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Ruthenium Complexes

Synthesis and Applications of (ONO Pincer)Ruthenium-Complex-Bound Norvalines

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Abstract: Two (ONO pincer)ruthenium-complex-bound norvalines, Boc–[Ru(pydc)(terpy)]Nva–OMe (**1**; Boc = *tert*-butyloxycarbonyl, terpy = terpyridyl, Nva = norvaline) and Boc–[Ru(pydc)(*t*Bu-terpy)]Nva–OMe (**5**), were successfully synthesized and their molecular structures and absolute configurations were unequivocally determined by single-crystal X-ray diffraction. The robustness of the pincer Ru complexes and norvaline scaffolds against acidic/basic, oxidizing, and high-temperature conditions enabled us to perform selective transformations of the *N*-Boc and *C*–OMe termini into various functional groups, such as alkyl amide, alkyl urea, and polyether groups, without the loss of the Ru center or enantiomeric purity. The resulting dialkylated Ru-bound norvaline, n-$C_{11}H_{23}CO$–L-[Ru(pydc)(terpy)]Nva–NH-n-$C_{11}H_{23}$ (L-**4**) was found to have excellent self-assembly properties in organic solvents, thereby affording the corresponding supramolecular gels. Ru-bound norvaline L-**1** exhibited a higher catalytic activity for the oxidation of alcohols by H_2O_2 than parent complex [Ru(pydc)(terpy)] (**11 a**).

Introduction

Metalated amino acids,[1] in which biologically important amino acid derivatives are tethered to functional organometallic compounds,[2] have attracted attention as promising bioorganometallic complexes for the fabrication of molecular functional materials.[3] Their unique properties, which originate from the bioorganic and organometallic moieties, provide such complexes with interesting properties for photochemical, electronic, magnetic, and catalytic applications. The first alanine and phenylalanine derivatives with ferrocene α-side chains were synthesized by Schlögl in 1957.[4] Although numerous metalated amino acids have since been developed for various applications, most of these derivatives were developed for use as biomarkers and biosensors.[5] The self-assembly and catalytic properties of metalated amino acids can be understood by the combination of amino acids and transition metal complexes, because these characteristics are inherent to both parts. How-

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*Supporting information for this article, including ^1H and ^{13}C NMR and HRMS (ESI-FT-ICR) spectra of all of the synthesized compounds, structure and crystallographic data of compounds L-**1**, D-**1**, **11 a**, **11 b**, L-**5**, and **20**, and XANES spectra of L-**1**, can be found under http://dx.doi.org/10.1002/asia.201600045.*

ever, few studies have investigated these properties for metalated amino acids.[1c,6,7] Recently, we synthesized a series of metalated amino acids that possessed (NCN pincer)palladium and (PCP pincer)palladium complexes and found that they exhibited unique self-assembly properties and excellent catalytic activities that were not observed in the parent complexes.[8,9] These results led us to design a new type of catalytically active amino acids with (ONO pincer)ruthenium complexes. Several pioneering studies have been reported on amino acids that were tethered to Ru complexes. Various Ru-complex-bound amino acids and peptides have been synthesized since Schachschneider and Knapp reported independently the metalated amino acids, in which a ruthenocene was attached covalently to the α-position of glycine[10a,c] and α-methyl group of alanine.[10b] Nevertheless, the research efforts mostly focused on amino acids and peptides in which the Ru complexes were bound to the N- or C-terminus, owing to their facile and convenient preparation.[5d,11] Contrarily, amino acids in which the Ru complexes were bound to the α-side chain have received little attention, despite their ability to conjugate a diverse array of peptides and proteins. Among the reported amino acids that have been tethered to a Ru complex through their α-side chain, amino acids[12] and peptides[13] that were bound to (η^6-arene)ruthenium complexes have been well-studied, owing to their facile and flexible preparation and their stability towards oxygen and moisture. These characteristics make such metalated amino acids and peptides potentially useful as synthetic auxiliary for aromatic nucleophilic substitution, which is a key macrocyclization step in the total synthesis of cyclic peptide antibiotics.[12b,c,13c] Strong coordination between the Ru and the S-containing side chains of cysteine and methionine has provided various Ru-bound amino acids.[14] The conjugation of (pyridyl)ruthenium complexes has been intensively explored to achieve Ru-bound amino acids with photoredox properties.[15] On the basis of their excellent photochemical properties, various molecular sensors have been developed that expanded their use in biochemistry. Despite the diverse applications of Ru-bound amino acids, no approach for their catalytic use was reported until Xu and Gilbertson's reports, in which alanine and its peptides that were conjugated with saturated IMes (SIMes)-type N-heterocyclic carbene (NHC)–Ru complex were successfully synthesized and showed catalytic activity for metathesis polymerization.[7a] Recently, histidine-[7b,c] and tyrosine-based amino acids[7d] that were bound to NHC–Ru complexes were developed and found to be catalytically active for the transfer hydrogenation of ketones and various metathesis reactions, respectively.

Ru-catalyzed oxidation reactions have attracted considerable attention in both industry and academia, owing to their high efficiencies and selectivities.[16] Although (dipyridyl)ruthenium[17] and (terpyridyl)ruthenium[18] complexes have shown excellent catalytic activity in various oxidation reactions, the catalytic application of amino acid conjugates of these complexes has remained unexplored. We envisaged that the integration of (pyridyl)ruthenium complexes into an appropriate amino acid would provide unique bioorganometallic compounds that could efficiently catalyze oxidation reactions. Recent progress in the application of pincer-type complexes[19] revealed that (pyridine-containing pincer)ruthenium complexes showed excellent catalytic activity with significant stability under various conditions, such as acidic/basic and high-temperature conditions, and even in the presence of oxidizing agents. Among the numerous reported pincer-type ruthenium complexes, we chose the ruthenium complex of ONO-pincer 2,6-pyridinedicarboxylate (pydc)[20] as the parent metal complex for tethering to the α-side chain of the amino acids, because of its facile preparation and suitable balance of robustness and high catalytic activity.

