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Synthesis, Structure, and Reactivity of a Rhenium Oxo–Vinylalkylidene Complex[†]

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The reaction of 3 equiv of $KOC(CF_3)_2Me$ with $ReOCl_3(PPh_3)_2$ in dichloromethane, followed by recrystallization from hexanes/THF, gives $ReO[OC(CF_3)_2Me]_3(THF)_2$ (1) in 35% yield. An X-ray diffraction study of 1 (monoclinic, $P2_1/n$, $a = 10.010(3)$ Å, $b = 29.247(6)$ Å, $c = 10.800(3)$ Å, $\beta = 117.09(1)°$, $Z = 4$) reveals a facial arrangement of the three alkoxide ligands around the metal center in a distorted octahedron. The ligand environment in 1 is quite crowded, as evidenced by an elongated Re—O bond between rhenium and one of the THF ligands. The reaction of 3,3-diphenylcyclopropene with 1 in dichloromethane gives initially a mixture of two isomeric rhenium oxo–vinylalkylidene complexes, of which the isomer *syn,mer*-$ReO[C(H)CH{=}CPh_2][OC(CF_3)_2Me]_3(THF)$ (**2b**) was isolated in 87% yield. An X-ray diffraction study of **2b** (triclinic, $P\bar{1}$, $a = 10.459(3)$ Å, $b = 10.913(3)$ Å, $c = 21.308(6)$ Å, $\alpha = 91.16(3)°$, $\beta = 102.05(2)°$, $\gamma = 117.98(2)°$, $Z = 2$) supports a pseudooctahedral structure with mutually trans vinylalkylidene and THF ligands. Complex **2b** does not react readily with internal or terminal olefins; however, the addition of $GaBr_3$ (1 equiv) to **2b** yields moderately active catalyst(s) that metathesize *cis*-2-pentene at ~6.7 turnovers min^{-1}. No propagating alkylidene species are observed during the metathesis reaction.

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, $ReO_2(CHCMe_3)(CH_2CMe_3)$, 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. We reasoned that if a rhenium(V) oxo complex with labile ligands could be prepared, it might react with cyclopropenes to give rhenium(VII) oxo–vinylalkylidene complexes.

In this paper 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 are also detailed.

Results and Discussion

Preparation of *fac*-$ReO[OC(CF_3)_2Me]_3(THF)_2$. The reaction of $ReOCl_3(PPh_3)_2$ with 3 equiv of $KOC(CF_3)_2Me$ in dichloromethane, followed by recrystallization from hexanes/THF (20:1), gives air-sensitive blue crystals of $ReO[OC(CF_3)_2CH_3]_3(THF)_2$ (1) in 35% yield (eq 1).[5] This

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[1] (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins,* 2nd ed.; Wiley: New York, 1985.

[2] Mol, J. C. *J. Mol. Catal.* **1991,** *65,* 145 and references therein.

[3] (a) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988,** 1489. (b) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992,** *114,* 3367.

[4] Titanium, zirconium: (a) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 610. Tungsten: (b) Johnson, L. K. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1992. (c) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993,** *115,* 8130. Ruthenium: (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992,** *114,* 3974. (e) Gagné, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics* **1992,** *11,* 3933. (f) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993,** *115,* 9858.

[5] Compound 1 also can be prepared from $ReOBr_3(PPh_3)_2$ in similar yield.

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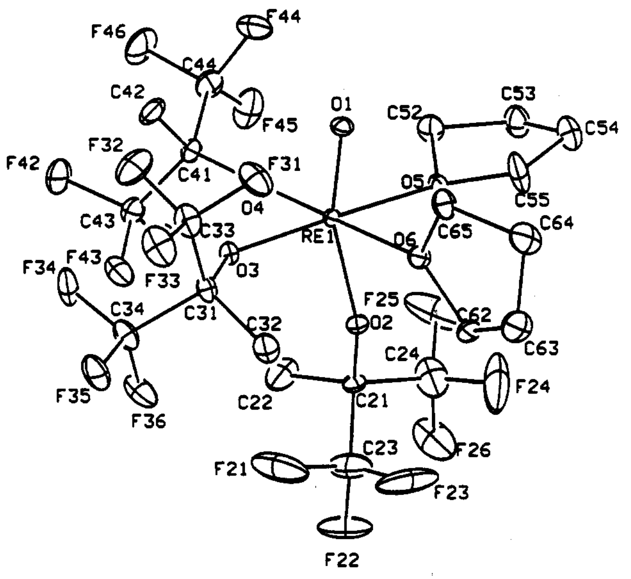
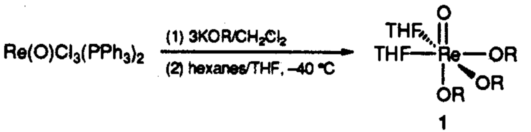


Figure 1. ORTEP drawing of *fac*-ReO[OC(CF$_3$)$_2$CH$_8$]$_3$-(THF)$_2$ (1).

