer B first with a diinitiator, a homopolymer B with two living termini is generated. Next monomer A is added and

polymerizes at both ends of block B to yield an ABA triblock. This process is routinely used to prepare styrene-isoprene-styrene and styrene-butadiene-styrene copolymers *via* anionic polymerization.¹⁸ Diinitiators for ROMP also have been prepared and include the di(titanacyclobutane) **4**¹⁹ and the di(tungsten benzylidene) **5**²⁰ complexes. Modeled after their mononuclear analogs, these species each generate two propagating centers.



We wanted to expand on this concept by designing and preparing other ROMP diinitiators. Herein we report the synthesis of a difunctional precursor based on 3,3-diphenylcyclopropene,²¹ an important alkylidene source. The impetus for choosing this cyclopropene stems from its versatility in the preparation of various alkylidene complexes some of which are ROMP catalysts.²² Ideally we want to prepare a diinitiator analogous to compound **3**, which is synthesized using the same cyclopropene chemistry. We reasoned that a complex with two ruthenium vinylalkylidene structures—a bis(ruthenaolefin)—would possess similar reactivity and tolerance of functional groups as its mononuclear cousin. Thus it should be possible to synthesize an ABA triblock copolymer, for example, of cyclobutene and norbornene (Scheme 2) with a ruthenium diinitiator, since a diblock copolymer of these monomers has been prepared with **3**.²³ Numerous functionalized norbornene compounds that are readily available also could be incorporated into ABA triblocks to generate a wide range of potentially interesting materials.

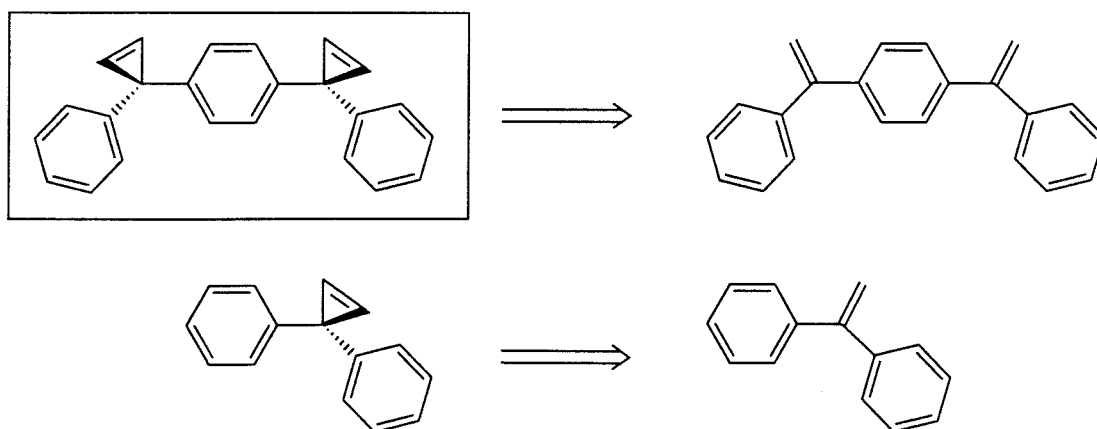
Scheme 2. Model Synthesis of ABA Triblock with Proposed Ruthenium Diinitiator



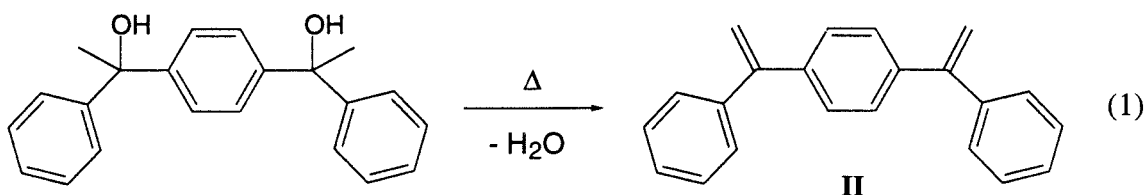
Results and Discussion

The synthesis of a compound containing two *gem*-disubstituted-cyclopropene moieties appeared straightforward given the relative facility of preparing 3,3-diphenylcyclopropene (DPCP).²¹ We also reasoned that if this difunctional compound has similar reactivity as DPCP, the reactions of this compound—a dialkylidene source—with appropriate transition metal complexes might afford dinuclear analogs of known ROMP initiators prepared from DPCP. The compound 1,4-di(1-phenylcycloprop-2-enyl)benzene (Scheme 3) was chosen as the target molecule, since it is the most structurally similar difunctional analog of DPCP. Also the divinyl analog of 1,1-diphenylethylene—the starting material for the three-step synthesis of DPCP—is readily available. Given the vinyl moieties of both starting materials have almost identical chemical environments, we concluded that the same preparative steps required for the synthesis of DPCP²¹ also would afford 1,4-di(1-phenylcycloprop-2-enyl)benzene. In particular, the two vinyl groups of 1,4-di(1-phenylvinyl)benzene would be transformed into cyclopropene structures in three steps: (1) cyclopropanation *via* dibromocarbene addition, (2) reduction to generate monobromocyclopropane rings, and (3) dehydrohalogenation to afford the dicyclopropene compound.

Scheme 3. Retro-synthesis of Target Dicyclopropene and Cyclopropene Analog

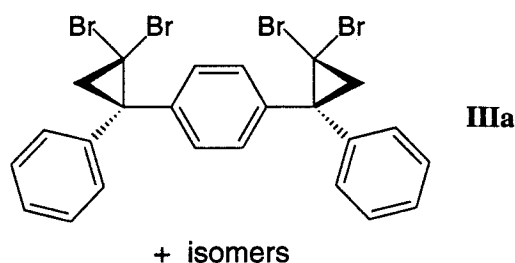


Preparation of 1,4-Di(1-phenylvinyl)benzene. The reaction of 1,4-diacetylbenzene with an excess of freshly prepared phenylmagnesium bromide in THF, followed by aqueous work-up, gives a viscous yellow mixture that primarily contains the diol 1,4-di(1-hydroxy-1-phenylethyl)benzene. Subsequent dehydration of this diol in hot toluene over P_2O_5 and recrystallization from hot acetone affords 1,4-di(1-phenylvinyl)benzene^R (**II**) in good yield (82%, non-optimized). The results of an 1H NMR study for the isolated product in benzene- d_6 indicate that one vinyl resonance (δ 5.26) and no methyl resonances are observed, consistent with complete dehydration of the diol (eq 1).



Preparation of 1,4-Di(2,2-dihalo-1-phenylcyclopropyl)benzene (X = Br, Cl). In method A, adapted from the synthesis of analog 1,1-dibromo-2,2-diphenylcyclopropane,^{21a} the dropwise addition of bromoform to a mixture of 1,4-di(1-phenylvinyl)benzene and KO^tBu in benzene affords a combination of starting material, a monocyclopropyl intermediate and the desired product, 1,4-di(2,2-dibromo-1-phenylcyclopropyl)benzene (**IIIa**). These components are observed in a ratio of roughly 1:2:2, respectively, consistent with TLC studies and mass uptake. Subjecting this product mixture again to the same reaction conditions, followed by work-up, gives **IIIa** in fair yield (64%, non-optimized). From an 1H NMR study of the isolated product in benzene- d_6 two overlapping methylene resonances (δ 2.43 and 2.42) and no vinyl resonances are observed. These results are consistent with the complete cyclopropanation of both vinyl moieties of the starting material **II**. The low yield could be explained by the poor solubilities of the products. In particular the weak solubility of the monocyclopropane intermediate significantly arrests the reaction midway and hampers the efforts to recover

and purify the dicyclopropane **IIIa**. Similar results—low yields and poor solubilities of the products—are obtained for this reaction in other solvents, e.g. dichloromethane and toluene. Efforts to optimize the synthesis of **IIIa**, other than changing the solvent, have yet to be fully investigated. At a higher temperature—above room temperature—the reaction may afford the dicyclopropane in higher yield.

