# **ORGANOMETALLICS**

Article

# Activation of Nitrous Oxide by Dinuclear Ruthenium Complexes

Alexander G. Tskhovrebov, Euro Solari, Rosario Scopelliti, and Kay Severin\*

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

# **Supporting Information**

**ABSTRACT:** The dinuclear Ru(II) complexes (arene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(C<sub>2</sub>H<sub>4</sub>)(PCy<sub>3</sub>) (arene = p-cymene or 1,3,5-C<sub>6</sub>H<sub>3</sub>iPr<sub>3</sub>) react with N<sub>2</sub>O under mild conditions to give OPCy<sub>3</sub> and the trinuclear complexes (arene)Ru( $\mu$ -Cl)<sub>3</sub>Ru( $\mu$ -Cl)<sub>3</sub>Ru(arene). The N-heterocyclic carbene complex (p-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(C<sub>2</sub>H<sub>4</sub>)(IMes) (IMes = 1,3-dimesitylimidazol-2-ylidene), on the other hand, reacts with N<sub>2</sub>O to give a mixed-valence Ru(II)/Ru(III) complex with a chelating alkoxy ligand. Dinitrogen complexes were identified as intermediates in all reactions. At elevated temperature, the carbene complex (p-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(C<sub>2</sub>H<sub>4</sub>)(IMes) is able to catalyze the oxidation of alcohols with N<sub>2</sub>O.



# INTRODUCTION

Nitrous oxide is a chemically very inert molecule. This feature has hampered its utilization as an oxidant or as a building block for more complex molecules. The use of N2O as an oxidant would be particularly appealing since  $N_2O$  has a high oxidation potential and the side product of oxidation reactions, dinitrogen, is environmentally benign. Not surprisingly, considerable efforts have been made to activate N2O chemically.<sup>1,2</sup> One possibility is the utilization of heterogeneous catalysts.<sup>3</sup> Several systems are known to catalyze oxidation reactions with N<sub>2</sub>O, but high temperatures and pressures are generally needed. The activation of N<sub>2</sub>O under mild conditions in homogeneous solution can be achieved with transition metal complexes.<sup>4,5</sup> Oxygen atom transfer reactions from N<sub>2</sub>O to transition metal complexes with concomitant release of N2 typically produce metal-oxo complexes, but the insertion of oxygen into metal-carbon and metal-hydrogen bonds has also been reported. So far, there are few metal complexes that bind  $N_2O$  intact ( $N_2O$  is a very poor ligand).<sup>6-8</sup> Reactions of  $N_2O$ that proceed with rupture of the N-N bond have been observed in some selected cases.9

[Ru(NH<sub>3</sub>)<sub>5</sub>(N<sub>2</sub>O)]<sup>2+</sup>, the first nitrous oxide complex, was reported more than 40 years ago.<sup>7f</sup> Despite this early success, there are still only a few Ru complexes that are able to react with N<sub>2</sub>O under ambient conditions.<sup>7,10</sup> At elevated temperature and pressure, however, Ru-porphyrin complexes can catalyze the oxidation of organic substrates with N<sub>2</sub>O, albeit with poor efficiency.<sup>11</sup> Below, we show that dinuclear Ru(II) complexes of the general formula (arene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl-(C<sub>2</sub>H<sub>4</sub>)L (L = PCy<sub>3</sub> or IMes) are able to react with N<sub>2</sub>O under mild conditions.

# RESULTS AND DISCUSSION

For several years, we have been interested in the chemistry of dinuclear complexes, in which two different metal fragments are connected by halogeno bridges.<sup>12</sup> In 2005, we described the

ruthenium ethylene complex (p-cymene)Ru $(\mu$ -Cl)<sub>3</sub>RuCl- $(C_2H_4)(PCy_3)$  (1).<sup>13</sup> It can be obtained by reaction of the commonly used starting material [(p-cymene)RuCl $(\mu$ -Cl)]<sub>2</sub> with one equivalent of PCy<sub>3</sub> in the presence of ethylene (Scheme 1).



The dimer **1** and the structurally related complex **2** turned out to be exceptionally active catalysts for atom transfer radical addition and polymerization reactions.<sup>13,14</sup> The high intrinsic activity of **1** was further evidenced by a reaction with acetylene, which resulted in the formation of a  $\mu$ -carbide complex,<sup>15</sup> and by the observation of an intramolecular C–H activation of the PCy<sub>3</sub> ligand.<sup>16</sup> In all cases, the reactions were initiated by loss of the labile ethylene ligand. In view of these results, it appeared interesting to test the reactivity of **1** and **2** toward N<sub>2</sub>O.

