# **Inorganic Chemistry**

# Mechanism of Me–Re Bond Addition to Platinum(II) and Dioxygen Activation by the Resulting Pt–Re Bimetallic Center

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## Supporting Information

**ABSTRACT:** Unusual cis-oxidative addition of methyltrioxorhenium (MTO) to  $[PtMe_2(bpy)]$ , (bpy = 2,2'-bipyridine) (1) is described. Addition of MTO to 1 first gives the Lewis acid—base adduct  $[(bpy)Me_2Pt-Re(Me)(O)_3]$  (2) and subsequently affords the oxidative addition product  $[(bpy)Me_3PtReO_3]$  (3). All complexes 1, MTO, 2, and 3 are in equilibrium in solution. The structure of 2 was confirmed by X-ray crystallography, and its dissociation constant in solution is 0.87 M. The structure of 3 was confirmed by extended X-ray absorption fine structure and X-ray absorption near-edge structure in tandem with one- and two-dimensional NMR spectroscopy augmented by deuterium and  ${}^{13}C$  isotope-labeling studies. Kinetics of formation of



compound 3 revealed saturation kinetics dependence on [MTO] and first-order in [Pt], complying with prior equilibrium formation of 2 with oxidative addition of Me–Re being the rate-determining step. Exposure of 3 to molecular oxygen or air resulted in the insertion of an oxygen atom into the platinum–rhenium bond forming [(bpy)Me<sub>3</sub>PtOReO<sub>3</sub>] (4) as final product. Density functional theory analysis on oxygen insertion pathways leading to complex 4, merited on the basis of Russell oxidation pathway, revealed the involvement of rhenium peroxo species.

# INTRODUCTION

The study of hetero-bimetallic systems has recently received increased attention because of their application in catalytic transformations, oxidation processes, and metalloproteins.1 Recent developments have focused on the cooperative influence of two dissimilar adjacent metal ions held together in close proximity.<sup>10–15</sup> Because of the possible "synergistic" effect of two different metal centers acting together, the related hetero-bimetallic systems can give rise to reaction pathways and/or products not possible in mononuclear analogues.<sup>16</sup> In this regard our previous research has revealed C-H activation by the pincer iridium complex X with methyltrioxorhenium  $(MTO)^{17}$  to give an Ir–Re bimetallic complex Z with net result of methyl transfer to Ir (Scheme 1).<sup>18,19</sup> We proposed that this reaction was initiated by coordination of MTO to iridium via the oxo ligand, followed by elimination of H<sub>2</sub> and subsequent C-H bond activation of the Me group on MTO by Ir to afford Y. Isomerization of Y in acetonitrile afforded Z with complete Me transfer from MTO to Ir. Herein, we report methyl transfer from MTO to  $[PtMe_2(bpy)]$  (bpy = 2,2'-bipyridine) (1) by unusual cis-oxidative addition to form the bimetallic complex 3 via Lewis acid-base complex  $[(bpy)Me_2Pt-Re(Me)(O)_3]$  (2) (Scheme 2). This pathway is in contrast to the well-established trans-oxidative addtion of electrophillic reagents to 1, a typical

Scheme 1. Reaction of MTO with Pincer Ir Complex X to Give Ir-Re Bimetallic Complex Z via Y with Net Methyl Transfer from Re to Ir



example of which is illustrated in Scheme 3, wherein reaction of 1 with methyl iodide is suggested to proceed via  $S_N^2$  mechanism, followed by the formation of a cationic species leading to the trans oxidative addition product.<sup>20–22</sup> On the one hand, the other pathway known for electrophillic substrates such as Ar–X (X = halogen) is radical pathway.<sup>21</sup> On the other hand, concerted cis-addition mechanisms on platinum complexes are known for nonpolar substrates such as H<sub>2</sub> and R–H (R = alkyl or aryl) or forced via intramolecular pathway.<sup>21</sup> The present article gives the first report illustrating an intermolecular cis-oxidative addition for the reaction of an electrophilic

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Scheme 3. trans-Oxidative Addition Mechanism for the Reaction of 1 with Methyliodide



substrate MTO to platinum(II). Exposure of the resulting bimetallic complex 3 to molecular oxygen/air resulted in rapid formation of  $[(bpy)Me_3PtOReO_3]$  (4). Density functional theory (DFT) investigation of this unique O<sub>2</sub> activation reaction, merited on the basis of Russell oxidation pathway,<sup>23</sup> involved pairing of a rhenium peroxo intermediate leading to the release of O<sub>2</sub> and the formation of two molecules of 4.