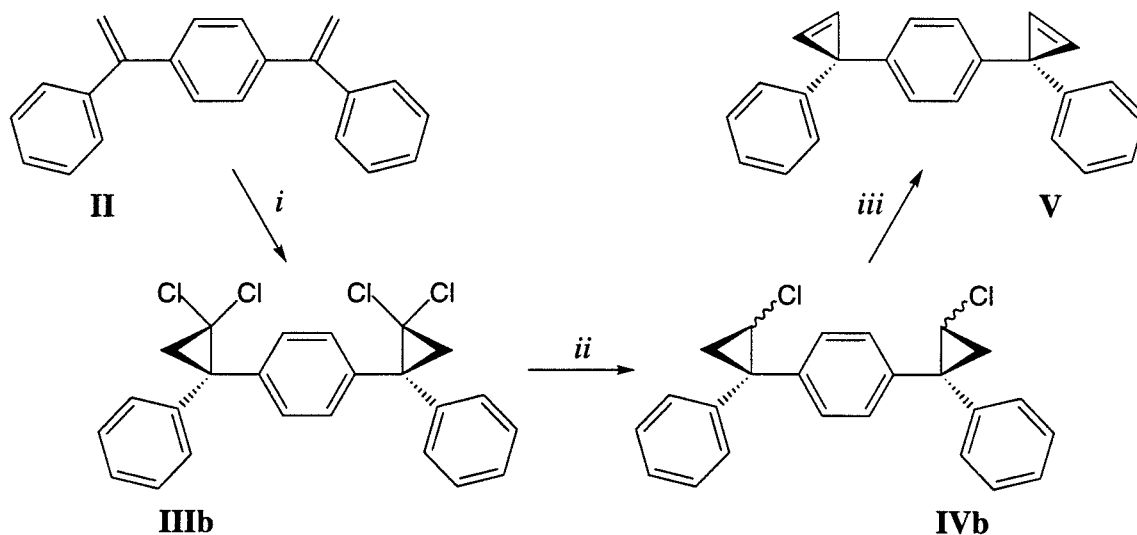


Preliminary results for the biphasic reaction²⁴ (method B) of a 50% NaOH solution and a solution of 1,4-di(1-phenylvinyl)benzene in bromoform in the presence of a phase transfer catalyst to give **IIIa** in excellent yield (97%) are encouraging. ¹H NMR results indicate that the isolated product is identical to **IIIa** obtained by method A and is relatively pure. The synthesis also does not require anhydrous conditions nor purification of the bromoform. However, like the earlier synthesis, these results are achieved with a second addition of reagents to ensure complete cyclopropanation of the two vinyl moieties. On a larger scale this biphasic preparation of **IIIa** may prove to be the method of choice due to its greater convenience and yield.

When chloroform is substituted for bromoform in the above biphasic reaction, the tetrachloro analog **IIIb** is afforded in very good yield (95%) and the reaction reaches completion within 1 h. An ¹H NMR study of the isolated product in benzene-*d*₆ indicates that a methylene resonance (δ 2.58, br) and no vinyl resonance are observed, also consistent with complete cyclopropanation of both vinyl groups in 1,4-di(1-phenylvinyl)benzene. Remarkably the product 1,4-di(2,2-dichloro-1-phenylcyclopropyl)benzene (**IIIb**) is highly soluble in most organic solvents.

Interest in preparing **IIIb** stems from promising results from the synthesis of 3-methyl-3-phenylcyclopropene developed by Grubbs and Maughon.²⁵ This cyclopropene synthesis involves a few facile, high-yielding steps that do not require rigorous exclusion of air and water. On the basis of these steps, a more convenient route to the proposed dicyclopropene **V** is envisioned (Scheme 4). Cyclopropanation of both vinyl structure (*i*) is achieved in the biphasic reaction (*vide supra*). Next reduction with a tin hydride source²⁶ (*ii*) would yield an intermediate with only monochlorocyclopropane rings as observed exclusively in the corresponding step of the 3-methyl-3-phenylcyclopropene synthesis. Finally, elimination of hydrogen chloride (*iii*) would afford 1,4-di(1-phenylcycloprop-2-enyl)-benzene (**V**), the same dicyclopropene proposed for use in syntheses of dialkylidene complexes.

Scheme 4. Proposed Alternate Synthesis of Dicyclopropene **V**.



(i) CHCl_3 , NaOH , PTC ; (ii) Bu_3SnCl , NaBH_4 , AIBN , PrOH ; (iii) KO^tBu , DMSO

Reduction of 1,4-Di(2,2-dichloro-1-phenylcyclopropyl)benzene. Treatment of **IIIb** with the catalytic tin hydride system²⁶ (Scheme 4) does not result in clean formation of the desired product 1,4-di(2-chloro-1-phenylcyclopropyl)benzene (**IVb**). Results from TLC and ^1H NMR studies indicate that the product mixture contains the

starting material—an estimated 25% of the mixture—and more than one product. The species are not entirely separable by flash chromatography and their similar solubilities have hampered other means of isolation, including recrystallization. Efforts to drive the reaction to completion have been unsuccessful thus far and largely limited to longer reaction times and increasing the quantity of the hydride source.

Preparation of 1,4-Di(2-bromo-1-phenylcyclopropyl)benzene. Reduction of 1,4-di(2,2-dibromo-1-phenylcyclopropyl)benzene (**IIIa**) in a refluxing mixture of diethylphosphite and triethylamine affords a mixture of starting material and the desired product 1,4-di(2-bromo-1-phenylcyclopropyl)benzene (**IVa**). Fortunately the unreacted starting material can be recovered by filtration. The product is isolated from the filtrate as an off-white solid in fair yield (60%, non-optimized). The single reduction of both dibromocyclopropane rings in **IIIa** to afford bromocyclopropane moieties is reflected in the ^1H NMR data (for the isolated product in benzene- d_6), in which new methine (δ 3.70-3.58, CHBrCH_2) and methylene (δ 1.93-1.72 and 1.39-1.15, CHBrCH_2) resonances in a 1:1:1 ratio are observed. The methylene resonance ascribable to **IIIa** is not observed in the ^1H NMR study of this product.

Preparation of 1,4-Di(1-phenylcycloprop-2-enyl)benzene. Preliminary results for the dehydrohalogenation of **IVa** are promising. The dropwise addition of a solution of KO^tBu in DMSO to a solution of **IVa** in DMSO, followed by work-up and recrystallization from hot acetone, affords yellow crystals of the desired product 1,4-di(1-phenylcycloprop-2-enyl)benzene (**V**) in excellent yield (91%). ^1H NMR results—the absence of upfield chemical shifts, ascribable to the cyclopropane ring of **IVa**, and observation of a new downfield shift (δ 7.47) for the isolated product in CDCl_3 —are indicative of the complete dehydrohalogenation of both cyclopropene moieties in **IVa** to give the dicyclopene **V**. The product is soluble in most organic solvents, an

observation that should not limit the development of syntheses of various dinuclear alkylidene complexes with this dicyclopene under conditions similar to those required for the preparation of their mononuclear analogs.

Conclusions and Outlook

In summary, the targeted compound 1,4-di(1-phenylcyclopropenyl)benzene can be prepared from 1,4-di(1-phenylvinyl)benzene. This synthesis is based upon the preparation of 3,3-diphenylcyclopropene from 1,1-diphenylethylene. However, the poor solubilities of products generated in the cyclopropanation (method A) of 1,4-di(1-phenylvinyl)benzene have complicated efforts to produce and isolate the desired product conveniently and in high yield. We reason that the third phenyl moiety of the product and intermediates contributes to the greater crystallinity and hence the lower solubility of these species than those of the diphenyl analogs. Preliminary results have demonstrated that the biphasic cyclopropanation using bromoform affords the desired dicyclopene intermediate both conveniently and in high yield. If this method can be applied to a larger scale synthesis with similar results, the biphasic cyclopropanation reaction will likely supersede the other cyclopropanation (method A) for future syntheses of the dicyclopene. Ultimately the alternate synthesis based on the work of Maughon and Grubbs may also provide a convenient method of preparing the dicyclopene. However, this outlook depends upon the ability to conveniently prepare and isolate the intermediate 1,4-di(2-chloro-1-phenylcyclopropyl)benzene *and* the complete dehydrohalogenation of this intermediate to give the desired dicyclopene. Further studies are in progress.

This dicyclopene has been developed for the purpose of preparing novel ROMP catalysts, specifically ones which would initiate polymer growth in two directions. In the future ABA-block copolymers might be generated from the proposed ROMP diinitiators by preparing the middle homopolymer (block B) first and changing monomer only once.

