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# Synthesis, characterization and reactivity of ReOMe<sub>2</sub>(bipy)X complexes

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#### Abstract

The complexes *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)Cl, where *cis* or *trans* refers to the Me–Re–Me regiochemistry, were observed to react as follows: (1) with the alkylating agents RMgCl (R = CH<sub>2</sub>SiMe<sub>3</sub> and CH<sub>2</sub>Ph) and RLi (R = Me) to give ReOMe<sub>2</sub>(bipy)R, and (2) with the alkoxides NaOR' (R' = Me and Et) to give *trans*-ReOMe<sub>2</sub>(bipy)(OR'). The complex ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>SiMe<sub>3</sub> was observed by <sup>1</sup>H NMR spectroscopy to undergo *trans* to *cis* isomerization, which proceeded via reversible first-order kinetics, with  $\Delta H^{\circ} = 1.60(4)$  kcal mol<sup>-1</sup> and  $\Delta S^{\circ} = 3.7(1)$  eu. At room temperature,  $\Delta G^{\circ} = 0.5(1)$  kcal mol<sup>-1</sup> and  $K_{eq} = 0.42(2)$ , indicating a weak thermodynamic preference for the *trans* isomer. The activation parameters for the *trans* to *cis* isomerization were  $\Delta H_1^{\dagger} = 26(2)$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger}_{-1} = 10(7)$  eu, and those for the reverse *cis* to *trans* isomerization were  $\Delta H^{\ddagger}_{-1} = 27(2)$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger}_{-1} = 14(7)$  eu. Treatment of a mixture of *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>SiMe<sub>3</sub> with anhydrous HCl gave ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)Cl; similar treatment of ReOMe<sub>3</sub>(bipy) and ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>Ph gave *cis*-ReOMe<sub>2</sub>(bipy)Cl. Exposure of ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)Cl to AgPF<sub>6</sub> in acetonitrile-d<sub>3</sub> gave the cationic nitrile adduct [ReOMe(bipy)-(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>]. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Rhenium(V); Oxo-alkyl; 2,2'-Bipyridine; Cis-trans isomerization

#### 1. Introduction

Transition-metal alkyl complexes are used to catalyze a variety of important organic transformations such as  $\alpha$ -olefin oligomerization and polymerization [1]. Mechanistic studies have shown, for example, that the polymerization of ethylene by cationic d<sup>0</sup> Ti and Zr complexes proceeds via the intermediacy of alkyl-metal species [2]. The recent use of late transition-metal complexes as catalyst precursors for the Ziegler–Natta polymerization of olefins [3–8] prompted us to examine the development of rhenium alkyl complexes for this purpose [9,10]. We report here the synthesis of ReOMe<sub>2</sub>(bipy)R (R = CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>Ph, and Me) and ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)Cl, explore the kinetics and

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mechanism(s) of the reversible isomerization between *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>SiMe<sub>3</sub>, and show that the removal of the chloride ligand from ReOMe(-bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)Cl in acetonitrile-d<sub>3</sub> affords the corresponding cationic Re(V) alkyl complex, [ReOMe-(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>]. We also prepare and characterize two *trans*-ReOMe<sub>2</sub>(bipy)(OR') complexes.

#### 2. Results and discussion

Scheme 1 summarizes the synthesis of the  $ReOMe_2(bipy)R$  and trans- $ReOMe_2(bipy)(OR')$  complexes starting from a mixture of trans- $ReOMe_2$ -(bipy)Cl (1a) and cis- $ReOMe_2(bipy)Cl$  (1b). For these reactions, the products and the yields were indistinguishable regardless of whether trans (1a) or cis (1b) was used as the starting material. Therefore, to simplify our synthetic efforts, we typically employed a mixture [9] of 1a and 1b in the reactions reported here.

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#### 2.1. Reactions of ReOMe<sub>2</sub>(bipy)Cl with Me<sub>3</sub>SiCH<sub>2</sub>MgCl and PhCH<sub>2</sub>MgCl

The reaction of a mixture of **1a** and **1b** with  $Me_3SiCH_2MgCl$  in diethyl ether afforded a mixture of *trans*-ReOMe\_2(bipy)CH\_2SiMe\_3 (**2a**) and *cis*-ReOMe\_2-(bipy)CH\_2SiMe\_3 (**2b**) in ~ 50% crude yield (Eq. (1)). The pure *trans* isomer **2a** was isolated from the mixture by precipitation as a blue solid from hexanes upon cooling to  $-78^{\circ}C$ . The *cis* isomer **2b**, which remained dissolved in the supernatant at  $-78^{\circ}C$ , could not be separated as a pure compound due to rapid equilibration between the two isomers. At room temperature,



both compounds were observed to be soluble in organic solvents and moderately air stable.

