

# Synthesis of *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)Cl and related cationic oxorhenium(v) complexes

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The purpose of this study was to prepare high oxidation-state rhenium oxomethyl complexes, including cationic compounds, and test selected examples for olefin polymerization activity. Reaction of ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl with pyridine *N*-oxide and 2,2'-bipyridine (bipy) gave *cis*-ReOMe<sub>2</sub>(bipy)Cl. Conversely, treatment of ReO(bipy)Cl<sub>3</sub> with AlMe<sub>3</sub> gave *trans*-ReOMe<sub>2</sub>(bipy)Cl. The compound *cis*-ReOMe<sub>2</sub>(bipy)Cl isomerized quantitatively to *trans*-ReOMe<sub>2</sub>(bipy)Cl upon heating in benzene ( $\Delta H^\ddagger = 29(3)$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = 6(9)$  e.u.; at 79 °C,  $k_{\text{obs}} = 1.34(9) \times 10^{-2}$  min<sup>-1</sup> and  $t_{1/2} = 52$  min). Reaction of *cis*-ReOMe<sub>2</sub>(bipy)Cl with AgX (X<sup>-</sup> = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, or BPh<sub>4</sub><sup>-</sup>) in acetonitrile gave the cationic acetonitrile adducts [ReOMe<sub>2</sub>(bipy)(CH<sub>3</sub>CN)]X. Treatment of the PF<sub>6</sub><sup>-</sup> salt with PR<sub>3</sub> (PR<sub>3</sub> = PMe<sub>3</sub>, P(OMe)<sub>3</sub>, PMe<sub>2</sub>Ph, P(*n*-Bu)<sub>3</sub>, and PMePh<sub>2</sub>) yielded the cationic PR<sub>3</sub> adducts *cis*-[ReOMe<sub>2</sub>(bipy)(PR<sub>3</sub>)]PF<sub>6</sub>. The BF<sub>4</sub><sup>-</sup> salt of the PMe<sub>3</sub> adduct, *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]BF<sub>4</sub>, was prepared by the reaction of ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl with [Ag(CH<sub>3</sub>CN)<sub>2</sub>][BF<sub>4</sub>] in acetonitrile followed by treatment with bipy in CH<sub>2</sub>Cl<sub>2</sub>. Single crystal X-ray crystallographic analyses of *cis*-ReOMe<sub>2</sub>(bipy)Cl, *trans*-ReOMe<sub>2</sub>(bipy)Cl, and *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]BF<sub>4</sub> revealed that they have distorted octahedral structures. Analogs of *cis*-ReOMe<sub>2</sub>(bipy)Cl, *trans*-ReOMe<sub>2</sub>(bipy)Cl, and *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]BF<sub>4</sub> were also prepared in which the bipy ligand was replaced with 1,10-phenanthroline (phen). An additional analog of *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]BF<sub>4</sub> was prepared in which the bipy ligand was replaced by 4,4'-dimethyl-2,2'-bipyridine. In preliminary experiments, ethylene was polymerized using both *cis*-ReOMe<sub>2</sub>(bipy)Cl and *trans*-ReOMe<sub>2</sub>(bipy)Cl as catalyst precursors.

## Introduction

Group 4 cationic alkyl metallocenes serve as highly active catalysts for the Ziegler–Natta polymerization of olefins.<sup>1,2</sup> Their catalytic activity is, however, substantially diminished upon exposure to polar functional groups, especially those containing oxygen.<sup>3–5</sup> In a different catalytic system, Schrock and co-workers have shown that rhenium-based olefin-metathesis catalysts are substantially more tolerant of polar functional groups than their early transition metal congeners.<sup>6–9</sup> On the basis of Schrock's observations and the recent successful use of late transition-metal complexes as catalyst precursors for olefin polymerization,<sup>10–15</sup> we felt that appropriately designed rhenium alkyl complexes might serve as functional-group-tolerant catalysts for the Ziegler–Natta polymerization of olefins. Furthermore, we reasoned that effective rhenium-based catalysts would require the following four components. First, a labile ligand that could be readily removed to afford a vacant coordination site on the metal center (to permit binding of the olefin). Second, a geometry that, upon being made coordinatively unsaturated, would leave an alkyl group adjacent to the vacant site (to permit olefin insertion and propagation). Third, a cationic metal center in a high oxidation state (to promote coordination of the olefin). Fourth, a stable ligand in the Re coordination sphere that could be easily tuned sterically and electronically, such as bipyridine and its derivatives.

There are few examples of cationic high oxidation-state rhenium–alkyl complexes.<sup>16</sup> We therefore targeted the development and study of a new class of complexes designed to meet our objectives. We report here the synthesis of *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)Cl, explore the kinetics and mechanism(s) of the thermal *cis* to *trans* isomerization, and show that the removal of the chlorine ligand from *cis*-ReOMe<sub>2</sub>(bipy)Cl yields coordinatively unsaturated cationic intermediates that can be trapped by acetonitrile. We also describe preliminary studies of the

polymerization of ethylene using *cis* and *trans*-ReOMe<sub>2</sub>(bipy)Cl as catalyst precursors, and demonstrate multiple pathways for the preparation of the cationic phosphine adducts *cis*-[ReOMe<sub>2</sub>(bipy)(PR<sub>3</sub>)]X.

## Results and discussion

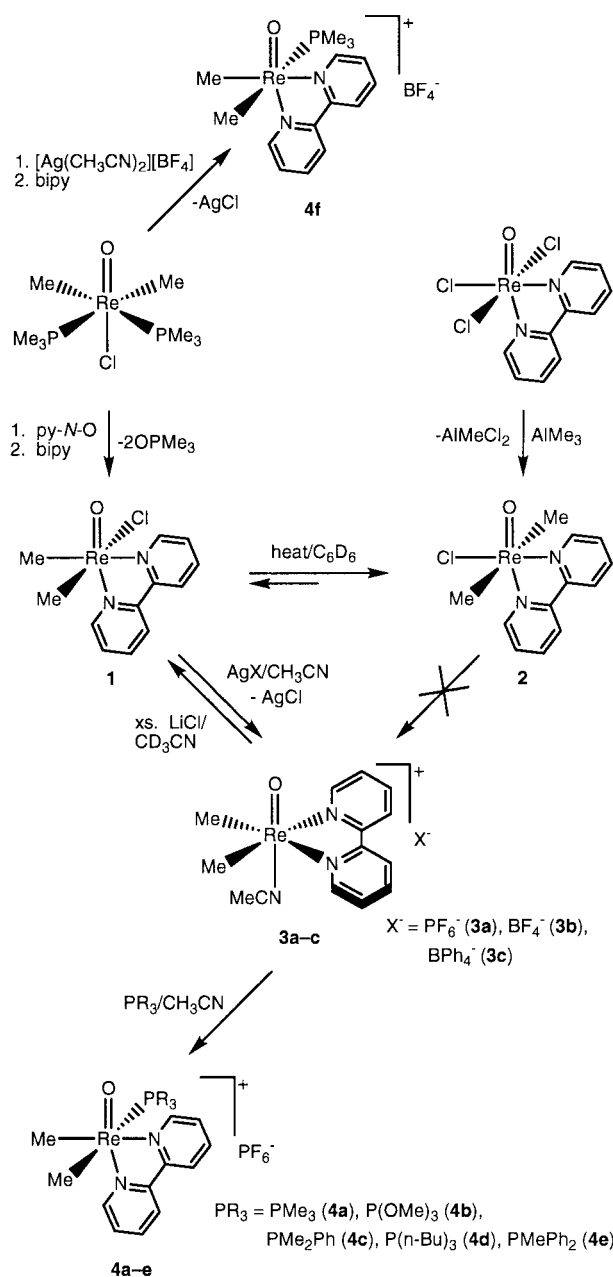
A summary of our synthetic results is presented in Scheme 1. A detailed description of the results and our corresponding observations are provided below.

### Synthesis of *cis*- and *trans*-ReOMe<sub>2</sub>(bipy)Cl

The compound *cis*-ReOMe<sub>2</sub>(bipy)Cl (**1**) was prepared by the reaction of ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl<sup>17</sup> with 2 equivalents of pyridine *N*-oxide and 1 equivalent of 2,2'-bipyridine in benzene. Crystallization from a saturated solution in benzene gave brown plates that were insoluble in *n*-pentane and hexanes. The 1,10-phenanthroline analog of **1**, *cis*-ReOMe<sub>2</sub>(phen)Cl, was prepared similarly.

The compound *trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**) was prepared by the reaction of ReOCl<sub>3</sub>(bipy) with 1 equivalent of AlMe<sub>3</sub> in dichloromethane at –78 °C. Upon crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexanes, **2** was obtained as brown crystals that were insoluble in hexanes and *n*-pentane. The 1,10-phenanthroline analog of **2**, *trans*-ReOMe<sub>2</sub>(phen)Cl, was prepared similarly. Compound **2** was also prepared by thermally isomerizing **1** in benzene (see below).