A suspension of complex 1 in THF under an atmosphere of  $N_2O$  was heated to 60 °C. After 24 h, the trinuclear complex 5 was obtained as a purple precipitate in 58% yield (Scheme 2). The remaining solution contained OPCy<sub>3</sub> along with some unidentified Ru complexes. To obtain more information about possible intermediates, we have performed a similar reaction with the more soluble triisopropylbenzene complex 2. Gentle heating (40 °C) of a suspension of complex 2 in THF under  $N_2O$  resulted in the formation of an orange solution, which

Received: August 15, 2012 Published: September 26, 2012

#### Scheme 2



gradually darkened. As in the case of the cymene complex 1, we were able to isolate a trinuclear complex (6) as the main product after 24 h (yield: 47%). Reactions performed in THF $d_8$  allowed the NMR spectroscopic identification of the dinitrogen complex 4 as an intermediate in the reaction. dinitrogen complex **4** as an interaction of  $[(1,3,5-C_6H_3iPr_3) RuCl(\mu-Cl)]_2$  with PCy<sub>3</sub> under an atmosphere of N<sub>2</sub>. Control reactions with pure 4 showed that it also reacts with  $N_2O$  to give complex 6 along with  $OPCy_3$ . It appears likely that a similar dinitrogen complex (3) is formed in reactions with complex 1, but the poor solubility of the cymene complexes prevented further solution-based studies. Overall, the results clearly demonstrate the ability of the dinuclear complexes 1 and 2 to activate  $N_2O$ . Oxygen atom transfer results in the formation of OPCy<sub>3</sub> (presumably via short-lived Ru-oxo complexes) along with N2. The latter is captured by  $(arene)Ru(\mu-Cl)_3RuCl(PCy_3)$  to give the intermediates 3 and 4, which also participate in reactions with  $N_2O$ .

The trinuclear Ru(II) complex **5** has been described before; it can be obtained by irradiation of  $[(p\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$ in chloroform.<sup>17</sup> The new complex **6** was analyzed by singlecrystal X-ray diffraction (Figure 1). Its structure is very similar to that of complex **5**: it features a central Ru( $\mu$ -Cl)<sub>3</sub>Ru( $\mu$ -Cl)<sub>3</sub>Ru core,<sup>18</sup> which is capped by two 1,3,5-triisopropylben-



Figure 1. Molecular structure of complex 6 in the crystal. Hydrogen atoms and cocrystallized solvent molecules are not shown for clarity. The thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Ru1–Cl1 2.4517(18), Ru1–Cl2 2.431(2), Ru1–Cl3 2.4575(19), Ru2–Cl1 2.4115(18), Ru2–Cl2 2.3879(19), Ru2–Cl3 2.4002(18); Cl(2)-Ru(2)-Cl(3) 82.64(7), Cl(2)-Ru(2)-Cl(2)A 180.0, Cl(2)A-Ru(2)-Cl(3) 97.36(7), Cl(2)-Ru(1)-Cl(3) 80.58(7), Ru(1)-Cl(1)-Ru(2) 82.32(5).

zene ligands. As observed for 5, the Ru–Cl bond lengths involving the terminal Ru atoms (2.43-2.46 Å) are longer than those to the central Ru atom (2.39-2.41 Å).

A crystallographic analysis of 4 has been published, <sup>12c</sup> but a solution-based analysis of 4 is missing so far. When a  $CD_2Cl_2$  solution of 4 under dinitrogen was investigated by <sup>31</sup>P NMR spectroscopy, three signals between 54 and 55 ppm were observed (Figure 2, bottom). Complex 4 contains two



Figure 2.  $^{31}\mathrm{P}$  NMR spectrum (CD\_2Cl\_2) of complex 4 at a dinitrogen pressure of 10 atm (top) and 1 atm (bottom).

stereogenic Ru centers and likely exists as a mixture of diastereoisomers. Two  $^{31}P$  NMR signals were thus expected. The third one can be attributed to the dinuclear complex 7. Evidence for a dynamic equilibrium between 4 and 7 was established by pressure-dependent NMR spectroscopy: at elevated dinitrogen pressure (10 atm), the intensity of the signal of 7 increased with respect to that of the signals of 4 (Figure 2, top).



The reactions of 1 and 2 with N<sub>2</sub>O are likely initiated by loss of the ethylene ligand and generation of a highly active (arene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(PCy<sub>3</sub>) species. These intermediates should also be accessible by reaction of [(arene)RuCl( $\mu$ -Cl)]<sub>2</sub> with one equivalent of PCy<sub>3</sub> in the absence of ethylene. In fact, stirring of a solution of [(arene)RuCl( $\mu$ -Cl)]<sub>2</sub> in THF at 65 °C under N<sub>2</sub>O for 24 h led to the formation of the trinuclear complexes 5 (yield: 46%) and 6 (yield: 34%) along with OPCy<sub>3</sub> (Scheme 4).