We successfully synthesized two (ONO pincer)ruthenium-complex-bound norvalines, Boc–[Ru(pydc)(terpy)]Nva–OMe (**1**)[21] and Boc–[Ru(pydc)(*t*Bu-terpy)]Nva–OMe (**5**; Boc = *tert*-butyloxycarbonyl, terpy = terpyridyl, Nva = norvaline),[21] in which Ru–pydc complexes were covalently conjugated to an N,C-termini-protected norvaline. Herein, we report the synthesis of (ONO pincer)ruthenium-complex-bound norvalines (**1**–**8**; Figure 1) and the single-crystal X-ray structure determination

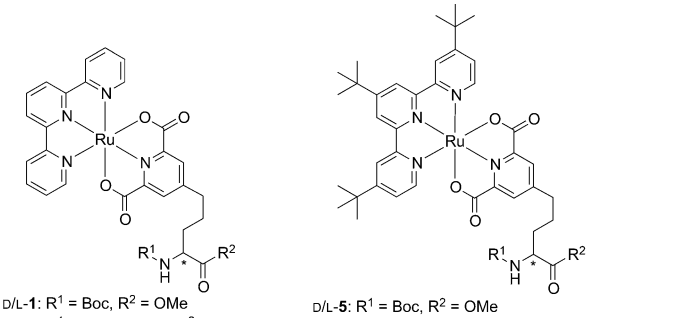


Figure 1. Molecular structures of a series of Ru-complex-bound norvaline derivatives.

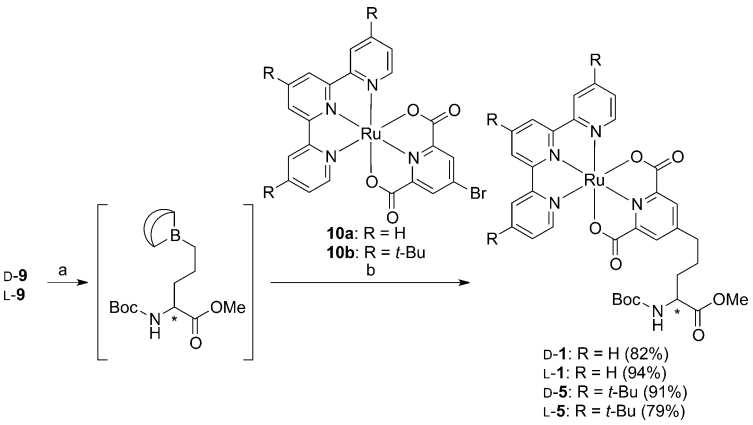
of complexes **1** and **5**. The preservation of chirality of the amino acid moiety was confirmed by chiral HPLC analysis after both the conjugation of the Ru complexes and the transformation of the N,C-termini in complexes **1** and **5**. The self-assembly behavior of these complexes, which was attributed to the inherent hydrogen-bonding properties of the amino acid moiety, was demonstrated by the formation of supramolecular organogels of the derivatives of Ru-bound norvaline L-**4**, which containes long alkyl chains at the N- and C-termini.

The combination of [Ru(pydc)(terpy)] and norvaline led us to develop a highly active bioorganometallic catalyst. The higher catalytic activity of Ru-bound norvaline L-**1** compared to the parent [Ru(pydc)(terpy)] (**11a**) was confirmed for the oxidation of various alcohols with H_2O_2 as the terminal oxidant. The origin of the enhanced catalysis of complex L-**1** was investigated by inductively coupled plasma–optical emission spectroscopy (ICP-OES).

Results and Discussion

Synthesis of (ONO Pincer)Ruthenium-Complex-Bound Norvalines

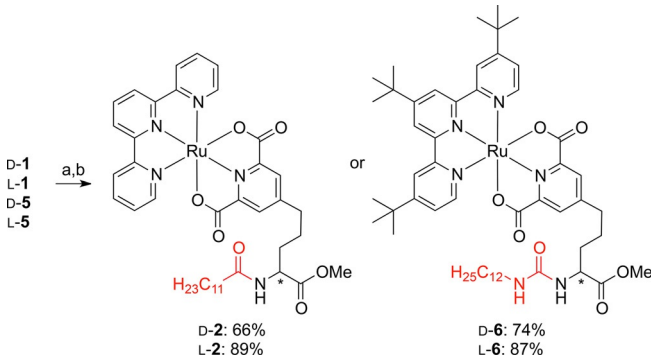
The Ru-complex-bound norvalines were designed to contain robust and catalytically active (ONO pincer)ruthenium complexes, [Ru(pydc)(terpy)][22] or [Ru(pydc)(*t*Bu-terpy)],[23] that were bound to the α-side chain of the norvaline derivatives through a chemically stable carbon–carbon bond. To conjugate the ruthenium complexes to the α-side chains of protected norvalines, we chose the Suzuki–Miyaura cross-coupling reaction. Modification of the methods reported by the groups of Taylor[24] and van Koten[25] and optimization of the reaction conditions allowed the successful cross-coupling of bromo-substituted (ONO pincer)ruthenium complexes **10a** and **10b** with borylated norvalines that were prepared from protected allylglycines D-**9** and L-**9** (Scheme 1). Thus, in the presence of catalytic amounts of $Pd(OAc)_2$ and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos), the in-situ-prepared 9-BBN adducts of protected D- and L-allylglycine (D-**9** and L-**9**) efficiently coupled with compounds **10a** and **10b** to give the desired functionalized amino acids (D-**1**, L-**1**, D-**5**, and L-**5**) in good yields without the decomposition of the Ru complex or the loss of chirality of the amino acid moiety. Retention of the absolute configuration of the α-carbon atom of the resulting complexes (D-**1**, L-**1**, D-**5**, and L-**5**) was further confirmed by chiral HPLC analysis and single-crystal X-ray diffraction.