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

	1	2b
formula	$C_{20}H_{25}F_{18}O_6Re$	$C_{31}H_{29}F_{18}O_5Re$
fw	889.64	1009.80
cryst dimens, mm	0.35 × 0.26 × 0.49	0.36 × 0.16 × 0.52
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	10.010(3)	10.459(3)
b, Å	29.247(6)	10.913(3)
c, Å	10.800(3)	21.308(6)
α, deg		91.16(3)
β, deg	117.09(1)	102.05(2)
γ, deg		117.98(2)
V, Å^3	2815.0	2080.7
Z	4	2
ρ_{calc}, g cm^{-3}	2.099	1.612
μ, cm^{-1}	45.25	30.69
T, °C	–70	–65
octants collcd	$\pm h,+k,+l$	$\pm h,\pm k,+l$
2θ range, deg	1.4–55.0	2.0–48.0
scan speed, deg min^{-1}	1.70–5.00	1.70–4.00
scan width, deg	1.20–2.20 ω	1.20–2.20 ω
total no. of rflns	6891	6707
no. of unique data, $I > 3\sigma(I)$	4447	4987
final no. of variables	406	496
R	0.035	0.054
R_w	0.038	0.056
GOF	1.45	5.40



(1)

OR = OC(CF$_3$)$_2$Me

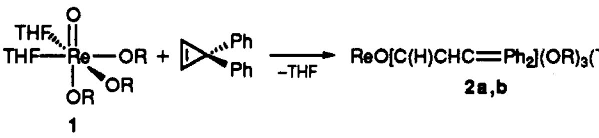
low yield can be accounted for in part by the additional recrystallization procedure needed to separate pure 1 from the triphenylphosphine byproduct. The ^{1}H NMR data for 1 in CD_2Cl_2 are consistent with a dynamic structure at room temperature where the THF and hexafluoro-*tert*-butoxide ligands rapidly 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. Experimental details are summarized in Table 1, and relevant bond distances and angles are listed in Table 2. 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 2. Selected Bond Distances and Angles for *fac*-ReO[OC(CF$_3$)$_2$CH$_3$]$_3$(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)

Preparation of *syn,mer*-ReO[C(H)CH=CPh$_2$][OC(CF$_3$)$_2$Me]$_3$(THF). Compound 1 and 3,3-diphenylcyclopropene undergo a rapid reaction in C_6D_6 at room temperature to give a blood red solution containing a mixture of two vinylalkylidene complexes (eq 2). The two



(2)

OR = OC(CF$_3$)$_2$Me

products are distinguishable by ^{1}H NMR spectroscopy, as characterized by pairs of downfield doublets (^{1}H NMR (C_6D_6): **2a**, δ 12.66, 9.49 (J = 13 Hz); **2b**, δ 12.31, 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 and ^{1}H and ^{13}C NMR data for **2b** are consistent with the stoichiometry ReO[C(H)CH=CPh$_2$][OC(CF$_3$)$_2$Me]$_2$(THF). Also a meridional geometry of the alkoxide ligands is reflected in the ^{1}H 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 3). 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

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[6] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[7] For representative Re=CH and Re=CH chemical shifts see ref 3 and: Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* 1991, *39*, 1.

