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Indra Kusuma, Takashi Komuro, and Hiromi Tobita\*

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## Diruthenium Complexes with a 1,8-Naphthyridine-Based Bis(silyl) Supporting Ligand: Synthesis and Structures of Complexes Containing $Ru^{II}_{2}(\mu-H)_{2}$ and $Ru^{I}_{2}$ Cores

Indra Kusuma, Takashi Komuro, and Hiromi Tobita\*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan

E-mail: tobita@m.tohoku.ac.jp

We designed a novel naphthyridine-based supporting 1 2 3 4 ligand involving two silyl coordinating moieties at 2,7-positions, <sup>*i*Bu</sup>NBSi, for the synthesis of dinuclear metal complexes. Reaction of a ligand precursor <sup>*i*Bu</sup>NBSi(H)<sub>2</sub> (1) with  $Ru_3(CO)_{12}$  gave a di- $\mu$ -hydridodiruthenium(II,II) complex (<sup>t-Bu</sup>NBSi)Ru<sub>2</sub>( $\mu$ -H)<sub>2</sub>(CO)<sub>4</sub> (2). Photoirradiation to 2 resulted in formation of a diruthenium(I,I) complex (<sup>t-Bu</sup>NBSi)Ru<sub>2</sub>(CO)<sub>6</sub> (3). The Si-Ru-Ru-Si linkage of 2 takes a zigzag arrangement, whereas that of 3 edents a result. 5 6 7 8 a zigzag arrangement, whereas that of 3 adopts a roughly 10 linear one.

11	Keywords:	2,7-Disubstituted	1,8-naphthyridine	
12	Diruthenium complex   Silyl ligand			

13 Development of supporting ligands for dinuclear 14 complexes is an important subject in coordination chemistry. 15 This is because dinuclear complexes display greater structural variety than mononuclear ones and also show 16 17 specific reactivity arising from cooperative effect of plural 18 metal centers for accommodation and activation of substrates.<sup>1</sup> 1,8-Naphthyridine (napy)<sup>2</sup> and its derivatives<sup>3,4</sup> 19 have been widely utilized as such supporting ligands, since 20 21 the napy backbone has a rigid structure and can hold two metal centers in proximity.<sup>2-4</sup> In particular, napy derivatives 22 23 with coordinating moieties at 2,7-positions (Chart 1)<sup>4</sup> have recently been attracted considerable attention as supporting 24 ligands for dinuclear-complex catalysts,<sup>4a,c-h</sup> where a dimetal 25 core is effectively stabilized by chelation to each metal 26 center. For example, Uyeda et al.<sup>1,4a,c-e</sup> and Bera et al.<sup>41</sup> 27 developed dinickel- and diruthenium-complex catalysts, 28 29 respectively, bearing napy-diimine type tetradentate ligands. 30 In these catalysts, each dimetal core is considered to 31 facilitate transformation of organic molecules effectively by 32 the cooperative effect. However, to the best of our 33 knowledge, previous 2,7-disubstituted napy ligands used for 34 the synthesis of dinuclear complexes were limited only to 35 ones having nitrogen-, oxygen-, or carbon-donor 36 coordinating moieties at the ends of 2,7-substituents.<sup>4</sup>



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39 As part of our continuous study on the design and synthesis of transition-metal complexes bearing a silyl-40 containing multidentate ligand,<sup>5</sup> this time, we focused on the 41

42 development of an unprecedented napy-based ligand having 43 two silyl ligand moieties in the substituents at 2,7-positions 44 for the synthesis of dimetal complexes. We have previously 45 synthesized a mononuclear ruthenium-carbonyl complex 46 bearing an SiNSi-type bis(silyl)-pyridine pincer ligand.<sup>5</sup> 47 Along this line, we developed 2,7-bis[(di-tert-48 butylsilyl)methyl]-1,8-naphthyridine as an SiNNSi-type tetradentate ligand precursor, abbreviated as <sup>*t*-Bu</sup>NBSi(H)<sub>2</sub> 49 (Chart 1), and examined the synthesis of diruthenium-50 51 carbonyl complexes. Since silyl ligands possess not only 52 strong  $\sigma$ -donating ability but also strong *trans* influence, the dimetal center bearing '-BuNBSi is expected to show some 53 specific structural and electronic features caused by 54 55 weakening of a metal-metal or metal-element bond(s) 56 located trans to silvl silicon atoms.<sup>6</sup>