Scheme 1. Synthesis of (ONO pincer)ruthenium-complex-bound norvalines **1** and **5**: a) 9-BBN, THF, 0 °C, 5 min then RT, 2 h; b) complex **10a**/**b**, $Pd(OAc)_2$, SPhos, K_3PO_4, THF/water/DMF (10:1:100 v/v/v), RT, 18 h.

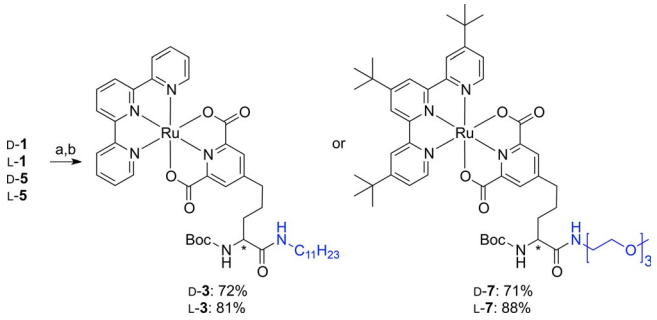
Modification of the N- and C-Termini

Both the N- and C-termini of complexes D-**1**, L-**1**, D-**5**, and L-**5** could be modified through a simple deprotection and condensation process that was first developed for peptide synthesis. Deprotection of the N-terminal Boc group in complexes D-**1** and L-**1** efficiently proceeded through treatment with HCl. Subsequent condensation of the resulting N-terminal-free Ru-bound norvaline with 1-dodecanoic acid by using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium hexafluorophosphate (DMT-MM·PF_6)[26] as a coupling reagent gave the corresponding alkylamide products (D-**2** and L-**2**) in 66% and 89% yield, respectively, whilst preserving the ruthenium complex intact (Scheme 2). The N-terminus of complexes D-**5** and L-**5** was successfully converted into 1-dodecylurea by Boc deprotection, followed by reaction with 1-dodecylisocyanate, thereby affording the corresponding complexes D-**6** and L-**6** in 74% and 87% yield, respectively.



Scheme 2. N-terminus functionalization of Ru-complex-bound norvalines D-**1**, L-**1**, D-**5**, and L-**5**: a) HCl, 1,4-dioxane, RT, 2 h; b) *N*,*N*-diisopropylethylamine (DIEA), DMT-MM·PF_6, 1-dodecanoic acid or 1-dodecylisocyanate, CH_2Cl_2, RT, 4 h.

The C-terminal methyl esters of complexes D-**1**, L-**1**, D-**5**, and L-**5** could be converted into various amides through sequential alkaline hydrolysis and condensation with an amine. Basic hydrolysis of the C-terminus of complexes D-**1** and L-**1** by using LiOH and subsequent condensation with 1-undecylamine afforded the corresponding *C*-*n*-undecylamides (D-**3** and L-**3**) in 72% and 81% yield, respectively. Similarly, the condensations of C-terminus-free ruthenium norvalines that were derived from complexes D-**5** and L-**5** with 2-[2-(2-methoxyethoxy)ethoxy]ethylamine gave the corresponding *C*-amido products (D-**7** and L-**7**) in 71% and 88% yield, respectively (Scheme 3). Notably, no loss



Scheme 3. C-terminus functionalization of Ru-complex-bound norvalines D-**1**, L-**1**, D-**5**, and L-**5**: a) LiOH·H_2O, THF/water (4:1 v/v), RT, 2 h; b) 1-undecylamine or 2-[2-(2-methoxyethoxy)ethoxy]ethylamine, DMT-MM·PF_6^-, Et_3N, $CHCl_3$, RT, 12 h.

or undesirable change in the ruthenium complex moiety was detected by NMR and UV/Vis spectroscopy after modification of the N- and C-termini. This result clearly confirmed the adequate robustness of (ONO pincer)ruthenium complexes, such as [Ru(pydc)(terpy)] and [Ru(pydc)(*t*Bu-terpy)], towards acidic and basic conditions by using fundamental peptide chemistry.

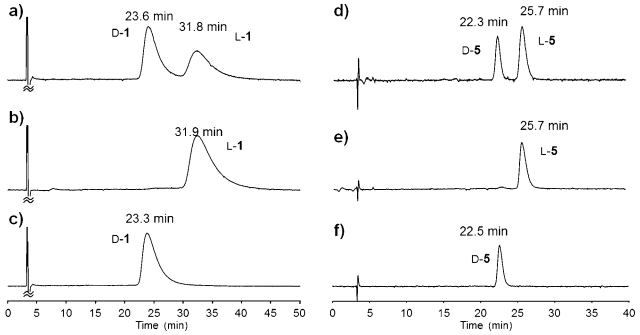


Figure 2. HPLC chromatograms of complexes D-**1** and L-**1** (column: Daicel CHIRALPAK AY-H (0.46 cm×25 cm); eluent: *n*-hexane/EtOH/MeOH/diethanolamine (DEA)/trifluoroacetic acid (TFA), 50:40:10:0.1:0.1 v/v/v/v/v; flow rate: 1.0 mL min^{-1}; 40 °C; UV detector: 313 nm) and D-**5** and L-**5** (column: Daicel CHIRALPAK ID (0.46 cm×25 cm); eluent: 0.1 M aq. KPF_6 (pH 2.0)/MeCN, 45:55 v/v; flow rate: 0.8 mL min^{-1}; 40 °C; UV detector: 313 nm): a) racemic mixture of D/L-**1**; b) L-**1**; c) D-**1**; d) racemic mixture of D/L-**5**; e) L-**5**; and f) D-**5**.