#### RESULTS AND DISCUSSION

**Characterization of Complex 2.** In the absence of dioxygen, upon mixing 1 and MTO in  $CD_2Cl_2$  or  $CDCl_3$  or tetrahydrofuran (THF) at 280 K, an equilibrium mixture of the Lewis acid-base adduct 2 and the cis-oxidative addition product 3 in addition to 1 and MTO was observed (Scheme 2). Increasing the temperature to higher than 280 K for prolonged period (30 min half-life at 298 K) leads to decomposition of 3, and the resulting compounds could not be characterized.

<sup>1</sup>H NMR chemical shifts of **2** could not be distinguished from **1** and MTO. However, a change from their original chemical shifts (before mixing) was observed upon increasing the concentration of MTO, indicating a fast exchange between **2**, **1**, and MTO. Even though the change in <sup>1</sup>H NMR chemical shifts is subtle, changes in <sup>195</sup>Pt{<sup>1</sup>H} and <sup>17</sup>O{<sup>1</sup>H} NMR chemical shifts were significant. A plot of <sup>195</sup>Pt{<sup>1</sup>H} NMR chemical shift versus [MTO] (Supporting Information Figure S1) affords a dissociation constant  $K_d = 0.87 \pm 0.08$  M.

Keeping the reaction mixture (THF) at -30 °C resulted in the precipitation of complex 2 in crystalline form. Single-crystal X-ray structure of 2 is shown in Figure 1. The Pt–Re bond is 2.8954(4) Å, which is longer than the average Pt–Re single bond indicating dative bonding.<sup>24,25</sup> The geometry of rhenium in 2 is trigonal bipyramidal with the three oxo ligands in one plane and the Me and Pt occupying the apical positions. The geometry around the Pt is slightly distorted square pyramid with the Pt–Re bond tilted by 7.53° from the normal to the mean square plane around platinum. Complex 2 is a combination of a soft Pt(II) center with a hard Lewis acid rhenium metal. Previously known are the combinations of MTO with hard Lewis bases<sup>26,27</sup> as well as 1 with soft Lewis



Figure 1. ORTEP drawing of the complexes 2 and 4. Ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

acids. It is noteworthy to mention that complexes of 1 with  $I_2$  and  $Me_3SnX$  or  $Me_3GeX$  (X = Cl, I) are known as intermediates in the pathway of oxidative addition reactions of 1.<sup>28</sup> Upon re-dissolution of crystals of 2 into solution, the equilibrium reactions in Scheme 2 are re-established, and 1, MTO, and 3 are observed.

**Characterization of Complex 3.** <sup>1</sup>H NMR spectrum of 3 was distinctly different from that of 1 and 2. The aromatic region showed well-defined eight proton signals (Supporting Information Figure S2) indicating a  $C_s$  symmetry and reflecting the two different equatorial ligands on Pt, CH<sub>3</sub>, and ReO<sub>3</sub>. Analogously  $C_1$  symmetry with the same NMR behavior was observed for the adduct of 1 with *m*-chloroperoxybenzoic acid reported earlier.<sup>29</sup> The three methyl groups were identified at 1.50 and 0.18 ppm with the ratio of 1:2 having 60 and 38 Hz coupling constants for Pt satellites, respectively (Figure 2). The



Figure 2.  $^{1}$ H NMR (expanded region) of the reaction mixture of 1+MTO, 2, and 3.