Experimental

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under an argon purge or using a nitrogen-filled Vacuum Atmospheres drybox. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4-Å molecular sieves. THF was degassed by sparging with nitrogen and then dried by passing through two columns of activated alumina under nitrogen. Likewise benzene, toluene, and hexane (HPLC grade) were sparged and passed through a column of Q-5 catalyst (Kaiser) and a column of activated alumina under nitrogen. DMSO was dried over CaH₂, vacuum-distilled with warming (30°C) and stored under argon.

Bromoform (Aldrich) was washed with a saturated CaCl₂ solution, distilled from CaCl₂, filtered through a plug of activated alumina and stored under argon. Bromobenzene (Aldrich) and triethylamine (Baker) were distilled from CaH₂ and stored under argon. Diethylphosphite (Aldrich) was vacuum-distilled at 35°C and stored under argon. Potassium *t*-butoxide (powder, Aldrich) was used without further purification and stored in the drybox. Cetyltrimethylammonium bromide (Aldrich), tributyltin chloride (Aldrich), AIBN (Kodak), sodium borohydride (Aldrich) and 1,4-diacetylbenzene (Aldrich) were used as received.

¹H NMR spectra were recorded on a General Electric QE-300 Plus (300.10 MHz) spectrometer. Chemical shifts are reported relative to an internal standard (TMS, δ 0.0). All coupling constants are reported in Hz.

1,4-Di(1-phenylvinyl)benzene (II). A freshly prepared solution of phenylmagnesium bromide (185 mmol) in THF (200 ml) was loaded into a 1000-ml three-neck flask fitted with an addition funnel and was chilled to -10 °C with an ice-saltwater bath. A solution of 1,4-diacetylbenzene (10.0 g, 61.7 mmol) in THF (90 ml) was transferred to the

addition funnel and added dropwise to the stirred Grignard reagent over a period of 2 h. Aliquots of THF (6x50 ml) were added periodically to the reaction mixture to ensure proper mixing. The bath was removed and the reaction mixture was stirred an additional 2 h while warming to room temperature. The reaction mixture was transferred slowly to a 2000-ml separatory funnel filled with a saturated NH_4Cl solution (200 ml) and water (50 ml). The aqueous phase was separated and extracted with ethyl acetate (3x150 ml). The organic phases were combined, dried over Na_2SO_4 , filtered and concentrated on a rotary evaporator. The resulting residue was dissolved into toluene (200 ml), to which was added freshly crushed P_2O_5 (ca. 5 g). The flask was fitted with a reflux condenser and then was heated to 60 °C for 1.5 h. The brownish solution was allowed to cool and decanted. A residue at the bottom of the flask was dissolved into water (75 ml) and extracted with ethyl acetate (3x50 ml). The organic phases were combined, dried over Na_2SO_4 , filtered and concentrated on a rotary evaporator to dryness. A tan-colored solid was recovered and recrystallized from hot acetone to yield a white crystalline solid (14.3 g, 82%). ^1H NMR (C_6D_6) δ 7.25-7.20 (m, H_{Ar}), 7.1-6.9 (m, H_{Ar}), 5.26 (dd, CH_2 , $J_{\text{HH}} = 10.2$, $J_{\text{HH}} = 1.2$).

1,4-Di(2,2-dibromo-1-phenylcyclopropyl)benzene (IIIa). Compound IIIa was prepared under anhydrous conditions (method A) and by a more convenient procedure (method B) which involved a biphasic system and phase transfer catalyst.

Method A. A 500-ml three-neck flask was charged with KO^tBu (8.85 g, 2.25 equiv) and fitted with an addition funnel in the drybox. Benzene (100 ml) was transferred to the flask, followed by slow addition of a solution of **II** (9.88 g, 35.0 mmol) in benzene (150 ml). The mixture had become amber-colored during the addition and was later chilled to 10 °C. A solution of bromoform (6.40 ml, 2.09 mol) in benzene (50 ml) was transferred to the addition funnel and then added dropwise to the rapidly stirred reaction mixture over a period of 4 h. The mixture became brownish within 5 min. Stirring was continued as the mixture was allowed to warm to room temperature. The reaction was followed by TLC

and was estimated to be 40% complete. Also three traces were observed and attributed to **II**, the monocyclopropyl intermediate and **IIIa**, the desired product. The contents of the reaction flask were poured into a 1000-ml separatory funnel to which was added chilled water (100 ml) and ethyl acetate (300 ml). The organic phase was collected and the aqueous layer was extracted with ethyl acetate (3x150 ml). The organic phases were combined, dried over Na_2SO_4 , filtered and concentrated on a rotary evaporator. The product was dried in vacuo overnight to yield a tan-colored solid (8.39 g, 38%). This product mixture was resubmitted to the same reaction conditions and was worked-up as before. The resulting brown residue was loaded onto a column of silica gel and eluted with 5% ethyl acetate/ petroleum ether. Selected fractions were combined and concentrated on a rotary evaporator to yield an off-white solid (14.1 g, 64%). $^1\text{H NMR}$ (C_6D_6) δ 7.34-6.97 (m, H_{Ar}), 2.43 and 2.42 (CH_2CBr_2).

Method B. Reagent-grade bromoform (Aldrich) was used as received for this procedure. On the benchtop **II** (1.00 g, 3.54 mmol) was dissolved into a minimum volume of bromoform (4 ml). To the rapidly stirred solution, cetyltrimethylammonium bromide (50 mg, 0.05 equiv) and a 50% NaOH solution (1.1 ml, 4 equiv) were added. Within 1 min the reaction mixture had become terra cotta in color. Stirring was continued for 2 h, at which time the reaction was determined by TLC to be greater than 60% complete. The reaction mixture was stirred for another hour without significant change to the extent of reaction. Bromoform (2 ml) and a 50% NaOH solution (1.1 ml) again were added to the reaction mixture which was stirred for 2 h. At this time the reaction was determined by TLC to have reached completion. The mixture was transferred to a 250-ml separatory funnel to which ethyl acetate (70 ml) and water (30 ml) were added. Then the contents were swirled gently. The organic phase was separated and washed with a saturated NaHCO_3 solution (3x20 ml), water (20 ml) and brine (20 ml). Subsequently the solution was dried over Na_2SO_4 , filtered and concentrated on a rotary evaporator to yield an off-white solid (2.16 g, 97%). This product was sufficiently pure for subsequent use.

1,4-Di(2,2-dichloro-1-phenylcyclopropyl)benzene (IIIb). Reagent-grade chloroform was used for this procedure which follows from method B. Cetyltrimethylammonium bromide (50 mg, 0.05 equiv) and then a 50% NaOH solution (1.1 ml, 4 equiv) were added to the rapidly stirred solution of **II** (1.00 g, 3.54 mmol) in chloroform (6-8 ml). The reaction mixture was stirred for 1 h, and then worked-up in the same manner as **IIIa**. The resulting off-white solid was washed on a fritted funnel with hot ethanol and dried in vacuo overnight to yield a white solid (1.51 g, 95%). $^1\text{H NMR}$ (C_6D_6) δ 7.40-6.95 (m, H_{Ar}), 2.58 (br, CH_2CCl_2).

1,4-Di(2-bromo-1-phenylcyclopropyl)benzene (IVa). A 100-ml three-neck flask was charged with **IIIa** (5.0 g, mol), evacuated and back-filled with argon. To the flask triethylamine (6.7 ml, 6.0 equiv) and diethylphosphite (5.9 ml, 5.7 equiv) were added and a reflux condenser was attached under argon. The mixture was stirred and heated to 90 °C for 9 h. Aliquots of the reaction mixture were studied by TLC after 3, 6 and 9 h. The results of the latter two samples were consistent with there being primarily one product in the mixture. Ethyl acetate (75 ml) was added to the reaction flask and stirred vigorously. The mixture was filtered and concentrated on the rotary evaporator to yield a red-brown residue. The filtrant was dried in vacuo to yield an off-white solid (1.85 g) which was determined to be **IIIa** and was saved for later usage. The concentrated filtrate was loaded onto a short column (15 cm) of silica gel and eluted with 5% ethyl acetate/petroleum ether. The elutant was concentrated on a rotary evaporator to yield an off-white solid (2.24 g, 60%). $^1\text{H NMR}$ (CDCl_3) δ 7.41-7.08 (m, H_{Ar}), 3.70-3.58 (m, CHBrCH_2), 1.93-1.72 and 1.39-1.15 (m, CHBrCH_2).