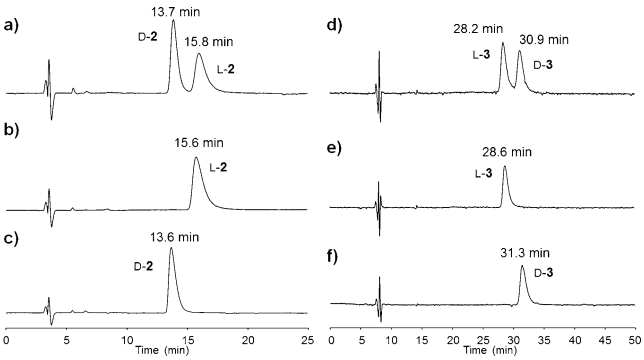


Figure 3. HPLC chromatograms of complexes D-**2** and L-**2** (column: Daicel CHIRALPAK ID (0.46 cm×25 cm); eluent: 0.1 M aq. KPF_6 (pH 2.0)/MeCN, 45:55 v/v; flow rate: 1.0 mL min^{-1}; 25 °C; UV detector: 254 nm) and D-**3** and L-**3** (column: Daicel CHIRALPAK ID (0.46×25 cm); eluent: 0.1 M aq. KPF_6 (pH 2.0)/MeCN, 30:70 v/v; flow rate: 0.8 mL min^{-1}; 25 °C; UV detector: 254 nm): a) racemic mixture of D/L-**2**; b) L-**2**; c) D-**2**; d) racemic mixture of D/L-**3**; e) L-**3**; and f) D-**3**.

Optical Purity of the Metalated Amino Acids

Preservation of the stereochemistry at the α-carbon atom of the amino acid moiety was verified by chiral HPLC analysis on a chiral column, such as CHIRALPAK AY-H and CHIRALPAC ID. Under the baseline-separation conditions for racemic mixtures of enantiomers D/L-**1** and D/L-**5**, we assessed the optical purity of Ru-bound norvalines that were synthesized from the corresponding D- and L-allylglycines (D-**9** and L-**9**), as shown in Figure 2. The almost-equal enantiomeric excesses of the starting Boc–allylgly–OH·$NHCy_2$ and complexes D-**1**, L-**1**, D-**5**, and L-**5** (>98% *ee*) indicated that no racemization occurred during the Suzuki–Miyaura cross-coupling reactions for ruthenium conjugation. Similarly, complete preservation of the enantiomeric purity throughout the N/C-termini transformation of D-**1** and L-**1** into D-**2**, L-**2**, D-**3**, and L-**3** was confirmed as shown in Figure 3. These results indicated that no racemization occurred under the acidic or basic deprotection conditions and also under the condensation conditions.

Single-Crystal X-ray Analysis

The precise molecular structures of (ONO pincer)ruthenium-complex-bound amino acids L-**1**, D-**1**, and L-**5** were determined by single-crystal X-ray analysis; fully mirror-image structures of complexes L-**1** and D-**1** were observed, as shown in Figure 4. We could not grow large single crystals of the metalated amino acids with good crystallinity, owing to the presence of multiple intermolecular interactions; indeed, to the best of our knowledge, only five X-ray structures of α-side-chain-metalated amino acids have been reported: ferrocenylalanine,[27] (arene)ruthenium-complex-bound amino acids with related dipeptides,[13a,c,d] and (NHC)ruthenium-bound histidine.[7a] Recently, microcrystal X-ray diffraction measurements based on synchrotron radiation at SPring-8 (BL02B1, BL38B1, and BL40XU[28]) enabled us to determine the molecular structures of (pincer)palladium-complex-bound norvalines from microscale (1–20 μm) crystals.[8] Microcrystal analysis of a square platelet crystal (dimensions: 25 μm×25 μm; thickness: 1 μm) allowed us to con-

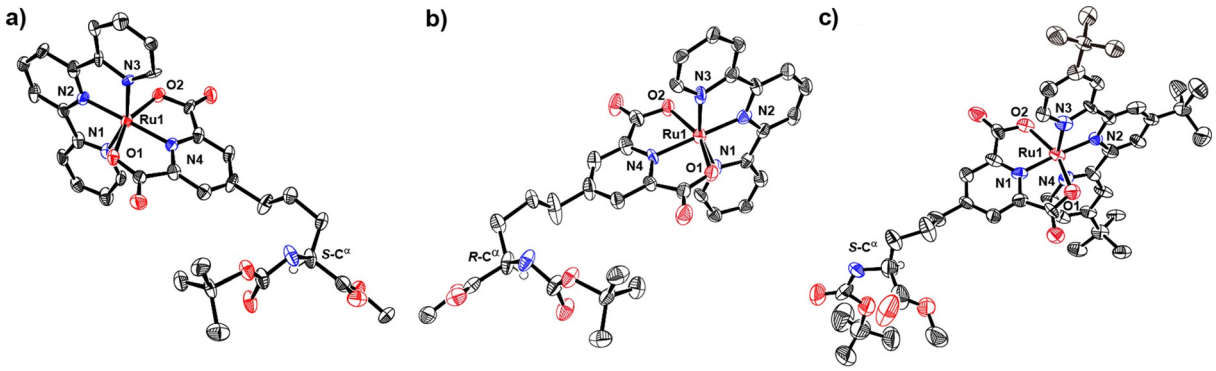


Figure 4. Molecular structures of ruthenium-based norvalines: a) L-**1**; b) D-**1**; c) L-**5**. Thermal ellipsoids are set at 50% probability.

Table 1. Crystallographic data for complexes L-**1**, D-**1**, and L-**5**.