assignment of the downfield chemical shift at 1.50 ppm to the equatorial methyl group is consistent with the trans effect of N atom commonly observed for the derivatives of complex 1.<sup>22,30</sup> The platinum coupling constant values are consistent with the values of 73 Hz (Me trans to N) and 44 Hz (Me trans to Me) observed for the analogous [PtMe<sub>4</sub>(bpy)] complex.<sup>30</sup> The Pt satellites for the methyl signals in 3 are broader than those observed for 1. Effect of chemical shift anisotropy  $(CSA)^{31}$  as a cause of broadening was negated with the observation of sharpening of platinum satellites upon increasing the NMR field strength (Supporting Information Figure S9). It is noteworthy to mention that CSA is a commonly observed phenomenon in Pt(II) complexes including our observation of CSA for complex 1 (Supporting Information Figure S8).<sup>32,33,31</sup> While the exact source for broadening of satellites in 3 could not be ascertained and is beyond the scope of this work, we attribute it to the spin rotation relaxation effect of Pt.<sup>34,35</sup>

NOESY spectrum of the reaction mixture (Figure 3) showed strong (A) and weak correlation (B) of equatorial and axial



Figure 3. Expanded NOESY spectrum of the reaction mixture of 1+MTO, 2, and 3.

methyl groups, respectively, with the aromatic protons for complex **3**. This is consistent with the shorter and longer distances between the equatorial (2.60 Å) and axial (3.22 Å) carbon atoms methyl groups with the aromatic protons as predicted by DFT (Supporting Information .xyz data). The correlation between the methyl group assigned to 1.50 ppm and only one of the aromatic protons (8.83 ppm) (A) conforms to structure **3** and negates the possibility of its isomer **3A** (Chart 1) as axial methyl group in **3A** are equidistance from the two pyridinyl rings.

Chart 1. NOESY Correlation for Complexes 1, 3, and 3' and Structure of 3A



For further confirmation of structure 3, <sup>13</sup>C-enriched MTO was used, and the corresponding complex 3' (Chart 1) was investigated by NMR. The <sup>1</sup>H NMR of 3' has two types of signals, a singlet and doublet (s, 0.18 ppm for CH<sub>3</sub> and d at 0.05, 0.31 ppm with a coupling constant of 129 Hz for  ${}^{13}CH_3$ ) for the two axial methyl groups due to the <sup>13</sup>C enrichment, which otherwise is the same when regular MTO was used. On the one hand, the NOESY spectrum of 3' (Supporting Information Figure S4) showed no correlation of <sup>13</sup>C-enriched methyl group with the other axial methyl confirming that the incoming CH<sub>3</sub> from MTO occupied the axial position. On the other hand, both the axial methyl groups on 3' showed correlation with the equatorial methyl group in the same NOESY spectrum validating the structure assignment. In comparison isomer 3A would feature correlation between the <sup>13</sup>C-enriched methyl group and the other two methyl groups. It is worth mentioning that similar correlations were used to pinpoint the structure of  $[Pt(bpy) (CH_3)_2I(PMe_3)]$  from its possible isomers.<sup>36</sup>

When  $CD_3ReO_3$  was used, the <sup>2</sup>H NMR showed a signal at 0.18 ppm corresponding to the axial methyl group. <sup>1</sup>H NMR of the same reaction mixture (Supporting Information Figure S5) showed the signals for axial and equatorial methyl groups with the ratio of 1:1. These are consistent with our proposed cisoxidative addition fashion of MTO to 1 to form 3. The exchange of methyl groups was observed only after several hours with the proportional distribution of  $CD_3$  groups and emergence of <sup>2</sup>H signals for 1 as well as 3.