A severe drawback of the phosphine complexes 1 and 2 with respect to catalytic applications is the possibility of autoxidation to give OPCy<sub>3</sub>. We anticipated that a complex featuring an N-heterocyclic carbene (NHC) ligand instead of PCy<sub>3</sub> would be more robust. A complex of this kind, (p-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(C<sub>2</sub>H<sub>4</sub>)(IMes) (8), has been described by Delaude



and Demonceau.<sup>19</sup> Similar to 1, complex 8 shows an interesting organometallic chemistry.<sup>19,20</sup> Placing a THF solution of complex 8 under an atmosphere of  $N_2O$  led to a slow color change from orange to dark orange, and after 12 h complex 10 was isolated from the reaction mixture in 74% yield. <sup>1</sup>H NMR monitoring showed that the reaction proceeds via the  $N_2$  complex 9, which then gradually disappeared (Scheme 5).

Scheme 5



Complex 10 was found to be paramagnetic, which hampered an NMR-spectroscopic analysis. However, we were able to characterize the product by single-crystal X-ray diffraction (Figure 3). Complex 10 features a  $\mu$ -alkoxy ligand, which is



Figure 3. Molecular structure of complex 10 in the crystal. Hydrogen atoms and cocrystallized solvent molecules are not shown for clarity. The thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Ru(2)-C(1) 2.016(8), R(2)-Cl(1) 2.428(2), Ru(2)-Cl(2) 2.528(2), Ru(2)-Cl(3) 2.320(2), Ru(2)-Cl(4) 2.328(2), Ru(1)-···Ru(2) 3.1492(12), Ru(1)-Cl(2) 2.426(2), Ru(1)-Cl(1) 2.478(2), O(1)-C(12) 1.433(10); C(1)-Ru(2)-O(1) 96.2(3), C(1)-Ru(2)-Cl(3) 96.8(2), C(1)-Ru(2)-Cl(4) 90.7(2), O(1)-Ru(2)-Cl(3) 164.33(17), O(1)-Ru(2)-Cl(4) 96.29(17), C(1)-Ru(2)-Cl(1) 92.9(2), Ru(1)-O(1)-Ru(2) 98.0(2), N(1)-C(1)-N(2) 104.0(7).

derived from oxidation of one of the *o*-methyl groups of the IMes ligand.<sup>21</sup> The same chelating carbene ligand was proposed to form during the aerobic oxidation of a Pd-IMes complex.<sup>22</sup> The formation of **10** proceeds likely via a highly reactive Ruoxo complex followed by an intramolecular C–H activation. Unfortunately, we were not able to establish the fate of the 'H' atom, which is formally liberated in this reaction.<sup>23</sup> Complex **10** can be described as a mixed-valence Ru(II)/Ru(III) complex,<sup>24</sup> in line with the observed paramagnetism. The observed Ru–O bond lengths (2.117(6) and 2.054(6) Å) are close to the values reported for other alkoxybridged Ru(II)/Ru(III) or Ru(II)/Ru(III) complexes.<sup>25</sup>

The observation of complexes 9 and 10 in reaction of the IMes complex 8 with N<sub>2</sub>O suggests a reaction pathway that is related to what was observed for 1 and 2: liberation of the ethylene ligand generates the highly reactive (p-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(IMes). Subsequent reaction with N<sub>2</sub>O provides a Ruoxo complex and N<sub>2</sub>. The oxo complex leads to autoxidation of the IMes ligand and N<sub>2</sub> is captured by remaining (p-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl(IMes) to give complex 9. The latter is slowly converted into 10, presumably by loss of N<sub>2</sub> followed by reaction with N<sub>2</sub>O. The ability of N<sub>2</sub>O to oxidize 9 into 10 was demonstrated in a control experiment with preformed 9, which is accessible by reaction of [(p-cymene)RuCl( $\mu$ -Cl)<sub>3</sub>]<sub>2</sub> with IMes under an atmosphere of N<sub>2</sub> (Scheme 6). Complex 9



was also characterized by single-crystal X-ray diffraction (Figure 4). The N–N bond length of the terminal dinitrogen ligand (1.073(2) Å) is shorter than what was found for N<sub>2</sub>-bridged 4 (1.120(4) Å),<sup>12c</sup> but close to the values for the terminal N<sub>2</sub>



Figure 4. Molecular structure of complex 9 in the crystal. Hydrogen atoms and cocrystallized solvent molecules are not shown for clarity. The thermal ellipsoids are set at 50% probability. Selected bond lengths (Å) and angles (deg): Ru(1)-N(1) 1.9304(18), Ru(1)-C(1) 2.034(2), Ru(1)-Cl(4) 2.3806(6), Ru(1)-Cl(3) 2.4211(6), Ru(1)-Cl(2) 2.4426(6), Ru(1)-Cl(1) 2.5138(6); N(1)-Ru(1)-C(1) 97.43(7), N(1)-Ru(1)-Cl(4) 89.21(5), C(1)-Ru(1)-Cl(4) 91.67(6), Cl(4)-Ru(1)-Cl(2) 170.496(17), Cl(3)-Ru(2)-Cl(1) 80.506(16), Ru(2)-Cl(1)-Ru(1) 82.441(16), N(4)-C(1)-N(3) 102.27(16).

complex  $[RuTp(N_2)(Ph_2P(CH_2)_2NMe_2)](CF_3SO_3)$  (e.g., 1.097(5) Å),<sup>26</sup>  $[TpRu(N_2)(PEt_3)_2](BPh_4)$  (1.010(2) Å),<sup>27</sup> or  $[CpRu(N_2)(1,2-bis(diisopropylphosphino)ethane)](BAr_4)$ (1.087(4) Å).<sup>28</sup> The Ru-N<sub>2</sub> fragment is slightly bent (Ru(1)-N(1)-N(2) = 169.15(17)°). The bond lengths and angles found for the NHC ligand are unremarkable.

