

**Figure 1.** The GVB(2/4)PP one-electron orbitals of the C=C bond in  $C_2F_4$  are shown for (i) (symmetry-constrained)  $\sigma$  and  $\pi$  bonds,  $E_{PP(2/4)} = -473.53219$  hartrees,  $E_{GVB-CI(2/4)} = -473.54944$  hartrees; (ii) skewed  $\sigma$  and  $\pi$  bonds (no symmetry constraints),  $E_{PP(2/4)} = -473.53242$  hartrees,  $E_{GVB-CI(2/4)} = -473.54899$  hartrees; and (iii) symmetric bent or "banana" bonds,  $E_{PP(2/4)} = -473.53226$  hartrees,  $E_{GVB-CI(2/4)} = -473.54924$  hartrees. Contours are plotted from  $-0.5$  to  $+0.5$  au, with increments every 0.05 au.

of in terms of the  $\sigma$  and  $\pi$  bond description.<sup>11</sup>

In conclusion, we report an accurate ab initio theoretical prediction of the bond energy of  $C_2F_4$  [ $D_{298}(C=C) = 64.5 \pm 2.5$  kcal/mol] and of the heat of formation of  $CF_2$  ( $\Delta H_{f,298}^\circ = -46.5 \pm 1.6$  kcal/mol), by using the newly-developed CCCI methods. The predicted bond energy helps distinguish between the large discrepancies in existing experimental values for  $D_{298}(C_2F_4)$ , ruling out one estimate (53.4 kcal/mol) and strongly supporting the 69.0 kcal/mol value. In addition, we find that the traditional picture of multiple bonds ( $\sigma$  and  $\pi$  bonds) is correct for  $C_2F_4$ .

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(11) The calculations on  $FC\equiv CF$  (ref 4), which find bent bonds  $\sim 2$  kcal/mol lower than  $\sigma\pi$  bonds, did not go beyond the GVB-PP description.

(12) Zero-point energies for  $CF_2$  were taken from ref 9b (4.3 kcal/mol) for the  $^1A_1$  state, while the zero-point motion of the  $^3B_1$  state was estimated ( $4.1 \pm 0.1$  kcal/mol) from the frequency shifts in  $C_2D_4$ ,<sup>9a</sup> going to  $CD_2$  (Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724) and the frequencies in  $C_2F_4$ . This leads to  $T_0(CF_2) = 57.3 \pm 0.1$  kcal/mol [ $\Delta E_{ST} = T_0(CF_2) = 57.5$  kcal/mol].

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## The Synthesis, Characterization, and Reactivity of a Novel Nitroruthenium(III) Complex

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Transition-metal nitro complexes have attracted much attention due to their ability to act as oxygen atom transfer agents and also because of the potential these reagents have as catalysts for the air oxidation of organic substrates.<sup>1,2</sup> These complexes have been shown to oxidize a number of organic<sup>3-10</sup> and inorganic substrates,<sup>11-16</sup> where the corresponding transition-metal nitrosyl complexes are formed along with the oxidized substrates. The metal nitrosyl species which is produced can be oxidized back to the original metal nitro complex by a symmetric cleavage of dioxygen.<sup>5,6,17-21</sup> While a variety of transition-metal nitro complexes have been studied, only one example of an isolable nitroruthenium(III) complex has appeared in the literature, with no

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discussion of reactivity with organic substrates.<sup>16a</sup> The reported ruthenium complex suffers from facile intermolecular disproportionation at the nitro ligand, where the nitroruthenium(III) complex disproportionates rapidly to the nitrosylruthenium(II) and (nitrate)ruthenium(III) complexes.<sup>12,15</sup> Through the utilization of phosphine ligands with octahedral nitroruthenium(III) complexes, we have found that the stability of a nitroruthenium(III) moiety can be greatly enhanced. We now wish to report the synthesis and characterization of a stable nitroruthenium(III) complex and the initial kinetic studies involving the oxidation of organic substrates by this nitroruthenium(III) species. This complex acts as an oxygen atom transfer agent in the oxidation of olefins and as an electron transfer agent in the oxidation of alcohols. Furthermore, no evidence for disproportionation at the nitro ligand has been found with this complex.

