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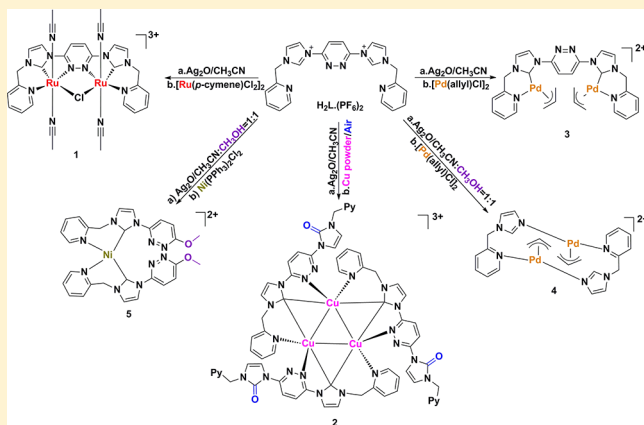
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## Pyridazine-Based N-Heterocyclic Carbene Complexes and Ruthenium-Catalyzed Oxidation Reaction of Alkenes

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## S Supporting Information

**ABSTRACT:**  $[\text{Ru}_2\text{Cl}(\text{L})(\text{CH}_3\text{CN})_4](\text{PF}_6)_3$  (**1**,  $\text{L} = 3,6$ -bis-(*N*-(pyridylmethyl)imidazolylikenyl)pyridazine),  $[\text{Cu}_3\text{L}^a_3](\text{PF}_6)_3$  (**2**,  $\text{L}^a = 3$ -(*N*-(pyridylmethyl)imidazolylikenyl)-6-(*N*-(pyridylmethyl)imidazolylikenyl)pyridazine),  $[\text{Pd}_2(\text{allyl})_2\text{L}](\text{PF}_6)_2$  (**3**),  $[\text{Pd}_2(\text{allyl})_2\text{L}^b_2](\text{PF}_6)_2$  (**4**,  $\text{L}^b = N$ -pyridylmethylimidazole), and  $[\text{NiL}^c_2](\text{PF}_6)_2$  (**5**,  $\text{L}^c = 3$ -(*N*-(pyridylmethyl)imidazolylikenyl)-6-methoxy-pyridazine) have been synthesized and fully characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. In complex **1**, ligand **L** binds to two Ru(II) centers, forming a well-behaved  $\text{Ru}_2(\text{L})\text{Cl}$  plane with a five-membered metallocyclic ring. Complex **2** is trinuclear, containing a triangular  $\text{Cu}_3$  unit bonded together by three 3-(*N*-(pyridylmethyl)imidazolylikenyl)-6-(*N*-(pyridylmethyl)imidazolylikenyl)pyridazine, where one imidazolylikenyl was oxidized into imidazolone. Deprotonation reaction with  $\text{Ag}_2\text{O}$  in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$  resulted in C–N cleavage of the imidazolium salt, and subsequent reaction with  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  gave **4** and **5**, respectively. Dinuclear Ru(II)-NHC complex **1** exhibits excellent catalytic activity for the oxidation of alkenes into diketones.



## ■ INTRODUCTION

Pyridazine-based transition metal complexes have received considerable attention in coordination chemistry because of their great structural diversity.<sup>1</sup> In many cases, the pyridazine-derived ligands are capable of incorporating two metal ions in close proximity via their diazine fragments in the presence of peripheral donating groups that are bonded to the diazine moiety.<sup>2</sup> Because of interesting structural, electrochemical, and catalytic properties of the dinuclear transition metal complexes, much effort has been devoted to developing the architecture of pyridazine-derived ligands.<sup>3</sup> N donors were commonly introduced to the systems in the form of nitrogen heterocyclic groups<sup>4</sup> and Schiff bases.<sup>5</sup> For instance, 3,6-dipyridylpyridazine (**A** in Figure 1) has shown to form predominantly dinuclear complexes.<sup>2e,4b</sup>

As alternatives to the traditional phosphine and nitrogen ligands, N-heterocyclic carbenes (NHCs) have gained increasing importance due to their unique properties.<sup>6</sup> Compared to the widely used phosphine complexes, the NHC complexes have shown remarkable stability toward air, moisture, and heat because of their strong  $\sigma$ -donating ability.<sup>7</sup> Additionally, the N-bonded functional groups are easily modified, and various functional groups such as pyridine,<sup>8</sup> pyrimidine,<sup>9</sup> pyrazole,<sup>10</sup> and phenanthroline<sup>11</sup> have been introduced to the NHC systems, as such kinds of donors are versatile for the assemblage of multinuclear complexes. A large number of transition metal

complexes with bichelating,<sup>12</sup> pincer,<sup>13</sup> tripodal,<sup>14</sup> or bridging NHC ligands<sup>15</sup> have been synthesized and showed great catalytic activities in C–C coupling,<sup>13b,16</sup> hydrogenation,<sup>13d,17</sup> and hydrosilylation reactions.<sup>12d,18</sup> Nevertheless, the pyridazine/NHC hybrid ligands are relatively less investigated.<sup>19</sup> 3,6-Diimidazolium-substituted pyridazine ligand precursors (**B**) have been used to prepare Ag(I) and Hg(II) complexes.<sup>19a,b,e</sup> Recently, our group has reported a series of dinuclear palladacyclic complexes derived from **B**, and C–N cleavage was observed.<sup>19e</sup> As an extension of our studies on functionalized NHCs,<sup>8e,10c,11a</sup> herein we present the synthesis and characterization of a modified pyridazine-functionalized imidazolium salt (**C**) in which two pyridine groups are attached to the imidazole rings as two additional coordination sites. The double-pincer ligand showed remarkable coordination diversity.

## ■ EXPERIMENTAL SECTION

All chemicals were obtained from commercial suppliers and used without further purification. 3,6-Di(1*H*-imidazol-1-yl)pyridazine (see Supporting Information) and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  were prepared according to the known procedure.<sup>20</sup> Elemental analyses were performed on a Flash EA1112 instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are

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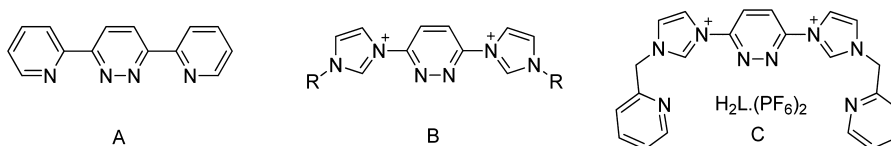


Figure 1. Pyridazine-containing ligand A and ligand precursors B and C.

expressed in ppm downfield to TMS at  $\delta = 0$  ppm, and coupling constants ( $J$ ) are expressed in Hz.