Notwithstanding their propensity to undergo autoxidation reactions, the complexes 1 and 8 were tested for their ability to catalyze the oxidation of cyclooctanol by N2O. The reactions were performed with 5 mol % of complex 1 or 8 in 1,2dichlorobenzene using a slightly elevated N2O pressure of 2 atm. Complex 1 did not show any catalytic activity, neither at room temperature nor at elevated temperature. Complex 2 was nearly inactive at 25 °C, but at 150 °C cyclooctanone was obtained in a yield of 65%. A control reaction performed under  $N_2$  containing 0.1 vol %  $O_2$  did not yield a significant amount of ketone. 3,5-Dimethoxybenzyl alcohol and 3-methylbenzyl alcohol were also oxidized by N2O at 150 °C to the corresponding aldehydes in yields of 55% and 20%, respectively. These preliminary results demonstrate that the NHC complexes have some potential as catalyst precursors. The achieved turnover numbers (4-13) are still low,<sup>29</sup> but more robust catalysts might be obtained by using NHC ligands, which are less prone to autoxidation.

# CONCLUSION

Dinuclear Ru(II) complexes of the general formula (arene)-Ru( $\mu$ -Cl)<sub>3</sub>RuCl(C<sub>2</sub>H<sub>4</sub>)L (L = PCy<sub>3</sub> or IMes) were found to react with N<sub>2</sub>O under mild conditions. In all cases, oxygen atom transfer to the ligand L was observed. For the PCy<sub>3</sub> complexes 1 and 2, the oxidation resulted in liberation of OPCy<sub>3</sub> and formation of trinuclear (arene)Ru( $\mu$ -Cl)<sub>3</sub>Ru( $\mu$ -Cl)<sub>3</sub>Ru(arene) complexes (5, 6). For the NHC complex 8, on the other hand, the oxidized IMes ligand remained attached to the Ru to give a chelating alkoxy ligand (10). Preliminary investigations show that the NHC complex 8 can be used as a precursor for the catalytic oxidation of alcohols with N<sub>2</sub>O, but the reactions require high temperature and catalyst loading.

# EXPERIMENTAL SECTION

General Procedures. Unless stated otherwise, the reactions were performed under an atmosphere of dry dinitrogen. Solvents were purified and dried according to standard procedures. The ligands 1,3dimesitylimidazol-2-ylidene (IMes) and PCy3 were obtained from Sigma-Aldrich. The complexes  $[(p-cymene)RuCl(\mu-Cl)]_{2}^{30}$  [(1,3,5- $C_6H_3iPr_3$ RuCl( $\mu$ -Cl)]<sub>2</sub>,<sup>31</sup> [(1,3,5-C\_6H\_3iPr\_3)Ru( $\mu$ -Cl)<sub>3</sub>RuCl- $(PCy_3)]_2(\mu \cdot N_2)$  (4),<sup>12c</sup> and (*p*-cymene)Ru( $\mu$ -Cl)<sub>3</sub>RuCl( $C_2H_4$ )(IMes) (8)<sup>19</sup> were prepared as described inadvertent oxidations by traces of O2, we have used N2O of high purity (99.999%), which was purchased from Air Liquide. NMR spectra were measured on a Bruker Avance DPX-400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz, <sup>31</sup>P: 162 MHz) spectrometer. NMR spectra at elevated pressure were obtained by using high-pressure quartz NMR tubes. Combustion analysis was performed with a Thermo Scientific Flash 2000 organic elemental analyzer. The GC measurements were performed with a GC/MS using a Varian 3800 spectrometer coupled to a Varian 2200 mass spectrometer. The IR spectrum of complex 9 was recorded on a Spectrum One FT-IR spectrometer from Perkin-Elmer.