The <sup>1</sup>H NMR spectrum of **2a** in benzene-d<sub>6</sub> exhibited resonances corresponding to the bipy ligand and a singlet at  $\delta$  2.67 corresponding to the methyl groups. The CH<sub>2</sub>SiMe<sub>3</sub> fragment gave rise to two singlets at  $\delta$ 4.81 (CH<sub>2</sub>Si) and 0.69 (SiMe<sub>3</sub>). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2a** showed a resonance at  $\delta$  41.5, which was assigned to the methylene carbon, and resonances at  $\delta$  9.4 and 2.1, which were assigned to the methyl carbons attached to rhenium and silicon, respectively. These data are consistent with a *trans*-Me–Re–Me geometry. We assigned the strong band in the IR spectrum at 978 cm<sup>-1</sup> to the terminal Re=O stretch [11–14].

Upon heating **2a** in benzene, an equilibrating mixture of **2a** and **2b** could be observed by <sup>1</sup>H NMR spectroscopy. The room temperature <sup>1</sup>H NMR spectrum of **2b** in benzene-d<sub>6</sub> exhibited eight resonances arising from the bipy ligand and two distinct singlets at  $\delta$  3.88 and 2.78 arising from the two non-equivalent methyl groups. The CH<sub>2</sub>SiMe<sub>3</sub> fragment gave rise to two doublets at  $\delta$  3.40 and 2.35 (corresponding to the AB quartet arising from the diastereotopic CH<sub>2</sub> group;  $J_{gem} = 11$  Hz) and a singlet at  $\delta$  0.46 (SiMe<sub>3</sub>). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2b** showed a resonance at  $\delta$ 26.4 (assigned to the methylene carbon), resonances at



Scheme 1. Summary of the synthetic work starting from a mixture of 1a and 1b.

stretch [11-14].

Table 1 Kinetic and thermodynamic data for the reversible *cis-trans* isomerization of **2a** and **2b** 

<i>T</i> (°C)	K <sub>eq</sub>	$10^3 k_{\rm obs}$ (min <sup>-1</sup> )	$\frac{10^3 k_1}{(\min^{-1})}$	$\frac{10^3 k_{-1}}{(\min^{-1})}$
55 60 65 75	$\begin{array}{c} 0.56 \pm 0.01 \\ 0.57 \pm 0.02 \\ 0.59 \pm 0.02 \\ 0.64 \pm 0.01 \end{array}$	$18.8 \pm 0.1 \\ 27.2 \pm 0.6 \\ 52 \pm 2 \\ 190.0 \pm 0.5$	$\begin{array}{c} 6.71 \pm 0.01 \\ 9.9 \pm 0.2 \\ 19.2 \pm 0.8 \\ 74.1 \pm 0.2 \end{array}$	$\begin{array}{c} 12.06 \pm 0.01 \\ 17.3 \pm 0.4 \\ 32 \pm 1 \\ 115.9 \pm 0.3 \end{array}$



Fig. 1. van't Hoff plot of the reversible cis-trans isomerization of **2a** and **2b** over the temperature range 55–75°C.

 $\delta$  21.7 and 12.9 (assigned to the two non-equivalent methyl carbons attached to rhenium), and a resonance at  $\delta$  2.0 (assigned to the three equivalent methyl carbons attached to silicon). These data are consistent with a *cis*-Me-Re-Me geometry. We assigned the strong band in the IR spectrum at 982 cm<sup>-1</sup> to the terminal Re=O stretch [11–14].

Treatment of a mixture of **1a** and **1b** with PhCH<sub>2</sub>MgCl in toluene at  $-78^{\circ}$ C gave *cis*-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>Ph (**3**), which could be precipitated from hexanes by cooling to  $-78^{\circ}$ C, affording a blue powder in  $\sim 53\%$  yield. Compound **3** was found to be stable upon heating to  $75^{\circ}$ C in benzene-d<sub>6</sub>, and showed no evidence of *cis* to *trans* isomerization.

The <sup>1</sup>H NMR spectrum for **3** in benzene-d<sub>6</sub> exhibited the expected resonances arising from the bipy ligand and two distinct singlets at  $\delta$  3.97 and 2.90 arising from the two non-equivalent methyl groups. The CH<sub>2</sub>Ph ligand gave rise to two doublets at  $\delta$  5.73 and 3.94 (corresponding to the AB quartet arising from the diastereotopic CH<sub>2</sub> group;  $J_{gem} = 12$  Hz). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **3** showed a resonance at  $\delta$  32.4, which was assigned to the methylene carbon, and reso-

#### 2.2. Reaction of ReOMe<sub>2</sub>(bipy)Cl with MeLi

The reaction of a mixture of **1a** and **1b** with MeLi in  $CH_2Cl_2$  at  $-78^{\circ}C$  gave ReOMe<sub>3</sub>(bipy) (4) as a blue– green powder in 92% yield (see Scheme 1). The <sup>1</sup>H NMR and IR spectroscopic data were consistent with those reported previously for this complex [12,15].

