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# Ruthenium-Mediated Double C–H Activation of Toluene with 1-Azidoadamantane

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**Supporting Information** 

**ABSTRACT:** Reaction of  $[L_{OEt}RuCl_2]_2 (L_{OEt}^- = [CpCo{P(O)(OEt)_2}_3]^-) (1)$  with the organic azides RN<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, followed by recrystallization from Et<sub>2</sub>O, afforded  $[L_{OEt}RuCl_2(NH_2R)]$  (R = Ph (2), 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (3), 1-adamantyl (Ad) (4)). Complex 1 can catalyze the reduction of 4-nitrophenyl azide to 4nitroaniline by cyclohexene. Heating 1 with AdN<sub>3</sub> in toluene at reflux led to formation of the cyclometalated Ru(III) complex  $[L_{OEt}Ru(\kappa_2C_r)R-AdN=CHC_6H_4)$ -Cl] (5), possibly via double C–H activation of toluene by an imido intermediate. The crystal structures of 3 and 5 have been determined.

 $[L_{OEt}RuCl_2]_2 \xrightarrow{AdN_3} reflux \\ - HCl \qquad Cl \qquad N \\ HCl \qquad Cl \qquad N \\ HCl \qquad HCl \qquad Cl \qquad N \\ HCl \qquad HCl \qquad HCl \qquad HCl \qquad HCl \qquad HCl \\ HCl \qquad HCl \qquad HCl \qquad HCl \qquad HCl \\ HCl \qquad HCl \qquad$ 

T he amination of hydrocarbons with organic azides has attracted much attention because it is atom economical and the byproduct,  $N_2$ , is environmentally benign.<sup>1,2</sup> In this connection, much effort has been devoted to develop efficient metal-based catalysts for inter- and intramolecular C–H amination with organic azides.<sup>3-11</sup> It is generally believed that high-valent imido complexes are the active intermediates in metal-catalyzed amination and aziridination reactions. In some cases, well-defined, reactive imido species that can effect C–H bond activation could be isolated from stoichiometric reactions of lower valent metal complexes with nitrene sources.<sup>3,4,10,11b,12</sup>

We are particularly interested in Ru imido complexes that have been shown to exhibit imido transfer activity.<sup>10,11,13-15</sup> For example, Ru(VI) bis(imido) species synthesized from Ru(II) carbonyl porphyrins and nitrene transfer agents are capable of aziridination and amination of hydrocarbon substrates.<sup>10,11</sup> In comparison with the porphyrin and related nitrogen chelate analogues, the imido chemistry of Ru cyclopentadienyl (Cp) complexes is not well developed. Matsuzaka and co-workers reported that dinuclear CpRu imido complexes can undergo C-N coupling with alkynes and activate P-H bonds, demonstrating that such complexes can display interesting organometallic chemistry.<sup>16</sup> In an effort to develop efficient catalysts for C-H amination with organic azides, we sought to synthesize Ru-imido complexes supported by the Kläui tripodal ligand  $[CpCo{P(O)(OEt)_2}_3]^-$  (Scheme 1, denoted as  $L_{OEt}^{-}$  hereafter), which has been recognized as an





oxygen analogue of Cp.<sup>17</sup> While high-valent Ru-L<sub>OEt</sub> complexes containing oxo<sup>18</sup> and nitrido<sup>19</sup> ligands have been isolated, analogous terminal imido complexes remain elusive.<sup>20</sup> In an attempt to synthesize Ru-L<sub>OEt</sub> imido species, we studied the reactions between  $[L_{OEt}RuCl_2]_2$  (1)<sup>21</sup> and organic azides. In this work, we found that the interaction of 1 with phenyl azide in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O gave a Ru(III) aniline complex, whereas that with 1-azidoadamantane (AdN<sub>3</sub>) in refluxing toluene yielded a cyclometalated complex,  $[L_{OEt}Ru(\kappa_2C_iN-AdN=CHC_6H_4)Cl]$ , presumably via double C–H bond activation of toluene by a reactive imido intermediate.

#### EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 and 121.5 MHz for <sup>1</sup>H and <sup>31</sup>P, respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H) and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Magnetic moments were determined by the Evans method<sup>22</sup> in chloroform solutions at room temperature. Elemental analyses were performed by Medac Ltd., Surrey, U.K. The compound [L<sub>OEt</sub>RuCl<sub>2</sub>]<sub>2</sub> (1) was synthesized as described elsewhere.<sup>21</sup>

Preparations of  $[L_{OEt}RuCl_2(NH_2R)]$  (R = Ph (2), 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (3), 1-Adamantyl (Ad) (4)). A mixture of 1 (100 mg, 0.07 mmol) and 2 equiv of RN<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was stirred at room temperature overnight. The solvent was removed in vacuo, and the residue was washed with cold hexane. Recrystallization from Et<sub>2</sub>O at room temperature overnight afforded deep red crystals.