**Complex 4.** Complex 4 was prepared as reported previously.<sup>12c</sup> In solution, the tetranuclear complex 4 is in equilibrium with the dinuclear complex 7. The assignment of the NMR signals was achieved by recording spectra at different N<sub>2</sub> pressure. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 1.24–2.33 (m, Cy's, CH(CH<sub>3</sub>)<sub>2</sub>), 3.04–2.93 (m, CH(CH<sub>3</sub>)<sub>2</sub>), 5.31 (s, tetranuclear complex), 5.41 (s, tetranuclear complex), 5.44 (s,

dinuclear complex). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): dinuclear complex 7: 22.08 (d, 37.1 Hz, Cy), 27.74 (d, 9.3 Hz, Cy), 28.76 (s Cy), 35.80 (d, 23.2 Hz, Cy), 26.43 and 31.49 (CH(CH<sub>3</sub>)<sub>2</sub>), 73.64 (CH, arene), 103.64 (C, arene); tetranuclear complex 4: 21.93–36.10 (Cy, CH(CH<sub>3</sub>)<sub>2</sub>), 72.51, 75.14 (CH, arene), 101.89, 104.17 (C, arene). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): dinuclear complex 7: 54.41; tetranuclear complex 4: 53.94 and 54.62.

**Complex 5.** Method A. A suspension of complex 1 (50 mg, 63  $\mu$ mol) in THF (20 mL) was heated at 60 °C under an atmosphere of N<sub>2</sub>O. After 24 h, the mixture was cooled to room temperature. Complex 5 precipitated in the form of a purple powder, which was isolated by filtration and washed with hexane. Yield: 23 mg, 58%.

*Method B.* A solution of  $[(p\text{-cymene})\text{RuCl}(\mu\text{-Cl})]_2$  (482 mg, 787  $\mu$ mol) and PCy<sub>3</sub> (221 mg, 787  $\mu$ mol) in THF (100 mL) was heated at 60 °C under an atmosphere of N<sub>2</sub>O. After 24 h, the mixture was cooled to room temperature. Complex **5** precipitated in the form of a purple powder, which was isolated by filtration and washed with hexane. Yield: 191 mg, 46%. The analytical data match what has been described before.<sup>17</sup>

**Complex 6.** Method A. A suspension of complex 2 (250 mg, 292  $\mu$ mol) in THF (10 mL) was heated at 40 °C under an atmosphere of N<sub>2</sub>O. After 24 h, the mixture was cooled to room temperature. Complex 6 precipitated in the form of a purple powder, which was isolated by filtration and washed with hexane. Yield: 86 mg, 47%.

*Method B.* A solution of  $[(1,3,5-C_6H_3iPr_3)RuCl(\mu-Cl)]_2$  (400 mg, 531 µmol) and PCy<sub>3</sub> (150 mg, 535 µmol) in THF (100 mL) was heated at 65 °C under an atmosphere of N<sub>2</sub>O. After 24 h, the mixture was cooled to room temperature. Complex 6 was isolated by filtration and washed with hexane. Yield: 111 mg, 34%. Anal. Calcd for  $C_{30}H_{48}Cl_6Ru_3$ : C 38.97; H 5.23. Found: C 38.48; H 5.08. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 1.38 (d, 6.7 Hz, 36 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.00 (sept, 6.7 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.28 (s, 6 H, CH, arene). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 22.04 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.48 (CH(CH<sub>3</sub>)<sub>2</sub>), 70.45 (CH, arene), 103.51 (C, arene). Single crystals were obtained by cooling a saturated CH<sub>2</sub>Cl<sub>2</sub> solution.

**Complex 9.** A solution of  $[(p-cymene)RuCl(\mu-Cl)]_2$  (400 mg, 654  $\mu$ mol) and IMes (200 mg, 654  $\mu$ mol) in toluene (25 mL) was heated at 70 °C under an atmosphere of dinitrogen. After 24 h, the mixture was cooled to room temperature. An orange precipitate formed, which was isolated by filtration and washed with hexane. Yield: 335 mg, 60%. Anal. Calcd for C31H38Cl4N4Ru2.0.5(toluene): C 48.37; H 4.94; N 6.54. Found: C 48.16; H 4.76; N 6.71. IR ( $\nu$ ): 2125 cm<sup>-1</sup> (N<sub>2</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, δ): 1.33 (d, 6.8 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11 (s, 6 H), 2.17 (s, 9 H, Me from o-Mes and p-cym), 2.39 (s, 6 H, Me from p-Mes), 2.89 (sept, 6.8 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.25 (m, 2 H), 5.45 (m, 2 H, CH's from p-cym), 6.96 (s, br, 2 H, CH from carbene), 7.01 (s, br, 4 H, CH from Mes). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 18.14, 20.90, 21.92, 22.28 (Me's), 30.92 (CH(CH<sub>3</sub>)<sub>2</sub>), 77.91, 77.97, 78.16, 78.32 (CH<sub>ar</sub> from p-cym), 95.33, 101.26 (C<sub>ar</sub> from p-cym), 125.46, 128.17, 128.68, 128.76, 128.98 (CH from carbene, C and CH from Mes), 175.72  $(C_{carb})$ . Single crystals were obtained by slow evaporation of a  $CH_2Cl_2$ solution.