### 2.3. Reaction of ReOMe<sub>2</sub>(bipy)Cl with sodium alkoxides

Treatment of a mixture of **1a** and **1b** in either benzene or toluene with an excess of sodium methoxide or ethoxide gave dark green *trans*-ReOMe<sub>2</sub>(bipy)(OR') complexes in low yields (Eq. (2)).



The compounds **5a** and **5b** were soluble in benzene and toluene and slightly soluble in hexanes. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **5a** and **5b** were consistent with a *trans*-Me–Re–Me geometry, and no *trans* to *cis* isomerization was detected (cf. **3**). The strong bands in the IR spectra of **5a** at 949 cm<sup>-1</sup> and of **5b** at 951 cm<sup>-1</sup> were assigned to the terminal Re=O stretches [11–14].

### 2.4. Kinetics of the reversible cis-trans isomerization of **2a** and **2b**

Complexes **2a** and **2b** were observed to exist as an equilibrium mixture in solution. Upon dissolving pure **2a** in benzene-d<sub>6</sub>, the rate of equilibration (or isomerization) was observed to increase with increasing temperature. To further examine the process, we monitored the rate of isomerization of **2a** to **2b** by <sup>1</sup>H NMR spectroscopy. Both the loss of **2a** and the appearance of **2b** could be modeled using standard reversible first-order kinetics [16]. The kinetic and thermodynamic data obtained from this model are listed in Table 1. The equilibrium constants indicate that **2a** is thermodynamically favored in this equilibrium. Fig. 1 shows a van't Hoff plot of  $\ln(K_{eq})$  versus 1/T, which gives  $\Delta H^{\circ} = 1.60(4)$  kcal mol<sup>-1</sup> and  $\Delta S^{\circ} = 3.7(1)$  eu. Fig. 2 shows Eyring plots of  $\ln(k_1/T)$  versus 1/T and  $\ln(k_{-1}/T)$ 

versus 1/T, which provide activation parameters of  $\Delta H_1^{\ddagger} = 26(2)$  kcal mol<sup>-1</sup> and  $\Delta S_{-1}^{\ddagger} = 10(7)$  eu for the forward isomerization and  $\Delta H_{-1}^{\ddagger} = 27(2)$  kcal mol<sup>-1</sup> and  $\Delta S_{-1}^{\ddagger} = 14(7)$  eu for the reverse process.

We previously reported analogous kinetic studies of the *cis-trans* isomerization of  $\text{ReOMe}_2(\text{bipy})\text{Cl}$  [9]. Given the similarities of the two systems, we believe that the mechanism of the present isomerization is analogous to that proposed for the  $\text{ReOMe}_2(\text{bipy})\text{Cl}$ system [9]. assigned to the terminal Re=O stretch [11–14]. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6** exhibited a resonance at  $\delta$  43.3, which were assigned to the methylene carbon, and resonances at  $\delta$  2.0 and 1.3, which was assigned to the methyl carbons attached to rhenium and silicon, respectively. Comparison of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6** to that of **4** and of ReO(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(bipy) [17] suggests that that **6** possesses structure **6a**, although structures **6b** and **6c** cannot be ruled out. Repeated attempts to obtain crystals of **6** suitable for X-ray crystallographic analysis were unsuccessful.



#### 2.5. Reaction of ReOMe<sub>2</sub>(bipy)R with anhydrous HCl

After bubbling anhydrous HCl for 1 min into a mixture of **2a** and **2b** dissolved in  $CH_2Cl_2$ , the complex ReOMe(bipy)( $CH_2SiMe_3$ )Cl (**6**) was isolated as a red-purple powder in ~ 90% yield (Eq. (3)).

The <sup>1</sup>H NMR spectrum of **6** in CD<sub>2</sub>Cl<sub>2</sub> exhibited a resonance at  $\delta$  4.66 arising from the methyl group attached to rhenium, and the CH<sub>2</sub>SiMe<sub>3</sub> ligand gave rise to two doublets at  $\delta$  7.34 and 6.92 (corresponding to the AB quartet arising from the diastereotopic CH<sub>2</sub> group;  $J_{gem} = 7$  Hz) and a singlet at  $\delta$  0.16 (SiMe<sub>3</sub>). The strong band in the IR spectrum at 993 cm<sup>-1</sup> was



Fig. 2. Eyring plots of the reversible cis-trans isomerization of **2a** and **2b** over the temperature range 55–75°C.