**Synthesis of  $H_2L \cdot (PF_6)_2$  ( $L = 3,6$ -bis(*N*-(pyridylmethyl)-imidazolylidenyl)pyridazine).** A solution of 3,6-di(1*H*-imidazol-1-yl)pyridazine (4.24 g, 20 mmol) and 2-(chloromethyl)pyridine (12.8 g, 100 mmol) in 50 mL of DMF was stirred at 120 °C for 12 h. The resulting white solid was collected by filtration and dissolved in 100 mL of water. Subsequent addition of an aqueous solution of  $NH_4PF_6$  (8.15 g, 50 mmol) to the solution afforded a white precipitate, which was collected by filtration and dried. Yield: 8.75 g, 64%. Anal. Calcd for  $C_{22}H_{20}F_{12}N_8P_2$ : C, 38.50; H, 2.94; N, 16.33. Found: C, 38.23; H, 2.91; N, 16.12.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  10.47 (s, NCHN, 2H), 8.81 (s,  $C_4N_2H_2$ , 2H), 8.69 (m, NCHCHN, 2H), 8.58 (d,  $J = 4.4$  Hz,  $o$ - $C_5H_4N$ , 2H), 8.17 (m, NCHCHN, 2H), 7.94 (m,  $p$ - $C_6H_4N$ , 2H), 7.61 (d,  $J = 8.0$  Hz,  $m$ - $C_6H_4N$ , 2H), 7.44 (m,  $m$ - $C_6H_4N$ , 2H), 5.77 (s,  $CH_2$ , 4H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  153.3, 152.0, 150.0, 138.0, 137.7, 125.2, 124.3, 124.0, 123.2, 120.4, 54.2.

**Synthesis of  $[Ru_2Cl(L)(CH_3CN)_4](PF_6)_3$ , 1.** A solution of  $H_2L \cdot (PF_6)_2$  (137 mg, 0.20 mmol) in 6 mL of acetonitrile was treated with  $Ag_2O$  (48 mg, 0.20 mmol) at 50 °C. After 5 h,  $Ag_2O$  disappeared completely, and  $[Ru(p\text{-cymene})Cl_2]_2$  (122 mg, 0.20 mmol) was added to the solution. After it was stirred for 12 h at room temperature, the solution was filtered. The filtrate was then concentrated to ca. 2 mL. Addition of  $Et_2O$  (20 mL) to the filtrate afforded a red precipitate, which was collected and washed with  $Et_2O$ . Yield: 63 mg, 26%. Anal. Calcd for  $C_{30}H_{30}ClF_{18}N_{12}P_3Ru_2 \cdot 0.5CH_3CN$ : C, 29.75; H, 2.54; N, 13.99. Found: C, 29.93; H, 2.53; N, 13.67.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  9.88 (d,  $J = 4.8$  Hz,  $o$ - $C_5H_4N$ , 2H), 8.78 (s,  $C_4N_2H_2$ , 2H), 8.61 (d,  $J = 2.4$  Hz, NCHCHN, 2H), 8.14 (t,  $J = 7.8$  Hz,  $p$ - $C_6H_4N$ , 2H), 7.98 (d,  $J = 2.0$  Hz, NCHCHN, 2H), 7.85 (d,  $J = 7.6$  Hz,  $m$ - $C_6H_4N$ , 2H), 7.70 (t,  $J = 6.4$  Hz,  $m$ - $C_6H_4N$ , 2H), 6.13 (s,  $CH_2$ , 4H), 2.06 (s,  $CH_3CN$ , 12H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  194.8 (Ru- $C_{carbene}$ ), 156.6, 155.3, 155.0, 138.7, 126.9, 125.4, 124.3, 124.1, 119.0, 118.1, 53.6, 3.0.

**Synthesis of  $[Cu_3L^a_3](PF_6)_3$ , (2,  $L^a = 3$ -(*N*-(pyridylmethyl)-imidazolylidenyl)-6-(*N*-(pyridylmethyl)imidazolylonyl)-pyridazine).** A solution of  $H_2L \cdot (PF_6)_2$  (137 mg, 0.20 mmol) in 6 mL of acetonitrile was treated with  $Ag_2O$  (48 mg, 0.20 mmol) at 50 °C. After 5 h,  $Ag_2O$  disappeared completely, and an excess of copper powder (0.2 g) was added to the solution. After it was stirred for 12 h at 50 °C, the solution was filtered to remove the excess copper powder. The filtrate was then concentrated to ca. 2 mL. Addition of  $Et_2O$  (20 mL) to the filtrate afforded a yellow precipitate, which was collected and washed with  $Et_2O$ . Yield: 56 mg, 45%. Anal. Calcd for  $C_{66}H_{54}Cu_3F_{18}N_{24}O_3P_3$ : C, 42.69; H, 2.93; N, 18.10. Found: C, 42.88; H, 2.73; N, 17.92.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  8.90 (d,  $J = 9.2$  Hz,  $C_6H_4N$ , 3H), 8.61 (d,  $J = 2.4$  Hz, NCHCHN, 3H), 8.46 (s, 3H), 8.37 (m, 3H), 8.08 (t,  $J = 7.6$  Hz, 3H), 7.91 (s, 3H), 7.86 (m, 3H), 7.76 (d,  $J = 7.6$  Hz, 3H), 7.35 (m, 9H), 6.98 (m, 6H), 6.83 (d,  $J = 2.8$  Hz, NCHCHN, 3H), 5.40 (s,  $CH_2$ , 6H), 5.16 (d,  $J = 16.8$  Hz,  $CH_2$ , 3H), 4.86 (d,  $J = 16.0$  Hz,  $CH_2$ , 3H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  167.7 (Cu- $C_{carbene}$ ), 156.1 (C=O), 152.2, 152.1, 152.0, 150.8, 149.2, 148.5, 140.2, 137.1, 126.3, 125.1, 124.7, 123.8, 123.2, 123.0, 122.6, 121.3, 115.3, 107.4, 53.8, 48.2. IR (KBr):  $\nu$ (C=O) 1702  $cm^{-1}$ .