Data for 2 are as follows. Yield: 45 mg (40% with respect to Ru).  $\mu_{\text{eff}} = 1.9 \ \mu_{\text{B}}$ . IR (KBr, cm<sup>-1</sup>): 3303, 3205 ( $\nu$ (N–H)). Anal. Calcd for C<sub>23</sub>H<sub>42</sub>Cl<sub>2</sub>CoNO<sub>9</sub>P<sub>3</sub>Ru: C, 34.51; H, 5.29; N, 1.75. Found: C, 34.28; H, 5.32, N, 1.86.

Data for 3 are as follows. Yield: 36 mg (31% with respect to Ru).  $\mu_{\text{eff}}$  = 1.8  $\mu_{\text{B}}$ . IR (KBr, cm<sup>-1</sup>): 3292, 3203 ( $\nu$ (N–H)). Anal. Calcd for

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C<sub>23</sub>H<sub>41</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>11</sub>P<sub>3</sub>Ru: C, 32.68; H, 4.89; N, 3.31. Found: C, 32.38; H, 4.55, N, 3.34.

Data for 4 are as follows. Yield: 50 mg (41% with respect to Ru).  $\mu_{\text{eff}}$  = 1.9  $\mu_{\text{B}}$ . IR (KBr, cm<sup>-1</sup>): 3285, 3232 ( $\nu$ (N–H)). MS (ESI): m/z 858 (M<sup>+</sup>). Anal. Calcd for C<sub>27</sub>H<sub>52</sub>Cl<sub>2</sub>CoNP<sub>9</sub>P<sub>3</sub>Ru: C, 37.77; H, 6.10; N, 1.63. Found: C, 37.62; H, 6.10, N, 1.92.

**Ru-Catalyzed Reduction of 4-Nitrophenyl Azide with Cyclohexene.** A mixture of 4-nitrophenyl azide (105 mg, 0.64 mmol) and 1 (18 mg, 0.013 mmol) was heated in neat cyclohexene (5 mL) at 60 °C overnight. The organic volatiles were pumped off, and the residue was subjected to silica column chromatography. The organic products, *N*-(2-cyclohexenyl)-4-nitroaniline (7% yield with respect to 4-nitrophenyl azide) and 4-nitroaniline (70%), were eluted with hexane and CH<sub>2</sub>Cl<sub>2</sub>, respectively, and characterized by NMR and IR spectroscopy.<sup>10b</sup>

**Preparation of**  $[L_{OEt}Ru(\kappa_2 N, C-AdN = CHC_6 H_4)CI]$  (5). A mixture of 1 (100 mg, 0.07 mmol) and 1-azidoadamantane (25 mg, 0.141 mmol) in toluene (5 mL) was heated at reflux overnight. The solvent was removed in vacuo, and the residue was washed with cold hexane. Recrystallization from Et<sub>2</sub>O afforded red crystals that were suitable for X-ray diffraction. Yield: 58 mg (45% with respect to Ru).  $\mu_{eff} = 2.0 \mu_{B}$ . Anal. Calcd for C<sub>34</sub>H<sub>56</sub>Cl<sub>2</sub>CoNO<sub>9</sub>P<sub>3</sub>Ru: C, 44.82; H, 6.19; N, 1.54. Found: C, 44.63; H, 6.10, N, 1.55.

**X-ray Crystallography.** Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda$  = 1.541 78 Å). The data were corrected for absorption using the program SADABS.<sup>23</sup> Structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL software package.<sup>24</sup>