Similar treatment of **3** and **4** with anhydrous HCl in  $CH_2Cl_2$  afforded *cis*-ReOMe<sub>2</sub>(bipy)Cl (**1b**) as the exclusive product as judged by <sup>1</sup>H NMR spectroscopy. Consequently, it appears that for these trialkyl rhenium complexes, the  $-CH_2Ph$  group is more readily lost from the Re center than is the  $-CH_3$  group, which is lost more readily than the  $-CH_2SiMe_3$  group.

## 2.6. Reaction of $ReOMe(bipy)(CH_2SiMe_3)Cl$ with $AgPF_6$

Treatment of **6** with AgPF<sub>6</sub> in acetonitrile-d<sub>3</sub> gave the green salt [ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>] (7) in ~99% yield as judged by <sup>1</sup>H NMR spectroscopy (Eq. (4)).

$$6 + AgPF_6 \xrightarrow[CD_3CN]{} OBC$$

 $[\text{ReOMe(bipy)(CH}_2\text{SiMe}_3)(\text{CD}_3\text{CN})][\text{PF}_6] + \text{AgCl} \quad (4)$ 

The salt was isolated as a dark blue-green oily powder that was insoluble in benzene, toluene, and hexanes. The salt was thermally stable to 60°C in acetonitrile, but readily decomposed when exposed to air. At room temperature under nitrogen in the solid state, the salt turned from a blue-green oily powder to a dark brown residue that was not characterized. The <sup>1</sup>H NMR spectrum for 7 in acetonitrile-d<sub>3</sub> exhibited a singlet at  $\delta$  4.43 arising from the methyl group attached to rhenium as well as the expected aromatic resonances. The CH<sub>2</sub>SiMe<sub>3</sub> ligand gave rise to two doublets at  $\delta$  7.26 and 6.80 (corresponding to the AB quartet arising from the diastereotopic  $CH_2$  group;  $J_{gem} = 8$  Hz) and a singlet at  $\delta$  0.12 (SiMe<sub>3</sub>). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 7 showed a resonance at  $\delta$  42.8, which was assigned to the methylene carbon, and a resonance at  $\delta$  11.9, which was assigned to the methyl carbon attached to rhenium. The methyl carbons of SiMe<sub>3</sub> could not be assigned due to overlapping resonances from CD<sub>3</sub>CN at  $\delta$  1.3. We assigned the band in the IR spectrum at 2272 cm<sup>-1</sup> to the C=N stretch of coordinated acetonitrile, which is distinct from the C=N bands of free acetonitrile (2294 and 2255 cm<sup>-1</sup>) [18]. The IR spectrum also exhibited broad overlapping bands over the region 790–1000 cm<sup>-1</sup>, precluding definitive assignment of the Re=O stretch. This latter spectral feature has been observed in related cationic rhenium(V) oxo-alkyl complexes [12]. From spectroscopic data alone, we cannot distinguish between the three plausible isomers of 7 shown below. We were unable to obtain crystals of 7 that were suitable for X-ray crystallographic analysis.



ReOMe<sub>2</sub>(2,2'-bipyridine)Cl (0.10 g, 0.24 mmol) was dissolved in diethyl ether (50 ml). The solution was frozen in liquid nitrogen, and Me<sub>3</sub>SiCH<sub>2</sub>MgCl (0.25 mmol) was added via microsyringe. The mixture was allowed to warm slowly to room temperature (r.t.). The solution gradually turned green over a period of 12 h. The green mixture was then filtered through a glass frit to remove a fine dark precipitate. The solvent was removed under vacuum, and the residue was extracted with hexanes (4 × 6 ml). The extracts were combined, and the volatiles removed under vacuum, giving a mixture of *cis* 

#### 3. Conclusions

The results presented here demonstrate a facile approach to the synthesis of a new class of rhenium oxo-alkyl complexes that contain chelating nitrogen ligands. Alkyl and alkoxide substitution of the chlorine atom from ReOMe<sub>2</sub>(bipy)Cl affords rhenium(V) oxo-trialkyl and alkoxide complexes, respectively. The oxo-trialkyl compounds react with anhydrous HCl to give halogenated complexes. Abstraction of the chlorine atom from ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)Cl with AgPF<sub>6</sub> in CD<sub>3</sub>CN affords the cationic rhenium(V) oxo-alkyl complex [ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>].

#### 4. Experimental

Unless otherwise stated, all reactions were performed using standard Schlenk and glovebox techniques. All glassware was either flame-dried under argon or ovendried. Solvents were purified by standard techniques and stored over molecular sieves under argon. The compounds *trans*-ReOMe<sub>2</sub>(bipy)Cl (**1a**) and *cis*-ReOMe<sub>2</sub>(bipy)Cl (**1b**) were prepared as described previously [9]. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 MHz instrument and referenced internally to the known resonances of the solvents. High resolution mass spectrometry (HRMS) was performed at Rice University on a Finniganmat MAT 95 spectrometer operating in the EI mode.