 $^{13}C{^{1}H}$  NMR of 3 showed 10 signals for the carbon atoms of bipyridine ligand consistent with  $C_{\rm s}$  symmetry. The platinum satellites with a Pt-C coupling constant of 349 Hz was observed for the axial methyl groups upon using <sup>13</sup>C-enriched MTO, which otherwise is absent when using regular MTO. The  $^{17}O{^{1}H}$  NMR showed a single chemical shift of 795 ppm and confirmed the presence of ReO<sub>3</sub> moiety in 3. However, no <sup>195</sup>Pt{<sup>1</sup>H} NMR signals could be observed, and we attribute this to the same spin rotation relaxation effect causing the broadening of platinum satellites in the <sup>1</sup>H NMR. Overall <sup>1</sup>H NMR and NOESY correlations including from <sup>13</sup>C-enriched MTO, deuterium-labeling studies as well as <sup>13</sup>C{<sup>1</sup>H} NMR characterization of complex 3 confirmed the presence of bipyridine as well as the three methyl groups along with their orientations, and the  ${}^{17}O{\{}^{1}H{\}}$  NMR confirmed the existence of ReO<sub>3</sub> group. However, the existence of Pt-Re bond and the question of oxidation state on platinum in the proposed structure of 3 could not be confirmed in the absence of singlecrystal X-ray structure. Hence, the use of X-ray absorption spectroscopy (extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES)) is warranted to establish the Pt-Re bond in 3. However, it was not straightforward, as complex 3 always exists as a mixture with 2 in solution and could not be isolated as a pure solid. Hence, the approach of deconvoluting EXAFS and XANES spectrum of 3 from spectra of 2 and the mixture was based on Beer's law with the help of NMR (concentration of 2:3) and DFT (structural comparison).

For complexes 1, 2, and MTO, pure solid samples were used to collect the XANES and EXAFS spectra. Under the reaction conditions of 1 with 5 equiv of MTO in a solvent mixture of THF/CH<sub>3</sub>CN (1:1) at 280 K at ~1 h after mixing the reagents under inert atmosphere (oxygen-free), the molar ratio of 3 to 2 is 58:42 as observed by NMR (see Supporting Information Figure S10 for reaction profile). Using the above reaction conditions, the EXAFS and XANES spectra of reaction mixture were collected. Then the spectrum of 3 was deconvoluted from the spectra of 2 and the reaction mixture based on Beer's law. Table 1 summarizes the XANES data for complexes 1, 2, 3 and compared with Pt metal and Pt(O)<sub>2</sub>. The calculated Pt L3 edge XANES spectrum of 3 (Supporting Information Figure S11) has a higher white line (height  $\approx 2.01$ ) compared with that of 2

Table 1. Summary of XANES Data for Complexes 1, 2, and 3 Compared with Pt Metal and  $PtO_2$ 

sample	edge energy (eV)	white line height	oxidation state
Pt foil	11 564.0	1.30	0
1	11 566.0	1.66	II
2	11 566.0	1.57	II
3	11 566.9	2.01	III
$PtO_2^{37}$	11 565.8	2.70	IV

(height  $\approx 1.66$ ); however, it is lower than that of PtO<sub>2</sub> (height 2.70),<sup>37</sup> indicating a formal +3 oxidation state of Pt in 3.

Figure 4 represents the comparison of R-space EXAFS spectra of 2 and 3. Table 2 compares bond lengths and



**Figure 4.** Comparison of R-space EXAFS spectra of **2** and **3**. (*k*-range = 2.62-8.80 Å<sup>-1</sup>; *k*-weight = 2).

Table 2. Comparison of Bond Lengths between EXAFS, X-ray, and DFT for Complexes 2 and 3

	complex 2			complex 3					
		bond length (Å)			bond length (Å)				
	coord.	EXAFS	X-ray	coord.	EXAFS	DFT			
Pt-Re	1	2.90	2.8954(4)	1	2.39	2.51			
Pt–N (N1, N2)	2	2.11	2.102, 2.104	2	2.09	2.2			
Pt-C (eq-Me) <sup>a</sup>	2	2.04	2.049, 2.024	1	2.03	2.16			
Pt-C $(ax-Me)^a$				2	2.11	2.16			
Pt-C (C2,C3) <sup>b</sup>	2	2.96	2.962, 2.967	2	2.99	3.05			
Pt–C (C4, C11) <sup>b</sup>	2	3.10	3.091, 3.101	3	3.11	3.16			
$^{a}eq$ = equatorial, $ax$ = axial. <sup>b</sup> See Figure 1 for atom labels.									

coordination numbers of **2** and **3** derived from the EXAFS analysis with single-crystal X-ray structure and DFT-calculated structures for **2** and **3**. EXAFS results of complex **2** are consistent with experimental X-ray single-crystal structure. The long Pt–Re distance of 2.90 Å in **2** is comparable with its X-ray structure distance of 2.8954(4) Å leading to a weak contribution in the Pt L3 edge R-space EXAFS spectrum (Supporting Information Figure S12). This is also confirmed by the Re edge EXAFS data (Supporting Information Figure S14).