57 We synthesized the target ligand precursor 2,7-bis[(di-58 *tert*-butylsilyl)methyl]-1,8-naphthyridine  $(^{t-Bu}NBSi(H)_2)$  (1) 59 by six step reactions as illustrated in Scheme 1. Known 2,7-60 dimethyl-1,8-naphthyridine (E) as the precursor of 1 was 61 prepared by a newly-designed synthetic route from easilyavailable 2-aminopyridine,<sup>7,8</sup> which results in moderate to 62 63 high yields of intermediates A-E. In the final step, the ligand precursor  $^{t-Bu}NBSi(H)_2$  (1) was obtained in 88% 64 isolated yield by dilithiation of the methyl groups of E with 65 66 *n*-butyllithium (2.2 equiv.) at -78 °C followed by coupling 67 with di-tert-butylchlorosilane (Scheme 1, see the Supporting 68 Information for detail). Compound 1 is the first example of 69 1,8-naphthyridine-based ligand precursor bearing а 70 (hydrosilyl)methyl groups at the 2,7-positions.



72 73 74 75 76 Scheme 1. Synthesis of the ligand precursor '-BuNBSi(H)<sub>2</sub> (1) from 2aminopyridine. Reactants: (*i*) pivaloyl chloride,  $Et_3N$ , <sup>7a</sup> (*ii*) (1) *n*-BuLi, (2) DMF; <sup>7a</sup> (*iii*) 3 N HCl; <sup>7a</sup> (*iv*) (1) acetone, (2) saturated KOH in MeOH;<sup>7b</sup> (v) (1) MeLi, (2) KMnO<sub>4</sub> in acetone;<sup>7c</sup> (vi) (1) n-BuLi (2.2 equiv.), (2) (t-Bu)<sub>2</sub>SiHCl (2.5 equiv.).

77 Compound 1 was characterized by NMR, IR, and mass 78 spectroscopy (see the Supporting Information). The <sup>1</sup>H 79 NMR spectrum of 1 shows only two doublet signals for the 80 ring protons of 1,8-naphthyridine at 7.83 and 7.20 ppm. An 81 Si–H signal appears as a triplet at 3.63 ppm ( ${}^{3}J_{\text{HH}} = 3.6 \text{ Hz}$ )

1 due to the coupling with two methylene protons (2.73 ppm, 2 doublet). Observation of one strong singlet signal for *tert*-3 butyl groups at 0.96 ppm shows that four *tert*-butyl groups 4 are equivalent. In the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of 1, a signal 5 appears at 14.6 ppm. These observations indicate that 6 compound 1 adopts a  $C_{2v}$ -symmetric structure in solution.

The ligand precursor  $^{i-Bu}NBSi(H)_2$  (1) reacted with 2/3 7 molar equiv. of Ru<sub>3</sub>(CO)<sub>12</sub> in toluene at 90 °C to give an air-8 stable diruthenium(II,II) complex  $(^{t-Bu}NBSi)Ru_2(\mu-H)_2(CO)_4$ 9 (2) as an orange powder in 31% isolated yield via Si-H 10 oxidative addition as well as ligand substitution (Scheme 11 2).<sup>9</sup> The <sup>1</sup>H NMR spectrum of **2** in  $C_6D_6$  shows a singlet 12 signal for two hydrido hydrogens at -6.21 ppm. The two 13 14 methylene protons on the same carbon atom (SiCH<sub>A</sub>H<sub>B</sub>) 15 were observed as two inequivalent doublets at 2.72 and 2.66 16 ppm ( ${}^{2}J_{\text{HH}} = 17.2 \text{ Hz}$ ), and the  ${}^{1}\text{H}$  signals for the *tert*-butyl 17 groups on each silicon atom also appeared inequivalently as two singlets at 1.41 and 0.99 ppm. The <sup>29</sup>Si{<sup>1</sup>H} NMR 18 spectrum of 2 exhibits a single signal for the silvl ligand 19 moieties at 73.8 ppm. These NMR data support that 20 21 complex 2 adopts a  $C_2$ -symmetric structure in solution 22 where the  $C_2$  axis passes through the midpoint between the 23 two metal centers and the central carbon atoms of the naphthyridine ring. The IR spectrum of 2 shows four 24 25 absorption bands for CO vibration at 2013, 1990, 1944, and 1927  $\text{cm}^{-1}$  in accordance with the structure of **2**. 26