### 4.1. Preparation of ReOMe<sub>2</sub>(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>) (**2a** and **2b**)

In a Schlenk flask, a mixture of cis- and trans-

and *trans* isomers as a dark blue–green powder (0.05 g, 50%). The dark blue–green powder was re-dissolved in hexanes (15 ml), and the volume of the solution was reduced by ca. a half. A blue precipitate formed after cooling the resulting solution for 6 h at  $-78^{\circ}$ C. The green supernatant was removed via cannula, and the residue was dried under vacuum to give pure *trans*-ReOMe<sub>2</sub>(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>) (**2a**) as a blue solid (yield 0.03 g, 30%). A mixture of *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>) in a 9:1 ratio (**2b**:**2a**, respectively) was further obtained as a green powder by removing the volatiles from the supernatant under vacuum.

#### 4.1.1. Analytical data for

#### trans-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>SiMe<sub>3</sub> (2a)

<sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  8.88 (dd, 1H,  $J_{HH} = 5$ ,  $J_{HH} = 3$ Hz, bipy), 7.93 (d, 1H,  $J_{HH} = 6$  Hz, bipy), 7.17 (dd, 1H,  $J_{HH} = 6$ ,  $J_{HH} = 4$  Hz, bipy), 6.72 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 6.50 (dt, 1H,  $J_{HH} = 7$ ,  $J_{HH} = 1$  Hz, bipy), 6.19 (m, 2H, bipy), 5.87 (dt, 1H,  $J_{HH} = 7$  Hz,  $J_{HH} = 1$  Hz, bipy), 4.81 (s, 2H,  $CH_2SiMe_3$ ), 2.67 (s, 6H,  $ReMe_2$ ), 0.69 (s, 9H,  $CH_2SiMe_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ ): 151.0, 150.6, 147.3, 146.5, 135.8, 135.2, 123.0, 121.6, 121.3, 121.1, 41.5 ( $CH_2SiMe_3$ ), 9.4 ( $ReMe_2$ ), 2.1 ( $CH_2SiMe_3$ ). IR (KBr, Nujol, cm<sup>-1</sup>): 1603 s, 1311 w, 1238 m, 1159 w, 1157 w, 1018 w, 978 s, 954 s, 851 s, 835 s, 758 s, 740 m, 723 m. *Anal.* Calc. for  $C_{16}H_{25}N_2OSiRe$ : C, 40.40; H, 5.30; N, 5.89. Found: C, 40.72; H, 5.21; N, 5.89%.

# 4.1.2. Analytical data for cis-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>SiMe<sub>3</sub>(2b)

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.81 (d, 1H,  $J_{HH} = 6$  Hz, bipy), 7.77 (d, 1H,  $J_{HH} = 5$  Hz, bipy), 7.19 (d, 1H,  $J_{HH} = 8$ Hz, bipy), 6.72 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 6.56 (dt, 1H,  $J_{HH} = 8$ ,  $J_{HH} = 1$  Hz, bipy), 6.27 (dt, 1H,  $J_{HH} = 6$ ,  $J_{\rm HH} = 1$  Hz, bipy), 6.18 (dt, 1H,  $J_{\rm HH} = 8$ ,  $J_{\rm HH} = 1$  Hz, bipy), 5.84 (dt, 1H,  $J_{\rm HH} = 7$ ,  $J_{\rm HH} = 1$  Hz, bipy), 3.88 (s, 3H, Re*Me*), 3.40 (d, 1H, 11 Hz, CH<sub>2</sub>SiMe<sub>3</sub>), 2.78 (s, 3H, Re*Me*), 2.35 (d, 1H, 11 Hz, CH<sub>2</sub>SiMe<sub>3</sub>), 0.46 (s, 9H, CH<sub>2</sub>Si*Me*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 150.3, 146.6, 146.5, 145.9, 139.0, 135.4, 123.7, 121.9, 121.8, 121.0, 26.4 (CH<sub>2</sub>SiMe<sub>3</sub>), 21.7 (Re*Me*), 12.9 (Re*Me*), 2.0 (CH<sub>2</sub>Si*Me*<sub>3</sub>). IR (KBr, Nujol, cm<sup>-1</sup>): 1605 s, 1330 s, 1259 m, 1240 s, 1159 m, 1016 m, 982 vs, 909 w, 851 s, 832 s, 812 s, 760 s, 725 m, 712 m. A satisfactory analysis was not obtained. *Anal.* Calc. for C<sub>16</sub>H<sub>25</sub>N<sub>2</sub>OSiRe: C, 40.40; H, 5.30; N, 5.89. Found: C, 39.82; H, 5.03; N, 5.66%.