**Synthesis of  $[Pd_2(allyl)_2L](PF_6)_2$ , 3.** A solution of  $H_2L \cdot (PF_6)_2$  (137 mg, 0.20 mmol) in 6 mL of acetonitrile was treated with  $Ag_2O$  (48 mg, 0.20 mmol) at 50 °C. After 5 h,  $Ag_2O$  disappeared completely, and  $[Pd(allyl)Cl]_2$  (74 mg, 0.20 mmol) was added to the solution. After it was stirred for 12 h at 50 °C, the solution was filtered. The filtrate was then concentrated to ca. 2 mL. Addition of  $Et_2O$  (20 mL) to the filtrate afforded a white precipitate, which was collected and washed with  $Et_2O$ . Yield: 171 mg, 87%. Anal. Calcd for  $C_{28}H_{28}F_{12}N_8P_2Pd_2$ : C, 34.34; H, 2.88; N, 11.44. Found: C, 34.17; H, 2.79; N, 11.29.  $^1H$  NMR (400 MHz,

$DMSO-d_6$ ):  $\delta$  8.97 (d,  $J = 4.8$  Hz,  $o$ - $C_5H_4N$ , 2H), 8.74 (s,  $C_4N_2H_2$ , 2H), 8.26 (d,  $J = 1.2$  Hz, NCHCHN, 2H), 8.17 (t,  $J = 7.8$  Hz,  $p$ - $C_6H_4N$ , 2H), 7.97 (d,  $J = 1.6$  Hz, NCHCHN, 2H), 7.88 (d,  $J = 8.0$  Hz,  $m$ - $C_6H_4N$ , 2H), 7.64 (t,  $J = 6.4$  Hz,  $m$ - $C_6H_4N$ , 2H), 5.76–5.56 (m,  $C_3H_5$  and  $CH_2$ , 6H), 4.52 (d,  $J = 8.0$  Hz,  $C_3H_5$ , 2H), 3.75 (d,  $J = 13.2$  Hz,  $C_3H_5$ , 2H), 3.37 (br,  $C_3H_5$ , 2H), 2.56 (br,  $C_3H_5$ , 2H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  177.5 (Pd- $C_{carbene}$ ), 154.9, 154.8, 153.0, 140.2, 126.1, 125.7, 125.2, 124.4, 120.7, 120.2, 74.4, 54.9, 51.0.

**Synthesis of  $[Pd_2(allyl)_2L^b](PF_6)_2$  (4,  $L^b = N$ -pyridylmethylimidazole).** A solution of  $H_2L \cdot (PF_6)_2$  (137 mg, 0.20 mmol) in 6 mL of  $CH_3CN/CH_3OH$  (1:1) was treated with  $Ag_2O$  (48 mg, 0.20 mmol) at 50 °C. After 5 h,  $Ag_2O$  completely disappeared, and  $[Pd(allyl)Cl]_2$  (74 mg, 0.20 mmol) was added to the solution. After it was stirred for 12 h at 50 °C, the solution was filtered. The filtrate was then concentrated to ca. 2 mL. Addition of  $Et_2O$  (20 mL) to the filtrate afforded a white precipitate, which was collected and washed with  $Et_2O$ . Yield: 62 mg, 69%. Anal. Calcd for  $C_{24}H_{28}F_{12}N_6P_2Pd_2$ : C, 31.91; H, 3.12; N, 9.30. Found: C, 32.20; H, 3.09; N, 9.13.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  8.83 (s, 2H), 8.19 (s, 2H), 8.05 (s, 2H), 7.63 (m, 4H), 2.27 (s, 2H), 6.48 (br,  $C_3H_5$ , 2H), 6.00 (m, 2H), 5.44 (s,  $CH_2$ , 4H), 4.26 (br,  $C_3H_5$ , 4H), 3.43 (br,  $C_3H_5$ , 4H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  155.3, 151.4, 141.0, 139.4, 128.7, 125.8, 124.9, 120.4, 119.1, 83.7, 63.0, 52.5.

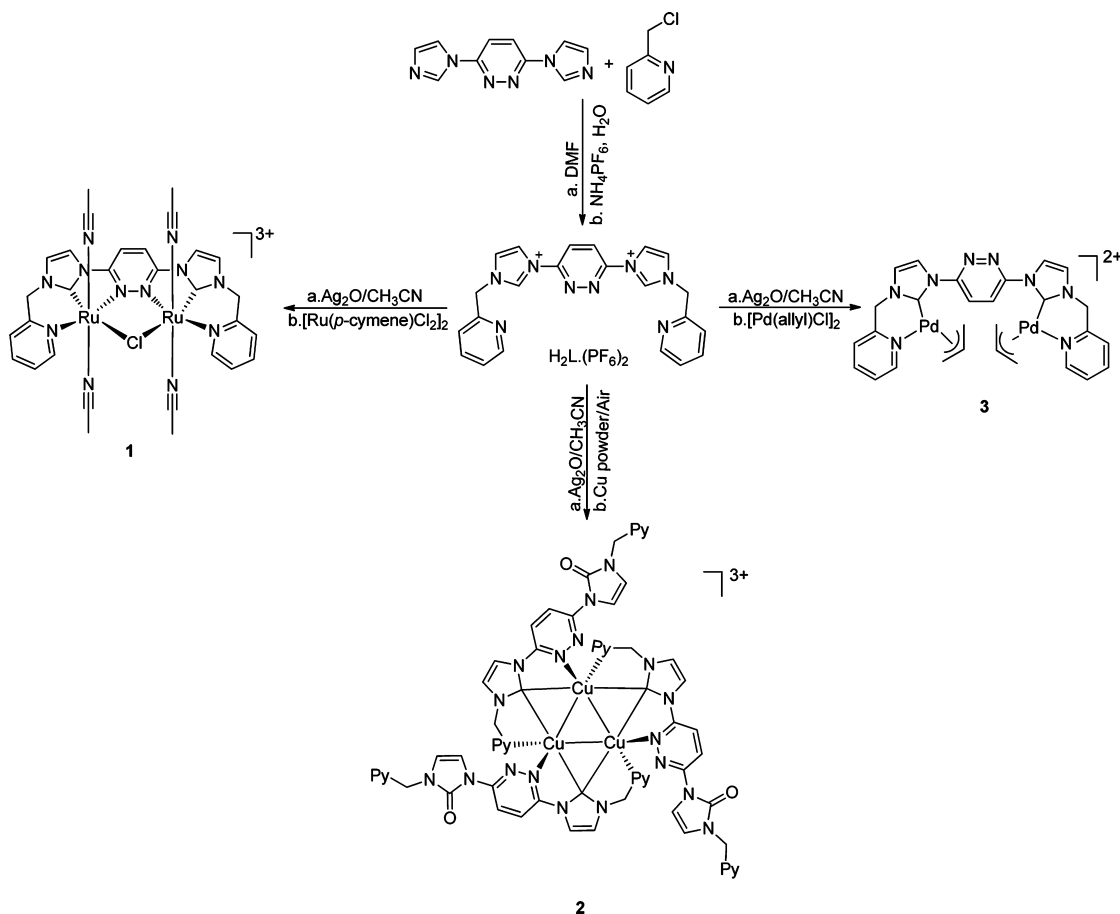
**Synthesis of  $[NiL^c_2](PF_6)_2$  (5,  $L^c = 3$ -(*N*-(pyridylmethyl)-imidazolylidenyl)-6-methoxyxypridazine).** A solution of  $H_2L \cdot (PF_6)_2$  (137 mg, 0.20 mmol) in 6 mL of  $CH_3CN/CH_3OH$  (1:1) was treated with  $Ag_2O$  (48 mg, 0.20 mmol) at 50 °C. After 5 h,  $Ag_2O$  completely disappeared, and  $Ni(PPh_3)_2Cl_2$  (131 mg, 0.20 mmol) was added to the solution. After it was stirred for 12 h at 50 °C, the filtrate was concentrated to ca. 2 mL. Addition of  $Et_2O$  (20 mL) to the filtrate afforded a yellow precipitate, which was collected and washed with  $Et_2O$ . Yield: 71 mg, 81%. Anal. Calcd for  $C_{28}H_{26}F_{12}N_{10}NiO_2P_2 \cdot 0.5CH_3CN$ : C, 38.54; H, 3.07; N, 16.27. Found: C, 38.71; H, 3.13; N, 16.08.  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ):  $\delta$  8.30–8.19 (m, 6H), 7.97 (d,  $J = 7.6$  Hz, 2H), 7.56 (m, 8H), 6.73 (d,  $J = 15.2$  Hz,  $CH_2$ , 2H), 5.93 (d,  $J = 14.8$  Hz,  $CH_2$ , 2H), 4.20 (s,  $CH_3$ , 6H).  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ ):  $\delta$  165.0 (Ni- $C_{carbene}$ ), 159.2, 154.1, 152.9, 149.4, 141.4, 137.0, 125.5, 125.2, 123.9, 121.9, 119.8, 55.3, 54.0.