Crystal structures of **1** (Fig. 1) and **2** (Fig. 2) were determined. The crystal data are presented in Table 1, and selected bond distances and angles are given in Tables 2 and 3, respectively. Compounds **1** and **2** possess distorted octahedral geometries in the solid state. In both structures, the Re–O,<sup>17–24</sup> Re–C<sup>17–20</sup> and Re–Cl<sup>17,21–24</sup> bond lengths are within the ranges of reported distances. The dative Re–N(1) bonds, which are *trans* to the triply bonded oxo ligands, are approximately 0.2 Å



Scheme 1

longer than the Re–N(2) bonds due to the strong *trans* influence of the oxo group. The Re atoms are displaced in the direction of the oxo ligands by 0.38 (1) and 0.42 (2) Å from the planes defined by C(11), C(12), N(2), and Cl.

In **1**, the O–Re–Cl and O–Re–C(12) bond angles, 101.5(4)° and 103.2(6)°, respectively, are slightly larger than the O–Re–C(11) and O–Re–N(2) bond angles, 98.3(5)° and 96.9(5)°, respectively, indicating that the oxo group is tilted slightly toward the pyridine moiety and the methyl group adjacent to it. In **2**, the O–Re–Cl, O–Re–C(11), and O–Re–C(12) bond angles, 101.8(3)°, 107.8(4)°, and 105.2(4)°, respectively, are markedly larger than the O–Re–N(2) bond angle, 90.9(5)°, indicating that here too the oxo group is tilted toward the pyridine fragment.

The room temperature  $^1\text{H}$  NMR spectra for **1** and **2** exhibited two and one resonance(s), respectively, arising from the methyl groups; spectra for both compounds also exhibited resonances arising from the eight bipy hydrogens. The IR spectra for the two compounds each showed one strong band that can be assigned to the Re–O stretch ( $989\text{ cm}^{-1}$  (**1**) and  $968\text{ cm}^{-1}$  (**2**)). These data are consistent with the solid state structures of **1** and **2**.

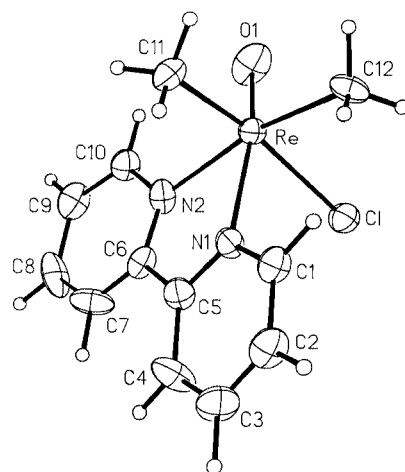


Fig. 1 Thermal ellipsoid plot of *cis*-ReOMe<sub>2</sub>(bipy)Cl (**1**) showing the atomic numbering scheme (40% probability ellipsoids with the hydrogens as spheres of arbitrary diameter).

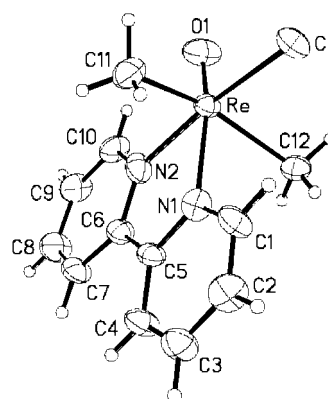


Fig. 2 Thermal ellipsoid plot of *trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**) showing the atomic numbering scheme (40% probability ellipsoids with the hydrogens as spheres of arbitrary diameter).

### Kinetics and mechanism(s) for the isomerization of *cis*-ReOMe<sub>2</sub>(bipy)Cl to *trans*-ReOMe<sub>2</sub>(bipy)Cl

Heating **1** in benzene-*d*<sub>6</sub> gave **2** as the sole product. The rate of isomerization, as measured quantitatively by  $^1\text{H}$  NMR spectroscopy, exhibited a first-order dependence on the concentration of **1**. The rate constant at 79 °C was calculated to be  $1.34(9) \times 10^{-2}\text{ min}^{-1}$  with  $t_{1/2} = 52\text{ min}$ . The data from the isomerization at several temperatures are shown in Fig. 3 in the form of an Eyring plot, which yielded  $\Delta H^\ddagger = 29(3)\text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 6(9)\text{ e.u.}$

To probe the mechanism of the isomerization, three separate solutions of **1** in benzene-*d*<sub>6</sub> containing approximately 2, 5, and 10 equivalents of bipyridine were monitored at 79 °C. The rates of isomerization were indistinguishable from the rate observed in the absence of added bipyridine. These results and the small positive entropy of activation for the process suggest that complete dissociation of the bipyridine ligand plays no role in the rate-determining step for the isomerization. A pathway that involves dissociation of a single nitrogen of the bipy ligand, however, might be involved.<sup>25</sup> Dissociation of the weak Re–N bond *trans* to the oxo ligand would yield a five-coordinate intermediate that could undergo rearrangements to move the methyl ligands into a mutually *trans* configuration followed by reattachment of the bipy nitrogen (Scheme 2). A “least motion” pathway through a TBPY structure in which both nitrogens remain attached to Re and the midpoint between the nitrogens defines an apical position *trans* to the oxo ligand also cannot be excluded. A pathway involving an intermediate with a *trans*-Me–Re=O configuration is unlikely given that this type of struc-

**Table 1** Crystal data for *cis*-ReOMe<sub>2</sub>(bipy)Cl·C<sub>6</sub>H<sub>6</sub> (**1**·C<sub>6</sub>H<sub>6</sub>), *trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**) and *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)][BF<sub>4</sub>] (**4f**)

Compound	<b>1</b> ·C <sub>6</sub> H <sub>6</sub>	<b>2</b>	<b>4f</b>
Empirical formula	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> OCIRe·C <sub>6</sub> H <sub>6</sub>	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> OCIRe	C <sub>15</sub> H <sub>23</sub> N <sub>2</sub> OPRe <sup>+</sup> BF <sub>4</sub> <sup>-</sup>
<i>M</i>	502.05	423.90	551.38
Crystal dimensions/mm	0.22 × 0.50 × 0.60	0.32 × 0.30 × 0.25	0.30 × 0.45 × 0.65
Space group	<i>P</i> <sub>2</sub> <sub>1</sub> (monoclinic)	<i>P</i> <sub>2</sub> <sub>1</sub> (monoclinic)	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i> (monoclinic)
<i>a</i> /Å	6.600(3)	11.835(1)	12.085(4)
<i>b</i> /Å	8.153(5)	7.599(1)	12.811(4)
<i>c</i> /Å	16.932(9)	15.037(2)	12.714(4)
$\beta$ /°	93.12(4)	97.60(1)	93.89(3)
<i>T</i> /°C	-50	-50	-50
<i>Z</i>	2	4	4
<i>V</i> /Å <sup>3</sup>	910	1340.5(3)	1964
<i>D</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.83	2.1	1.86
$\mu$ /cm <sup>-1</sup>	69.2	92.49	63.9
<i>R</i> , <i>R</i> <sub>w</sub>	0.038, 0.039	0.019, 0.051	0.048, 0.042

**Table 2** Selected bond distances (Å) and angles (°) for *cis*-ReOMe<sub>2</sub>(bipy)Cl (**1**·C<sub>6</sub>H<sub>6</sub>)

Re–O1	1.672(11)	Re–C1	2.428(3)
Re–N1	2.321(11)	Re–N2	2.134(12)
Re–C11	2.111(14)	Re–C12	2.180(13)
O1–Re–C1	101.5(4)	C11–Re–C1	160.1(4)
O1–Re–C11	98.3(5)	C12–Re–C1	86.6(4)
O1–Re–C12	103.2(6)	C12–Re–N1	90.7(4)
O1–Re–N2	96.9(5)	C12–Re–N2	159.9(5)
O1–Re–N1	166.1(5)	C1–Re–N1	78.2(3)
C11–Re–C12	86.9(5)	C1–Re–N2	90.3(3)
C11–Re–N2	89.3(5)	N1–Re–N2	69.3(4)
C11–Re–N1	83.1(5)		