#### 4.2. Preparation of cis-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>Ph (3)

In a Schlenk flask, a mixture of cis- and trans-ReOMe<sub>2</sub>(2,2'-bipyridine)Cl (0.17 g, 0.40 mmol) was dissolved in toluene (50 ml). The solution was cooled to - 78°C, and PhCH<sub>2</sub>MgCl (0.40 mmol of a 1 M solution in diethyl ether) was added via a microsyringe. The mixture was allowed to warm slowly to r.t. The solution gradually became deep green over a period of 12 h. The resulting solution was then filtered through a glass frit to remove a fine dark precipitate. The volatiles were removed under vacuum, and the residue was extracted with benzene  $(4 \times 6 \text{ ml})$ . The extracts were combined, and the benzene was removed under vacuum. The resulting dark green solid was extracted with hexanes  $(4 \times 15 \text{ ml})$ , and the extracts combined and filtered. The volume of the extracts was reduced in half and then cooled to  $-78^{\circ}$ C for 12 h to give a blue precipitate. The green supernatant was removed via cannula and the blue precipitate was dried under vacuum to give 0.10 g (53% yield) of cis-ReOMe<sub>2</sub>(bipy)CH<sub>2</sub>Ph. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.55 (dd, 1H,  $J_{HH} = 5$ ,  $J_{HH} = 1$  Hz, bipy), 7.75 (d, 1H,  $J_{\rm HH} = 6$  Hz, bipy), 6.88 (d, 1H,  $J_{\rm HH} = 7$  Hz, bipy), 6.64 (d, 1H,  $J_{\rm HH} = 8$  Hz, bipy), 6.56-6.47 (m, 4 H), 6.22-6.10 (m, 4 H), 5.90 (dt, 1H,  $J_{\rm HH} = 7$ ,  $J_{\rm HH} = 1$  Hz, bipy), 5.73 (d, 1H,  $J_{\rm HH} = 12$  Hz, CH<sub>2</sub>Ph), 3.97 (s, 3H, ReCH3), 3.94 (d, 1H,  $J_{HH} = 12$ Hz,  $CH_2Ph$ ), 2.90 (s, 3H,  $ReCH_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 153.8, 149.6, 149.5, 146.2, 145.1, 135.0, 134.2, 126.8, 126.7, 122.3, 121.2, 121.1, 120.9, 120.0, 32.4 (CH<sub>2</sub>Ph), 21.3 (ReMe; trans to equatorial N), 9.4 (ReMe; cis to equatorial N). IR (KBr, Nujol,  $cm^{-1}$ ): 1605 s, 1312 m, 1261 m, 1209 m, 1157 m, 1045 m, 1015 m, 999 m, 970 vs, 909 w, 756 vs, 723 m, 700 s. HRMS Calc. for  $C_{18}H_{18}N_2ORe [M-15]^+$ : 465.0979. Found: 465.0982.

#### 4.3. Preparation of ReOMe<sub>3</sub>(bipy) (4)

In a Schlenk flask, a mixture of *cis*- and *trans*-ReOMe<sub>2</sub>(2,2'-bipyridine)Cl (0.31 g, 0.74 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and cooled to  $-78^{\circ}$ C. An

aliquot of MeLi (0.75 mmol in hexanes) was added via syringe. The mixture was allowed to warm to r.t., and the initially dark solution gradually became blue–green over a period of 3 h. The volatile components were removed under vacuum and the residue extracted with benzene ( $5 \times 20$  ml). The extracts were combined and filtered. The solvent was removed from the filtrate under vacuum to yield 0.27 g of ReOMe<sub>3</sub>(bipy) as a blue–green powder (90% yield). The IR and <sup>1</sup>H NMR spectra were consistent with those reported in the literature [15,18]. We report the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum collected in C<sub>6</sub>D<sub>6</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 150.4, 149.7, 146.9, 145.9, 135.9, 135.1, 122.8, 121.9, 121.4, 121.1, 21.2 (Re*Me*), 8.8 (Re*Me*<sub>2</sub>).