**General Procedure for Preparations of Diketones.** In a glass tube, a mixture of **1** (6 mg, 0.005 mmol), alkene (0.5 mmol), and NaI (23 mg, 0.15 mmol) in 3.0 mL of  $CH_3CN$  was stirred. To the solution was added TBHP (1 mL, 65% solution in water) via a syringe at room temperature. The stirring was continued at room temperature for 10 min. The reaction was quenched by adding a saturated  $Na_2SO_3$  solution and then extracted with dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate. After filtration, the solvent was removed under vacuum, and the residue was purified by column chromatograph on silica gel (ethyl acetate/petroleum ether) to afford the desired product.

**X-ray Structural Determination.** Single-crystal X-ray diffraction data were collected at 298(2) K on a Siemens Smart/CCD area-detector for **1** and **2** or an Oxford Diffraction Gemini A Ultra diffractometer for **3–5** with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) by using an  $\omega$ - $2\theta$  scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using SMART and SAINT or Oxford Diffraction CrysAlisPro software.<sup>21</sup> The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F_2$  using the SHELXTXL package.<sup>22</sup> Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C–H distances of 0.93–0.97 Å and  $U_{iso}(H) = 1.2$ – $1.5U_{eq}(C)$ . Disordered solvents in the lattice for **2** could not be modeled successfully and were removed from their reflection data with

Table 1. Summary of the Crystallographic Data for 1–5

	[Ru <sub>2</sub> Cl(L)(CH <sub>3</sub> CN) <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub> , <b>1</b>	[Cu <sub>3</sub> L <sup>a</sup> ](PF <sub>6</sub> ) <sub>3</sub> , <b>2</b>	[Pd <sub>2</sub> (allyl) <sub>2</sub> L](PF <sub>6</sub> ) <sub>2</sub> , <b>3</b>	[Pd <sub>2</sub> (allyl) <sub>2</sub> L <sup>b</sup> ](PF <sub>6</sub> ) <sub>2</sub> , <b>4</b>	[NiL <sup>c</sup> ](PF <sub>6</sub> ) <sub>2</sub> , <b>5</b>
formula	C <sub>32</sub> H <sub>33</sub> ClF <sub>18</sub> N <sub>13</sub> P <sub>3</sub> Ru <sub>2</sub>	C <sub>66</sub> H <sub>54</sub> Cu <sub>3</sub> F <sub>18</sub> N <sub>24</sub> O <sub>3</sub> P <sub>3</sub>	C <sub>28</sub> H <sub>28</sub> F <sub>12</sub> N <sub>8</sub> P <sub>2</sub> Pd <sub>2</sub>	C <sub>28</sub> H <sub>34</sub> F <sub>12</sub> N <sub>8</sub> P <sub>2</sub> Pd <sub>2</sub>	C <sub>30</sub> H <sub>29</sub> F <sub>12</sub> N <sub>11</sub> NiO <sub>2</sub> P <sub>2</sub>
fw	1272.21	1856.86	979.32	985.37	924.29
cryst syst	monoclinic	cubic	orthorhombic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 3	<i>Pb</i> cn	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	10.8610(15)	20.2458(19)	14.4781(8)	8.9307(2)	20.0236(9)
<i>b</i> , Å	12.0263(19)	20.2458(19)	15.6757(8)	14.1680(3)	13.0568(6)
<i>c</i> , Å	36.135(3)	20.2458(19)	15.4845(8)	14.3697(3)	15.1251(10)
$\alpha$ , deg	90	90	90	90	90
$\beta$ , deg	92.3010(10)	90	90	100.477(2)	97.998(5)
$\gamma$ , deg	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	4716.0(11)	8298.6(13)	3514.3(3)	1787.89(7)	3915.9(4)
<i>Z</i>	4	4	4	2	4
<i>D</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.792	1.486	1.851	1.830	1.568
reflns collected	24 118	39 544	14 479	8935	22 692
reflns indep, <i>R</i> <sub>int</sub>	8292, 0.0633	4876, 0.1440	3133, 0.0301	3143, 0.0210	6895, 0.0498
goodness-of-fit on <i>F</i> <sup>2</sup>	1.065	0.922	1.110	1.043	1.037
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0543, 0.1060	0.0660, 0.1680	0.0734, 0.2021	0.0382, 0.1005	0.0658, 0.1806
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1047, 0.1331	0.0920, 0.1823	0.0945, 0.2233	0.0447, 0.1064	0.0899, 0.2032

Scheme 1. Synthesis of the Imidazolium Salt, [Ru<sub>2</sub>Cl(L)(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>)<sub>3</sub> (**1**), [Cu<sub>3</sub>L<sup>a</sup>](PF<sub>6</sub>)<sub>3</sub> (**2**), and [Pd<sub>2</sub>(allyl)<sub>2</sub>L](PF<sub>6</sub>)<sub>2</sub> (**3**)

SQUEEZE.<sup>23</sup> Further details of the structural analysis are summarized in Table 1.