**Table 3** Selected bond distances (Å) and angles (°) for *trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**)

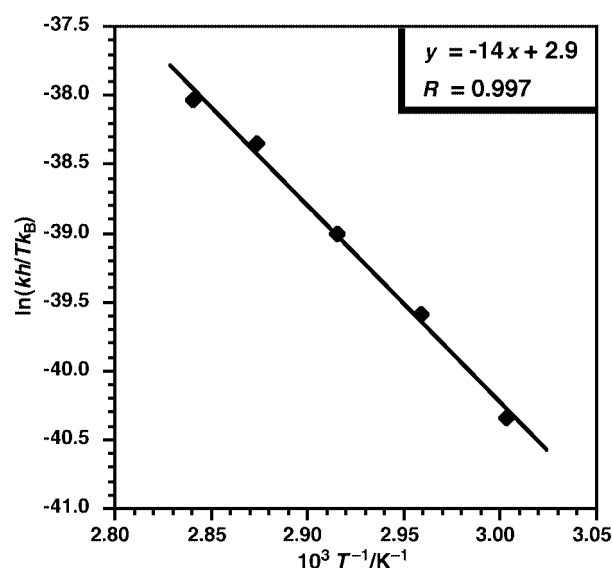
Re–O1	1.644(9)	Re–C1	2.421(4)
Re–N1	2.264(10)	Re–C11	2.140(10)
Re–N2	2.051(12)	Re–C12	2.158(10)
O1–Re–C11	107.8(4)	C11–Re–N1	75.5(4)
O1–Re–C12	105.2(4)	C12–Re–C1	82.9(3)
O1–Re–C1	101.8(3)	C12–Re–N2	96.1(4)
O1–Re–N2	90.9(5)	C12–Re–N1	75.0(3)
O1–Re–N1	164.4(4)	C1–Re–N1	93.7(3)
C11–Re–C12	146.0(4)	C1–Re–N2	167.1(4)
C11–Re–C1	82.5(4)	N1–Re–N2	73.7(5)
C11–Re–N2	91.6(5)		

ture is unprecedented for transition metal oxo alkyls, and is probably disfavored energetically.

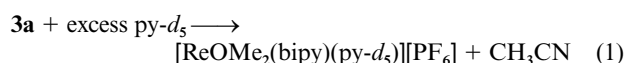
### Synthesis and NMR characterization of [ReOMe<sub>2</sub>(bipy)-(CH<sub>3</sub>CN)]X **3**

The reaction of **1** with AgX (X = PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and BPh<sub>4</sub><sup>-</sup>) in acetonitrile gave the cationic Re(v) complexes [ReOMe<sub>2</sub>(bipy)-(CH<sub>3</sub>CN)]X (**3a–c**). The compounds were isolated as dark blue-green oily powders, which were insoluble in benzene, toluene, and hexanes. When stored at room temperature in the glove box, the compounds decomposed over a period of 24 h. For this reason, elemental analyses were not attempted. The complexes were thermally stable in acetonitrile, however, and although sensitive to the presence of oxygen as solids and in solution, they were soluble and remarkably stable in degassed water.

The reaction of **3a** with excess LiCl in CD<sub>3</sub>CN regenerated compound **1** (Scheme 1). To determine the number of CH<sub>3</sub>CN ligands coordinated in **3**, we treated **3a** with excess pyridine-*d*<sub>5</sub> in benzene-*d*<sub>6</sub> (eqn. (1)), and monitored the initially heterogeneous exchange reaction by <sup>1</sup>H NMR spectroscopy. Integration of the CH<sub>3</sub>CN resonance *versus* an internal standard

**Fig. 3** Eyring plot of the isomerization of **1** to **2**, where *k* is the rate constant, *h* is Planck's constant, *k<sub>B</sub>* is Boltzmann's constant, and *T* is the temperature in Kelvin.

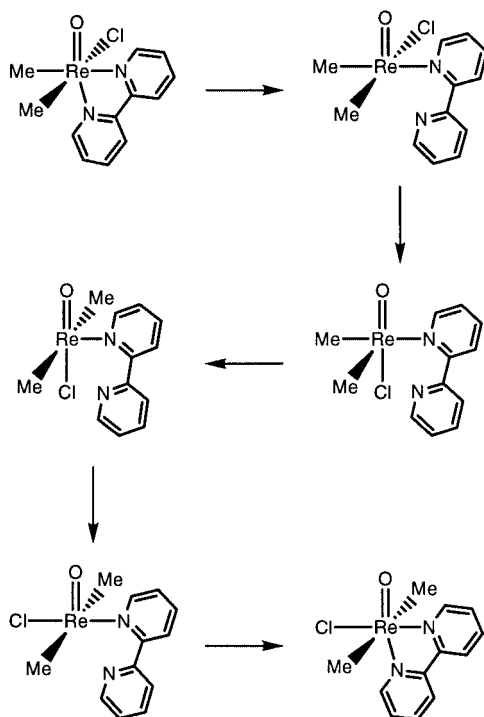
(C<sub>6</sub>Me<sub>6</sub>) indicated that one CH<sub>3</sub>CN group was attached to Re, which is consistent with the proposed formulation of **3**.



The <sup>1</sup>H NMR spectra of **3a–c** in CD<sub>3</sub>CN and **3a** in CD<sub>2</sub>Cl<sub>2</sub> at temperatures as low as -70 °C indicated in all cases that the methyl groups were equivalent, and that the bipy ligand was bisected by a mirror plane rendering the two halves of the ligand equivalent. These data are consistent with the structure shown in Scheme 1. It should be noted, however, that the analogous compound [ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]<sup>+</sup>, which we characterize below by X-ray crystallography, possesses a *cis* Me–Re–Me configuration. If **3** possesses a structure similar to [ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)]<sup>+</sup>, a low energy fluxional process could perhaps rationalize the NMR spectra observed for **3**.

### Synthesis of *cis*-[ReOMe<sub>2</sub>(bipy)(PR<sub>3</sub>)]PF<sub>6</sub> (**4a–e**)

Reactions of **3a** with PMe<sub>3</sub>, P(OMe)<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, PMe<sub>2</sub>Ph, and PMePh<sub>2</sub> in CH<sub>3</sub>CN afforded the complexes *cis*-[ReOMe<sub>2</sub>(bipy)(PR<sub>3</sub>)]PF<sub>6</sub> (**4a–e**). As judged by <sup>1</sup>H NMR spectroscopy, the reaction failed to give analogs of **4** when phosphines with large cone angles<sup>26</sup> (e.g., PPh<sub>3</sub>, PCy<sub>3</sub>, P(*i*-Pr)<sub>3</sub>, and P(*t*-Bu)<sub>3</sub>) were used. Complexes **4a** and **4b** dissolved readily in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, and THF but not in *n*-pentane, hexanes, benzene, or diethyl ether. While the solubility of complexes **4a** and **4b** was



Scheme 2

similar to that of **4c–e**, the latter complexes also exhibited slight solubility in benzene and diethyl ether. In contrast to **1**, complexes **4a–e** failed to convert to the *trans* isomer upon heating. The *cis* configuration of **4b**, for example, was maintained even upon heating to 100 °C for more than 3 h in CD<sub>3</sub>CN. It is not clear why the *cis* isomer of **4** is apparently more stable than the *trans* geometry given that the opposite preference is shown by ReOMe<sub>2</sub>(bipy)Cl (*i.e.*, **2** is thermodynamically favored over **1**).

The PR<sub>3</sub> adducts **4a–e** were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Resonances were assigned based on NMR spectroscopic studies of the analogous structurally characterized BF<sub>4</sub><sup>−</sup> salt, *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>−</sup> (see next section). The assignments of the Re–methyl resonances are presented in Table 4 for each adduct.

#### Synthesis and X-ray structure determination of *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>−</sup> (**4f**)

The complex *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>−</sup> (**4f**) was prepared by the reaction of ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl with [Ag(CH<sub>3</sub>CN)<sub>2</sub>] [BF<sub>4</sub>]<sup>−</sup> and 2,2′-bipyridine in acetonitrile. Alternatively, **4f** was prepared from **1** by reaction with [Ag(CH<sub>3</sub>CN)<sub>2</sub>] [BF<sub>4</sub>]<sup>−</sup> in acetonitrile followed by the addition of PMe<sub>3</sub>. The compound dissolved readily in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN but not in hexanes, benzene, or diethyl ether.

Crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether produced moderately air-sensitive brown crystals of **4f**, which were characterized by X-ray crystallography. A thermal ellipsoid plot is shown in Fig. 4, the crystal data are presented in Table 1, and selected bond distances and angles are provided in Table 5. Compound **4f** possesses a distorted octahedral geometry with *cis* methyl groups. The Re–O, Re–C and Re–N bond lengths are not markedly different from those of neutral **1** and **2**. The Re–P bond length, 2.439(4) Å, is within the range of reported values.<sup>17–19,21–23,27</sup> As observed in **1** and **2**, the Re–N(2) bond length is *ca.* 0.2 Å longer than the Re–N(1) bond length due to the *trans* influence of the oxo group. The O–Re–C(1) and O–Re–C(2) bond angles, 104.1(6)° and 101.0(6)°, respectively, are slightly larger than the O–Re–P and O–Re–N(1) bond angles, 99.0(4)° and 97.4(5)°, indicating that the oxo group is slightly tilted toward the PMe<sub>3</sub> and bipy ligands.