#### 4.4. Preparation of trans-ReOMe<sub>2</sub>(bipy)(OMe) (5a)

In a Schlenk flask, a mixture of cis- and trans-ReOMe<sub>2</sub>(2,2'-bipyridine)Cl (0.10 g, 0.24 mmol) and NaOMe (2 equiv.) was dissolved in either benzene or toluene (20 ml). The dark purple solution slowly turned to turquoise over a period of 15 h. The volatile components were removed under reduced pressure, and the residue was extracted with hexanes  $(4 \times 5 \text{ ml})$  and filtered. The solvent was removed from the filtrate under vacuum to yield trans-ReOMe<sub>2</sub>(bipy)(OMe) (5a) as a blue-green powder (yield 0.04 g, 40%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.59 (d, 1H,  $J_{\rm HH} = 6$  Hz, bipy), 8.02 (d, 1H,  $J_{\rm HH} = 6$  Hz, bipy), 7.30 (d, 1H,  $J_{\rm HH} = 8$  Hz, bipy), 6.83 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 6.56 (dt, 1H,  $J_{HH} = 9$ ,  $J_{HH} =$ 1 Hz, bipy), 6.20 (dt, 1H,  $J_{HH} = 8$ ,  $J_{HH} = 1$  Hz, bipy), 6.03 (dt, 1H,  $J_{HH} = 8$ ,  $J_{HH} = 1$  Hz, bipy), 5.84 (dt, 1H,  $J_{\rm HH} = 6, J_{\rm HH} = 1$  Hz, bipy), 5.25 (s, 3H, OMe), 2.27 (s, 6H, Re $Me_2$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 149.2, 146.9, 146.4, 145.9, 136.0, 135.2, 122.3, 121.4, 121.0, 120.5, 69.1 (ReOMe), 16.1 (Re $Me_2$ ). IR (KBr, Nujol, cm<sup>-1</sup>): 1604 s, 1566 m, 1314 m, 1263 m, 1240 m, 1159 m, 1030 s, 1003 m, 949 vs, 912 m, 758 vs, 725 s. Anal. Calc. for C<sub>13</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Re: C, 37.22; H, 4.08; N, 6.68. Found: C, 37.43; H, 3.85; N, 6.35%.

#### 4.5. Preparation of trans-ReOMe<sub>2</sub>(bipy)(OEt) (5b)

This compound was prepared using the method used to prepare **5a**. The complex was isolated as a blue– green powder (yield 0.05 g, 50%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 8.59 (d, 1H,  $J_{HH} = 6$  Hz, bipy), 8.16 (d, 1H,  $J_{HH} = 5$ Hz, bipy), 7.30 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 6.82 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 6.56 (dt, 1H,  $J_{HH} = 8$ ,  $J_{HH} = 1$  Hz, bipy), 6.19 (dt, 1H,  $J_{HH} = 7$ ,  $J_{HH} = 1$  Hz, bipy), 6.02 (dt, 1H,  $J_{HH} = 7$ ,  $J_{HH} = 1$  Hz, bipy), 5.83 (dt, 1H,  $J_{HH} = 6$ ,  $J_{HH} = 1$  Hz, bipy), 5.43 (q, 2H,  $J_{HH} = 7$  Hz, OCH<sub>2</sub>Me), 2.28 (s, 6H, ReMe<sub>2</sub>), 1.76 (t, 3H, 7 Hz, OCH<sub>2</sub>Me). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 149.2, 147.8, 146.6, 145.8, 136.0, 135.2, 122.3, 121.4, 120.9, 120.5, 74.7 (ReOCH<sub>2</sub>CH<sub>3</sub>), 21.0 (ReOCH<sub>2</sub>CH<sub>3</sub>), 16.2 (ReMe<sub>2</sub>). IR (KBr, Nujol, cm<sup>-1</sup>): 1603 s, 1566 m, 1310 m, 1262 m, 1155 m, 1092 m, 1045 s, 1001 m, 951 vs, 908 m, 758 s, 723 s. *Anal.* Calc. for C14H19N2O2Re: C, 38.79; H, 4.42; N, 6.46. Found: C, 38.76; H, 4.42; N, 6.46%.