#### RESULTS AND DISCUSSION

Reactions of 1 with Aryl Azides. Treatment of  $[L_{OEt}RuCl_2]_2$  (1) with phenyl azide in  $CH_2Cl_2$  at room temperature resulted in a color change from orange to green in 2 h. Evaporation of the solvent afforded a paramagnetic green oily material that did not crystallize. No reaction was found between this green oil and PPh<sub>3</sub>. This green species is probably a phenyl azide adduct rather than an imido complex. Transition-metal complexes containing organic azide ligands are well-known.<sup>25</sup> The IR spectrum of the reaction mixture showed a band at 2126 cm<sup>-1</sup> (cf. 2129 cm<sup>-1</sup> for free phenyl azide) assignable to the azido group. A similar N-N stretching frequency (2106 cm<sup>-1</sup>) has been found for a recently reported Ru aryl azide complex, in which the azide ligand binds to Ru in an  $\eta^1$  mode.<sup>15</sup> While this green species is stable in CH<sub>2</sub>Cl<sub>2</sub> solution for hours, recrystallization from Et<sub>2</sub>O overnight afforded air-stable red crystals characterized as the known compound [L<sub>OEt</sub>RuCl<sub>2</sub>(NH<sub>2</sub>Ph)] (2).<sup>21</sup> Similarly, the reaction of 1 with 4-nitrophenyl azide, followed by recrystallization from Et<sub>2</sub>O, afforded the 4-nitroaniline complex  $[L_{OEt}RuCl_2(NH_2C_6H_4NO_2-4)]$  (3), which has been characterized by X-ray diffraction<sup>26</sup> (Figure 1). The Ru–O, Ru–Cl, and Ru-N distances in 3 (average 2.059, 2.3387(14) and 2.106(5) Å, respectively) are similar to those in [L<sub>OFt</sub>RuCl<sub>2</sub>(NH<sub>2</sub>Ph)].<sup>21</sup> It seems unlikely that the phenyl azide was initially reduced to aniline that subsequently binds to Ru, because no free aniline was detected during the course of the reaction. Also, the reaction of 1 with aniline resulted in a color change from orange to dark red only; no green intermediate was observed. Reduction of Ru-bound aryl azide to aniline by organic solvents to give an amine complex has been reported previously.<sup>10a</sup> Therefore, we believe that the aniline ligands in 2 and 3 were formed by Ru-mediated reduction of the nitrene intermediates (derived from the corresponding aryl azide precursors) with  $Et_2O$ .



**Figure 1.** Molecular structure of 3. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Ru1-O8 = 2.045(3), Ru1-O7 = 2.058(4), Ru1-O9 = 2.073(4), Ru1-N1 = 2.106(5), Ru1-Cl1 = 2.3387(14), Ru-Cl2 = 2.3387(14).

The possibility of using **1** as a catalyst for the allylic amination of cyclohexene<sup>10</sup> has been explored. Treatment of 4nitrophenyl azide with 2 mol % of **1** in neat cyclohexene at room temperature resulted in a red solution (possibly containing **3**); no allylic amination product was found. Heating the reaction mixture at 60 °C overnight led to isolation of 4nitroaniline (70%) along with a small amount of *N*-(2-cyclohexenyl)-4-nitroaniline (ca. 7%) (Scheme 2). In the

### Scheme 2. Ru-Catalyzed Reduction of 4-Nitrophenyl Azide with Cyclohexene



absence of the Ru catalyst, the reaction between 4-nitrophenyl azide and cyclohexene at 60 °C afforded 4-nitroaniline in very low yield (<5%). Thus, while 1 is a poor catalyst for the allylic amination, it can catalyze the reduction of 4-nitrophenyl azide with cyclohexene at 60 °C with a turnover number of 35 (with respect to 1). Gallo and co-workers reported that a Ru(VI) imido porphyrin complex can abstract hydrogen atoms from cyclohexene.<sup>10a</sup> Therefore, the 1-mediated reduction of aryl azide possibly involves the formation of a nitrene intermediate that abstracts hydrogen atoms from cyclohexene to give aniline.

Reaction of 1 with 1-Azidoadamantane. Treatment of 1 with 1-azidoadamantane (AdN<sub>3</sub>) in organic solvents such as CH<sub>2</sub>Cl<sub>2</sub> and toluene at room temperature, followed by recrystallization from Et<sub>2</sub>O, afforded the amine complex  $[L_{OEt}RuCl_2(NH_2Ad)]$  (4). On the other hand, refluxing 1 with AdN<sub>3</sub> in toluene led to isolation of the cyclometalated Ru(III) complex  $[L_{OEt}Ru(\kappa_2 N, C-AdN = CHC_6H_4)Cl]$  (5) in 45% yield (with respect to Ru). In contrast with AdN<sub>3</sub>, refluxing 1 with phenyl azide in toluene gave 2 as the sole isolated product. 1 also reacted with AdN<sub>3</sub> in other alkylbenzenes such as ethylbenzene and isopropylbenzene under the same conditions to give dark red materials. However, we were not able to characterize and crystallize the paramagnetic red products in these reactions. The crystal structure of 5 has been determined.<sup>27</sup> Figure 2 shows the molecular structure of 5. The geometry around Ru is pseudo-octahedral. The C47-N1 bond distance of the cyclometalated ligand (1.296(4) Å) is consistent with an imine C=N double bond.