The room temperature <sup>1</sup>H NMR spectrum of **4f** in

Table 4 NMR data for the methyl groups of [ReOMe<sub>2</sub>(bipy)(PR<sub>3</sub>)]<sub>n</sub>X<sub>n−4</sub><sup>−a</sup>

	<sup>1</sup> H NMR (ppm)	<sup>13</sup> C- <sup>1</sup> H NMR (ppm)
<b>4a</b>	4.16 (d, <i>J</i> <sub>PH</sub> = 6.6 Hz)	
	2.87 (d, <i>J</i> <sub>PH</sub> = 2.1 Hz)	
<b>4b</b>	4.01 (d, <i>J</i> <sub>PH</sub> = 5.4 Hz)	12.1 (d, <i>J</i> <sub>PC</sub> = 8.1 Hz)
	2.69 (d, <i>J</i> <sub>PH</sub> = 3.6 Hz)	26.0 (d, <i>J</i> <sub>PC</sub> = 29.3 Hz)
<b>4c</b>	4.15 (d, <i>J</i> <sub>PH</sub> = 6.0 Hz)	12.9 (d, <i>J</i> <sub>PC</sub> = 3.8 Hz)
	2.88 (d, <i>J</i> <sub>PH</sub> = 1.2 Hz)	20.2 (d, <i>J</i> <sub>PC</sub> = 22.9 Hz)
<b>4d</b>	4.24 (d, <i>J</i> <sub>PH</sub> = 6.3 Hz)	14.1 (d, <i>J</i> <sub>PC</sub> = 4.7 Hz)
	2.93 (d, <i>J</i> <sub>PH</sub> = 1.2 Hz)	21.6 (d, <i>J</i> <sub>PC</sub> = 21.9 Hz)
<b>4e</b>	4.50 (d, <i>J</i> <sub>PH</sub> = 7.2 Hz)	15.4 (d, <i>J</i> <sub>PC</sub> = 4.0 Hz)
	3.21 (d, <i>J</i> <sub>PH</sub> = 1.2 Hz)	20.2 (d, <i>J</i> <sub>PC</sub> = 22.8 Hz)
<b>4f</b>	4.15 (d, <i>J</i> <sub>PH</sub> = 6.6 Hz)	12.9 (d, <i>J</i> <sub>PC</sub> = 3.8 Hz)
	2.86 (d, <i>J</i> <sub>PH</sub> = 2.1 Hz)	20.0 (d, <i>J</i> <sub>PC</sub> = 19.4 Hz)

<sup>a</sup> Data shown are for the PF<sub>6</sub><sup>−</sup> salts except for **4f** (the BF<sub>4</sub><sup>−</sup> analog of **4a**). For each compound, the data in the top row correspond to the Me group *cis* to the PR<sub>3</sub> ligand, and those in the bottom row correspond to the Me group *trans* to the PR<sub>3</sub> ligand.<sup>17</sup>

Table 5 Selected bond distances (Å) and angles (°) for *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>−</sup> (**4f**)

Re–O	1.674(10)	Re–P	2.439(4)
Re–C1	2.092(16)	Re–C2	2.067(15)
Re–N2	2.302(10)	Re–N1	2.131(9)
O–Re–P	99.0(4)	C1–Re–P	156.7(5)
O–Re–N1	97.4(5)	N1–Re–C2	161.4(5)
O–Re–C1	104.1(6)	N2–Re–C2	91.0(5)
O–Re–C2	101.0(6)	P–Re–C2	87.3(4)
O–Re–N2	167.9(4)	P–Re–N1	92.9(3)
C1–Re–C2	85.6(6)	P–Re–N2	79.9(3)
C1–Re–N1	87.0(5)	N1–Re–N2	70.8(4)
C1–Re–N2	78.1(5)		

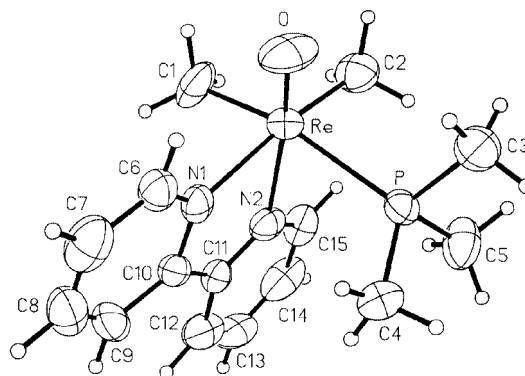


Fig. 4 Thermal ellipsoid plot of the cation from *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>−</sup> (**4f**) showing the atomic numbering scheme (40% probability ellipsoids with the hydrogens as spheres of arbitrary diameter).

acetonitrile-*d*<sub>3</sub> exhibited two doublets arising from the two methyl groups in addition to a doublet arising from the three methyl groups of the PMe<sub>3</sub> ligand. Resonances attributable to bipyridine were also observed. Coupling to phosphorus was maintained on the NMR time scale at room temperature, which is inconsistent with rapid dissociation of the ligand. The Re–Me group *cis* to PMe<sub>3</sub> appeared at δ 4.15 (d, *J*<sub>PH</sub> = 6.6 Hz) in the <sup>1</sup>H NMR spectrum and at δ 12.9 (d, *J*<sub>CP</sub> = 3.8 Hz) in the <sup>13</sup>C NMR spectrum. In contrast, the Re–Me group *trans* to PMe<sub>3</sub> appeared at δ 2.86 (d, *J*<sub>PH</sub> = 2.1 Hz) in the <sup>1</sup>H NMR spectrum and δ 20.0 (d, *J*<sub>CP</sub> = 19.4 Hz) in the <sup>13</sup>C NMR spectrum.<sup>17</sup> The <sup>31</sup>P NMR spectrum for **4f** showed only one resonance at δ −34.9. We assign the strong band in the IR spectrum at 993 cm<sup>−1</sup> to the terminal Re=O stretch. The spectroscopic data are consistent with the solid state structure.

Analogs of **4f** in which the bipy ligand was replaced by 1,10-phenanthroline (phen) and 4,4′-dimethyl-2,2′-bipyridine (4,4′-

Me<sub>2</sub>bipy) were prepared by a procedure similar to the one used to prepare **4f**. The room temperature <sup>1</sup>H and <sup>13</sup>C NMR spectra for both *cis*-[ReOMe<sub>2</sub>(phen)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>-</sup> and *cis*-[ReOMe<sub>2</sub>(4,4'-Me<sub>2</sub>bipy)(PMe<sub>3</sub>)] [BF<sub>4</sub>]<sup>-</sup> in CD<sub>3</sub>CN exhibited two distinct Re–methyl groups, which is consistent with the assigned *cis* Me–Re–Me configuration.

### Polymerization of ethylene by using **1** and **2** as catalyst precursors

The addition of *ca.* 3400 equivalents of methylaluminoxane (MAO) to a solution of *ca.* 5 μmol of **1** or **2** in toluene formed a homogeneous green solution, suggesting the abstraction of the chlorine ligand.<sup>28</sup> Saturation of this solution with ethylene at 140 psi for 30 min yielded, after workup, a small amount (*e.g.*, 0.02–0.05 g) of polyethylene (PE). Control experiments in which **1** and **2** were omitted afforded substantially less PE (*e.g.*, 0.001 g). The calculated activities were typically 0.8–2.1 g of PE (mmol of cat)<sup>-1</sup> atm<sup>-1</sup> h<sup>-1</sup>. Attempts to polymerize ethylene by using **3a**, **3c** or **4a** as catalyst and an ethylene pressure of 1–2 atm failed to produce polymer.

In practice, the polymerization of ethylene can proceed *via* either free radical or coordination polymerization mechanisms.<sup>29,30</sup> The free-radical mechanism, however, typically requires minimum pressures of *ca.* 500 atmospheres of ethylene.<sup>31</sup> Given the relatively low pressures of ethylene employed in the present work (140 psi), we can reasonably exclude the participation of the free radical pathway in the studies reported here. Although the observed activities are low compared to the recently reported Ni and Pd catalyst systems,<sup>10,12</sup> the present work represents, to our knowledge, the first examples of rhenium-based catalysts that effect the coordination polymerization of olefins. We anticipate an increase in catalytic activity through modification of the rhenium ligand environment.

### Conclusion

The results presented here demonstrate the synthesis of neutral rhenium oxomethyl complexes that contain chelating nitrogen ligands. Abstraction of the chlorine atom from these complexes affords coordinatively unsaturated cationic species in which a methyl moiety is adjacent to the vacant site. The cationic complexes are soluble and stable in water. Preliminary studies suggest that the complexes catalyze (albeit poorly) the coordination polymerization of ethylene.