	L-**1**	D-**1**	L-**5**
formula	$C_{35}H_{37}N_5O_9Ru$	$C_{35}H_{37}N_5O_9Ru$	$C_{45}H_{57}N_5O_8Ru$
M_w [g mol^{-1}]	772.78	772.78	897.02
crystal size [mm^3]	0.025×0.025×0.001	0.04×0.03×0.005	0.03×0.03×0.005
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2 (#5)	*C*2 (#5)	$P2_1$ (#4)
a [Å]	24.6010	24.4882(13)	18.8290(3)
b [Å]	16.0450	15.9351(9)	13.4152(3)
c [Å]	17.6000	17.3743 (9)	19.7391(4)
β [°]	91.8700	92.497(7)	116.0060(10)
V [Å^3]	6943.4258	6773.4(6)	4481.15(16)
Z	8	8	4
T [°C]	−173.0	−173.0	−173.0
total reflns	20607	29699	77473
unique reflns	11246	15082	14274
no. of parameters	876	925	1469
R [$I>2\sigma(I)$]/all	0.0607/0.0698	0.0584/0.0776	0.0643/0.1187
wR_2 [$I>2\sigma(I)$]	0.1683	0.1338	0.1781
GOF	1.065	1.021	1.001
Flack parameter	0.11(5)	0.02(2)	−0.13(3)
radiation (λ [Å])	synchrotron (0.71000) BL38B1; SPring-8	synchrotron (0.35540) BL02B1; SPring-8	synchrotron (0.71069) BL40XU; SPring-8

firm the absolute configurations of enantiomers D-**1** and L-**1** from their refined Flack χ parameters ($\chi=0.11(5)$ for L-**1**; 0.02(2) for D-**1**), with good agreement between the crystallographic parameters for complexes L-**1** and D-**1** (Table 1). These crystal structures revealed that the (ONO pincer)ruthenium-complex moieties in complexes D-**1** and L-**1** retained almost the same bond lengths and angles as in the parent [Ru(pydc)(terpy)] (**11 a**).[29] Thus, the structures of these ruthenium-complex moieties did not undergo any significant change upon conjugation with the amino acid moieties, which indicated that the chemical and physical properties in the metalated amino acids had been retained. The similar structure of the Ru(pydc)(*t*Bu-terpy) moieties in compound L-**5** compared to the parent ruthenium complex (**10 b**)[30] was also confirmed by X-ray structural analysis, along with determination of the absolute configuration.

Electrochemical Properties

The redox behavior of (ONO pincer)ruthenium-complex-bound norvalines L-**1** and L-**5** was investigated by using cyclic voltammetry (CV) on the basis of the activity of the Ru(pydc)(terpy) and Ru(pydc)(*t*Bu-terpy) units. The corresponding (ONO pincer)ruthenium complexes [Ru(pydc)(terpy)] (**11 a**)[22] and [Ru(pydc)(*t*Bu-terpy)] (**11 b**)[23] were also synthesized and their redox properties were compared with those of complexes L-**1** and L-**5** (Table 2). A reversible single-electron oxidation process was observed for each ruthenium complex and attributed to the metal-centered redox of the Ru^{II}/Ru^{III} couple. The oxidation potential decreased from +0.067 to −0.048 V on moving from complex L-**1** to L-**5**, and from +0.079 to +0.002 on moving from complex **11 a** to **11 b**. The larger change in oxidation potential (0.115 V) between complexes L-**1** and L-**5** compared to that between complexes **11 a** and **11 b** (0.077 V) was attributed to stabilization of the Ru^{III} state by the electron-donating *t*Bu-terpy ligand. Similarly, the *t*Bu-terpy ligand led to lower reduction potentials for complexes L-**1**/L-**5** (0.144 V) and complexes **11 a**/**11 b** (0.091 V). Notably, introducing amino acid moieties caused small-but-evident changes in the redox properties of complexes L-**1** and L-**5**. Negative potential shifts were found in both the oxidation and reduction processes for the pairs L-**1** and **11 a** (0.012 and 0.007 V, respectively) and L-**5** and **11 b** (0.050 and 0.060 V, respectively). These results indicated that the amino-acid moiety affected the electronic state of the ruthenium complexes, despite negligible changes in their structure, as discussed below in the discussion of their catalytic properties.

Table 2. Electrochemical properties of the Ru complexes.

Complex	$E_{1/2}$ (*V* vs Fc/Fc$^+$)	
Boc–L-[Ru(pydc)(terpy)]Nva–OMe (L-**1**)	+0.067	−1.974
[Ru(pydc)(terpy)] (**11 a**)	+0.079	−1.967
Boc–L-[Ru(pydc)(*t*Bu-terpy)]Nva–OMe (L-**5**)	−0.048	−2.118
[Ru(pydc)(*t*Bu-terpy)] (**11 b**)	+0.002	−2.058

Self-Assembly Properties

The hydrophobic functionalization of amino acids and peptides gives rise to their supramolecular organization in organic solutions, based on their inherent hydrogen-bonding properties. In particular, amino acids[31] and peptides[32] with long conjugated alkyl chains undergo efficient self-assembly to afford well-ordered supramolecular architectures. Recently, we reported that *N*-/*C*-aliphatic Pd- and Pt-bound amino acids and peptides showed excellent self-assembly properties in organic solutions to afford supramolecular gels that possessed well-regulated metal arrays.[1c,8,9] To investigate the self-assembly properties of Ru-bound amino acids, aliphatic (ONO pincer)ruthenium-complex-bound norvalines L-**4** and L-**8** were synthesized by the N-/C-terminus transformations of compounds L-**2** and L-**6** in 65% and 45% yield, respectively [Eq. (1) and (2)]. The resulting double-tailed amino acid L-**4** exhibited sonication-induced self-assembly properties. Under ultrasonic irradiation (0.45 W cm^{-2} at 40.0 kHz), a solution of complex L-**4** in chlorobenzene/acetone/EtOH (18:5:2, v/v/v; 2.4×10^{-2} M) readily lost fluidity to afford a supramolecular gel (Figure 5 a, b). Similar ultrasound-induced gelation was demonstrated in our earlier reports on Pd- and Pt-bound glutamic acids and their peptides.[9] Importantly, the observed sol/gel transition was completely reversible upon further heating (melting)/sonication cycles, thereby indicating that noncovalent-bonding interactions, such as hydrogen bonding and π–π stacking, played a dominant role in