28 Scheme 2. Synthesis of diruthenium complexes 2 and 3.

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29 Single crystal X-ray structure analysis revealed that 30 complex 2 has two octahedrally-coordinated Ru centers bridged by two hydrido ligands and a "-BuNBSi ligand in a µ-31  $\kappa^{2}(Si,N)$ : $\kappa^{2}(Si,N)$  coordination mode (Figure 1a).<sup>10</sup> The Si-32 33 Ru-Ru-Si linkage adopts a zigzag arrangement (Figure 1b) 34 possibly due to the presence of the two µ-hydrido ligands 35 that bridge the two octahedral Ru centers. The Ru-Ru distance (2.6994(5) Å) is close to that of a di- $\mu$ -hydridodiruthenium complex  $[(\eta^5-C_5Me_5)Ru(\mu-H)(CO)]_2$ 36 37 (2.6920(3) Å) having the same electron count.<sup>11</sup> Positions of 38 39 two bridging hydrido hydrogens were determined by a 40 differential Fourier map and refined, but the values of Ru-H 41 bond distances (Ru(1)-H(1) 1.69(5) Å, Ru(1)-H(2) 1.88(8) Å, Ru(2)–H(1) 1.86(6) Å, and Ru(2)–H(2) 1.83(8) Å) could 42 43 not be compared with each other due to their large standard

44 deviations. To gain a more insight into the detailed structure 45 of the Ru<sub>2</sub>H<sub>2</sub> core, the hydrido-ligand positions were also investigated by the DFT calculation of a simplified model 46 complex (<sup>Me</sup>NBSi)Ru<sub>2</sub>( $\mu$ -H)<sub>2</sub>(CO)<sub>4</sub> (2'), which has two 47 48 methyl groups on each silicon atom instead of tert-butyl 49 groups, at the B3PW91 level using a mixed basis set, i.e. 50 LANL2DZ (for Ru) and 6-31G(d,p) (for the other atoms) 51 (see the Supporting Information). In the optimized structure 52 of 2', two Ru atoms are asymmetrically bridged by a pair of 53 hydrido ligands where the Ru-H bonds trans to Si (1.909 Å 54 each) are longer than those trans to CO (1.765 Å each) 55 probably due to strong trans influence of the silyl ligand moieties. According to the recent suggestion of bond 56 57 classification for bridging hydrido complexes with M-H-M 3c-2e bonds by Green, Green, and Parkin,<sup>12</sup> we can 58 59 represent the structure of 2 as depicted in Scheme 2 by 60 application of the "half-arrow" method. Since the <sup>1</sup>H and 61 Si NMR spectra show that 2 has a pseudo  $C_2$ -symmetric 62 structure (vide supra), the zigzag Si-Ru-Ru-Si arrangement 63 of 2 is considered to be maintained in solution.



65 Figure 1. Crystal structure of 2: (a) side view and (b) top view. 66 Thermal ellipsoids are drawn at the 50% probability level, and all the 67 hydrogen atoms except hydrido hydrogens are omitted for clarity. 68 Selected bond distances (Å) and angles (°) and selected torsion angles 69 (°): Ru(1)-Ru(2) 2.6994(5), Ru(1)-Si(1) 2.3891(13), Ru(2)-Si(2) 2.3887(11), Ru(1)-N(1) 2.202(3), Ru(2)-N(2) 2.186(4), Ru(1)-H(1) 70 71 72 73 74 1.69(5), Ru(1)-H(2) 1.88(8), Ru(2)-H(1) 1.86(6), Ru(2)-H(2) 1.83(8); Ru(2)-Ru(1)-Si(1) 134.17(3), Ru(1)-Ru(2)-Si(2) 130.81(3), Si(1)-Ru(1)-N(1) 80.97(10), Si(2)-Ru(2)-N(2) 80.62(10), Si(1)-Ru(1)-H(2) 175(2), Si(2)-Ru(2)-H(1) 167.7(17); N(1)-Ru(1)-Ru(2)-N(2) 75 15.81(14), C(2)-Ru(1)-Ru(2)-C(4) 6.6(2), Ru(1)-N(1)-C(18)-C(17) 76 170.0(3), Ru(2)-N(2)-C(18)-C(17) 168.5(3).