### Experimental

Unless otherwise stated, all reactions were performed in flame-dried or oven-dried glassware by using standard Schlenk and glovebox techniques. Toluene and benzene were distilled from Na. Dichloromethane was distilled from CaH<sub>2</sub>. Hexanes, THF, and diethyl ether were distilled from Na/benzophenone and stored over molecular sieves under argon until they were needed. Rhenium metal was purchased from Cleveland Refectory Materials and used as received. MAO (10% in toluene) was purchased from Aldrich. The compounds ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl and ReO(bipy)Cl<sub>3</sub> were prepared as described in the literature.<sup>17,24</sup> The complex ReO(phen)Cl<sub>3</sub> was prepared using a modification of the literature procedure.<sup>21</sup> NMR spectra were recorded on a 300-MHz instrument. Phosphorus NMR spectra were referenced to external H<sub>3</sub>PO<sub>4</sub> with positive chemical shifts reported downfield of this resonance.

### Syntheses

***cis*-ReOMe<sub>2</sub>(bipy)Cl (**1**)**. ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl (0.17 g, 0.40 mmol) was dissolved in benzene (40 mL), and pyridine *N*-oxide (0.077 g, 0.81 mmol) was added to the solution. The brown solution changed slowly to red-orange over a period of 8 h. An

aliquot of 2,2'-bipyridine (0.063 g, 0.40 mmol) was then added, giving a deep red solution that gradually turned to deep red-purple over a period of 40 h. The mixture was then filtered through a glass frit to remove dark precipitates. The filtrate was evaporated to dryness under reduced pressure, and the residue was washed (3 × 20 mL) with a mixture of hexane/benzene (3:1) to remove OPMe<sub>3</sub>. The remaining solid was held under vacuum for 4 h and then dissolved in benzene (50 mL). The volume of the solution was reduced under vacuum to *ca.* 15 mL. Dark red-brown plates crystallized from solution after 12 h at room temperature (yield 0.080 g, 60%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.93 (d, 1 H, *J* = 5.7 Hz, bipy), 8.34 (d, 1 H, *J* = 8.1 Hz, bipy), 8.18 (d, 1 H, *J* = 5.4 Hz, bipy), 7.91 (d, 1 H, *J* = 7.8 Hz, bipy), 7.81 (dt, 1 H, *J* = 7.5 Hz, *J* = 0.9 Hz, bipy), 7.59 (dt, 1 H, *J* = 6.9 Hz, *J* = 1.2 Hz, bipy), 7.44 (dt, 1 H, *J* = 8.1 Hz, *J* = 0.9 Hz, bipy), 7.09 (dt, 1 H, *J* = 6.3 Hz, *J* = 0.9 Hz, bipy), 5.19 (s, 3 H, ReMe), 4.91 (s, 3 H, ReMe). <sup>13</sup>C-<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 155 (s, bipy), 150.5 (s, bipy), 150.6 (s, bipy), 147 (s, bipy), 141 (s, bipy), 138 (s, bipy), 126 (s, bipy), 124 (s, bipy), 123 (s, bipy), 122 (s, bipy), 18.6 (s, ReMe), 10.8 (s, ReMe). IR (KBr, Nujol, cm<sup>-1</sup>): 1606 m, 1342 w, 1313 w, 1238 m, 1188 w, 989 s, 908 w, 819 m, 787 s, 726 s. Calc. for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>OClRe·*x*C<sub>6</sub>H<sub>6</sub>: C, 36.30; H, 3.48; N, 6.36. Found: C, 36.57; H, 3.26; N, 5.92%. The value of *x* (0.22) was determined in CD<sub>3</sub>CN by integration of the <sup>1</sup>H NMR resonance of benzene *vs.* those of ReOMe<sub>2</sub>(bipy)Cl.

***trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**)**. Into a 200 mL Schlenk reaction flask was added ReO(bipy)Cl<sub>3</sub> (1.00 g, 2.15 mmol) and 100 mL of dichloromethane. This suspension was cooled to -78 °C, and AlMe<sub>3</sub> (1.10 mL, 2.20 mmol, 2 M in toluene) was added slowly *via* syringe. The mixture was stirred at room temperature for 2 h. The volatile materials were removed under vacuum, and the residue was extracted with toluene (5 × 20 mL). The toluene solution was filtered through a glass frit. Vacuum distillation afforded a brown powder that was subjected to flash chromatography in air (alumina, 10 cm × 2.5 cm). Elution with dichloromethane produced a clearly visible red band on the column. Evaporation of the fractions corresponding to the red band gave *trans*-ReOMe<sub>2</sub>(bipy)Cl as a brown powder (yield 0.42 g, 46% yield). Crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/hexanes (1:5, 20 mL) at room temperature (24 h) gave the product as brown crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.57 (d, 1 H, *J* = 7.8 Hz, bipy), 8.21 (d, 1 H, *J* = 5.7 Hz, bipy), 8.09 (d, 1 H, *J* = 7.8 Hz, bipy), 7.83 (m, 2 H, bipy), 7.39 (m, 2 H, bipy), 6.98 (m, 1 H, bipy), 2.92 (s, 6 H, ReMe<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 151 (s, bipy), 147.4 (s, bipy), 147.1 (s, bipy), 147.0 (s, bipy), 140 (s, bipy), 137 (s, bipy), 124 (s, bipy), 123 (s, bipy), 122 (s, bipy), 121 (s, bipy), 10.8 (s, ReMe). IR (KBr, Nujol, cm<sup>-1</sup>): 1604 s, 1568 m, 1315 m, 1276 w, 1261 m, 1236 w, 1195 w, 1157 w, 1045 w, 1024 w, 1005 w, 968 s, 918 w, 761 s, 725 m. Calc. for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>OClRe: C, 34.00; H, 3.33; N, 6.60. Found: C, 34.01; H, 3.07; N, 7.11%.

***cis*-ReOMe<sub>2</sub>(phen)Cl**. The complex ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl (0.010 g, 0.024 mmol) was dissolved in toluene (5 mL), and pyridine *N*-oxide (0.004 g, 0.05 mmol) was added. The brown solution changed slowly to red-orange over a period of 2 h. The solvent was removed under reduced pressure, and the residue was dried for 3 h. The residue was then dissolved in toluene (5 mL), and 1,10-phenanthroline (0.004 g, 0.024 mmol) was added to the orange solution. The resulting deep red solution turned gradually to deep red-purple over a period of 8 h. The mixture was filtered through a glass frit. The filtrate was evaporated to dryness under reduced pressure, and the residue was washed with a mixture of benzene/hexane (1:3, 6 × 10 mL) to remove OPMe<sub>3</sub>. The resulting solid was held under vacuum for 4 h and then extracted into cold (<0 °C) diethyl ether (30 mL). The cold extracts were filtered through a glass frit, and the resulting deep blue solution was evaporated to dryness under vacuum to give

the product as a deep purple powder (0.004 g, 40%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.07 (d, 1 H,  $J = 5.1$  Hz, phen), 8.58 (d, 1 H,  $J = 4.8$  Hz, phen), 8.50 (d, 1 H,  $J = 8.4$  Hz, phen), 8.13–8.00 (m, 3 H, phen), 7.60–7.53 (m, 2 H, phen), 5.54 (s, 3 H, ReMe), 5.15 (s, 3 H, ReMe).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CDCl}_3$ ):  $\delta$  150, 147, 142, 140, 137, 135.0, 131, 129, 128.5, 126, 125, 122, 19.1 (ReMe), 0.3 (ReMe). IR (KBr,  $\text{cm}^{-1}$ ): 1629 m, 1577 m, 1516 m, 1429 s, 1300 m, 1248 m, 1145 m, 1109 m, 1057 w, 997 m, 956 s, 908 s, 848 s, 723 s.

**trans-ReOMe<sub>2</sub>(phen)Cl.** This compound was prepared by a procedure analogous to that used for the preparation of **2**. The compound was isolated as a purple powder in 55% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.60 (dd, 1 H,  $J = 5.4$  Hz,  $J = 1.2$  Hz, phen), 8.26 (dd, 1 H,  $J = 8.1$  Hz,  $J = 1.5$  Hz, phen), 8.09 (d, 1 H,  $J = 9$  Hz, phen), 7.93 (m, 2 H, phen), 7.78 (dd, 1 H,  $J = 8.1$  Hz,  $J = 5.7$  Hz, phen), 7.59 (d, 1 H,  $J = 8.7$  Hz, phen), 7.34 (dd, 1 H,  $J = 5.7$  Hz,  $J = 8.1$  Hz, phen), 3.10 (s, 6 H, ReMe<sub>2</sub>).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CDCl}_3$ ):  $\delta$  147, 145, 139, 135, 130, 129.0, 128.9, 128.3, 128.2, 126, 123, 121, 9.7 (ReMe). IR (KBr,  $\text{cm}^{-1}$ ): 3086 w, 3053 w, 2926 vs, 2858 s, 1629 m, 1601 m, 1577 m, 1429 s, 1249 m, 1190 m, 1145 m, 1124 m, 1080 w, 1058 w, 974 s, 912 m, 844 s, 759 m, 717 s. Calc. for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{OClRe}$ : C, 37.54; H, 3.15; N, 6.25. Found: C, 37.91; H, 2.70; N, 6.54%.