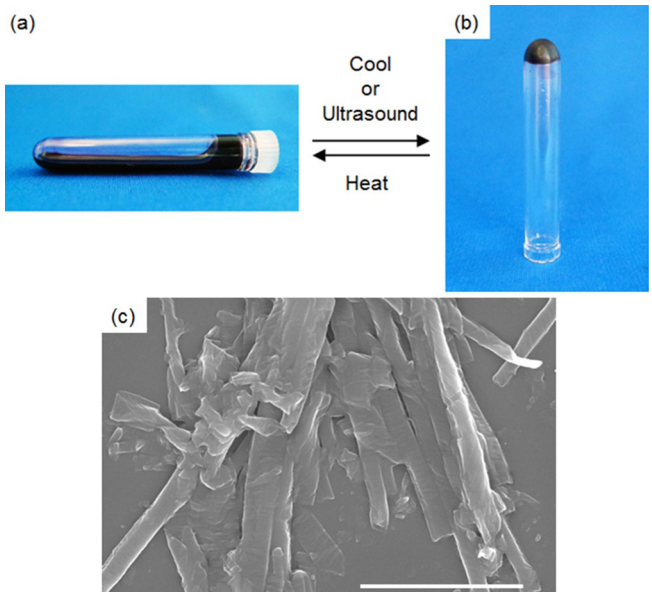
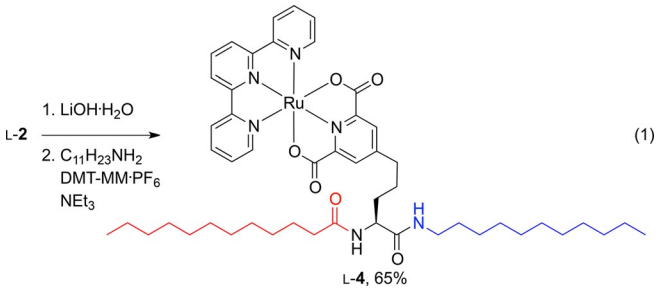
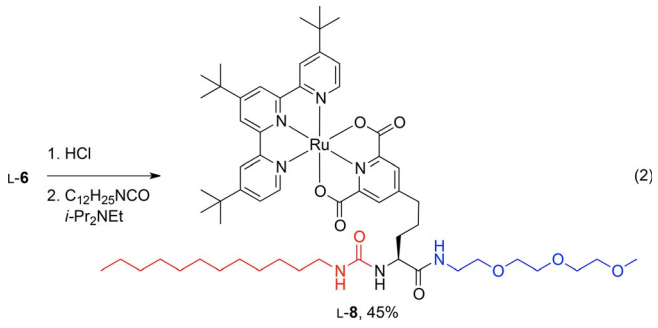


Figure 5. Photograph of the solution state (a) and gel state (b) of complex L-**4** (2.4×10^{-2} M) in chlorobenzene/acetone/EtOH (18:5:2); c) SEM image of the xerogel of complex L-**4**. Scale bar: 5.0 μm.

the formation of the supramolecular gels.[8c,9a,c] The formation of typical belt-like supramolecular aggregates was observed in the SEM image of the xerogel of complex L-**4** (Figure 5c). Although the urea moiety was commonly expected to show excellent hydrogen-bond-forming ability, complex L-**8** showed no self-assembly properties in any organic or aqueous solvent or under any external stimuli.



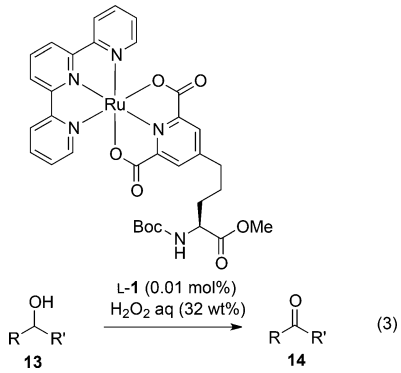
(1)



(2)

Catalytic Properties of Ruthenium-Bound Norvaline L-1

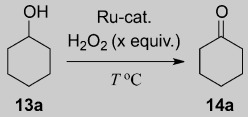
The combination of pydc and pyridyl ligands in Ru complexes affords highly active oxidation catalysts. Bhattacharya and co-workers reported a pioneering work on mild and selective oxidation reactions, including alkene epoxidation and alcohol oxidation, by using (ONO pincer)ruthenium complexes that contained the bipyridine (bpy) ligand of [Ru(pydc)(bpy)].[33] Nishiyama and co-workers employed a combination of bis(oxazolynyl)pyridine (pybox) and *N*,*N*,*N*-terdentate terpyridine (terpy) ligands to yield a highly stable (ONO pincer)ruthenium complex, [Ru(pybox)(terpy)], which was a highly efficient catalyst for a diverse range of oxidation reactions.[22,34] Beller and co-workers successfully demonstrated the efficiency of [Ru(pydc)(terpy)] for the catalysis of various oxidation reactions with appropriate terpy derivatives.[35]



(3)

To assess the catalytic properties of (ONO pincer)ruthenium-complex-bound norvaline L-**1**, oxidation reactions of alcohols were performed with hydrogen peroxide (H_2O_2) as a "green" oxidant [Eq. (3)].[36] The catalytic activity of complex L-**1** was first demonstrated for the oxidation of cyclohexanol (**13a**). The oxidation of compound **13a** proceeded efficiently in the presence of a small amount of complex L-**1** (0.01 mol%) to selectively afford the corresponding cyclohexanone (**14a**). As shown in Table 3, the influence of reaction temperature and the number of equivalents and addition rate of H_2O_2 were examined. For the treatment of compound **13a** with two equivalents of H_2O_2 and 0.01 mol% of complex L-**1**, the yield of compound **14a** negligibly increased from 50% to 51% on increasing the reaction temperature from 25 °C to 40 °C (Table 3, entries 1 and 2); on further increasing the temperature to 80 °C, the yield dropped to 30% (Table 3, entry 3). When the amount of H_2O_2 was decreased to one equivalent, the yield decreased to 36%, whereas the yield increased slightly to 56% when four equivalents of H_2O_2 were used (Table 3, entries 4 and 5). No improvement in yield was achieved by the slow addition of H_2O_2 (Table 3, entry 6). The lower yields at 80 °C and with one equivalent of H_2O_2 could be explained by the competitive and unproductive decomposition of H_2O_2, which is a common problem in H_2O_2-based oxidation reactions. Based on these results, we chose the conditions listed in Table 3, entry 1 (at 25 °C with 2.0 equiv of H_2O_2) as our optimal conditions for the L-**1**-catalyzed alcohol-oxidation reaction. To our delight, complex L-