Observations on the Reduction of IIIb. A 25-ml round-bottomed flask was loaded successively with **IIIb** (200 mg, 446 μmol), 1-propanol (15 ml), tributyltin

chloride (24 μ l, 0.2 equiv), AIBN (20 μ l) and NaBH₄ (42.2 mg, 2.5 equiv) - the latter was added slowly with stirring. The flask was fitted with a reflux condenser. The mixture was heated to reflux for 1 h. Aliquots of the reaction mixture were studied by TLC after 30 min and 1 h. Four traces were observed in each and did not differ significantly between the two samples. The hot solution was allowed to cool to room temperature, transferred to a 125-ml separatory funnel and diluted with diethyl ether (50 ml). The organic layer was washed with water (5x30 ml) and brine (30 ml), dried over Na₂SO₄ and concentrated on a rotary evaporator to yield an off-white residue (280 mg crude). In ¹H NMR studies a methylene resonance (δ 2.58) attributed to the *gem*-dichlorocyclopropane structures of the starting material was observed with moderate intensity. Also several overlapping multiplets were observed - consistent with the TLC results which indicated that the crude mixture contained more than one product.

1,4-Di(1-phenylcycloprop-2-enyl)benzene (V). A 25-ml three-neck flask was charged with **IVa** (446 mg, 953 μ mol) and purged with argon. DMSO (5 ml) was added to the flask and stirred vigorously. In the drybox a 25-ml flask was loaded with potassium *t*-butoxide (225 mg, 2.1 equiv) and capped with septum. DMSO (5 ml) was added to the base and stirred vigorously until complete dissolution had occurred. Under positive argon pressure the base was transferred dropwise to the reaction flask chilled to 15-20 °C *via* a fine cannula (22 gauge) over a period of 30 min, during which time the mixture turned yellow and then brown. The residual base was rinsed with DMSO (5 ml) and added to the mixture. The cooling bath was removed and the mixture was allowed to warm to room temperature for 1 h. When an aliquot of the reaction mixture was checked by TLC, only one spot was observed. The mixture was transferred to a 125-ml separatory funnel to which chilled water (20 ml) was added carefully. The flask was washed with a 2:1 petroleum ether/ether mixture (25 ml) and added to the separatory funnel. The organic phase was collected and the aqueous phase was extracted with 2:1 petroleum ether/ ether

(3x25 ml). The organic phases were combined, dried over Na_2SO_4 , filtered and concentrated to dryness on a rotary evaporator. The product was recrystallized from hot acetone to yield yellow crystals (265 mg, 91%). $^1\text{H NMR}$ (CDCl_3) 7.47 (s, C_3H_2), 7.32-7.15 (m, H_{Ar}), 7.08 (s, C_6H_4).

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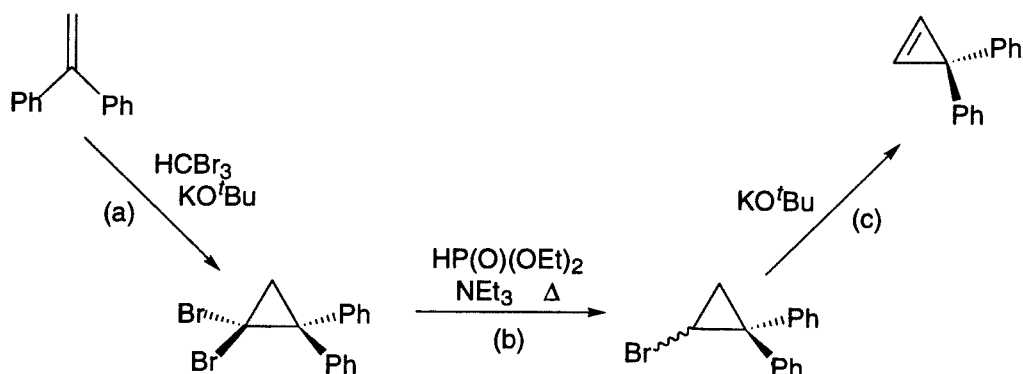
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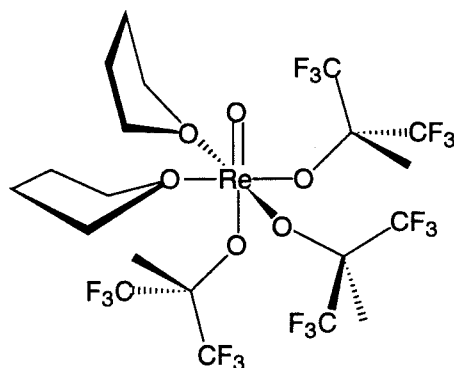
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Appendix

Data for X-ray Diffraction Studies

A. X-ray Diffraction Study of *fac*-ReO[OC(CF₃)₂CH₃]₃(THF)₂ (1).

(See Chapter 1, Figure 1 for the ORTEP plot.)

Table A.1. Crystal Data and Summary of Data Collection and Refinement.

formula	C ₂₀ H ₂₅ F ₁₈ O ₆ Re	μ , cm ⁻¹	45.25
fw	889.64	<i>T</i> , °C	-70
cryst dimens, mm	0.35 x 0.26 x 0.49	octants colld	±h,+k,+l
cryst system	monoclinic	2 θ range, deg	1.4-55.0
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	scan speed, deg min ⁻¹	1.70-5.00
<i>a</i> , Å	10.010(3)	scan width, deg	1.20-2.20 ω
<i>b</i> , Å	29.247(6)	total no. rflns	6891
<i>c</i> , Å	10.800(3)	unique data, <i>I</i> > 3 σ (<i>I</i>)	4447
β , deg	117.09(1)	final no. variables	406
<i>V</i> , Å ³	2815.0	<i>R</i>	0.035
<i>Z</i>	4	<i>R</i> _w	0.038
ρ_{calc} , g cm ⁻³	2.099	GOF	1.45

Table A.2. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (\AA^2)

atom	x	y	z	B_{iso}^a
Re(1)	5939.3(3)	6073.2(1)	5629.6(3)	1.7(1)
F(21)	6615(11)	7489(2)	5705(9)	10.3(5)
F(22)	7260(8)	7726(2)	4161(8)	8.2(4)
F(23)	5109(7)	7461(2)	3590(10)	10.6(4)
F(24)	5507(10)	6794(4)	2109(6)	13.1(4)
F(25)	7529(11)	6408(2)	3030(10)	11.6(6)
F(26)	7687(10)	7108(2)	2643(7)	10.0(4)
F(31)	3921(6)	6021(2)	7622(5)	5.3(2)
F(32)	5930(6)	6042(2)	9523(6)	6.2(2)
F(33)	4169(6)	6510(2)	9181(5)	5.7(2)
F(34)	7789(5)	6733(2)	10000(5)	5.2(2)
F(35)	6052(6)	7230(2)	9577(5)	5.0(2)
F(36)	7284(6)	7235(2)	8408(5)	5.3(2)
F(41)	11019(5)	6248(2)	7720(6)	5.6(2)
F(42)	11378(6)	6012(2)	9749(5)	6.6(2)
F(43)	9710(6)	6518(2)	8661(5)	5.1(2)
F(44)	8871(8)	5011(2)	7050(6)	7.8(3)
F(45)	10373(6)	5419(2)	6592(5)	6.1(2)
F(46)	11042(6)	5188(2)	8677(6)	7.1(2)
O(1)	5277(5)	5570(1)	5864(5)	2.6(2)
O(2)	6215(5)	6623(1)	4761(4)	2.3(1)
O(3)	6357(5)	6387(2)	7367(4)	2.2(1)
O(4)	8083(5)	5919(1)	6474(4)	2.0(1)
O(5)	5810(5)	5757(1)	3749(4)	2.5(1)
O(6)	3522(5)	6260(2)	4384(5)	2.6(1)
C(21)	7089(8)	6923(2)	4456(7)	2.6(2)
C(22)	8714(11)	6914(4)	5499(11)	6.4(4)
C(23)	6489(15)	7402(3)	4414(14)	6.2(5)
C(24)	6959(15)	6797(5)	3037(12)	6.9(5)
C(31)	5526(8)	6639(3)	7860(7)	2.8(2)
C(32)	4264(9)	6935(3)	6828(8)	3.8(3)
C(33)	4894(9)	6307(3)	8563(9)	3.9(3)
C(34)	6683(9)	6962(3)	8989(9)	3.7(3)
C(41)	9126(8)	5770(3)	7800(7)	2.9(2)
C(42)	8498(9)	5621(3)	8799(8)	4.1(3)
C(43)	10299(9)	6144(3)	8468(8)	3.9(3)
C(44)	9872(11)	5353(3)	7512(10)	5.2(3)
C(52)	6916(9)	5415(3)	3831(8)	3.7(3)
C(53)	6428(10)	5281(3)	2327(8)	4.3(3)
C(54)	4774(10)	5334(3)	1653(9)	4.5(3)
C(55)	4413(9)	5631(4)	2568(9)	5.5(3)
C(62)	2906(8)	6628(2)	3350(8)	3.4(2)
C(63)	1239(10)	6596(3)	2820(10)	5.2(3)
C(64)	963(9)	6104(3)	2983(11)	5.4(3)
C(65)	2285(8)	5974(3)	4335(8)	3.9(3)