**[ReOMe<sub>2</sub>(bipy)(CH<sub>3</sub>CN)][PF<sub>6</sub>] (3a).** Cold acetonitrile (20 mL,  $<0^\circ\text{C}$ ) was added to a mixture of **1** (0.020 g, 0.047 mmol) and  $\text{AgPF}_6$  (0.013 g, 0.047 mmol). The solution turned green, and a white precipitate appeared. The mixture was warmed slowly to room temperature as it was stirred (1 h), and then the mixture was filtered. The filtrate was evaporated to dryness under vacuum to give the product as a blue-green oily powder (yield 0.014 g, 53%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.75 (d, 2 H,  $J = 5.7$  Hz, bipy), 8.42 (d, 2 H,  $J = 8.1$  Hz, bipy), 8.03 (t, 2 H,  $J = 7.5$  Hz, bipy), 7.67 (t, 2 H,  $J = 6.3$  Hz, bipy), 4.75 (s, 6 H, ReMe), 1.96 (s, 3 H, CH<sub>3</sub>CN).  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  155, 151, 143, 128, 125, 13.3. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1606 s, 1305 w, 1165 w, 1074 (br), 966 s, 839 s, 765 w, 723 s, 688 m, 584 s.

**[ReOMe<sub>2</sub>(bipy)(CH<sub>3</sub>CN)][BF<sub>4</sub>] (3b).** This compound was prepared by a procedure analogous to that used to prepare **3a**.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.76 (d, 2 H,  $J = 6.5$  Hz, bipy), 8.45 (d, 2 H,  $J = 8.1$  Hz, bipy), 8.05 (t, 2 H,  $J = 7.8$  Hz, bipy), 7.66 (t, 2 H,  $J = 6.9$  Hz, bipy), 4.75 (s, 6 H, ReMe), 1.96 (s, 3 H, CH<sub>3</sub>CN). IR (solution in  $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2295 w, 1607 s, 1476 s, 1447 s, 1919 m, 1284 w, 1244 w, 1165 m, 1061 (br), 1003 s, 963 s, 895 w, 772 s, 731 s.

**[ReOMe<sub>2</sub>(bipy)(CH<sub>3</sub>CN)][BPh<sub>4</sub>] (3c).** This compound was prepared by a procedure analogous to that used to prepare **3a**.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.67 (broad, 2 H, bipy), 8.36 (d, 2 H,  $J = 8.1$  Hz, bipy), 7.94 (t, 2 H,  $J = 7.8$  Hz, bipy), 7.58 (broad, 2 H,  $J = 6.9$  Hz, bipy), 7.25 (m, PPh<sub>4</sub>), 6.99 (t,  $J = 7.2$  Hz, PPh<sub>4</sub>), 6.84 (t,  $J = 7.2$  Hz, PPh<sub>4</sub>), 4.85 (s, 6 H, ReMe). IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1670 m, 1605 s, 1580 m, 1314 m, 1298 m, 1269 m, 1149 s, 1084 w, 1017 m, 993 s, 963 m, 947 m, 914 m, 858 w, 766 s, 735 s, 708 s, 611 m.

**cis-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)] [PF<sub>6</sub>] (4a).** A mixture of **1** (0.010 g, 0.024 mmol) and  $\text{AgPF}_6$  (0.007 g, 0.03 mmol) in  $\text{CD}_3\text{CN}$  (0.5 mL) was added to an NMR tube, which was then sealed. The green solution was frozen, and  $\text{PMe}_3$  (0.09 mmol) was added *via* a calibrated vacuum manifold. The tube was sealed and the solution was allowed to warm to room temperature. Upon warming, the solution turned from green to red. After 12 h, the solution was evaporated to dryness, and the dark red residue was dissolved in  $\text{CD}_3\text{CN}$ . Integration of the  $^1\text{H}$  NMR resonances *vs.* an internal standard of  $\text{C}_6\text{M}_6$  indicated a yield of *ca.* 95%. The  $^1\text{H}$  NMR spectrum was indistinguishable from that obtained for the analogous  $\text{BF}_4^-$  salt, **4f**, described in detail below.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.06 (d, 1 H,  $J = 5.7$  Hz, bipy),

8.62 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.34 (d, 1 H,  $J = 9.0$  Hz, bipy), 8.11–7.97 (m, 3 H, bipy), 7.77 (dt, 1 H,  $J = 6.6$  Hz,  $J = 1.4$  Hz, bipy), 7.41 (dt, 1 H,  $J = 6.9$  Hz,  $J = 1.1$  Hz, bipy), 4.16 (d, 3 H,  $^3J_{\text{PH}} = 6.6$  Hz, ReMe), 2.87 (d, 3 H,  $^3J_{\text{PH}} = 2.1$  Hz, ReMe), 1.34 (d, 9 H,  $J_{\text{PH}} = 11.1$  Hz,  $\text{RePMe}_3$ ).

**cis-[ReOMe<sub>2</sub>(bipy)(P(OMe)<sub>3</sub>)] [PF<sub>6</sub>] (4b).** To a green solution of **3a**, which was prepared *in situ* from 0.019 g (0.45 mmol) of **1** in  $\text{CH}_3\text{CN}$  (15 mL), was added  $\text{P(OMe)}_3$  (0.47 mmol) *via* microsyringe. The solution, which immediately became dark brown, was stirred for 3 h and then filtered. The filtrate was evaporated to dryness under reduced pressure, and the resultant dark oily residue was washed with hexanes ( $2 \times 20$  mL), diethyl ether ( $2 \times 10$  mL) and benzene ( $2 \times 10$  mL), leaving a dark powder (yield 0.19 g, 62%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.11 (d, 1 H,  $J = 5.7$  Hz, bipy), 8.63 (d, 1 H,  $J = 8.7$  Hz, bipy), 8.32 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.10 (m, 3 H, bipy), 7.78 (m, 1 H, bipy), 7.45 (t, 1 H,  $J = 6.9$  Hz, bipy), 4.01 (d, 3 H,  $J_{\text{PH}} = 5.4$  Hz, ReMe), 3.37 (d, 9 H,  $J_{\text{PH}} = 11.1$  Hz,  $\text{ReP(OMe)}_3$ ), 2.69 (d, 3 H,  $J_{\text{PH}} = 3.6$  Hz, ReMe).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  154, 153, 151.4, 150, 142, 141.7, 127.6, 127.5, 126, 125, 55.2 (d,  $^2J_{\text{PC}} = 6.4$  Hz,  $\text{ReP(OMe)}_3$ ), 26.0 (d,  $^2J_{\text{PC}} = 29.3$  Hz, ReMe), 12.1 (d,  $^2J_{\text{PC}} = 8.1$  Hz, ReMe).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  98.7. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1607 s, 1523 m, 1319 m, 1273 m, 1240 m, 1179 m, 1132 w, 1047 s, 1026 s, 997 s, 902 m, 839 s, 771 s, 681 m. A satisfactory analysis was not obtained.

**cis-[ReOMe<sub>2</sub>(bipy)(PMePh<sub>2</sub>)] [PF<sub>6</sub>] (4c).** A dark green powder was prepared in 61% yield by a procedure analogous to that used to prepare **4b**.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.92 (d, 1 H,  $J = 5.7$  Hz, bipy), 8.14 (d, 1 H,  $J = 8.1$  Hz, bipy), 7.98–7.96 (m, 2H), 7.86 (d, 1 H,  $J = 5.7$  Hz, bipy), 7.78 (dt, 1 H,  $J = 7.7$  Hz,  $J = 1.1$  Hz, bipy), 7.70–7.60 (m, 3 H), 7.55 (m, 1 H), 7.35–7.27 (m, 2 H), 7.09–7.03 (m, 2 H), 6.77–6.71 (m, 2 H), 4.50 (d, 3 H,  $J_{\text{PH}} = 7.2$  Hz, ReMe), 3.21 (d, 3 H,  $J_{\text{PH}} = 1.2$  Hz, ReMe), 1.84 (d, 3 H,  $J_{\text{PH}} = 11.1$  Hz,  $\text{RePMePh}_2$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  153, 152, 150, 148, 141.4, 141, 133.5, 133.3, 132.6 (d,  $J_{\text{CP}} = 3$  Hz), 131.7 (d,  $J_{\text{CP}} = 3.2$  Hz), 131.1, 131, 130.2 (d,  $J_{\text{CP}} = 49.6$  Hz), 130, 139.8, 129.7, 129.5, 129.2 (d,  $J_{\text{CP}} = 45.9$  Hz), 127, 126.5, 124.2, 124, 20.2 (d,  $^2J_{\text{PC}} = 22.8$  Hz, ReMe), 15.4 (d,  $J_{\text{PC}} = 4.0$  Hz, ReMe), 12.9 (d,  $J_{\text{PC}} = 32.6$  Hz,  $\text{RePMePh}_2$ ).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -10.5. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1607 s, 1317 m, 1242 m, 1163 m, 1099 m, 997 s, 887 m, 839 vs, 768 s, 741 s, 729 s, 694 m. A satisfactory analysis was not obtained.