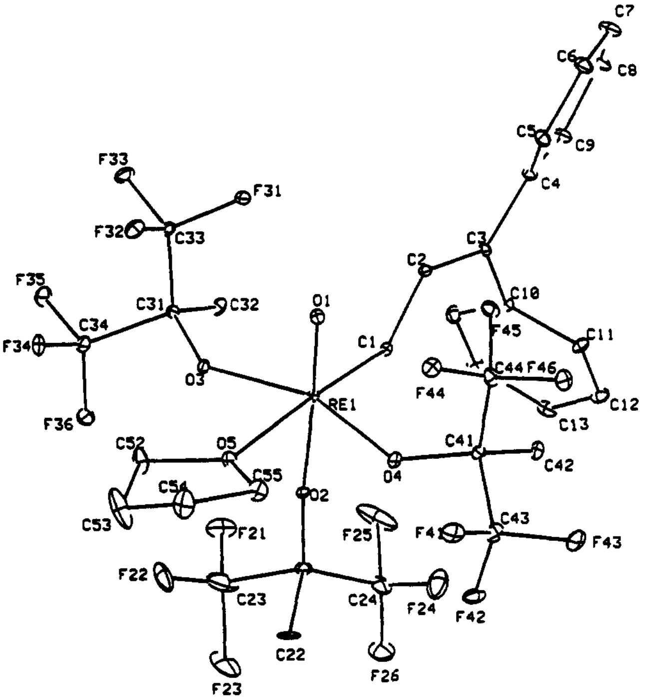


Figure 2. ORTEP drawing of *syn,mer*-ReO[C(H)=CHCPh$_2$][OC(CF$_3$)$_2$CH$_3$]$_3$(THF) (**2b**).

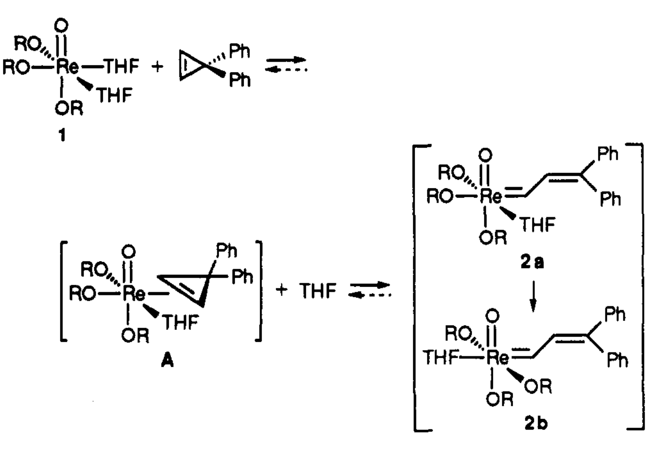
Table 3. Selected Bond Distances and Angles for *syn,mer*-ReO[C(H)CH=CPh$_2$][OC(CF$_3$)$_2$CH$_3$]$_3$(THF) (2b)

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)

(1.674 Å) and Re=C$_\alpha$ (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 a shorter Re–O(2) bond distance (1.909 Å) and a 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.

Isomerization. There are four possible isomers for the stoichiometry ReO[C(H)CH=CPh$_2$][OC(CF$_3$)$_2$Me]$_3$(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 on the basis of 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 Re(C-*t*-Bu)(CH-*t*-Bu)(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; addition of THF does not alter the rate of interconversion.[3b] Therefore, it seems reasonable to identify compound **2a** as the *syn,fac* isomer on the basis of these arguments.

Scheme 1



OR = OC(CF$_3$)$_2$Me

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 the intermediate olefin complex **A**. Though no olefin complexes are observed in the reaction mixture, these species are plausible intermediates on the basis of 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 to or faster than 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 rearrangements 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**, pre-

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(8) When 50 equiv of THF-d_8 was added after 1 min to the freshly prepared mixture of vinylalkylidene species **2a,b** in an NMR tube, a significant decrease in the rate of isomerization ($t_{1/2}$ = 18 h) was observed.

(9) (a) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998. (b) Visser, J. P.; Schipperjin, A. J.; Lukas, J.; Bright, D.; DeBoer, J. *J. Chem. Soc. D* **1971**, 1266. (c) Fredericks, S.; Thomas, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 350. (d) Lehmkuhl, H.; Kruger, P. C.; Tsay, Y. H.; Benn, R.; Mynott, R. *Liebigs Ann. Chem.* **1981**, 1147.

(10) Li, R. T.; Nguyen, S. T.; Grubbs, R. H. Manuscript in preparation.

(11) The isomerization of **2a** to **2b** is written as an irreversible process on the basis of the observation that conversion of pure **2b** to **2a** could not be promoted photochemically or thermally.

sumably the *fac* form, or whether it also is accessed directly by rearrangement of a *mer* olefin complex.