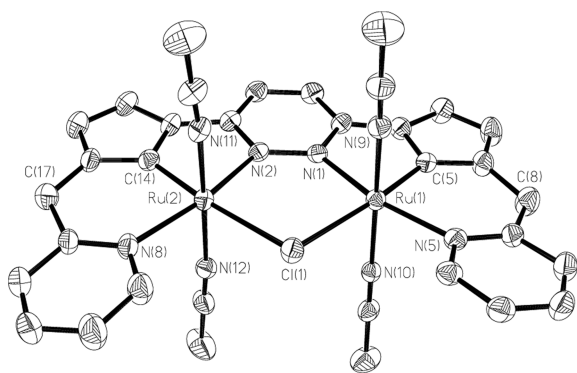
## RESULTS AND DISCUSSION

**Synthesis of the Imidazolium Salt.** The pyridazine-functionalized bis(NHC) ligand precursor ( $H_2L \cdot (PF_6)_2$ ) was reported by us in 2007, but it was obtained in very poor yield (4.5%).<sup>19c</sup> In this work, the imidazolium salt was prepared by

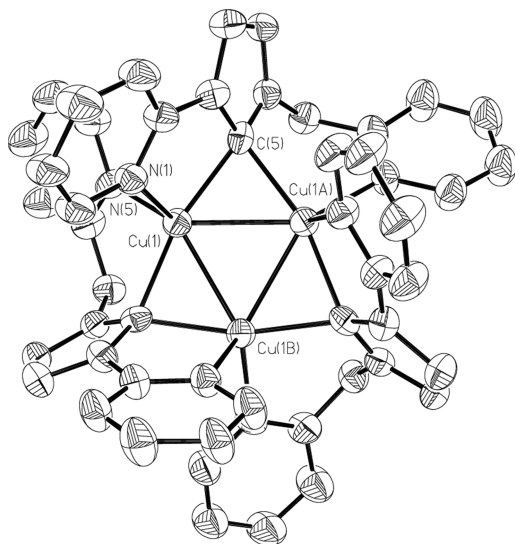
heating 3,6-di(1H-imidazol-1-yl)pyridazine and 2-(chloromethyl)pyridine in DMF and subsequent anion exchange reaction in water (Scheme 1). The imidazolium salt was isolated as a white solid in 64% yield.

**Synthesis and Characterization of [Ru<sub>2</sub>Cl(L)(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>)<sub>3</sub> (**1**).** Reaction of the imidazolium salt  $H_2L \cdot (PF_6)_2$  ( $L = 3,6$ -bis(*N*-(pyridylmethyl)imidazolylidenenyl)pyridazine) with  $Ag_2O$  in  $CH_3CN$  at 50 °C afforded a colorless solution of  $[Ag_6(L)_4]$ -





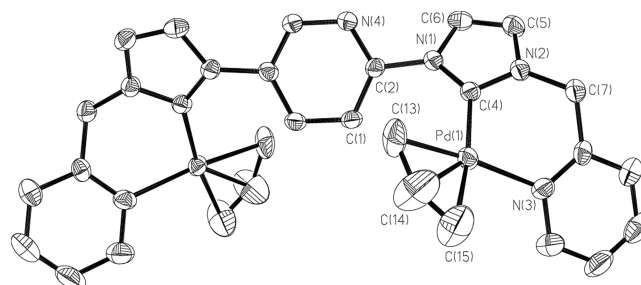
**Figure 2.** Thermal ellipsoids of  $[\text{Ru}_2\text{Cl}(\text{L})(\text{CH}_3\text{CN})_4](\text{PF}_6)_3$  (**1**) shown at the 30% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)–C(5) 1.900(7), Ru(1)–N(9) 2.020(6), Ru(1)–N(10) 2.036(6), Ru(1)–N(1) 2.053(5), Ru(1)–N(5) 2.110(6), Ru(1)–Cl(1) 2.5101(18), Ru(2)–C(14) 1.885(7), Ru(2)–N(12) 2.033(6), Ru(2)–N(11) 2.033(7), Ru(2)–N(2) 2.067(5), Ru(2)–N(8) 2.117(6), Ru(2)–Cl(1) 2.5044(18), C(5)–Ru(1)–Cl(1) 172.6(2), C(14)–Ru(2)–Cl(1) 173.1(2), Ru(2)–Cl(1)–Ru(1) 98.01(6).



**Figure 3.** Thermal ellipsoids of  $[\text{Cu}_3\text{L}_3](\text{PF}_6)_3$  (**2**) shown at the 30% probability level with hydrogen atoms, uncoordinated pyridine, and imidazolone rings omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)–Cu(1)#1 2.495(2), Cu(1)–Cu(1)#2 2.495(1), Cu(1)–C(5)#1 2.046(7), Cu(1)–C(5) 2.072(7), Cu(1)–N(5) 2.101(6), Cu(1)–N(1) 2.142(6), C(14)–O(1) 1.232(11), C(5)#1–Cu(1)–C(5) 164.6(3), C(5)#1–Cu(1)–N(5) 96.0(3), C(5)–Cu(1)–N(5) 98.8(3), C(5)#1–Cu(1)–N(1) 100.8(2), C(5)–Cu(1)–N(1) 80.6(2), N(5)–Cu(1)–N(1) 100.0(2), Cu(1)#1–Cu(1)–Cu(1)#2 60.0. Symmetry code: #1  $-y+1, z-1/2, -x+3/2$ ; #2  $-z+3/2, -x+1, y+1/2$ .

$(\text{PF}_6)_3$ .<sup>19c</sup> Subsequent addition of  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  to the solution gave  $[\text{Ru}_2\text{Cl}(\text{L})(\text{CH}_3\text{CN})_4](\text{PF}_6)_3$  (**1**) as a red solid in 26% yield. The  $^1\text{H}$  NMR spectrum of **1** exhibits two doublets at 8.61 and 7.98 ppm due to the imidazolidene backbone protons. In its  $^{13}\text{C}$  NMR spectrum, the carbenic carbon resonance signal was observed at 194.8 ppm as a singlet.

The details of the molecular structure of **1** were established by an X-ray diffraction study. As shown in Figure 2, the cation contains two Ru(II) ions, one L ligand, one chloride, and four acetonitrile molecules. As expected, the ligand L coordinates in a

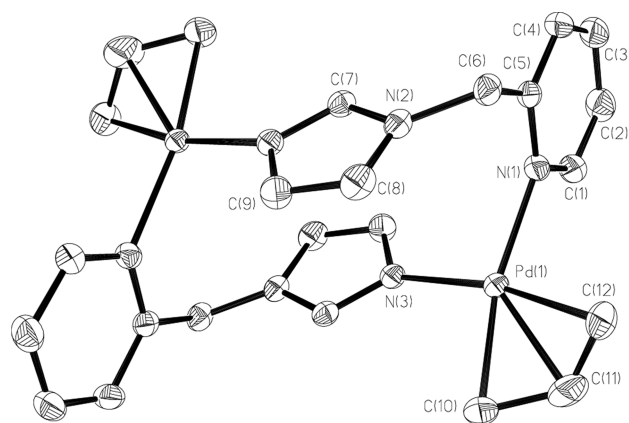
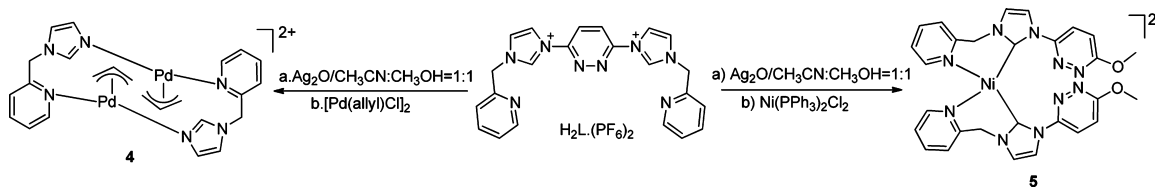