Table A.2 (cont.). Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (\AA^2)

atom	x	y	z	B_{iso}^a
H(22)	9258	7126	5238	5.5
H(22')	9110	6615	5536	5.5
H(22'')	8816	6993	6392	5.5
H(32)	3787	7090	7293	5.5
H(32')	3552	6748	6113	5.5
H(32'')	4662	7153	6433	5.5
H(42)	9299	5529	9662	5.5
H(42')	7826	5372	8405	5.5
H(42'')	7979	5870	8950	5.5
H(52)	6853	5157	4334	5.5
H(52')	7882	5552	4205	5.5
H(53)	6674	4970	2285	5.5
H(53')	6843	5489	1920	5.5
H(54)	4320	5043	1575	5.5
H(54')	4450	5477	773	5.5
H(55)	3918	5899	2074	5.5
H(55')	3804	5468	2881	5.5
H(62)	3146	6571	2608	5.5
H(62')	3252	6914	3793	5.5
H(63)	749	6676	1863	5.5
H(63')	950	6777	3390	5.5
H(64)	987	5932	2246	5.5
H(64')	66	6074	3074	5.5
H(65)	2085	6053	5087	5.5
H(65')	2520	5661	4308	5.5

^a B_{iso} is the mean of the principle axes of the thermal ellipsoid.

Table A.3. Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)^a

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Re(1)	19.5(1)	20.0(1)	22.4(1)	0.4(1)	6.4(1)	0.6(1)
F(21)	237(10)	47(4)	191(8)	-13(5)	169(8)	-25(4)
F(22)	126(5)	38(3)	193(7)	0(3)	110(5)	-31(4)
F(23)	65(4)	65(4)	266(11)	31(3)	69(6)	87(6)
F(24)	163(8)	262(12)	38(4)	-113(9)	17(5)	-4(5)
F(25)	252(11)	69(5)	254(11)	-54(6)	232(10)	-64(6)
F(26)	228(9)	111(5)	101(5)	-86(6)	128(6)	-34(4)
F(31)	72(3)	72(4)	75(4)	-33(3)	49(3)	-26(3)
F(32)	72(4)	104(5)	72(4)	9(4)	44(3)	38(4)
F(33)	67(3)	101(4)	74(4)	-20(3)	55(3)	-27(3)
F(34)	50(3)	89(4)	38(3)	8(3)	1(2)	-26(3)
F(35)	64(3)	68(3)	59(3)	0(3)	28(3)	-33(3)
F(36)	78(4)	57(3)	79(4)	-32(3)	46(3)	-28(3)
F(41)	37(3)	79(4)	91(4)	-15(3)	25(3)	4(3)
F(42)	56(3)	88(4)	57(3)	-6(3)	-19(3)	9(3)
F(43)	66(3)	52(3)	64(3)	-15(3)	20(3)	-17(3)
F(44)	115(5)	33(3)	99(5)	5(3)	5(4)	-1(3)
F(45)	69(4)	104(5)	53(3)	47(3)	21(3)	1(3)
F(46)	83(4)	88(4)	66(4)	55(4)	3(3)	17(3)
O(1)	30(2)	24(2)	39(3)	-6(2)	11(2)	2(2)
O(2)	32(2)	25(2)	31(2)	-1(2)	16(2)	4(2)
O(3)	25(2)	33(3)	25(2)	-1(2)	11(2)	-4(2)
O(4)	23(2)	23(2)	27(2)	0(2)	8(2)	4(2)
O(5)	32(3)	26(2)	30(2)	2(2)	9(2)	-7(2)
O(6)	23(2)	33(2)	38(3)	0(2)	8(2)	0(2)
C(21)	42(4)	25(4)	33(4)	-4(3)	20(3)	7(3)
C(22)	51(6)	86(8)	75(7)	-36(5)	1(5)	34(6)
C(23)	113(10)	43(6)	115(10)	2(6)	82(9)	16(6)
C(24)	108(10)	108(10)	67(7)	-56(8)	58(7)	-10(7)
C(31)	33(4)	46(4)	28(4)	-4(3)	14(3)	-12(3)
C(32)	39(4)	50(5)	48(5)	14(4)	13(4)	-11(4)
C(33)	43(s)	69(6)	47(5)	-10(4)	31(4)	-13(4)
C(34)	46(5)	51(5)	49(5)	-6(4)	28(4)	-22(4)
C(41)	27(4)	38(4)	31(4)	5(3)	3(3)	4(3)
C(42)	48(5)	52(5)	40(4)	1(4)	5(4)	22(4)
C(43)	41(4)	46(5)	42(4)	2(4)	3(4)	7(4)
C(44)	58(6)	49(6)	56(6)	27(5)	-3(5)	4(5)
C(52)	47(5)	44(5)	47(5)	20(4)	18(4)	-7(4)
C(53)	52(5)	62(6)	46(5)	11(4)	18(4)	-14(4)
C(54)	56(6)	72(6)	44(5)	11(5)	23(4)	-20(5)
C(55)	38(5)	96(8)	50(5)	9(5)	-2(4)	-44(5)
C(62)	35(4)	31(4)	43(4)	10(3)	1(3)	7(3)
C(63)	37(5)	63(6)	74(6)	12(4)	3(4)	6(5)
C(64)	28(4)	61(6)	87(7)	-3(5)	1(4)	-7(6)
C(65)	30(4)	60(6)	47(5)	-10(4)	8(3)	-8(4)

^aAnisotropic displacement exponent takes the form: $-2\pi^2(h^2a^2U_{11} + \dots + 2(hka*b*U_{12} + \dots))$

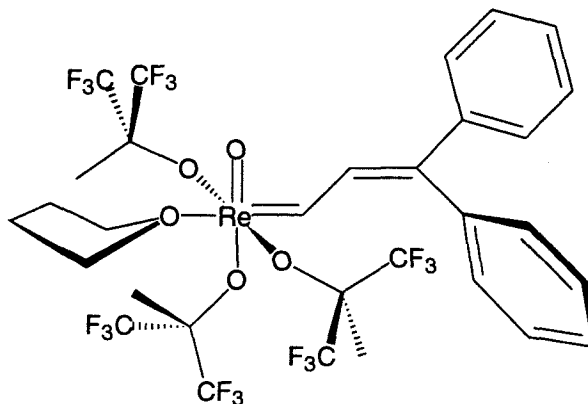
Table A.4. Interatomic Distances (Å) with Esd's

Re(1)-O(1)	1.681(4)	F(46)-C(44)	1.358(9)
Re(1)-O(2)	1.943(4)	O(2)-C(21)	1.381(7)
Re(1)-O(3)	1.956(4)	O(3)-C(31)	1.386(8)
Re(1)-O(4)	1.964(4)	O(4)-C(41)	1.403(7)
Re(1)-O(5)	2.180(4)	O(5)-C(52)	1.465(8)
Re(1)-O(6)	2.236(4)	O(5)-C(55)	1.447(8)
F(21)-C(23)	1.370(13)	O(6)-C(62)	1.469(8)
F(22)-C(23)	1.326(10)	O(6)-C(65)	1.474(9)
F(23)-C(23)	1.269(13)	C(21)-C(22)	1.498(11)
F(24)-C(24)	1.338(14)	C(21)-C(23)	1.518(12)
F(25)-C(24)	1.275(15)	C(21)-C(24)	1.523(12)
F(26)-C(24)	1.350(11)	C(31)-C(32)	1.518(10)
F(31)-C(33)	1.333(9)	C(31)-C(33)	1.536(11)
F(32)-C(33)	1.331(10)	C(31)-C(34)	1.561(10)
F(33)-C(33)	1.329(9)	C(41)-C(42)	1.538(11)
F(34)-C(34)	1.330(9)	C(41)-C(43)	1.524(10)
F(35)-C(34)	1.334(8)	C(41)-C(44)	1.534(11)
F(36)-C(34)	1.319(9)	C(52)-C(53)	1.519(10)
F(41)-C(43)	1.340(10)	C(53)-C(54)	1.482(12)
F(42)-C(43)	1.367(8)	C(54)-C(55)	1.480(11)
F(43)-C(43)	1.304(9)	C(62)-C(63)	1.500(11)
F(44)-C(44)	1.341(11)	C(63)-C(64)	1.491(13)
F(45)-C(44)	1.315(12)	C(64)-C(65)	1.506(11)