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. On the basis of 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 co-workers 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 $GaBr_3$ and **2b** can metathesize 100 equiv of *cis*-2-pentene at the rate of ~6.7 turnovers min^{-1} at room temperature. The addition of $AlCl_3$, $GaCl_3$, and $B(C_6F_5)_3$ to **2b** also can induce modest metathesis activity, whereas the addition of $AlBr_3$ only results in a slight enhancement of activity. 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 catalyst[16] 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 intermediate[17] 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 NMR (C_6D_6): δ 13.20 (d, Re=C*H*, J = 11 Hz), 9.35 (d, C*H*=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 an adduct, a metal halide, or a cationic complex (*vide supra*) 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 1 h, 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, the 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**. We are currently investigating the metathesis of functionalized and cyclic olefins and the modification of the ligand environment in this system.

Experimental Section

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 H_2SO_4, dried over $MgSO_4$ and CaH_2, and distilled from sodium benzophenone ketyl solubilized with tetraglyme. Dichloromethane and dichloromethane-d_2 (Cambridge Isotopes) were distilled from CaH_2 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. $AlBr_3$, $AlCl_3$, $GaBr_3$, and $GaCl_3$ (Strem) were sublimed prior to use. $KOC(CF_3)_2Me$ was prepared from 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (PCR) and potassium hydride in diethyl ether. $B(C_6F_5)_3$ was prepared from boron trichloride and (pentafluorophenyl)lithium in diethyl ether. $ReOCl_3(PPh_3)_2$[20] and 3,3-diphenylcyclopropene[21] were prepared by literature methods.

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[12] On the basis of ^1H NMR experiments with an internal standard, **2b** is unreactive toward acetone, acetonitrile, benzaldehyde, and ethyl acetate. For example, 10 equiv of benzaldehyde was combined with **2b** (10 mg) in C_6D_6 and monitored over a period of 24 h at 25 °C. There was no significant change measured in the composition of the mixture or the 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.

[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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NMR spectra were recorded on a General Electric QE-300 Plus (^{1}H, 300.10 MHz; ^{13}C, 75.49 MHz) spectrometer. Chemical shifts are reported relative to residual protons in deuterated solvents ($CDHCl_2$, δ 5.32; C_6D_5H, δ 7.15). All coupling constants are reported in Hz. Elemental analyses were performed by Oneida Research Service of Whitesboro, NY.

***fac*-ReO[OC(CF$_3$)$_2$Me]$_3$(THF)$_2$ (1).** $KOC(CF_3)_2Me$ (3.26 g, 14.8 mmol) was added to a stirred suspension of yellow $Re(O)Cl_3(PPh_3)_2$ (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 × 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: ^{1}H 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); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 123.77 (CF_3, J_{CF} = 289), 94.92 ($OCMe(CF_3)_2$, J_{CF} = 29), 73.88 (THF C_α), 25.19 (THF C_β), 16.56 (CH_3). Anal. Calcd for $C_{20}H_{25}F_{18}O_6Re$: C, 27.00; H, 2.83. Found: C, 27.37; H, 2.79.

***syn,mer*-ReO[C(H)CH═CPh$_2$][OC(CF$_3$)$_2$Me]$_3$(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: ^{1}H NMR (CD_2Cl_2) δ 12.15 (d, 1, $Re{=}CH$, J = 11), 9.13 (d, 1, $CH{=}CPh_2$, 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); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 280.13 ($Re{=}CH$, J_{CH} = 1.47), 163.15 ($CH{=}CPh_2$), 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_{CF} = 289), 81.86 and 81.44 ($OC(CF_3)_2Me$), 70.06 (THF C_α), 25.61 (THF C_β), 15.66 (CH_3). Anal. Calcd for $C_{31}H_{29}F_{18}O_5Re$: C, 36.87; H, 2.89. Found: C, 37.07; H, 2.50.

Isomerization of Vinylalkylidene Complexes 2a,b. In this ^{1}H 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. 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, $CH{=}CPh_2$, J = 13); **2b**, δ 12.31 (d, 1, $Re{=}CH$, J = 11), 9.33 (d, 1, $CH{=}CPh_2$, 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 2 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 μL, 100 equiv) and the Lewis acid were added to a solution of **2b** (7.5 mg) and mesitylene (2 μL) in C_6D_6 (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. ^{1}H 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(CF$_3$)$_2$Me]$_3$(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 Kα radiation (λ = 0.710 73 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 1. 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 1. 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═CPh$_2$][OC(CF$_3$)$_2$Me]$_3$(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 1. 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(C—H) = 0.95 Å. The final residuals for **2b** are listed in Table 1. 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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Supplementary Material Available: Tables of final positional and thermal parameters and complete listings of bond distances and angles for 1 and 2 and an additional ORTEP diagram of 2 (14 pages). Ordering information is given on any current masthead page.

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