**Figure 2.** Molecular structure of **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angle (deg): Ru1-O7 = 2.099(2), Ru1-O8 = 2.305(2), Ru1-O9 = 2.073(2), Ru1-N1 = 2.076(3), Ru1-C(41) = 1.979(3), Ru1-Cl1 = 2.3184(8), N1-C47 = 1.296(4); C47-N1-C31 = 119.9(3).

The Ru–C (1.979(3) Å) and Ru–N (2.076(3) Å) distances compare well with those in the mixed-valence cyclometalated complex [(phen)(ppy)ClRu( $\mu$ -O)RuCl(ppy)(phen)](PF<sub>6</sub>) (ppy = 2-(2-pyridyl)phenyl; Ru–C 1.98(2) and 2.022(18) Å, Ru–N(ppy) 2.020(17) and 2.065(13) Å).<sup>28</sup> The Ru–O bond opposite to carbon (2.305(2) Å) is apparently longer than the other two Ru–O bonds (2.073(2) and 2.099(2) Å), indicative of the trans influence of the phenyl ring.

While C–H amination of hydrocarbons by imido complexes is well documented, to our knowledge this is the first report of metal-mediated C–H amination coupled with cyclometalation of an alkylbenzene. Previous studies suggested that the active species in Ru-mediated C–H amination are high-valent Ru imido complexes that can activate C–H bonds via a hydrogen atom abstraction pathway.<sup>10,11</sup> We believe that a similar mechanism is involved in the formation of **5** (Scheme 3). The interaction of **1** with AdN<sub>3</sub> affords an azide adduct that is transformed to the Ru–imido intermediate **A** on heating. Hydrogen atom abstraction of toluene by **A** gives a Ru amide and benzyl radical intermediates. Recombination of the radical





pairs yields the amine complex **B**. Intramolecular C-H activation of the phenyl ring in **B** affords the metallacycle **C**. Finally, oxidative dehydrogenation to the amino group yields the cyclometalated imine complex **5**.

In summary, we have found that reaction of the Ru(III) chloride complex 1 with organic azides in the presence of  $Et_2O$  or cyclohexene at room temperature afforded Ru(III) amine complexes. 1 can catalyze the reduction of 4-nitrophenyl azide with cyclohexene at 60 °C. Reaction of 1 with AdN<sub>3</sub> in refluxing toluene led to formation of a Ru(III) complex with a cyclometalated imine ligand, presumably via double C–H activation of toluene by a Ru imido intermediate. Currently, effort is being made to characterize/trap reactive Ru–L<sub>OEt</sub> imido complexes and to explore their C–H activation reactivity.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

CIF files giving crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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(26) Crystal data for 3: formula,  $C_{34}H_{55}$ ClCoNO<sub>9</sub>P<sub>3</sub>Ru;  $M_r$  = 910.15, a = 9.43240(10) Å; b = 19.9781(3) Å; c = 21.2265(3) Å;  $\beta = 98.4760(10)^\circ$ , V = 3956.26(9) Å<sup>-3</sup>; Z = 4; crystal system, monoclinic; space group,  $P2_1/n$ ; T = 173(2) K;  $\mu = 8.572$  mm<sup>-1</sup>; F(000) = 1884; 12 778 reflections collected; 7012 unique reflections;  $R_{int} = 0.0318$ ; GOF = 1.006; R1 ( $I > 2\sigma(I)$ ) = 0.0395; wR2 (all data) = 0.1028.

(27) Crystal data for  $\mathbf{5} \cdot \text{CH}_2\text{Cl}_2$ : formula,  $\text{C}_{24}\text{H}_{41}\text{Cl}_4\text{CoN}_2\text{O}_{11}\text{P}_3\text{Ru}$ ;  $M_r = 928.30$ ; a = 13.9067(2) Å; b = 21.2398(3) Å; c = 12.3711(2) Å; V = 3654.12(9) Å<sup>-3</sup>; Z = 4; crystal system, orthorhombic; space group,  $Pna2_1$ ; T = 173(2) K;  $\mu = 11.316$  mm<sup>-1</sup>; F(000) = 1884; 11 241 reflections collected; 5084 unique reflections;  $R_{\text{int}} = 0.0533$ ; GOF = 1.024; R1  $(I > 2\sigma(I)) = 0.0371$ ; wR2 (all data) = 0.0794.

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