Table A.5. Intramolecular Angles (Deg) with Esd's

O(1)-Re(1)-O(2)	161.8(2)	F(22)-C(23)-C(21)	113.9(8)
O(1)-Re(1)-O(3)	101.2(2)	F(23)-C(23)-C(21)	116(1)
O(1)-Re(1)-O(4)	98.7(2)	F(24)-C(24)-C(21)	109(1)
O(1)-Re(1)-O(5)	84.7(2)	F(25)-C(24)-C(21)	113(1)
O(1)-Re(1)-O(6)	84.9(2)	F(26)-C(24)-C(21)	110.1(9)
O(2)-Re(1)-O(3)	93.4(2)	F(31)-C(33)-C(31)	110.0(6)
O(2)-Re(1)-O(4)	92.8(2)	F(32)-C(33)-C(31)	113.7(6)
O(2)-Re(1)-O(5)	82.1(2)	F(33)-C(33)-C(31)	114.0(8)
O(2)-Re(1)-O(6)	82.0(2)	F(34)-C(34)-C(31)	112.3(7)
O(3)-Re(1)-O(4)	87.2(2)	F(35)-C(34)-C(31)	112.5(6)
O(3)-Re(1)-O(5)	171.3(2)	F(36)-C(34)-C(31)	109.4(6)
O(3)-Re(1)-O(6)	99.3(2)	F(41)-C(43)-C(41)	112.8(7)
O(4)-Re(1)-O(5)	85.6(2)	F(42)-C(43)-C(41)	111.1(7)
O(4)-Re(1)-O(6)	171.8(2)	F(43)-C(43)-C(41)	111.8(7)
O(5)-Re(1)-O(6)	87.4(2)	F(44)-C(44)-C(41)	108.5(8)
Re(1)-O(2)-C(21)	152.3(4)	F(45)-C(44)-C(41)	115.0(8)
Re(1)-O(3)-C(31)	135.6(4)	F(46)-C(44)-C(41)	112.8(7)
Re(1)-O(4)-C(41)	133.9(4)	O(2)-C(21)-C(22)	113.5(6)
Re(1)-O(5)-C(52)	120.7(4)	O(2)-C(21)-C(23)	107.9(6)
Re(1)-O(5)-C(55)	123.6(4)	O(2)-C(21)-C(24)	108.3(6)
Re(1)-O(6)-C(62)	126.9(4)	O(3)-C(31)-C(32)	117.7(6)
Re(1)-O(6)-C(65)	123.0(4)	O(3)-C(31)-C(33)	108.0(6)
C(52)-O(5)-C(55)	106.2(5)	O(3)-C(31)-C(34)	105.1(6)
C(62)-O(6)-C(65)	109.4(5)	O(4)-C(41)-C(42)	116.8(6)
F(21)-C(23)-F(22)	106(1)	O(4)-C(41)-C(43)	108.3(6)
F(21)-C(23)-F(23)	105(1)	O(4)-C(41)-C(44)	104.2(6)
F(22)-C(23)-F(23)	108(1)	O(5)-C(52)-C(53)	104.3(6)
F(24)-C(24)-F(25)	109(1)	O(S)-C(55)-C(54)	107.8(7)
F(24)-C(24)-F(26)	109(1)	O(6)-C(62)-C(63)	104.7(7)
F(25)-C(24)-F(26)	107(1)	O(6)-C(65)-C(64)	104.2(7)
F(31)-C(33)-F(32)	105.6(8)	C(22)-C(21)-C(23)	108.5(8)
F(31)-C(33)-F(33)	106.7(6)	C(22)-C(21)-C(24)	108.6(8)
F(32)-C(33)-F(33)	106.2(7)	C(23)-C(21)-C(24)	110.0(8)
F(34)-C(34)-F(35)	107.7(6)	C(32)-C(31)-C(33)	109.3(6)
F(34)-C(34)-F(36)	107.8(7)	C(32)-C(31)-C(34)	107.5(6)
F(35)-C(34)-F(36)	106.8(7)	C(33)-C(31)-C(34)	108.9(6)
F(41)-C(43)-F(42)	106.3(7)	C(42)-C(41)-C(43)	110.1(6)
F(41)-C(43)-F(43)	108.1(7)	C(42)-C(41)-C(44)	108.0(7)
F(42)-C(43)-F(43)	106.3(7)	C(43)-C(41)-C(44)	109.0(7)
F(44)-C(44)-F(45)	107.9(8)	C(52)-C(53)-C(54)	104.0(7)
F(44)-C(44)-F(46)	105.3(8)	C(53)-C(54)-C(55)	107.0(7)
F(45)-C(44)-F(46)	106.7(8)	C(62)-C(63)-C(64)	104.4(7)
F(21)-C(23)-C(21)	107.8(9)	C(63)-C(64)-C(65)	103.3(7)

B. X-ray Diffraction Study of *syn,mer*-ReO[C(H)=CHCPh₂][OC(CF₃)₂CH₃]₃(THF) (2b).



(See Chapter 1, Figure 2 for the ORTEP plot.)

Table B.1. Crystal Data and Summary of Data Collection and Refinement.

formula	C ₃₁ H ₂₉ F ₁₈ O ₅ Re	ρ_{calc} , g cm ⁻³	1.612
fw	1009.80	μ , cm ⁻¹	30.69
cryst dimens, mm	0.36 x 0.16 x 0.52	T , °C	-65
cryst system	triclinic	octants colld	$\pm h, \pm k, +l$
space group	$P\bar{1}$ (no. 2)	2θ range, deg	2.0-48.0
a , Å	10.459(3)	scan speed, deg min ⁻¹	1.70-4.00
b , Å	10.913(3)	scan width, deg	1.20-2.20 ω
c , Å	21.308(6)	total no. rflns	6707
α , deg	91.16(3)	unique data, $I > 3\sigma(I)$	4987
β , deg	102.05(2)	final no. variables	496
γ , deg	117.98(2)	R	0.054
V , Å ³	2080.7	R_w	0.056
Z	2	GOF	5.40

Table B.2. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (\AA^2)