**Figure 4.** Thermal ellipsoids of  $[\text{Pd}_2(\text{allyl})_2\text{L}](\text{PF}_6)_2$  (**3**) shown at the 30% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)–C(4) 2.022(9), Pd(1)–C(14) 2.083(11), Pd(1)–C(13) 2.088(10), Pd(1)–N(3) 2.101(8), Pd(1)–C(15) 2.168(12), C(4)–Pd(1)–C(14) 138.3(4), C(4)–Pd(1)–C(13) 102.7(4), C(14)–Pd(1)–C(13) 35.7(4), C(4)–Pd(1)–N(3) 87.9(3), C(14)–Pd(1)–N(3) 133.9(4), C(13)–Pd(1)–N(3) 168.4(3), C(4)–Pd(1)–C(15) 170.1(4), C(14)–Pd(1)–C(15) 32.7(4), C(13)–Pd(1)–C(15) 67.8(4), N(3)–Pd(1)–C(15) 101.3(4). Symmetry code: #1  $-x, y, -z-1/2$ .

double-pincer fashion, forming a well-behaved  $\text{Ru}_2(\text{L})\text{Cl}$  plane, whereas four acetonitrile molecules occupy the axial positions. Each Ru(II) center is hexacoordinated in an octahedral sphere by one carbon, four nitrogen atoms, and one chloride. Two ruthenium centers are bridged by a pyridazine and a chloride, forming a five-membered metallocyclic ring. The Ru–Cl–Ru angle ( $98.01(6)^\circ$ ) is slightly smaller than the reported Ru–Cl–Ru angle ( $99.67(6)^\circ$ ).<sup>3c</sup> The Ru–C distances are 1.900(7) and 1.885(7) Å, which are significantly shorter than those of reported Ru–NHC complexes, which normally range from 1.91 to 2.10 Å.<sup>8e,11c,24</sup> The Ru···Ru distance is 3.785 Å, slightly longer than the value of a similar reported example (3.671 Å).<sup>3c</sup>

**Synthesis and Characterization of  $[\text{Cu}_3\text{L}_3](\text{PF}_6)_3$  (**2**).** In the past few years, a number of pyridazine-based dinuclear Cu(II) complexes have been established that show interesting magnetic and structural properties.<sup>2a–c,3a,5a</sup> However, very few corresponding Cu(I) complexes have been reported.<sup>2d,e</sup> Recently, direct synthesis of Cu–NHC complexes by using copper powder has been reported by our group, and the method was suitable for both Cu(I) and Cu(II) complexes.<sup>8d,10d</sup> Interestingly, treatment of a solution of  $[\text{Ag}_6(\text{L})_4](\text{PF}_6)_6$  with an excess of copper powder in air led to the isolation of  $[\text{Cu}_3\text{L}_3](\text{PF}_6)_3$  (**2**,  $\text{L}^a = 3\text{-(N-(pyridylmethyl)imidazolyliidenyl)-6-(N-(pyridylmethyl)imidazolyloonyl)pyridazine}$ ) as a yellow crystalline solid, an unexpected trinuclear copper product other than a dinuclear copper complex like **1**. One NHC carbon has been oxidized into a carbonyl group, which could be confirmed by a strong absorption band at  $1702\text{ cm}^{-1}$  in its IR spectrum and a singlet at 156.1 ppm in its  $^{13}\text{C}$  NMR spectrum. Such oxidation has been previously observed in the preparation of copper complexes.<sup>25</sup> The  $^1\text{H}$  NMR spectrum exhibits a singlet at 5.40 ppm ascribed to the  $\text{CH}_2$  groups between the imidazolone and pyridine rings, whereas two doublets of AB pattern were observed at 5.16 and 4.86 ppm, indicating that the two H atoms of the  $\text{CH}_2$  groups between imidazolyliene and pyridine rings are magnetically inequivalent.

The structure of trinuclear copper(I) complex **2** is depicted in Figure 3. The cation consists of three Cu(I) ions and three  $\text{L}^a$  ligands with a beautiful spiral divergence-shaped conformation. Unlike **1**, one-half of the ligand is coordinated to coppers in a tridentate fashion by one carbon and two nitrogen atoms, and the other half is left uncoordinated within which the carbenic carbon

Scheme 2. Synthesis of  $[\text{Pd}_2(\text{allyl})_2\text{L}^b](\text{PF}_6)_2$  (**4**) and  $[\text{NiL}^c](\text{PF}_6)_2$  (**5**)

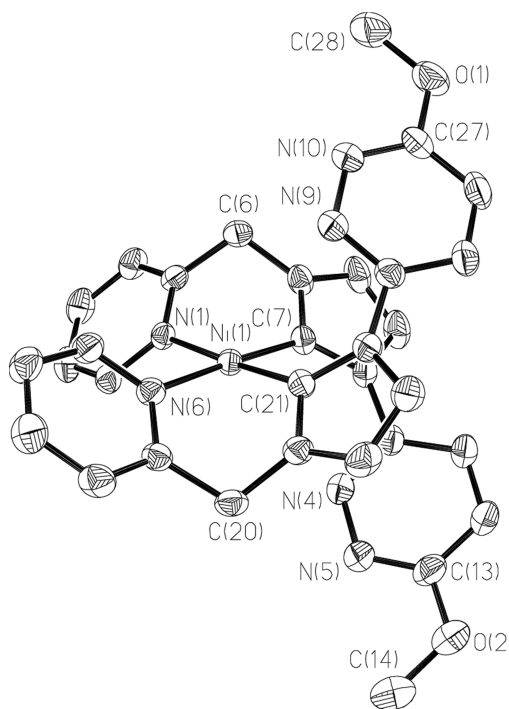
**Figure 5.** Thermal ellipsoids of  $[\text{Pd}_2(\text{allyl})_2\text{L}^b](\text{PF}_6)_2$  (**3**) are shown at the 30% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Pd(1)–C(11) 2.104(6), Pd(1)–N(3) 2.106(3), Pd(1)–C(10) 2.110(5), Pd(1)–C(12) 2.136(5), Pd(1)–N(1) 2.142(3), C(11)–Pd(1)–N(3) 133.2(2), C(11)–Pd(1)–C(10) 38.5(2), N(3)–Pd(1)–C(10) 99.28(17), C(11)–Pd(1)–C(12) 36.9(2), N(3)–Pd(1)–C(12) 167.86(18), C(10)–Pd(1)–C(12) 68.8(2), C(11)–Pd(1)–N(1) 129.2(2), N(3)–Pd(1)–N(1) 93.10(13), C(10)–Pd(1)–N(1) 167.39(17), C(12)–Pd(1)–N(1) 98.91(17). Symmetry code: #1  $-x+1, -y, -z+2$ .