For complex **3**, Pt L3 edge EXAFS fitting gave Pt–Re distance of 2.39 Å, which is in good agreement with the DFT-calculated Pt–Re bond distance of 2.51 Å and is shorter than that in **2**. Besides, the coordination numbers derived from the EXAFS analysis are also in good agreement with square pyramidal and octahedral geometry of Pt in **2** and **3**, respectively. Overall the combination of NMR with EXAFS and XANES studies established the structure of **3** without ambiguity.

**Kinetics and Thermodynamics of Formation of 3.** The equilibrium reaction of 1+MTO to 2 and 3 (Scheme 2) was monitored by <sup>1</sup>H NMR. Under excess MTO and limiting 1, the rate of reaction follows pseudo-first-order rate equation, and the observed rate constants  $k_{\Psi}$  plateau as [MTO] increases (Figure 5). The observed saturation kinetics, zero-order



Figure 5. Dependence of rate of conversion between 1 and 3 on [MTO].

dependence on [MTO], is consistent with the equilibrium between 1 and 2 and is much faster than the conversion of 2 to 3. Under conditions of excess MTO, the majority of Pt is present as 2 rather than 1. Therefore, the kinetic studies represent the equilibrium between 2 and 3 as the rate determining step with first-order dependence on [2] or the limiting reagent being [1].

The dependence of the equilibrium constant (*K*) for the conversion of **2** to **3** on temperature was investigated by <sup>1</sup>H NMR over the range of 269–285 K, and the data were fitted to the Von't Hoff relationship (eq 1).

$$\ln K = -\Delta H^0 / RT + \Delta S^0 / R \tag{1}$$

The thermodynamic parameters  $\Delta H^0 = -9.5 \pm 0.6$  kcal mol<sup>-1</sup> and  $\Delta S^0 = -34 \pm 2$  cal mol<sup>-1</sup> K<sup>-1</sup> were obtained (Supporting Information Figure S15). The reaction is favored by enthalpy and is entropically disfavored. Despite it being a unimolecular reaction, changes in the coordination environment of the bimetallic complexes 2 and 3 have a significant effect on entropy. This is consistent with the observation of much longer metal–metal bond in 2 than in 3. At 298 K, the equilibrium constant is 0.34 with 2 at 3 times the concentration of 3, and at 250 K, 3 is 8 times the concentration of 2.

Activation parameters ( $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$ ) were obtained in accordance with the Eyring relationship (eq 2) by following the kinetics of formation of **3**, the oxidative addition product, at different temperatures 269–285 K (Supporting Information Figure S16).

$$\ln(k_{\Psi}/T) = -\Delta H^{\ddagger}/RT + \ln(k_{\rm B}/h) + \Delta S^{\ddagger}/R$$
(2)

The enthalpy and entropy of activation were  $\Delta H^{\ddagger} = 7 \pm 1$ kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger} = -37 \pm 5$  cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. The large value of  $\Delta S^{\ddagger}$  is attributed to the need for significant reorganization from 2 to undergo Me–Re addition to make 3.

Mechanism of cis-Oxidative Addition via Berry Pseudorotation. The experimental studies of the equilibrium reaction of complex 1 with MTO to form complexes 2 and 3 described above provided the following insights on the mechanism:

- 1. Kinetic saturation in [MTO] established prior equilibrium of complex 2 en route to form the oxidative addition product complex 3.
- 2.  $\Delta G^0$  value of 0.6 kcal/mol at 298 K for the equilibrium between 2 and 3 demonstrating comparable stability.
- 3. Measured  $\Delta G^{\ddagger}$  value of 18  $\pm$  3 kcal/mol at 298 K is comparable to the value from an earlier report on methyl transfer from MTO to an Ir pincer complex.<sup>18</sup>