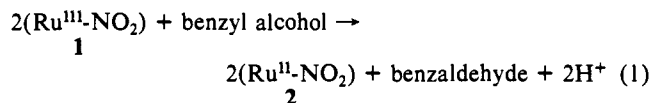
The synthesis of the active oxidizing agent in this study, *trans*-[Ru<sup>III</sup>(NO<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>(trpy)]<sup>2+</sup> (**1**) (where PMe<sub>3</sub> = trimethylphosphine and trpy = 2,2',2''-terpyridine), proceeds as follows. The starting material Ru<sup>III</sup>(Cl)<sub>3</sub>(trpy)<sup>22a</sup> is reduced by triethylamine in the presence of trimethylphosphine to ultimately yield *trans*-[Ru<sup>II</sup>(Cl)(PMe<sub>3</sub>)<sub>2</sub>(trpy)]<sup>+</sup>, by methods similar to published procedures.<sup>22</sup> This complex is then reacted with sodium nitrite in an ethanol/water mixture to give *trans*-[Ru<sup>II</sup>(NO<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>(trpy)]<sup>+</sup> (**2**). The oxidation of **2** with cerium(IV) in water then affords the desired nitroruthenium(III) complex, **1**. Elemental analysis of complexes **1**, **2**, **3**, and **4** as perchlorate salts gave satisfactory results.<sup>23</sup> The addition of excess perchloric acid to **2** in acetonitrile yields the nitrosylruthenium complex *trans*-[Ru(NO)(PMe<sub>3</sub>)<sub>2</sub>(trpy)]<sup>3+</sup> (**3**). The controlled potential electrolysis, or reaction with zinc amalgam, of **3** in acetonitrile produced [Ru(NO)(PMe<sub>3</sub>)<sub>2</sub>(trpy)]<sup>2+</sup> (**4**), which is stable at room temperature in the absence of oxygen. Interestingly, complex **4** reacts with oxygen to produce the nitroruthenium(II) complex, **2**, and the nitrosylruthenium complex, **3**. This observation is consistent with a slow air oxidation of **4** to **1**, followed by a rapid reaction of **1** with **4** remaining in solution, producing an equal mixture of complexes **2** and **3**. In an independent experiment, complex **1** was reacted with **4** and produced upon mixing quantitative amounts of **2** and **3**, respectively.

The configuration of the trimethylphosphine ligands in the paramagnetic complex **1** was suggested by NMR experiments on the diamagnetic precursor, complex **2**. The proton decoupled carbon-13 NMR spectrum of complex **2** displayed the expected number of resonances due to the trpy ligand and two trimethylphosphine ligands, assuming a trans geometry of the phosphine ligands around the ruthenium center.<sup>24</sup> The bonding mode of the nitro ligands in complexes **1** and **2**, in KBr pellets, was investigated through the use of infrared spectroscopy. The ν(N–O) bands for complex **1** were observed at 1480 and 1316 cm<sup>-1</sup> and at 1433 and 1281 cm<sup>-1</sup> for complex **2**, indicative of N-bound nitro coordination.<sup>25,26</sup>

The cyclic voltammogram<sup>27</sup> of complex **2** shows one reversible ruthenium(III)/(II) couple at +1.03 V versus SSCE, where the Δ*E*<sub>p</sub>, the peak potential difference, is 60 mV, and the ratio of peak currents, *ipc/ipa*, is equal to 1.0. The cyclic voltammogram of

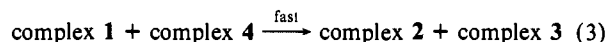
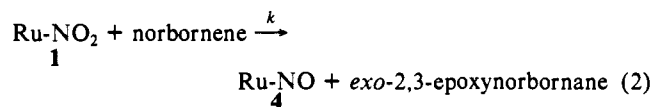
the nitroruthenium(III) complex, **1**, is identical with that found for complex **2**, with the same voltammetric *E*<sub>1/2</sub>. Coulometric analysis of complex **2** in acetonitrile at 5 °C yielded an *n* value of 1.10 for the exhaustive oxidation at +1.40 V versus SSCE and *n* = 1.04 for the return reduction of the species. The cyclic voltammograms of the nitrosylruthenium complexes **3** and **4** are identical, where both display a reversible couple at +0.25 V versus SSCE. The magnetic moment of **1** was examined by the Gouy method at room temperature, and a value of 2.05 μ<sub>B</sub> was found for this complex. This value is in close agreement with values for other low-spin ruthenium(III) octahedral complexes.<sup>28</sup>

The nitroruthenium(III) complex, **1**, acts as an oxidant toward a number of organic substrates.<sup>29</sup> Complex **1** reacts with benzyl alcohol in H<sub>2</sub>O (pH = 6.8) to produce benzaldehyde and the analogous ruthenium(II)–nitro complex, **2**, as depicted in eq 1.