atom	x	y	z	B_{iso}^a
Re(1)	3494.8(5)	4209.0(4)	2028.7(2)	2.4(1)
F(21)	5336(13)	2593(15)	827(6)	10.7(7)
F(22)	4358(26)	3837(12)	259(7)	17.0(12)
F(23)	3508(30)	1760(15)	-173(7)	21.9(15)
F(24)	1151(21)	296(14)	1073(10)	15.9(10)
F(25)	3609(31)	757(19)	1401(6)	20.5(18)
F(26)	2051(17)	-264(12)	425(6)	12.1(7)
F(31)	6793(8)	6338(8)	3273(3)	5.7(3)
F(32)	7074(9)	7950(8)	2680(4)	6.8(4)
F(33)	8902(8)	7607(9)	3077(4)	7.3(4)
F(34)	7712(10)	7662(10)	1540(5)	8.0(4)
F(35)	9315(9)	7068(11)	1942(5)	8.7(4)
F(36)	7415(10)	5691(11)	1195(4)	8.8(4)
F(41)	-1526(9)	2960(12)	1422(5)	8.1(5)
F(42)	-1284(8)	1269(11)	1050(4)	8.2(4)
F(43)	-2512(8)	936(11)	1769(5)	8.9(4)
F(44)	424(9)	4518(9)	2560(4)	6.2(3)
F(45)	1324(8)	3476(9)	3198(3)	5.8(3)
F(46)	-1058(9)	2633(10)	2892(4)	7.4(4)
O(1)	3594(8)	5340(7)	2604(4)	3.8(3)
O(2)	3321(7)	3016(7)	1312(3)	3.2(2)
O(3)	5493(7)	5484(7)	1910(3)	3.9(3)
O(4)	1276(7)	3165(8)	1802(4)	3.8(3)
O(5)	2909(9)	5479(8)	1274(4)	4.5(3)
C(1)	3891(10)	3061(10)	2623(5)	2.7(3)
C(2)	4171(11)	3236(10)	3314(5)	3.0(3)
C(3)	4246(11)	2221(10)	3670(5)	3.0(4)
C(4)	4375(14)	2366(12)	4373(5)	4.0(4)
C(5)	3821(15)	3121(14)	4658(6)	5.0(5)
C(6)	3988(19)	3278(16)	5325(7)	6.4(7)
C(7)	4747(22)	2696(18)	5704(6)	7.1(8)
C(8)	5262(23)	1952(18)	5438(6)	7.6(9)
C(9)	5065(17)	1749(14)	4774(6)	5.3(6)
C(10)	4150(13)	951(11)	3364(5)	3.5(4)
C(11)	2869(13)	-328(12)	3292(6)	4.5(4)
C(12)	2780(17)	-1503(13)	3002(7)	5.8(6)
C(13)	3911(23)	-1467(16)	2758(6)	6.3(8)
C(14)	5169(22)	-220(18)	2845(8)	7.1(9)
C(15)	5301(16)	994(13)	3136(7)	5.4(6)
C(21)	2931(14)	2075(14)	765(6)	4.9(5)
C(22)	1566(20)	2404(19)	201(6)	8.6(8)
C(23)	4247(32)	2557(51)	419(12)	18.1(24)
C(24)	2257(38)	646(21)	901(9)	10.5(13)
C(31)	6971(12)	5868(12)	2227(5)	3.8(4)
C(32)	7263(13)	4710(13)	2427(7)	4.9(5)
C(33)	7446(12)	6938(13)	2807(6)	4.2(4)
C(34)	7852(16)	6579(19)	1709(8)	6.8(6)

Table B.2 (cont.). Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (\AA^2)

atom	x	y	z	B_{iso}^a
C(41)	155(11)	2345(13)	2111(6)	4.0(4)
C(42)	207(14)	1061(14)	2333(7)	5.5(5)
C(43)	-1298(15)	1876(18)	1572(9)	6.5(7)
C(44)	215(15)	3247(16)	2691(7)	5.4(6)
C(52)	3952(19)	6561(19)	988(9)	7.7(8)
C(53)	2971(39)	7014(34)	558(15)	16.3(23)
C(54)	1736(25)	6701(24)	782(13)	11.0(12)
C(55)	1487(17)	5500(18)	1121(8)	7.5(7)
H(1)	3887	2289	2405	2.7
H(2)	4303	4079	3525	3.0
H(5)	3318	3531	4392	5.0
H(6)	3582	3772	5515	6.4
H(7)	4932	2866	6160	7.2
H(8)	5756	1537	5708	7.5
H(9)	5384	1172	4590	5.3
H(11)	2055	-374	3440	4.5
H(12)	1908	-2378	2969	5.8
H(13)	3809	-2281	2534	6.3
H(14)	5988	-173	2698	7.1
H(15)	6208	1854	3189	5.4
H(22)	560	1785	219	8.6
H(22')	1622	2341	-235	8.6
H(22'')	1713	3324	315	8.6
H(32)	8284	5081	2646	4.9
H(32')	7050	4084	2054	4.9
H(32'')	6657	4214	2707	4.9
H(42)	-583	561	2536	5.5
H(42')	1137	1331	2634	5.5
H(42'')	100	464	1971	5.5
H(52)	4350	6174	730	7.7
H(52')	4679	7303	1319	7.7
H(53)	2721	6591	130	15.9
H(53')	3544	8012	579	15.9
H(54)	906	6449	427	11.1
H(54')	1913	7454	1084	11.1
H(55)	1227	5615	1513	7.5
H(55')	736	4671	842	7.5

^a B_{iso} is the mean of the principle axes of the thermal ellipsoid.

Table B.3. Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)^a

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re(1)	33.1(2)	29.7(2)	33.2(2)	18.2(2)	7.7(1)	4.3(1)
F(21)	113(8)	201(13)	122(9)	114(9)	0(7)	-41(9)
F(22)	425(29)	75(7)	158(13)	82(12)	190(17)	51(8)
F(23)	591(37)	127(11)	109(10)	143(17)	157(16)	-10(8)
F(24)	223(18)	91(9)	264(20)	19(10)	150(17)	-14(10)
F(25)	616(41)	258(19)	75(8)	363(26)	47(14)	35(9)
F(26)	238(15)	101(8)	113(9)	85(9)	22(9)	-15(7)
F(31)	64(4)	79(5)	48(4)	17(4)	13(3)	-5(4)
F(32)	86(6)	56(5)	111(7)	34(4)	18(5)	-11(4)
F(33)	46(4)	101(6)	88(6)	11(4)	-1(4)	-24(5)
F(34)	93(7)	79(6)	103(7)	10(5)	43(5)	39(5)
F(35)	50(5)	135(8)	105(7)	5(5)	39(5)	2(6)
F(36)	96(7)	123(8)	76(6)	9(6)	53(5)	-16(6)
F(41)	66(5)	142(9)	104(7)	64(6)	-1(5)	7(6)
F(42)	48(5)	141(9)	85(6)	25(5)	-3(4)	-40(6)
F(43)	33(4)	138(9)	128(8)	12(5)	18(5)	2(6)
F(44)	76(5)	78(5)	102(6)	49(4)	32(4)	-2(5)
F(45)	73(5)	100(6)	60(4)	51(5)	24(4)	9(4)
F(46)	62(5)	118(7)	108(7)	36(5)	53(5)	16(5)
O(1)	61(5)	38(4)	57(5)	33(4)	22(4)	7(3)
O(2)	43(4)	33(4)	37(4)	12(3)	10(3)	-5(3)
O(3)	35(4)	45(4)	53(4)	9(3)	7(3)	16(3)
O(4)	31(4)	55(5)	64(5)	26(4)	8(3)	15(4)
O(5)	67(5)	55(5)	61(5)	40(4)	13(4)	23(4)
C(1)	31(5)	31(5)	49(6)	21(4)	12(4)	2(4)
C(2)	41(6)	34(5)	35(5)	18(5)	4(4)	0(4)
C(3)	44(6)	38(6)	36(5)	23(5)	7(4)	10(4)
C(4)	71(8)	46(6)	41(6)	31(6)	14(5)	3(5)
C(5)	83(9)	63(8)	59(8)	44(7)	24(7)	20(6)
C(6)	120(13)	77(10)	53(8)	51(10)	29(8)	8(7)
C(7)	154(16)	98(12)	42(7)	86(12)	7(9)	3(7)
C(8)	174(18)	107(13)	42(8)	103(13)	13(9)	17(8)
C(9)	107(11)	68(8)	41(7)	61(8)	4(7)	2(6)
C(10)	59(7)	40(6)	53(6)	38(6)	16(5)	11(5)
C(11)	52(7)	37(6)	70(8)	21(6)	-1(6)	-4(6)
C(12)	86(10)	43(7)	75(9)	30(7)	-9(8)	0(6)
C(13)	144(15)	68(10)	52(8)	75(11)	15(9)	8(7)
C(14)	154(16)	81(11)	101(12)	90(12)	79(12)	31(9)
C(15)	81(9)	51(8)	78(9)	32(7)	33(8)	12(7)
C(21)	61(8)	66(8)	47(7)	24(7)	10(6)	-11(6)
C(22)	118(13)	114(14)	33(7)	26(11)	-28(8)	-42(8)
C(23)	118(22)	439(57)	78(17)	97(30)	18(15)	-43(26)
C(24)	237(29)	70(12)	72(12)	50(16)	61(16)	-14(9)

Table B.3 (cont.). Anisotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)^a