Overall, reaction of 1+MTO to form 2 and then 3 are reversible in solution with the former being faster. Formation of 2 from 1+MTO is analogous to the previously observed complexation of 1 with Lewis acids such as I<sub>2</sub> preceding oxidative addition.<sup>28</sup> Conversion of complex 2 to 3 occurs possibly via a Berry pseudorotation followed by methyl transfer by pushing one of the equatorial methyls on Pt to the axial position. Berry rotation in trigonal bipyramidal geometry is a commonly observed phenemenon.<sup>38,39</sup>

Activation of Molecular Oxygen by Complex 3. Note that both MTO and complex 1 are stable toward oxygen and air. However, introduction of oxygen/air to the mixture of 1+MTO or 3 at -78 °C resulted in the formation of complex 4 (Scheme 2) in 78% yield along with the formation of some methanol (20%). This is one of the rare examples MeOH formation from O<sub>2</sub> as oxidant.<sup>40–45</sup> Complex 4 was characterized by <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and <sup>195</sup>Pt{<sup>1</sup>H} NMR as well as by single-crystal X-ray (Figure 2). X-ray structure of complex 4 features the rhenium metal center with tetrahedral geometry, typical for the perrhenate anion, whereas the platinum center has octahedral geometry, which is characteristic for Pt(IV).

The source of oxygen in 4 was confirmed by electrospray ionization (ESI) mass spectrometry using 50% <sup>18</sup>O-enriched dioxygen gas. The  $\text{Re}(^{18}\text{O})\text{O}_3^-$  ion showed the expected isotope pattern (Supporting Information Figure S17). The parent ion of 4 was not observed in the mass spectrum due to fragmentation of 4 into  $[(\text{bpy})\text{PtMe}_3]^+$  and  $\text{ReO}_4^-$  even under mild ESI conditions.

On the one hand, insertion of molecular oxygen into M-Me bond with the formation of M-OOMe via radical or excimer formation is documented in the literature.<sup>46–49</sup> On the other hand, insertion of an oxygen atom from O2 as observed in complex 4 is intriguing given that complex 3 possesses Ptmethyl bonds that can be susceptible to forming Pt-OOMe. Reaction of molecular oxygen with 3 was instantaneous with no observable intermediates (NMR time scale) and complete consumption of 3 leading to the formation of complex 4. For analogous reactions of oxygen on the rhenium center having redox-active catecholate and amidophenolate ligands, Lippert et al. proposed the formation of mononuclear  $\eta^1$ -superoxo species followed by binuclear trans-µ-1,2-peroxo-bridged complex and disproportion leading to the rhenium oxo species.<sup>50</sup> We investigated the mechanism of reaction of complex 3 with molecular oxygen by DFT.

Scheme 4 represents two possible pathways A and B. Both scenarios involve interaction of dioxygen with rhenium in two different orientations. Pathway A: edge-on  $O_2$  attack on complex 3 with Re–O–O angle equal to  $77^{\circ}$  (Figure 6A); pathway B: point-on  $O_2$  attack on complex 3, with a Re–O–O angle equal to  $173^{\circ}$  (Figure 6B).

Scheme 4. Possible Pathways A and B for the Reaction of 3 with Molecular Oxygen



A B Figure 6. Interaction of dioxygen with rhenium in complex 3 via edge-

on attack (A) and point-on attack (B); rhenium-green, platinum-blue, nitrogen-turquoise blue, oxygen-red, carbon-black, hydrogen-white.

Figure 7 represents the energy profile of pathway A with reaction of 3 with molecular oxygen (triplet-blue, singlet-red).



Figure 7. Energy profile of the pathway A with reaction of 3 with molecular oxygen (singlet-red, triplet-blue).