**Complex 10.** Method A. Complex 8 (130 mg, 160  $\mu$ mol) was dissolved in THF (20 mL) under N<sub>2</sub>. The reaction flask (250 mL) was purged and then filled with N<sub>2</sub>O, and the mixture was stirred overnight. The addition of hexane (10 mL) led to the formation of a dark orange precipitate, which was isolated, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane, washed with hexane, and dried under vacuum. Yield: 95 mg, 74%.

Method  $\tilde{B}$ . Complex 9 (150 mg, 185  $\mu$ mol) was dissolved in THF (20 mL) under N<sub>2</sub>. The reaction flask (250 mL) was purged and then filled with N<sub>2</sub>O, and the mixture was stirred overnight. The addition of hexane (10 mL) led to the formation of a dark orange precipitate, which was isolated, recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane, washed with hexane, and dried under vacuum. Yield: 110 mg, 68%. Anal. Calcd for C<sub>31</sub>H<sub>37</sub>N<sub>2</sub>OCl<sub>4</sub>Ru<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C 43.55; H 4.45; N 3.17. Found: C 43.44; H 4.48; N 3.32. Single crystals were obtained by slow diffusion of hexane into a solution of **10** in CH<sub>2</sub>Cl<sub>2</sub>.

**Catalysis Experiments.** Mesitylene was used as a standard. Under an atmosphere of dinitrogen, the substrate (1.0 mmol) and mesitylene (1.0 mmol) were added to a solution of the corresponding catalyst (50  $\mu$ mol) in 1,2-dichlorobenzene (20 mL). The reaction flask (250 mL) was purged and then filled with N<sub>2</sub>O (2 atm), and the solution was stirred at the given temperature for 18 h. The resulting mixture was analyzed by gas chromatography.

*Crystallographic Investigations.* Data collections for all compounds have been measured at low temperature using Mo K $\alpha$  radiation on a Bruker APEX II CCD. Semiempirical<sup>32</sup> absorption correction was applied to all data sets. Structure solutions, refinements, and geometrical calculations have been carried out by SHELXTL.<sup>33</sup> All structures were refined using full-matrix least-squares on  $F^2$  with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with  $U_{\rm iso} = aU_{\rm eq}$  (where *a* is 1.5 for  $-CH_3$  and -OH moieties and 1.2 for others).

#### ASSOCIATED CONTENT

#### **S** Supporting Information

An X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: kay.severin@epfl.ch.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The work was supported by the Swiss National Science Foundation and by the École Polytechnique Fédérale de Lausanne (EPFL).

## REFERENCES

(1) Leont'ev, A. V.; Fomicheva, O. A.; Proskurnina, M. V.; Zefirov, N. S. *Russ. Chem. Rev.* **2001**, *70*, 91–104.

(2) Lee, D.-H.; Mondal, B.; Karlin, K. D. In Activation of Small Molecules; Tolman, W. B., Ed.; Wiley-VCH: Weinheim, 2006; pp 43–79.

(3) (a) Panov, G. I.; Dubkov, K. A.; Kharitonov, A. S. In Modern Heterogeneous Oxidation Catalysis; Noritaka, M., Ed.; Wiley-VCH: Weinheim, 2009; pp 217–252. (b) Parmon, V. N.; Panov, G. I.; Noskov, A. S. Catal. Today 2005, 100, 115–131.

(4) Tolman, W. B. Angew. Chem., Int. Ed. 2010, 49, 1018-1024.

(5) For selected recent examples see: (a) Horn, B.; Limberg, C.; Herwig, C.; Feist, M.; Mebs, S. *Chem. Commun.* **2012**, DOI: 10.1039/ c2cc33846g. (b) Andino, J. G.; Caulton, K. G. *J. Am. Chem. Soc.* **2011**, 133, 12576–12583. (c) Yonke, B. L.; Reeds, J. P.; Zavalij, P. Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 12342–12346. (d) Demir, S.; Montalvo, E.; Ziler, J. W.; Meyer, G.; Evans, W. J. *Organometallics* **2010**, *29*, 6608–6611. (e) Yu, H.; Jia, G.; Lin, Z. *Organometallics* **2009**, 28, 1158–1164.

(6) (a) Pomowski, A.; Zumft, W. G.; Kroneck, P. M. H.; Einsle, O. Nature 2011, 477, 234–237. (b) Piro, N. A.; Lichterman, M. F.; Harman, W. H.; Chang, C. J. J. Am. Chem. Soc. 2011, 133, 2108–2111.
(7) (a) Paulat, F.; Kuschel, T; Näther, C.; Praneeth, V. K. K.; Sander, O.; Lehnert, N. Inorg. Chem. 2004, 43, 6979–6994. (b) Pamplin, C. B.; Ma, E. S. F.; Safari, N.; Rettig, S. J.; James, B. R. J. Am. Chem. Soc. 2001, 123, 8596–8597. (c) Bottomley, F.; Brooks, W. V. F. Inorg. Chem. 1977, 16, 501–502. (d) Bottomly, F.; Crawford, J. R. J. Am. Chem. Soc. 1972, 94, 9092–9095. (e) Armor, J. N.; Taube, H. Chem. Commun. 1971, 287–288. (f) Armor, J. N.; Taube, H. J. Am. Chem. Soc. 1969, 91, 6874–6876.