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Photoreaction of complex 2 in benzene at 7 °C for 20 h
under argon using a 450 W medium pressure mercury lamp
gave an air stable (hexacarbonyl)diruthenium complex (<sup>t</sup>

 $^{Bu}$ NBSi)Ru<sub>2</sub>(CO)<sub>6</sub> (3) as a dark brown powder in 47% 1 2 isolated yield (Scheme 2). Since the number of CO ligands 3 increased from four in complex 2 to six in complex 3, we 4 next examined the photoreaction of 2 under a CO 5 atmosphere (1 atm). As was expected, the reaction time until completion was dramatically shortened from 20 h to 1 h, 6 7 and the NMR yield of 3 was improved from 52% to 62%. 8 Although we have not characterized Ru-containing 9 byproducts formed in these photoreactions, the conversion 10 from 2 to 3 is considered to proceed via the following three processes: (1) photo-induced CO dissociation, which is well 11 established for carbonyl complexes, from complex 2, (2) 12 13 photo-induced reductive elimination of two hydrido ligands from 2 possibly as  $H_2$  together with the formation of coordinatively unsaturated species, <sup>13,14</sup> and (3) coordination 14 15 16 of liberated CO to this species giving 3.<sup>15</sup>

17 Unlike complex 2 whose Ru centers adopt the 18 oxidation number of +2, the Ru centers in complex 3 have the oxidation number of +1, demonstrating that <sup>ABu</sup>NBSi can 19 support the dinuclear ruthenium center with some different 20 oxidation states. The  ${}^{29}$ Si{ ${}^{1}$ H} NMR spectrum of **3** shows a 21 signal for the silvl coordinating moieties at 102.3 ppm. This 22 23 signal is shifted downfield in comparison with that of 2 by 24 28.5 ppm. The IR spectrum of 3 exhibits six terminal CO absorption bands at 2050, 2011, 1986, 1973, 1954, and 1927 25 cm<sup>-1</sup>. Complex **3** has a characteristic color of dark brown, 26 27 which is significantly different from that of 2 (orange). The 28 UV-vis spectrum of 3 (Figure S11) shows two weak 29 absorption maxima in a longer-wavelength region (> 450 nm), i.e. 480 and 717 nm, whereas that of 2 (Figure S7) did 30 31 not show any absorption maxima in this region. These 32 absorption maxima are presumably attributable to metal  $(d^{7})$ 33 to ligand (napy) charge transfer in accordance with the 34 assignments in previous reports for related diruthenium(I,I) complexes having napy-based multidentate ligands.<sup>3a,b</sup> 35

The molecular structure of 3 was determined by single 36 37 crystal X-ray structure analysis, revealing that complex 3 has two octahedrally-coordinated ruthenium centers bridged 38 by <sup>t-Bu</sup>NBSi (Figure 2a).<sup>10</sup> In contrast to di-µ-hydrido 39 complex 2, the Si-Ru-Ru-Si linkage in 3 adopts a roughly 40 41 linear arrangement in which each of the silvl silicon atoms is located trans to the Ru-Ru bond. The Ru-Ru bond 42 43 distance of 2.8579(3) Å is similar to that of a bis(silyl) 44 diruthenium(I,I) complex {(Me<sub>3</sub>SiO)<sub>3</sub>Si}(CO)<sub>4</sub>Ru- $Ru(CO)_4$ {Si(OSiMe<sub>3</sub>)<sub>3</sub>} (2.909(1) Å).<sup>16</sup> Nevertheless, this 45 distance is far longer than those of Ru(I)-Ru(I) complexes 46 with napy-based ligands (normally shorter than 2.7 Å).<sup>3a-d,4g</sup> 47 48 This elongation is obviously caused by strong trans 49 influence of the silyl ligands at the axial positions leading to 50 large destabilization of the Ru-Ru  $\sigma$ -bonding orbital as 51 expected from the proposal by Bera et al. for related Ru(I)-52 Ru(I) complexes having N- or O-coordinating axial donors supported by two 2-substituted napy-based ligands.<sup>3a</sup> The 53 Ru(CO)<sub>3</sub>-Ru(CO)<sub>3</sub> fragment of **3** adopts a staggered 54 55 conformation in order to avoid steric repulsion between CO ligands bound to two different metal centers; e.g. the C(2)-56 57 Ru(1)-Ru(2)-C(5) torsion angle = 31.50(11)°. This 58 conformation renders the Si-Ru-Ru-Si linkage tilted 59 against the naphthyridine ring (Figure 2b) as reflected in the

- 60 dihedral angle of  $24.10(7)^{\circ}$  between the least-squares plane
- 61 defined by the Ru(1), Ru(2), Si(1), and Si(2) atoms and that
- 62 of the 1,8-naphthyridine ring.