Similarly, the oxidation of 1-butanol by complex **1** under identical conditions yields butyraldehyde and complex **2**. The second-order rate constants for these reactions were found to be 1.3 M<sup>-1</sup> s<sup>-1</sup> and 2.5 × 10<sup>-1</sup> M<sup>-1</sup> s<sup>-1</sup> at 5 °C, respectively. Through spectroscopic monitoring, these reactions were observed to proceed isobestically from complex **1** to **2**. Additionally, from pH measurements for the reaction of complex **1** with benzyl alcohol in water, it was determined that one proton was produced for every molecule of complex **2** formed. In *o*-dichlorobenzene, the oxidation of benzyl alcohol with complex **1** proceeded cleanly with the production of a stoichiometric amount of the nitroruthenium(II) complex, **2**. The second-order rate constant for this reaction was found to be 2.9 × 10<sup>-4</sup> M<sup>-1</sup> s<sup>-1</sup> at 22 °C. By conducting the kinetic experiments over a range of temperatures, activation parameters were calculated for this reaction, and values for Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> were obtained as 21.1 ± 0.7 kcal/mol and -3.5 ± 2.3 eu, respectively.

The oxidation of norbornene by complex **1** can be described by the following equations



The oxidation of norbornene at 5 °C in acetonitrile yielded a second-order rate constant of 2.6 × 10<sup>-1</sup> M<sup>-1</sup> s<sup>-1</sup>, giving *exo*-2,3-epoxynorbornane as the organic product. The electronic spectrum for the reaction mixture confirmed the quantitative production of 50% complex **2** and 50% complex **3**, where the formation of the mixture was found to occur isobestically, indicating a 1:1 ratio of metal products evolved throughout the reaction. Thus, the slow step of the olefin oxidation is represented by eq 2, followed quickly by reaction 3. It is the fast electron transfer (upon mixing) between complexes **1** and **4** that is responsible for the equal distribution of complexes **2** and **3** observed for the oxidation of norbornene.

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(23) Anal. Calcd for **1**, [Ru<sup>III</sup>(NO<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>(trpy)](ClO<sub>4</sub>)<sub>2</sub> (C<sub>21</sub>H<sub>29</sub>N<sub>4</sub>O<sub>10</sub>P<sub>2</sub>Cl<sub>2</sub>Ru): C, 34.48; H, 4.00. Found: C, 34.24; H, 4.04. Calcd for **2**, [Ru<sup>II</sup>(NO<sub>2</sub>)(PMe<sub>3</sub>)<sub>2</sub>(trpy)](ClO<sub>4</sub>) (C<sub>21</sub>H<sub>29</sub>N<sub>4</sub>O<sub>5</sub>P<sub>2</sub>ClRu): C, 39.91; H, 4.62. Found: C, 39.90; H, 4.62. Calcd for **3**, [Ru(NO)(PMe<sub>3</sub>)<sub>2</sub>(trpy)](ClO<sub>4</sub>)<sub>3</sub> (C<sub>21</sub>H<sub>29</sub>Cl<sub>3</sub>N<sub>4</sub>O<sub>13</sub>P<sub>2</sub>Ru): C, 30.95; H, 3.59. Found: C, 31.02; H, 3.64. Calcd for **4**, [Ru(NO)(PMe<sub>3</sub>)<sub>2</sub>(trpy)](ClO<sub>4</sub>)<sub>2</sub> (C<sub>21</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>9</sub>P<sub>2</sub>Ru): C, 35.26; H, 4.08. Found: C, 34.67; H, 4.14.

(24) <sup>13</sup>C proton-decoupled NMR (CDCl<sub>3</sub>): δ 9.4, 10.0, 10.6, 123.0, 124.2, 127.0, 136.0, 137.6, 153.6, 155.6, 156.8.

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(27) Electrochemical measurements were made with a platinum electrode versus a saturated sodium chloride electrode (SSCE) in 0.1 M Et<sub>4</sub>NClO<sub>4</sub> solutions in acetonitrile; *E*<sub>1/2</sub> values are equal to (E<sub>p,a</sub> + E<sub>p,c</sub>)/2. Δ*E*<sub>p</sub> = E<sub>p(oxidation)</sub> – E<sub>p(reduction)</sub> at a scan rate rate of 100 mV/s.