**cis-[ReOMe<sub>2</sub>(bipy)(P(*n*-Bu)<sub>3</sub>)] [PF<sub>6</sub>] (4d).** This dark brown solid was prepared in 33% yield by a procedure analogous to that used to prepare **4b**.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.90 (d, 1 H,  $J = 5.7$  Hz, bipy), 8.64 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.34 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.09 (dt, 1 H,  $J = 7.5$  Hz,  $J = 0.9$  Hz, bipy), 8.03 (d, 1 H,  $J = 6.0$  Hz, bipy), 7.98 (dt, 1 H,  $J = 7.7$  Hz,  $J = 1.1$  Hz, bipy), 7.77 (dt, 1 H,  $J = 6.0$  Hz,  $J = 1.3$  Hz, bipy), 7.41 (dt, 1 H,  $J = 6.9$  Hz,  $J = 1.5$  Hz, bipy), 4.24 (d, 3 H,  $J_{\text{PH}} = 6.3$  Hz, ReMe), 2.93 (d, 3 H,  $J_{\text{PH}} = 1.2$  Hz, ReMe), 1.22 (m, 18 H,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ), 0.78 (t, 9 H,  $J = 7.2$  Hz,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  154, 153, 151, 149, 142, 141, 143 (m), 128, 127, 125.3, 125.1, 25.8 (d,  $^3J_{\text{PC}} = 3.7$  Hz,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ), 24.9 (d,  $^2J_{\text{PC}} = 13.5$  Hz,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ), 24.6 (d,  $J_{\text{PC}} = 26.7$  Hz,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ), 21.6 (d,  $J_{\text{PC}} = 21.9$  Hz, ReMe), 14.1 (d,  $^2J_{\text{PC}} = 4.7$  Hz, ReMe), 13.8 (s,  $\text{P(CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_3$ ).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -21.85. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1607 s, 1317 m, 1240 m, 1163 m, 1132 m, 1096 m, 1067 m, 1049 m, 993 s, 959 m, 936 m, 843 vs, 789 s, 723 m.

**cis-[ReOMe<sub>2</sub>(bipy)(PMe<sub>2</sub>Ph)] [PF<sub>6</sub>] (4e).** This dark powder was prepared in 63% yield by a procedure analogous to that used to prepare **4b**.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.95 (d, 1 H,  $J = 6.3$  Hz, bipy), 8.11 (d, 1 H,  $J = 8.1$  Hz, bipy), 7.9 (m, 3 H), 7.8 (m, 1 H), 7.67 (dt, 1 H,  $J = 7.2$  Hz,  $J = 0.9$  Hz, bipy), 7.35 (dt, 1 H,  $J = 7.2$  Hz,  $J = 1.5$  Hz, bipy), 7.24 (dt, 1 H,  $J = 7.5$  Hz,  $J = 1.5$

Hz, bipy), 7.0 (m, 2 H), 6.6 (m, 2 H), 4.15 (d, 3 H,  $J_{\text{PH}} = 6.0$  Hz, *ReMe*), 2.88 (d, 3 H,  $J_{\text{PH}} = 1.2$  Hz, *ReMe*), 2.09 (d, 3 H,  $J_{\text{PH}} = 10.8$  Hz, *RePMe<sub>2</sub>Ph*), 1.81 (d, 3 H,  $J_{\text{PH}} = 10.8$  Hz, *RePMe<sub>2</sub>Ph<sub>2</sub>*).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  153, 152, 150, 148, 141.5, 141, 132 (d,  $J_{\text{CP}} = 50.7$  Hz), 131 (d,  $J_{\text{CP}} = 2.6$  Hz), 129.8, 129.7, 129.6, 129.5, 128, 127, 124.7, 124.6, 20.2 (d,  $^2J_{\text{PC}} = 22.9$  Hz, *ReMe*), 15.9 (d,  $J_{\text{PC}} = 29.9$  Hz, *RePMe<sub>A</sub>Me<sub>B</sub>Ph<sub>2</sub>*), 12.9 (d,  $J_{\text{PC}} = 3.8$  Hz, *ReMe*), 10.3 (d,  $J_{\text{PC}} = 33.6$  Hz, *RePMe<sub>A</sub>Me<sub>B</sub>Ph<sub>2</sub>*).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -24.6. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1607 s, 1317 m, 1165 w, 1130 w, 997 s, 950 m, 916 m, 841 vs, 765 s, 746 m, 694 m.

***cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)](BF<sub>4</sub>) (4f).** *Method A.* Cold acetonitrile (70 mL) was added to a mixture of ReOMe<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>Cl (0.38 g, 0.90 mmol) and [Ag(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>) (0.25 g, 0.90 mmol) at 0 °C. The solution was stirred for 1 h and then filtered. The filtrate was evaporated to dryness under vacuum to yield a dark oil. The oil was dissolved in dichloromethane (50 mL), and 2,2'-bipyridine (0.14 g, 0.90 mmol) was added to the solution. The solution was stirred for 24 h, and the solvent was removed under vacuum. The dark oily residue was washed with hexanes (2 × 20 mL), diethyl ether (2 × 10 mL), and benzene (2 × 10 mL), leaving a brown powder. Crystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether (1:5, 20 mL) at room temperature (24 h) afforded the product as brown crystals (yield 0.28 g, 60%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.06 (d, 1 H,  $J = 5.7$  Hz, bipy), 8.63 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.35 (d, 1 H,  $J = 8.7$  Hz, bipy), 8.13–7.96 (m, 3 H, bipy), 7.78 (dt, 1 H,  $J = 5.7$  Hz,  $J = 1.2$  Hz, bipy), 7.42 (dt, 1 H,  $J = 6.9$  Hz,  $J = 1.0$  Hz, bipy), 4.15 (d, 3 H,  $^3J_{\text{PH}} = 6.6$  Hz, *ReMe*), 2.86 (d, 3 H,  $^3J_{\text{PH}} = 2.1$  Hz, *ReMe*), 1.34 (d, 9 H,  $J_{\text{PH}} = 10.8$  Hz, *RePMe<sub>3</sub>*).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  9.09 (d, 1 H,  $J = 6.0$  Hz, bipy), 8.65 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.36 (d, 1 H,  $J = 8.1$  Hz, bipy), 8.09–7.94 (m, 3 H, bipy), 7.78 (t, 1 H,  $J = 6.7$  Hz, bipy), 7.40 (t, 1 H,  $J = 6.6$  Hz, bipy), 4.31 (d, 3 H,  $J_{\text{PH}} = 6.3$  Hz, *ReMe*), 3.02 (d, 3 H,  $J_{\text{PH}} = 2.1$  Hz, *ReMe*), 1.35 (d, 9 H,  $J_{\text{PH}} = 11.1$  Hz, *RePMe<sub>3</sub>*).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  154, 153, 152, 149, 146, 142.4, 141.7, 128.2, 127.6, 126, 20.0 (d,  $^2J_{\text{PC}} = 19.4$  Hz, *ReMe*), 15.3 (d,  $J_{\text{PC}} = 33.8$  Hz, *RePMe<sub>3</sub>*), 12.9 (d,  $^2J_{\text{PC}} = 3.8$  Hz, *ReMe*).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -34.9. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1606 m, 1317 w, 1294 m, 1101 m, 1055 s, 993 (sh), 964 s, 954 s, 860 m, 796 w, 771 (sh), 750 m, 729 m. Calc. for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>OPRe<sup>+</sup>BF<sub>4</sub><sup>-</sup>: C, 32.68; H, 4.21; N, 5.08. Found: C, 32.71; H, 4.01; N, 4.95%.

*Method B.* The procedure used was analogous to that used to prepare **4a**, but employed [Ag(CH<sub>3</sub>CN)<sub>2</sub>](BF<sub>4</sub>) rather than AgPF<sub>6</sub> as the silver(i) salt (64% yield). The  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ) for this product was identical to that obtained for **4f** when prepared *via* Method A.