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64 Figure 2. Crystal structure of 3: (a) side view and (b) top view. 65 Thermal ellipsoids are drawn at the 50% probability level, and all the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and 66 67 angles (°) and selected torsion angles (°): Ru(1)-Ru(2) 2.8579(3), Ru(1)-Si(1) 2.4411(6), Ru(2)-Si(2) 2.4377(7), Ru(1)-N(1) 2.1892(19), 68 69 Ru(2)-N(2) 2.1980(19); Ru(2)-Ru(1)-Si(1) 160.807(18), Ru(1)-70 Ru(2)-Si(2) 160.797(18); N(1)-Ru(1)-Ru(2)-N(2) 28.12(7), C(2)-71 Ru(1)-Ru(2)-C(5) 31.50(11), Ru(1)-N(1)-C(20)-C(19) -160.03(16), 72 Ru(2)-N(2)-C(20)-C(19)-160.16(16).

73 In the <sup>1</sup>H NMR spectrum of **3** in  $C_6D_6$  at room temperature, each of the methylene and tert-butyl protons of 74 75 <sup>*t*-Bu</sup>NBSi showed one singlet signal at 2.80 ppm for CH<sub>2</sub> and 76 1.14 ppm for *t*-Bu. Variable temperature <sup>1</sup>H NMR spectra in 77 CD<sub>2</sub>Cl<sub>2</sub> (see Figure S12) demonstrated that both of the CH<sub>2</sub> 78 and t-Bu signals gradually broadened as the solution was 79 cooled from 300 K to 220 K. These observations prove the 80 fluxionality of 3 in solution that causes the exchange of two 81 protons in the methylene groups and of two tert-butyl 82 groups bound to each silicon atom. This fluxional behavior 83 probably occurs through flip of the Si-Ru-Ru-Si linkage 84 across the naphthyridine-ring plane.

In conclusion, we have successfully synthesized and characterized the first 1,8-naphthyridine-based SiNNSi-type chelate ligand precursor, <sup>*i*-Bu</sup>NBSi(H)<sub>2</sub>, and dinuclear ruthenium-<sup>*i*-Bu</sup>NBSi complexes **2** and **3**. The <sup>*i*-Bu</sup>NBSi ligand was found to support two different kinds of diruthenium cores, i.e. Ru(II)–Ru(II) in **2** and Ru(I)–Ru(I) in **3**. The **91** Ru(II)–Ru(II) complex **2** has a zigzag arrangement of the

1 Si-Ru-Ru-Si linkage, whereas the Ru(I)-Ru(I) complex 3 2 takes a roughly linear Si-Ru-Ru-Si linkage with a long Ru-Ru bond distance. Studies on the synthesis of other 3 dinuclear transition-metal complexes having '-BuNBSi and 4 5 on the reactivity of complexes 2 and 3 toward organic compounds are in progress. 6

8 This work was supported by JSPS KAKENHI Grant 9 Numbers JP25410058, JP15H03782, and JP16K05714 from 10 the Japan Society for the Promotion of Science (JSPS). We also acknowledge the Research and Analytical Center for 11 Giant Molecules, Tohoku University, 12 for mass 13 spectroscopic measurements and elemental analysis. 14

15 Supporting Information available is on 16 http://dx.doi.org/10.1246/cl.\*\*\*\*\*.

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- 9 During the reaction of 1 with Ru<sub>3</sub>(CO)<sub>12</sub>, an insoluble black solid of unidentified byproducts was also formed.
- 68 69 70 71 72 73 74 75 76 77 78 79 80 10 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1812369 (for 2) and CCDC-1812370 (for 3). Copies of the data can be obtained free of charge via CCDC Website.
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