#### 4.6. Preparation of $ReOMe(bipy)(CH_2SiMe_3)Cl$ (6)

In a Schlenk flask, a mixture of cis- and trans-ReOMe<sub>2</sub>(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>) (0.10 g, 0.21 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml). Over the course of 1 min, HCl was bubbled through the solution. The initially blue-green solution became red, and the volatiles were removed under vacuum. The residue was extracted with benzene  $(3 \times 20 \text{ ml})$ , and the extracts were combined and filtered. The volatiles were removed from the filtrate under vacuum to give a red-purple powder (0.09 g, 90%), which could be recrystallized from a mixture of benzene/hexanes (1/3) at r.t. to give dark red crystals of 6. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.03 (d, 1H, J<sub>HH</sub> = 6 Hz, bipy), 8.33 (m, 2H, bipy), 7.82 (d, 1H,  $J_{\rm HH} = 8$ Hz, bipy), 7.90 (d, 1H,  $J_{\rm HH} = 7$  Hz, bipy), 7.58 (dt, 1H,  $J_{\rm HH} = 7$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.48 (dt, 1H,  $J_{\rm HH} = 8$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.34 (d, 1H,  $J_{\rm HH} = 7$  Hz,  $CH_2SiMe_3$ ), 7.06 (dt, 1H,  $J_{HH} = 7$ ,  $J_{HH} = 1$  Hz, bipy), 6.92 (d, 1H,  $J_{\rm HH} = 7$  Hz,  $CH_2SiMe_3$ ), 4.66 (s, 3H, Re*Me*), 0.16 (s, 9H, CH<sub>2</sub>Si*Me*<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (CD2Cl2): 154.9, 150.5, 148.1, 140.9, 141.0, 138.7, 125.9, 124.0, 122.9, 121.6, 43.3 (CH<sub>2</sub>SiMe<sub>3</sub>), 2.0 (ReMe), 1.3  $(CH_2SiMe_3)$ . IR (KBr, Nujol, cm<sup>-1</sup>): 1605 s, 1570 w, 1313 m, 1240 s, 1159 w, 1022 w, 993 s, 961 m, 849 s, 831 s, 762 s, 707 m, 680 m. Anal. Calc. for C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>OSiReCl: C, 36.32; H, 4.47; N, 5.65. Found: C, 36.21; H, 4.32; N, 5.67%.

## 4.7. Preparation of [ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>] (7)

In a nitrogen-filled glove box, ReOMe(bipy)-(CH<sub>2</sub>SiMe<sub>3</sub>)Cl (10 mg) and 1.5 equiv. of AgPF<sub>6</sub> were weighed into a weighing dish and then dissolved in acetonitrile- $d_3$ . The resulting green solution was transferred to a NMR tube, which was then capped with a rubber septum. <sup>1</sup>H NMR spectra were recorded and integrated relative to C<sub>6</sub>Me<sub>6</sub> as an internal standard, which indicated a 99% yield of the cationic Re(V) complex, [ReOMe(bipy)(CH<sub>2</sub>SiMe<sub>3</sub>)(CD<sub>3</sub>CN)][PF<sub>6</sub>]. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  8.93 (d, 1H,  $J_{HH} = 6$  Hz, bipy), 8.53 (d, 1H,  $J_{HH} = 6$  Hz, bipy), 8.51 (d, 1H,  $J_{HH} = 8$  Hz, bipy), 8.32 (d, 1H,  $J_{\rm HH} = 8$  Hz, bipy), 8.07 (dt, 1H,  $J_{\rm HH} = 8$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.95 (dt, 1H,  $J_{\rm HH} = 8$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.72 (dt, 1H,  $J_{\rm HH} = 7$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.47 (dt, 1H,  $J_{\rm HH} = 7$ ,  $J_{\rm HH} = 1$  Hz, bipy), 7.26 (d, 1H,  $J_{\rm HH} = 8$  Hz,  $CH_2 SiMe_3$ ), 6.80 (d, 1H,  $J_{\rm HH} = 8$  Hz, CH<sub>2</sub>SiMe<sub>3</sub>), 4.43 (s, 3H, ReMe), 0.12 (s, 9H,  $CH_2SiMe_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 151.5, 150.2, 143.1, 142.6, 142.2, 127.8, 127.3, 127.2, 124.8, 124.6,

124.1, 42.8 ( $CH_2SiMe_3$ ), 11.9 (ReMe). IR (KBr, CD<sub>3</sub>CN solution, cm<sup>-1</sup>): 2303 s, 2272 s, 2255 s, 1607 m, 1319 m, 1246 m, 1163 w, 1125 w, 1038 m, 1005 m, 837 vs, 770 m, 559 m. Due to the solid-state lability of 7 (vide supra), an elemental analysis was not attempted.

### 4.8. Kinetics and thermodynamic studies of the reversible isomerization of **2a** and **2b**

The isomerization of 2a to 2b was monitored by <sup>1</sup>H NMR spectroscopy. Solutions of 2a in benzene- $d_6$  were heated in sealed NMR tubes directly in the probe cavity. The initial concentration of 2a varied between 0.034 and 0.066 M. Periodically, <sup>1</sup>H NMR spectra were recorded, and the methyl resonances of 2a and 2b were integrated relative to 0.001 M C<sub>6</sub>Me<sub>6</sub> as an internal standard. The temperature was held within  $\pm 0.1$  °C of one of the following temperatures: 55, 60, 65 and 75°C. The isomerization reaction followed reversible first-order kinetics approaching equilibrium and showed fits of data to a common plot of  $-\ln\{1 - [cis]/[cis]_{eq}\}$  versus time [16]. The equilibrium constants at each temperature were obtained when no further change in each spectrum was observed. The errors in these values were estimated from typical linear regression analysis [19,20].

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