Complex  $3 + {}^{3}O_{2}$  was considered as zero-energy ground level ( $\Delta G = 0$ ). By using the Yamaguchi spin contamination correction,  ${}^{51}$  energy of complex  $3 + {}^{1}O_{2}$  was calculated as 22.5 kcal/mol. In both cases of triplet and singlet oxygen, upon decreasing the distance between  $O_{2}$  and complex 3, they rearranged to give perrhenate intermediates  ${}^{3}Q$  and  ${}^{1}Q$ , respectively. The singlet peroxo complex  ${}^{1}Q$  is 42.6 kcal/mol downhill in energy than its triplet state  ${}^{3}Q$  facilitating the spin crossover. Structural comparison of  ${}^{1}Q$  and  ${}^{3}Q$  is given in Supporting Information (Figures S18 and S19 and Table S5). The triplet–singlet spin crossover at the minimum-energy crossing point (MECP) was at 12.7 kcal·mol. This triplet-singlet spin crossover is well-known for peroxo intermediates

from the reaction of molecular oxygen with Pd(0) and Re (V) complexes.<sup>52-56</sup>

Next, two molecules of  ${}^{1}\mathbf{Q}$  were paired with ReO<sub>5</sub> groups facing each other with one oxygen of the peroxo bond placed at 1.36 Å from the other oxygen of the same group in the other  ${}^{1}\mathbf{Q}$  molecule (Figure 8). The approach of pairing of two  ${}^{1}\mathbf{Q}$ s is



Figure 8. Pairing of two molecules of complex <sup>1</sup>Q; rhenium-green, platinum-blue, nitrogen-turquoise-blue, oxygen-red, carbon-black, hydrogen-white.

merited on the basis of Russell mechanism, where pairing of two peroxo radicals results in a six-membered cyclic intermediate.<sup>23</sup> During the optimization, the two <sup>1</sup>Q molecules moved away from each other releasing an O<sub>2</sub> molecule, concurrent with the formation of two molecules of 4a, an isomer of the experimentally observed complex 4. The energy for this process is -32.36 kcal/mol. Once O<sub>2</sub> is liberated, complex 4a was found at -36.52. kcal/mol from the reference. No transition state was observed for this step. The sequence of optimization and the change in significant bond lengths in this process are given in Supporting Information (Figure S20). This computational methodology of pairing molecules for coercing a reaction has precedence in the literature.<sup>57</sup>

However, pathway B, with the point-on attack, was not feasible with no reaction with oxygen, as oxygen was moving away from complex 3 during the optimization. Therefore, pathway B was eliminated. Overall, the proposed pathway A going from 3 to 4 via  ${}^{1}Q$  (Scheme 4, Figure 7) is downhill in energy without having any transition states. This is consistent with the experimental observation of instantaneous and complete consumption of 3 from its reaction with oxygen even at -78 °C.

## CONCLUSION

We have described herein an unusual cis-oxidative addition pathway for the reaction of 1 with MTO leading to the formation of 3 via Lewis-acid complex 2. Structure of 3 was unambiguously established via a combination of XANES, EXAFS, and NMR spectroscopy including NOESY and <sup>17</sup>O NMR. Kinetic saturation in [MTO] established complex 2 as the intermediate in the formation of 3. This fundamental study contrasts with known oxidative addition pathways of complex 1 in the following manner: Following Lewis acid-base complexation, cis-addition of Me-Re bond occurs rather than the often-encountered trans-oxidative addition pathway via cationic species. The extraordinary reaction of 3 with molecular oxygen affords clean oxygen insertion into the Pt-Re bond, leading to complex 4. DFT analysis of this reaction favored the peroxo species  ${}^{1}Q$  as intermediate. Addition of two molecules of  ${}^{1}Q$ resulted in the formation of two molecules of 4a with liberation of a dioxygen molecule. Overall the reaction of complex 3 with

oxygen was downhill in energy with the absence of transition state between 3 and  ${}^{1}Q$  as well as between  ${}^{1}Q$  and 4a, which is consistent with the experimental observation of instantaneous and complete consumption of 3 leading to the formation of 4 even at -78 °C.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02801.

Eyring plot, Van't Hoff plot, EXAFS fitting results, XANES spectra, reaction profile, NMR spectra, tabulated crystal data and structure refinement, selected bond lengths and angles, discussion of experimental details, procedures of syntheses, discussion of DFT calculations, illustrations of complexes, tabulated bond length changes, description of reaction sequence, additional references (PDF)

X-ray crystallographic information (CIF) DFT data (TXT)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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#### Notes

The authors declare no competing financial interest.

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