Table 3. Ru-complex-catalyzed oxidation of cyclohexanol into cyclohexanone.[a]



Entry	Catalyst	*x* [equiv]	*T* [°C]	Conversion[b] [%]	Yield[c] [%]
1	L-**1**	2.0	25	51	50
2	L-**1**	2.0	40	57	51
3	L-**1**	2.0	80	30	30
4	L-**1**	1.0	25	36	36
5	L-**1**	4.0	25	59	56
6[d]	L-**1**	2.0	40	44	36
7	**11a**	2.0	25	17	14
8[e]	L-**1**	2.0	25	43	41
9[e]	**11a**	2.0	25	43	42
10[f]	L-**1**	2.0	25	75	69
11[f]	**11a**	2.0	25	46	45
12	**12**	2.0	25	13	10
13	none	2.0	25	3	0

[a] Reaction conditions: cyclohexanol (5.0 mmol), H_2O_2 (32 wt%, *x* equiv), ruthenium catalyst (0.01 mol%), 4 h; [b] conversion of cyclohexanol; [c] GC yield determined by using methyl nonanoate as an internal standard; [d] slow addition of H_2O_2 over 4 h; [e] BTBAC (0.125 mmol) was added; [f] SDS (0.125 mmol) was added.

1 showed substantially higher catalytic activity than parent complex **11a** (Table 3, entry 7 vs entry 1). The contribution of the amino acid moiety to the enhancement in catalytic activity was examined by using the parent complex, [Ru(pydc)(terpy)] (**11a**) as a catalyst. Under the above-optimized conditions with compound **11a**, the oxidation of cyclohexanol (**13a**) gave the corresponding product in considerably lower yield (14%) compared to the L-**1**-catalyzed oxidation reaction (Table 3, entry 7). This enhancement in catalytic activity of complex L-**1** compared to compound **11a** seemed somewhat larger than that inferred from the small differences between their electrochemical properties (Table 2). The electronic effect of the *n*-alkyl side chain of the norvaline moiety was not directly related to the increased catalytic activity, because the redox potential of the Ru center strongly correlated to the reactivity of high-valence Ru–oxo species, which have been postulated to be the catalytically active species in this oxidation reaction.[17d,18d] To evaluate the electrochemical influence of the *n*-alkyl side chain of the norvaline moiety, a *n*-butyl-substituted complex, [Ru(*n*Bu-pydc)(terpy)] (**12**),[37] was prepared, in which the electron-donating ability of the *n*-butyl group was expected to impart similar redox properties as complex L-**1**. However, there was no enhancement in the compound-**12**-catalyzed oxidation of substrate **13a**; only 10% formation of compound **14a** was observed (Table 3, entry 12).

The oxidation reaction proceeded in an aqueous/organic biphasic system, in which the liquid organic substrates dispersed in the aqueous hydrogen peroxide and each phase could be readily distinguished by the naked eye, as shown in Figure 6. Quantification of the relative ruthenium content in the two phases was performed by using ICP-OES analysis. The aqueous/organic distribution ratio of ruthenium in the L-**1**-catalyzed oxidation reaction mixture was 53:47. In contrast, in the reaction mixture with compound **11a**, dominant distribution in the aqueous phase was observed (97:3). These results suggested that a phase-transfer mechanism was involved in the ruthenium-bound-norvaline-catalyzed oxidation reaction. We concluded that the hydrophobic amino acid moiety and hydrophilic high-valence ruthenium complex moiety made complex L-**1** amphiphilic; thus, complex L-**1** showed phase-transfer properties for facilitating the transport of alcohols into the aqueous H_2O_2 phase, whilst also carrying the oxidized product into the organic phase. We anticipated that the stronger hydrophilic nature of the high-valence ruthenium species that were derived from complex **11a** would contribute to this phenomenon. The addition of surfactants, such as benzyltributylammonium chloride (BTBAC) and sodium dodecylsulfonate (SDS), enhanced the catalytic activity of the parent ruthenium complex (**11a**), to give compound **14a** in 42% and 45% yield, which were comparable to the results with complex L-**1** (Table 3, entries 9 and 11 vs entry 1). These results suggested that the observed enhancement in the catalytic activity of complex L-**1** compared to compound **11a** could be explained by surfactant effects from the hydrophobic amino acid moiety of Boc–Nva–OMe, rather than the electron-donating effect of the alkyl side chain.

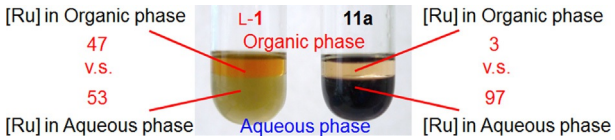


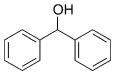
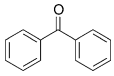
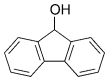
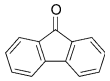
Figure 6. Photograph of two biphasic reaction mixtures that were obtained from the oxidation of cyclohexane catalyzed by compounds L-**1** and **11a**. Ru content was determined by ICP-OES analysis.