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(31)	38(6)	56(7)	41(6)	16(5)	10(5)	8(5)
C(32)	39(6)	54(7)	90(9)	21(6)	14(6)	2(7)
C(33)	33(6)	53(7)	58(7)	11(5)	3(5)	-1(6)
C(34)	54(9)	85(11)	77(10)	-2(8)	25(8)	-2(9)
C(41)	29(6)	64(8)	54(7)	19(5)	9(5)	8(6)
C(42)	53(7)	59(8)	89(10)	18(6)	30(7)	17(7)
C(43)	4(8)	92(11)	109(13)	31(8)	20(8)	2(10)
C(44)	58(8)	90(11)	75(9)	42(8)	34(7)	22(8)
C(52)	105(2)	114(13)	134(14)	83(11)	68(11)	86(12)
C(53)	308(37)	294(35)	267(32)	278(34)	219(30)	240(30)
C(54)	125(17)	135(18)	203(24)	93(15)	46(17)	98(18)
C(55)	79(10)	103(12)	114(13)	62(10)	-3(9)	44(10)

^aAnisotropic displacement exponent takes the form: $-2\pi^2(h^2a^2U_{11} + \dots + 2(hka*b*U_{12} + \dots))$

Table B.4. Interatomic Distances (Å) with Esd's

Re(1)-O(1)	1.674(7)	C(1)-C(2)	1.430(13)
Re(1)-O(2)	1.909(6)	C(2)-C(3)	1.378(13)
Re(1)-O(3)	1.968(7)	C(3)-C(4)	1.473(14)
Re(1)-O(4)	1.986(7)	C(3)-C(10)	1.470(14)
Re(1)-O(5)	2.315(7)	C(4)-C(5)	1.400(16)
Re(1)-C(1)	1.917(10)	C(4)-C(9)	1.389(16)
F(21)-C(23)	1.264(32)	C(5)-C(6)	1.392(17)
F(22)-C(23)	1.403(50)	C(6)-C(7)	1.383(20)
F(23)-C(23)	1.366(28)	C(7)-C(8)	1.338(20)
F(24)-C(24)	1.177(29)	C(8)-C(9)	1.383(17)
F(25)-C(24)	1.535(35)	C(10)-C(11)	1.385(15)
F(26)-C(24)	1.315(18)	C(10)-C(15)	1.371(16)
F(31)-C(33)	1.331(13)	C(11)-C(12)	1.367(18)
F(32)-C(33)	1.348(14)	C(12)-C(13)	1.372(21)
F(33)-C(33)	1.326(12)	C(13)-C(14)	1.351(23)
F(34)-C(34)	1.306(20)	C(14)-C(15)	1.384(18)
F(35)-C(34)	1.333(17)	C(21)-C(22)	1.842(22)
F(36)-C(34)	1.295(17)	C(21)-C(23)	1.574(28)
F(41)-C(43)	1.344(18)	C(21)-C(24)	1.443(24)
F(42)-C(43)	1.291(17)	C(31)-C(32)	1.484(17)
F(43)-C(43)	1.362(17)	C(31)-C(33)	1.510(16)
F(44)-C(44)	1.344(16)	C(31)-C(34)	1.568(17)
F(45)-C(44)	1.331(15)	C(41)-C(42)	1.511(18)
F(46)-C(44)	1.348(14)	C(41)-C(43)	1.551(18)
O(2)-C(21)	1.391(13)	C(41)-C(44)	1.536(18)
O(3)-C(31)	1.402(12)	C(52)-C(53)	1.496(26)
O(4)-C(41)	1.404(13)	C(53)-C(54)	1.366(28)
O(5)-C(52)	1.433(16)	C(54)-C(55)	1.451(23)
O(5)-C(55)	1.466(16)		

Table B.5. Intramolecular Angles (Deg) with Esd's

O(1)-Re(1)-O(2)	174.4(4)	F(35)-C(34)-C(31)	111(1)
O(1)-Re(1)-O(3)	93.7(3)	F(36)-C(34)-C(31)	111(1)
O(1)-Re(1)-O(4)	93.3(3)	F(41)-C(43)-C(41)	112(1)
O(1)-Re(1)-O(5)	87.7(3)	F(42)-C(43)-C(41)	112(1)
O(2)-Re(1)-O(3)	85.7(3)	F(43)-C(43)-C(41)	111(1)
O(2)-Re(1)-O(4)	85.2(3)	F(44)-C(44)-C(41)	113(1)
O(2)-Re(1)-O(5)	86.7(3)	F(45)-C(44)-C(41)	112(1)
O(3)-Re(1)-O(4)	156.5(3)	F(46)-C(44)-C(41)	112(1)
O(3)-Re(1)-O(5)	79.7(3)	O(2)-C(21)-C(22)	102(1)
O(4)-Re(1)-O(5)	78.3(3)	O(2)-C(21)-C(23)	111(2)
O(1)-Re(1)-C(1)	94.7(4)	O(2)-C(21)-C(24)	112(1)
O(2)-Re(1)-C(1)	90.9(4)	O(3)-C(31)-C(32)	116(1)
O(3)-Re(1)-C(1)	102.4(3)	O(3)-C(31)-C(33)	108(1)
O(4)-Re(1)-C(1)	99.3(3)	O(3)-C(31)-C(34)	103(1)
O(5)-Re(1)-C(1)	176.7(3)	O(4)-C(41)-C(42)	115(1)
Re(1)-O(2)-C(21)	170.0(7)	O(4)-C(41)-C(43)	103(1)
Re(1)-O(3)-C(31)	136.3(6)	O(4)-C(41)-C(44)	110(1)
Re(1)-O(4)-C(41)	136.7(6)	O(5)-C(52)-C(53)	102(1)
Re(1)-O(5)-C(52)	125.4(8)	O(5)-C(55)-C(54)	106(1)
Re(1)-O(5)-C(55)	124.2(8)	C(1)-C(2)-C(3)	121.6(9)
C(52)-O(5)-C(55)	109(1)	C(2)-C(3)-C(4)	120(1)
Re(1)-C(1)-C(2)	128.5(7)	C(2)-C(3)-C(10)	121.7(9)
F(21)-C(23)-F(22)	118(3)	C(4)-C(3)-C(10)	118.1(9)
F(21)-C(23)-F(23)	129(4)	C(3)-C(4)-C(5)	122(1)
F(22)-C(23)-F(23)	99(3)	C(3)-C(4)-C(9)	120(1)
F(24)-C(24)-F(25)	117(2)	C(5)-C(4)-C(9)	118(1)
F(24)-C(24)-F(26)	111(2)	C(4)-C(5)-C(6)	121(1)
F(25)-C(24)-F(26)	103(2)	C(5)-C(6)-C(7)	118(1)
F(31)-C(33)-F(32)	105(1)	C(6)-C(7)-C(8)	121(1)
F(31)-C(33)-F(33)	106(1)	C(7)-C(8)-C(9)	121(1)
F(32)-C(33)-F(33)	105(1)	C(4)-C(9)-C(8)	120(1)
F(34)-C(34)-F(35)	105(1)	C(3)-C(10)-C(11)	120(1)
F(34)-C(34)-F(36)	109(1)	C(3)-C(10)-C(15)	122(1)
F(35)-C(34)-F(36)	108(1)	C(11)-C(10)-C(15)	118(1)
F(41)-C(43)-F(42)	108(1)	C(10)-C(11)-C(12)	120(1)
F(41)-C(43)-F(43)	107(1)	C(11)-C(12)-C(13)	122(1)
F(42)-C(43)-F(43)	107(1)	C(12)-C(13)-C(14)	117(1)
F(44)-C(44)-F(45)	106(1)	C(13)-C(14)-C(15)	122(1)
F(44)-C(44)-F(46)	107(1)	C(10)-C(15)-C(14)	120(1)
F(45)-C(44)-F(46)	107(1)	C(22)-C(21)-C(23)	102(2)
F(21)-C(23)-C(21)	106(2)	C(22)-C(21)-C(24)	111(2)
F(22)-C(23)-C(21)	99(3)	C(23)-C(21)-C(24)	117(2)
F(23)-C(23)-C(21)	101(2)	C(32)-C(31)-C(33)	110(1)
F(24)-C(24)-C(21)	114(2)	C(32)-C(31)-C(34)	110(1)
F(25)-C(24)-C(21)	98(2)	C(33)-C(31)-C(34)	110(1)
F(26)-C(24)-C(21)	114(2)	C(42)-C(41)-C(43)	109(1)
F(31)-C(33)-C(31)	111(1)	C(42)-C(41)-C(44)	109(1)
F(32)-C(33)-C(31)	114(1)	C(43)-C(41)-C(44)	111(1)
F(33)-C(33)-C(31)	115(1)	C(52)-C(53)-C(54)	110(2)
F(34)-C(34)-C(31)	113(1)	C(53)-C(54)-C(55)	106(2)

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