was oxidized to a carbonyl group. The Cu–Cu–Cu angles are all  $60^\circ$ , in accordance with a perfect equilateral triangle consisting of three copper atoms. Each carbenic carbon is coordinated to two Cu(I) centers, and the Cu(I)–C distances are 2.046(7) and 2.072(7) Å, which are comparable to those of the reported Cu(I)-NHC examples (1.86–2.11 Å).<sup>7d,8d,14c,25,26</sup> The Cu–Cu bond length of 2.495 Å is within the normal range of those previously observed for similar trinuclear Cu(I)-NHC complexes (2.47–2.52 Å).<sup>25,26b</sup> The Cu–N<sub>pyridazine</sub> and Cu–N<sub>pyridine</sub> distances are 2.142(6) and 2.101(6), respectively.

**Synthesis and Characterization of  $[\text{Pd}_2(\text{allyl})_2\text{L}^b](\text{PF}_6)_2$  (**3**).** The carbene transfer reaction of  $[\text{Ag}_6(\text{L})_4](\text{PF}_6)_6$  with  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  afforded **3** as a white solid in 87% yield. The  $^1\text{H}$  NMR spectrum shows a singlet at 8.74 ppm due to the pyridazine backbone protons, showing no difference from that of **1** (8.78 ppm). In its  $^{13}\text{C}$  NMR spectrum, a singlet was observed at 177.5 ppm, ascribed to the NHC carbons, which is consistent with the reported values in the range 206.3–149.5 ppm for Pd-NHC complexes.<sup>27</sup>

The structure of **3** was further confirmed by X-ray diffraction and is depicted in Figure 4. Each Pd(II) center is coordinated by one carbenic carbon, one allyl group, and one pyridine group. The NHC-pyridine unit binds to palladium in a bidentate fashion with a bite angle of  $87.9(3)^\circ$ . The Pd–C<sub>carbene</sub> distances are 2.022(9) Å, showing no difference from those of the reported examples.<sup>28</sup>

**Synthesis and Characterization of  $[\text{Pd}_2(\text{allyl})_2\text{L}^b](\text{PF}_6)_2$  (**4**) and  $[\text{NiL}^c](\text{PF}_6)_2$  (**5**).** As shown in Scheme 2, when the deprotonation reaction of the imidazolium salt ( $\text{H}_2\text{L}^c(\text{PF}_6)_2$ )

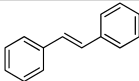
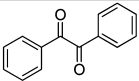
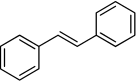
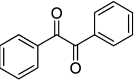
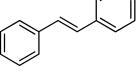
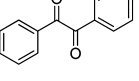
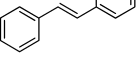
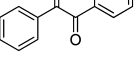
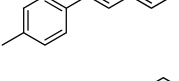
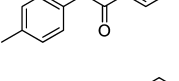
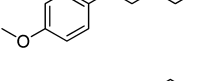
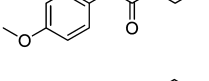
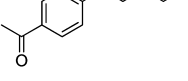
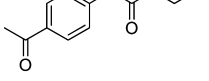
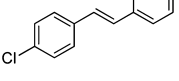
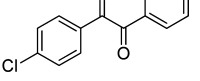
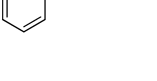
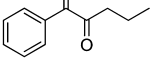

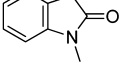
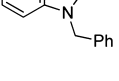
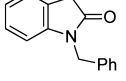
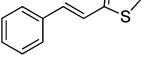
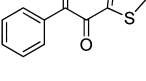
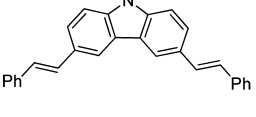
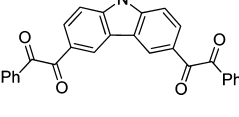


**Figure 6.** Thermal ellipsoids of  $[\text{NiL}^c](\text{PF}_6)_2$  (**5**) shown at the 30% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–C(7) 1.857(4), Ni(1)–C(21) 1.859(4), Ni(1)–N(6) 1.936(4), Ni(1)–N(1) 1.955(3), C(13)–O(2) 1.331(7), C(14)–O(2) 1.432(9), C(27)–O(1) 1.343(6), C(28)–O(1) 1.428(8), C(7)–Ni(1)–C(21) 90.59(19), C(7)–Ni(1)–N(6) 177.26(18), C(21)–Ni(1)–N(6) 87.73(17), C(7)–Ni(1)–N(1) 87.18(16), C(21)–Ni(1)–N(1) 176.59(17), N(6)–Ni(1)–N(1) 94.60(15).

with  $\text{Ag}_2\text{O}$  proceeded in a mixed solvent of  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{OH}$ , C–N cleavage between the pyridazine and the imidazole ring occurred due to nucleophilic substitution of one *N*-pyridylmethylimidazole by a methoxyl group.<sup>19e</sup> When the resulting solution was subsequently treated with  $[\text{Pd}(\text{allyl})\text{Cl}]_2$ , complex **4** was obtained in 69% yield. Although many efforts have been devoted to the isolation of the palladium complex bearing  $\text{L}^c$  ( $\text{L}^c = 3\text{-(N-(pyridylmethyl)imidazolylidene)-6-methoxypyridazine}$ ), unfortunately, we failed to isolate any Pd-NHC species. However, when  $\text{Ni(PPh}_3)_2\text{Cl}_2$  was added to the mixed solution after deprotonation reaction, complex **5** supported by  $\text{L}^c$  was isolated in 81% yield, which could be easily confirmed by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. The  $^1\text{H}$  resonances of **4** are all consistent with its formulation. In its  $^1\text{H}$  NMR spectrum, the allyl group and the *N*-pyridylmethylimidazole could be easily identified. The  $^1\text{H}$  NMR spectrum of **5** exhibits two doublets of AB pattern at 6.73 and 5.93 ppm, revealing that two protons of the  $\text{CH}_2$  linker are magnetically inequivalent, and both show apparent downfield shifts in comparison to those of **2** at 5.16 and 4.86 ppm. The