(8) For organic molecules that are able to bind  $N_2O$  see: (a) Tskhovrebov, A. G.; Solari, E.; Wodrich, M.; Scopelliti, R.; Severin, K. Angew. Chem., Int. Ed. **2012**, 51, 232–234. (b) Neu, R. C.; Otten, E.; Lough, A.; Stephan, D. W. Chem. Sci. **2011**, 2, 170–176. (c) Neu, R. C.; Otten, E.; Stephan, D. W. Angew. Chem., Int. Ed. **2009**, 48, 9709–9712. (d) Otten, E.; Neu, R. C.; Stephan, D. W. J. Am. Chem. Soc. 2009, 131, 9918–9919.

(9) (a) Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. J. Am. Chem. Soc. 2012, 134, 1471–1473. (b) Reeds, J. O.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. J. Am. Chem. Soc. 2011, 133, 18602–18605. (c) Cherry, J.-P. F.; Johnson, A. R.; Baraldo, L. M.; Tsai, Y.-C.; Cummins, C. C.; Kryatov, S. V.; Rybak-Akimova, E. V.; Capps, K. B.; Hoff, C. D.; Haar, C. M.; Nolan, S. P. J. Am. Chem. Soc. 2001, 123, 7271–7286. (d) Johnson, A. R.; Davis, W. M.; Cummins, C. C.; Serron, S.; Nolan, S. P.; Musaev, D. G.; Morokuma, K. J. Am. Chem. Soc. 1998, 120, 2071–2085. (e) Laplaza, C. E.; Odom, A. L.; Davis, W. M.; Cummins, C. C. J. Am. Chem. Soc. 1995, 117, 4999– 5000. (f) Heinemann, C.; Schwarz, H. Chem.—Eur. J. 1995, 1, 7–11. (10) (a) Walstrom, A.; Pink, M.; Fan, H.; Tomaszewski, J.; Caulton, K. G. Inorg. Chem. 2007, 46, 7704–7706. (b) Kaplan, A. W.; Bergman, R. G. Organometallics 1998, 17, 5072–5085. (c) Groves, J. T.; Roman, J. S. J. Am. Chem. Soc. 1995, 117, 5594–5595.

(11) (a) Tanaka, H.; Hashimoto, K.; Suzuki, K.; Kitaichi, Y.; Sato, M.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1905–1914.
(b) Hashimoto, K.; Tanaka, H.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2002**, 582–583. (c) Hashimoto, K.; Kitaichi, Y.; Tanaka, H.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2001**, 922–923.

(12) For selected references see: (a) Albrecht, C.; Gauthier, S.; Wolf, J.; Scopelliti, R.; Severin, K. Eur. J. Inorg. Chem. 2009, 1003–1010.
(b) Quebatte, L.; Scopelliti, R.; Severin, K. Eur. J. Inorg. Chem. 2006, 231–236. (c) Quebatte, L.; Haas, M.; Solari, E.; Scopelliti, R.; Nguyen, Q. T.; Severin, K. Angew. Chem., Int. Ed. 2005, 44, 1084–1088.
(d) Quebatte, L.; Scopelliti, R.; Severin, K. Angew. Chem., Int. Ed. 2004, 43, 1520–1524. (e) Gauthier, S.; Quebatte, L.; Scopelliti, R.; Severin, K. Chem.—Eur. J. 2004, 10, 2811–2821. (d) Severin, K. Chem.—Eur. J. 2002, 8, 1515–1518.

(13) Quebatte, L.; Solari, E.; Scopelliti, R.; Severin, K. Organometallics 2005, 24, 1404–1406.

(14) (a) Wolf, J.; Thommes, K.; Briel, O.; Scopelliti, R.; Severin, K. *Organometallics* **2008**, 27, 4464–4474. (b) Haas, M.; Solari, E.; Nguyen, Q. T.; Gauthier, S.; Scopelliti, R.; Severin, K. *Adv. Synth. Catal.* **2006**, 348, 439–442.

(15) Solari, E.; Antonijevic, S.; Gauthier, S.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2007**, 367–371.

(16) Solari, E.; Gauthier, S.; Scopelliti, R.; Severin, K. *Organometallics* **2009**, *28*, 4519–4526.

(17) Goerissen, R.; Koelle, U.; Spaniol, T. P. Polyhedron 1992, 11, 2317–2320.

(18) For other complexes containing a  $Ru(\mu-Cl)_3Ru(\mu-Cl)_3Ru$  unit see: (a) Cotton, A. F.; Torralba, R. C. *Inorg. Chem.* **1991**, 30, 4386–4391. (b) Cotton, A. F.; Torralba, R. C. *Inorg. Chem.* **1991**, 30, 3293–3304. (c) Cotton, A. F.; Matusz, M.; Torralba, R. C. *Inorg. Chem.* **1989**, 28, 1516–1520.