***cis*-[ReOMe<sub>2</sub>(phen)(PMe<sub>3</sub>)](BF<sub>4</sub>).** This compound was isolated as a greenish brown powder in 65% yield using a procedure analogous to that used to prepare **4f** (Method A).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  9.37 (dd, 1 H,  $J = 4.8$  Hz,  $J = 1.2$  Hz, phen), 8.67 (d, 1 H,  $J = 8.1$  Hz,  $J = 1.2$  Hz, phen), 8.55 (dd, 1 H,  $J = 8.1$  Hz,  $J = 1.2$  Hz, phen), 8.39 (dd, 1 H,  $J = 6.9$  Hz,  $J = 1.5$  Hz, phen), 8.21 (s, 2 H, phen), 8.15 (dd, 1 H,  $J = 7.5$  Hz,  $J = 5.1$  Hz, phen), 7.77 (dd, 1 H,  $J = 8.1$  Hz,  $J = 5.4$  Hz, phen), 4.34 (d, 3 H,  $J_{\text{PH}} = 6.9$  Hz, *ReMe*), 2.89 (d, 3 H,  $J_{\text{PH}} = 2.1$  Hz, *ReMe*), 1.23 (d, 9 H,  $J_{\text{PH}} = 11.1$  Hz, *RePMe<sub>3</sub>*).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  151, 149, 145, 144, 141, 140, 132, 129, 128.5, 126, 128, 126, 19.9 (d,  $^2J_{\text{PC}} = 20.3$  Hz, *ReMe*), 14.9 (d,  $J_{\text{PC}} = 32.8$  Hz, *RePMe<sub>3</sub>*), 12.5 (d,  $^2J_{\text{PC}} = 3.7$  Hz, *ReMe*).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -35.8. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1630 m, 1605 m, 1572 w, 1520 m, 1427 s, 1296 m, 1226 w, 1145 m, 1098 s, 1059 vs, 1001 s, 964 s, 908 w, 844 s, 775 w, 748 m, 723 s, 677 m. Calc. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>OPRe<sup>+</sup>BF<sub>4</sub><sup>-</sup>: C, 35.49; H, 4.03; N, 4.87. Found: C, 35.26; H, 3.82; N, 4.72%.

***cis*-[ReOMe<sub>2</sub>(4,4'-Me<sub>2</sub>bipy)(PMe<sub>3</sub>)](BF<sub>4</sub>).** This compound was isolated as a greenish brown powder in 43% yield by using a procedure analogous to that used to prepare **4f** (Method A).  $^1\text{H}$

NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.46 (d, 1 H,  $J = 6$  Hz, bipy), 8.46 (s, 1 H, bipy), 8.17 (s, 1 H, bipy), 7.77 (d, 1 H,  $J = 4.5$  Hz, bipy), 7.61 (d, 1 H,  $J = 5.7$  Hz, bipy), 7.23 (d, 1 H,  $J = 6$  Hz, bipy), 4.18 (d, 3 H,  $J_{\text{PH}} = 6.9$  Hz, *ReMe*), 2.92 (s, 3 H, bipy-*Me*), 2.85 (d, 3 H,  $J_{\text{PH}} = 2.1$  Hz, *ReMe*), 2.47 (s, 3 H, bipy-*Me*), 1.23 (d, 9 H,  $J_{\text{PH}} = 11.4$  Hz, *RePMe<sub>3</sub>*).  $^{13}\text{C}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  155, 154, 153, 152, 150, 148, 129, 128, 125, 21.3, 20.7, 20.2 (d,  $^2J_{\text{PC}} = 22.2$  Hz, *ReMe*), 14.9 (d,  $^2J_{\text{PC}} = 32.5$  Hz, *RePMe<sub>3</sub>*), 11.8 (d,  $^2J_{\text{PC}} = 3.5$  Hz, *ReMe*).  $^{31}\text{P}$ - $\{^1\text{H}\}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  -35.4. IR (KBr, Nujol,  $\text{cm}^{-1}$ ): 1620 m, 1591 s, 1306 w, 1283 m, 1248 w, 1059 m, 1004 s, 995 m, 961 s, 825 s, 737 s, 723 s. A satisfactory analysis was not obtained. Calc. for C<sub>17</sub>H<sub>27</sub>N<sub>2</sub>OPRe<sup>+</sup>BF<sub>4</sub><sup>-</sup>: C, 35.24; H, 4.70; N, 4.82. Found: C, 34.55; H, 4.68; N, 4.45%.

#### Kinetics for the thermal isomerization of **1** to **2**

The isomerization of **1** to **2** was monitored *in situ* by  $^1\text{H}$  NMR spectroscopy. Solutions of **1** in benzene-*d*<sub>6</sub> were heated in sealed NMR tubes directly in the probe cavity. The initial concentration of **1** varied between 0.004 and 0.008 M. Periodically,  $^1\text{H}$  NMR spectra were recorded, and the methyl resonances of **1** and **2** were integrated relative to 0.001 M C<sub>6</sub>H<sub>6</sub> as an internal standard. For a given study, the temperature was held within  $\pm 0.1$  °C of one of the following temperatures: 333, 338, 343, 348, and 352 K. The rate constants calculated for the disappearance of **1** were 1.25, 2.72, 4.94, 9.63, and  $13.4 \times 10^{-3}$  min<sup>-1</sup>, respectively. Each rate constant represents the average of 2–3 runs except at 333 K (only one run). The resulting activation parameters were calculated to be  $\Delta H^\ddagger = 29(3)$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = 6(9)$  e.u. The errors in these values were estimated from typical linear regression analysis.<sup>32</sup> Rate constants for the loss of **1** in benzene-*d*<sub>6</sub> in the presence of 2, 5, and 10 equivalents of bipy at 79 °C were 1.11, 1.24, and  $1.00 \times 10^{-2}$  min<sup>-1</sup>, respectively. The corresponding rate constants for the appearance of **2** were 1.14, 1.10, and  $1.28 \times 10^{-2}$  min<sup>-1</sup>, respectively.

#### Polymerization of ethylene by using **1** and **2** as catalyst precursors

In a typical experiment, complex **1** or **2** (*ca.* 4.7  $\mu\text{mol}$ ) was dissolved in a solution of toluene (10 mL) in a Fisher–Porter pressure reactor. Approximately 3400 equivalents of MAO (10% in toluene) were then added. The resulting homogeneous green solution was stirred for 5 min and then saturated with ethylene (140 psi). The mixture was allowed to stir for 30 min under a constant pressure of ethylene. The pressure was released, and a solution of methanol and 4 M HCl (1:1, v/v) was added, causing precipitation of a white solid. The white solid was collected by filtration, washed with methanol, and dried under vacuum to afford 0.02–0.05 g of polyethylene. IR (KBr, pellet,  $\text{cm}^{-1}$ ): 2919 s, 2851 s, 1632 s, 1474 s.

#### X-Ray structure determinations of *cis*-ReOMe<sub>2</sub>(bipy)Cl·C<sub>6</sub>H<sub>6</sub> (1·C<sub>6</sub>H<sub>6</sub>), *trans*-ReOMe<sub>2</sub>(bipy)Cl (**2**), and *cis*-[ReOMe<sub>2</sub>(bipy)(PMe<sub>3</sub>)](BF<sub>4</sub>) (**4f**)

Crystals for analyses of **1**·C<sub>6</sub>H<sub>6</sub> (dark brown flat slab), **2** (dark red cone) and **4f** (dark brown prismatic block) were grown from saturated benzene, CH<sub>2</sub>Cl<sub>2</sub>/hexanes, and CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether, respectively. The X-ray data for **1** and **4f** were collected on a Nicolet R3m/V diffractometer, and the data for **2** were collected on a Siemens P4 diffractometer. The crystals were manipulated under mineral oil during the mounting procedure. The data for **1** and **4f** were collected using the  $\theta$ - $2\theta$  scan technique, and the data for **2** were collected using the  $\omega$  scan technique. During data reduction, Lorentz and polarization corrections were applied, as well as a semi-empirical absorption correction.

In the analysis of **1**·C<sub>6</sub>H<sub>6</sub>, the space group *P*2<sub>1</sub> was assumed from the outset since the unitary structure factors displayed acentric statistics. The benzene moiety in the lattice did not

refine well due to slight positional disorder. Eventually the benzene moiety was treated as an ideal rigid body with 100% occupancy, using anisotropic thermal motion to account for most of the disorder. The absolute configuration about Re was determined by refinement of a coefficient multiplying  $\Delta f''$ , which indicated conclusively that the configuration shown in Fig. 1 is correct. The final difference map showed a maximum peak of about  $1.8 \text{ e } \text{\AA}^{-3}$  located near Re.

The analysis of **2** was routine. The final difference maps showed a maximum peak of about  $1.04 \text{ Re e } \text{\AA}^{-3}$  located near Re.

In solving the structure of **4f**, the C(1) and C(2) methyl groups were initially treated as ideal rigid bodies and allowed to rotate independently. The C(2) group refined to unreasonable values, however, and the attached hydrogen atoms were eventually fixed in the orientation found in the difference map. No attempt was made to model the heavily disordered anion using ideal rigid bodies. The final difference map showed a maximum peak of about  $2.5 \text{ e } \text{\AA}^{-3}$  located near Re.

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