Table 2. Ruthenium-Catalyzed Oxidation of Alkenes to  $\alpha$ -Diketones<sup>a</sup>

$$R_1-CH=CH-R_2 \xrightarrow[\text{TBHP, solvent, rt}]{\text{Ru, NaI}} R_1-C(=O)-C(=O)-R_2$$

entry	alkene	solvent	oxidant	product	yield (%) <sup>b</sup>
1		toluene	TBHP		62
2		CH <sub>3</sub> CN	TBHP		92
3		CH <sub>3</sub> CN	O <sub>2</sub>		N.D.
4		CH <sub>3</sub> CN	H <sub>2</sub> O <sub>2</sub>		N.D.
5		CH <sub>3</sub> CN	TBHP		88
6		CH <sub>3</sub> CN	TBHP		87
7		CH <sub>3</sub> CN	TBHP		67
8		CH <sub>3</sub> CN	TBHP		84
9		CH <sub>3</sub> CN	TBHP		66
10		CH <sub>3</sub> CN	TBHP		69
11		CH <sub>3</sub> CN	TBHP		83
12		CH <sub>3</sub> CN	TBHP		75
13		CH <sub>3</sub> CN	TBHP		58 <sup>c</sup>

<sup>a</sup>Reaction conditions: alkene 0.5 mmol, Ru 0.005 mmol (1 mol %), NaI 0.15 mmol (30 mol %), TBHP 1 mL, CH<sub>3</sub>CN 3 mL, room temperature, 10 min. <sup>b</sup>Isolated yield. <sup>c</sup>Dialkene 0.5 mmol, Ru 0.01 mmol (2 mol %), NaI 0.30 mmol (60 mol %), TBHP 2 mL, CH<sub>3</sub>CN 6 mL.

methyl group appears as a singlet at 4.20 ppm. Complex **5** shows a typical resonance signal at 165.0 ppm for the NHC carbon in its  $^{13}\text{C}$  NMR spectrum, which is consistent with other Ni-NHC complexes, ranging from 152.3 to 190.6 ppm.<sup>7g,8c,10c,15a,29</sup>

The solid-state structure of **4** determined by X-ray diffraction analysis is shown in Figure 5. The cation is composed of two palladium ions, two allyl groups, and two *N*-pyridylmethylimidazole molecules. Two Pd(II) centers are linked by the two *N*-pyridylmethylimidazole molecules, forming a 14-membered metallocyclic ring. The N–Pd–N angle is 93.10(13)°. Two imidazole rings are completely parallel to each other. The distance between the two palladium atoms is 5.880 Å, much shorter than that of **3** (7.881 Å). The Pd–N<sub>imidazole</sub> and Pd–N<sub>pyridine</sub> distances are 2.106(3) and 2.142(3) Å, respectively.

The molecular structure of **5** determined by X-ray diffraction is depicted in Figure 6. Structural analysis of the cationic  $[\text{Ni}(\text{L}^{\text{c}})_2]^{2+}$  reveals that the two chelates adopt a *cis* arrangement around the Ni(II) center. Both NHC rings are nearly coplanar with their *trans*-positioned pyridine rings, with small dihedral angles of 4.48° and 6.40°, respectively. The Ni–C distances (1.857(4) and 1.859(4) Å) are quite normal as compared to many known tetracoordinate nickel(II)-NHC complexes.<sup>9b,15a,29a,30</sup> The Ni–N distances are 1.936(4) and 1.955(3) Å.

**Catalytic Properties.** Ruthenium complexes of NHCs have increasingly gained interest as catalysts for a number of important reactions.<sup>6a,c,f</sup> Although plenty of ruthenium complexes of NHC ligands have been reported to be active catalysts for olefin metathesis,<sup>6d,f,7b,31</sup> isomerization,<sup>32</sup> polymerization,<sup>24a,33</sup> hydrogenation,<sup>34</sup> and C–H activation reactions,<sup>35</sup> the bimetallic Ru-NHC complexes as catalysts for oxidation reactions of alkenes have not been reported. Herein, we investigated the activity of **1** in oxidation of alkenes.

With the bimetallic Pd-NHC complexes **3** and **4** in hand, we first synthesized various alkenes through Heck coupling reaction of aromatic halide and olefins under standard conditions (see Supporting Information). The results shown in Table S1 illustrate that complex **3** is more active than **4**, with excellent catalytic activities for aryl bromides bearing electron-withdrawing groups and aryl iodides. Considering the applications of ruthenium complexes in oxidation reactions,<sup>3b–d,36</sup> the activity of **1** in oxidation of alkenes at low catalyst loadings was investigated under very mild conditions. The results are summarized in Table 2. The catalytic activity of **1** for the oxidation reaction of (*E*)-1,2-diphenylethene was first examined. The reaction could proceed smoothly at room temperature in toluene under air, and benzil was obtained in 62% yield (entry 1). The yield could be significantly increased to 92% by employing  $\text{CH}_3\text{CN}$  as solvent (entry 2). TBHP is crucial since no benzil was detected when  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  was used as oxidant (entries 3, 4). Various alkenes were then tested under the optimized conditions. The reactions were completed at room temperature within 10 min. Generally, alkenes bearing electron-donating groups afforded higher yields than those with electron-withdrawing groups (entries 5–8). It is worth mentioning that the *N*-substituted indoles have also been successfully applied in high yields (entries 10, 11). Moreover, heterocyclic alkenes, such as those with thiophene and carbazole, can also be employed, giving the target products in moderate yields (entries 12, 13).

Many efforts have been devoted to constructing cooperative metal catalysts because such catalysts are believed to exhibit

higher catalytic activity in organic transformations.<sup>10c,d</sup> The high activity of diruthenium complex **1** in oxidation of alkenes is tentatively ascribed to the Ru···Ru cooperative effect. The dinucleating ability of the pyridazine moiety, the strong donating ability of carbenes, and the hexadentate structural property greatly ensure the stability of **1** in oxidation state, which would potentially increase its catalytic activity in oxidation reactions.

## CONCLUSION

In summary, we have described the synthesis and structural characterization of Ru(II), Cu(I), Pd(II), and Ni(II) complexes containing pyridazine-based *N*-heterocyclic carbenes. The ligand shows diversified reactivity toward different metal ions. A diruthenium and dipalladium complexes bridged by 3,6-bis(*N*-(pyridylmethyl)imidazolylidene)pyridazine were obtained through carbene transfer reactions. However, the carbene transfer reaction toward Cu(I) afforded an unexpected trinuclear Cu(I)-NHC complex due to oxidation of a NHC to imidazolone. C–N bond cleavage was observed, giving a dinuclear palladacyclic complex and a mononuclear nickel complex containing *N*-pyridylmethylimidazole and 3-(*N*-(pyridylmethyl)imidazolylidene)-6-methoxypyridazine, respectively. Additionally, the dinuclear Ru(II) complex is a very efficient catalyst for oxidation of alkenes.

## ASSOCIATED CONTENT

### Supporting Information

CIF files giving X-ray crystallographic data for **1**–**5**, experimental details of Heck coupling reactions, and electrochemical studies of **1**. 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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