(19) Sauvage, X.; Borguet, Y.; Noels, A. F.; Delaude, L.; Demonceau, A. Adv. Synth. Catal. 2007, 349, 255–265.

(20) Borguet, Y.; Sauvage, X.; Zaragoza, G.; Demonceau, A.; Delaude, L. Organometallics 2011, 30, 2730–2438.

(21) For reviews on the degradation of metal-NHC complexes see:
(a) Praetorius, J. M.; Crudden, C. M. RSC Catal. Ser. 2010, 77–118.
(b) Crudden, C. M.; Allen, D. P. Coord. Chem. Rev. 2004, 248, 2247–2273.

(22) Konnick, M. M.; Stahl, S. S. J. Am. Chem. Soc. 2008, 130, 5753–5762.

 $(23)\ ^1H$  NMR data suggest that water is not formed during the reaction.

(24) For examples of mixed-valence Ru(II)( $\mu$ -Cl)<sub>3</sub>Ru(III) complexes see: (a) Borguet, Y.; Sauvage, X.; Zaragoza, G.; Demonceau, A.; Delaude, L. *Beilstein J. Org. Chem.* **2010**, *6*, 1167–1173. (b) Gauthier, S.; Quebatte, L.; Scopelliti, R.; Severin, K. *Inorg. Chem. Commun.* **2004**, 7, 708–712. (c) Batista, A. A.; Porcu, O. M.; Nascimento, O. R.; Barbosa, V. M.; Oliva, G. *J. Coord. Chem.* **1993**, *30*, 345–355. (d) Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1986**, *25*, 234–240. (e) Contreras, R.; Elliot, G. G.; Heath, G. A.; Lindsay, A. J.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *215*, C6–C10.

# **Organometallics**

(25) (a) Bardwell, D. A.; Horsburgh, L.; Jeffery, J. C.; Joulie, L. F.;
Ward, M. D.; Webster, I.; Yellowlees, L. J. J. Chem. Soc., Dalton Trans.
1996, 2527–2531. (b) Bardwell, D.; Jeffery, J. C.; Joulie, L.; Ward, M. D. J. Chem. Soc., Dalton Trans.
1993, 2255–2256. (c) Kölle, U.; Kossakowski, J.; Boese, R. J. Organomet. Chem.
1989, 378, 449–455. (d) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. J. Am. Chem. Soc.
1989, 111, 4712–4718. (e) Gould, R. O.; Stephenson, T. A.; Tocher, D. A. J. Organomet. Chem.
1984, 263, 375–384.

(26) Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076–1083.

(27) Jimenez Tenorio, M. A.; Jimenez Tenorio, M.; Carmen Puerta, M.; Valerga, P. J. Chem. Soc., Dalton Trans. **1998**, 3601–3608.

(28) Aneetha, H.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Mereiter, K. Organometallics 2002, 21, 628-635.

(29) Transition metal-catalyzed oxidations with N<sub>2</sub>O in homogeneous solution often show very poor turnover numbers. See ref 11 and (a) Chernysheva, A. N.; Beloglazkina, E. K.; Moiseeva, A. A.; Antipin, R. L.; Zyk, N. V.; Zefirov, N. S. *Mendeleev Commun.* **2012**, *22*, 70–72. (b) Ettedgui, J.; Neumann, R. J. Am. Chem. Soc. **2009**, *131*, 4–5. (c) Beloglazkina, E. K.; Majouga, A. G.; Moiseeva, A. A.; Zyk, N. V.; Zefirov, N. S. *Mendeleev Commun.* **2019**, *131*, 4–5. (c) Beloglazkina, E. K.; Majouga, A. G.; Moiseeva, A. A.; Zyk, N. V.; Zefirov, N. S. *Mendeleev Commun.* **2009**, *19*, 69–71. (d) Ben-Daniel, R.; Neumann, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 92–95. (e) Ben-Daniel, R.; Weiner, L.; Neumann, R. J. Am. Chem. Soc. **2002**, *124*, 8788–8789.

(30) (a) Bennett, M. A.; Robertson, G. B.; Smith, A. K. J. Organomet. Chem. **1972**, 43, C41–C43. (b) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. Inorg. Synth **1982**, 21, 74–78.

(31) Hull, J. W.; Gladfelter, W. L. Organometallics 1984, 3, 605–613.
(32) Blessing, R. H. Acta Crystallogr., Sect. A 1995, 51, 33–38.

(33) Sheldrick, G. M. SHELXTL 6.1.4; University of Göttingen: Götttingen, Germany, 1997; Bruker AXS, Inc.: Madison, WI, USA, 2003.

# ■ NOTE ADDED AFTER ASAP PUBLICATION

The abstract graphic in the version of this paper published on Sep 26, 2012 has been corrected and the revised version reposted on Sep 27, 2012.

Article