Scope of the Alcohol-Oxidation Reaction Catalyzed by a Ruthenium-Bound Norvaline

The catalytic activity of Ru-bound norvaline L-**1** was investigated for the oxidation of a variety of secondary alcohols. As shown in Table 4, aliphatic secondary alcohols cycloheptanol (**13b**) and 2-cyclohexen-1-ol (**13c**) were oxidized into their corresponding cyclic ketones (**14b** and **14c**) in 35% and 21% yield, respectively (Table 4, entries 1 and 2). The efficiency of this reaction was demonstrated by the oxidations of benzylic secondary alcohols 1-phenylethanol (**13d**), 1-indanol (**13e**), 1,1-diphenylmethanol (**13f**), and fluorenol (**13g**), which efficiently proceeded to afford acetophenone (**14d**), 1-indanone (**14e**), benzophenone (**14f**), and fluorenone (**14g**) in 87%, 81%, 76%, and 58% yield, respectively (Table 4, entries 3–6). Notably, the parent [Ru(pydc)(terpy)] (**11a**) showed lower catalytic activities for all of the substrates examined under these conditions (the yields are shown in the parentheses in Table 4 and Table 5).

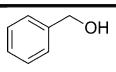
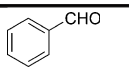
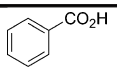
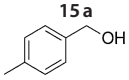
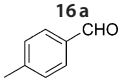
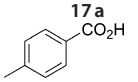
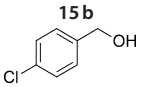
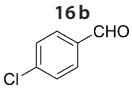
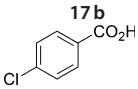
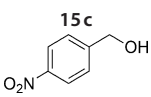
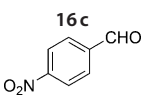
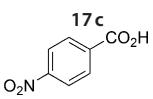
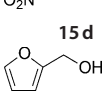
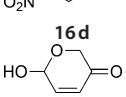
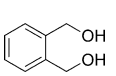
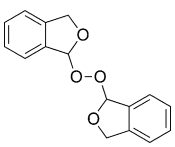
The substrate scope for the oxidation of primary alcohols was also evaluated (Table 5). In the presence of Ru-bound nor-

Table 4. Oxidation of secondary alcohols catalyzed by Ru-bound norvaline complexes.[a]

Entry	Substrate	T [°C]	t [h]	Product	Yield [%][b]
1	 **13b**	60	24	 **14b**	35 (6)
2	 **13c**	70	24	 **14c**	21 (13)
3	 **13d**	25	4	 **14d**	87[c] (19)
4	 **13e**	25	24	 **14e**	81 (24)
5[d,f]	 **13f**	25	24	 **14f**	76 (2)
6[e,f]	 **13g**	70	24	 **14g**	58 (41)

[a] Reaction conditions: alcohol (5.0 mmol), H_2O_2 (32 wt%, 2.0 equiv), complex L-**1** (0.01 mol%); values in parentheses denote results with Ru catalyst **11a**. [b] Yields determined by ^{1}H NMR spectroscopy. [c] Yield of the isolated product. [d] CH_2Cl_2 (1.0 mL) was used as the solvent. [e] Complex L-**1** (0.1 mol%) in EtOAc (2.5 mL). [f] EtOAc (0.5 mL) was used as the solvent.

Table 5. Oxidation of alcohols catalyzed by Ru-bound norvaline complexes.[a]

Entry	Substrate	T [°C]	t [h]	Product	Yield [%][b]	Product	Yield [%][b]
1	 **15a**	25	4	 **16a**	36 (70)	 **17a**	59 (11)
2	 **15b**	40	24	 **16b**	16	 **17b**	4
3	 **15c**	40	24	 **16c**	71[c]	 **17c**	23[c]
4	 **15d**	40	24	 **16d**	69[c]	 **17d**	20[c]
5[d]	 **15e**	25	0.5	 **18**	57[f]		
6[e]	 **15f**	25	24	 **19**	9 (7)	 **20**	66 (38)

[a] Reaction conditions: alcohol (5.0 mmol), H_2O_2 (32 wt%, 2.0 equiv), complex L-**1** (0.01 mol%); values in parentheses denote results with Ru catalyst **11a**. [b] Yields determined by ^{1}H NMR spectroscopy. [c] Yield of the isolated product. [d] CH_2Cl_2 (1.0 mL) was used as the solvent. [e] Complex L-**1** (0.1 mol%) in EtOAc (2.5 mL). [f] EtOAc (0.5 mL) was used as the solvent.

valine L-**1**, the oxidation of primary benzylic alcohols proceeded to afford the corresponding aldehydes, carboxylic acids, and their derivatives. The oxidation of substituted benzyl alcohols **15a**–**15d** proceeded to give the corresponding aldehydes (**16a**–**16d**), along with carboxylic acids **17a**–**17d** as over-oxidation products (Table 5, entries 1–4). Interestingly, over-oxidation of the aldehydes was partly suppressed by using parent [Ru(pydc)(terpy)] (**11a**) as the catalyst, with which the oxidation of compound **15a** gave compound **16a** in 70% yield, with a small amount of compound **17a** (11% yield). The oxidation of 2-furanylmethanol (**15e**) proceeded along with oxidative rearrangement to give 6-hydroxy-2*H*-pyran-3(6*H*)-one (**18**) in 57% yield (Table 5, entry 6).[38] Notably, 1,2-benzenedimethanol (**15f**) gave bis(1,3-dihydroisobenzofuran-1-yl)peroxide (**20**) as the main product, with a small amount of lactone **19** (Table 5, entry 7). The formation of peroxide **20** was reasonably ascribed to the Lewis-acid-catalyzed dehydrative etherification of diols.[39]

Conclusion

We have successfully synthesized (ONO pincer)ruthenium-complex-bound norvalines through the formation of chemically robust C–C bonds between the propyl side chains of norvalines and [Ru(pydc)(terpy)] or [Ru(pydc)(*t*Bu-terpy)] complexes. The chemically robust nature of the Ru-complex-bound norvalines enabled the facile installation of various functionalities at the N- and C-termini by using common deprotection/condensation protocols without metal leaching. Chiral HPLC and single-crystal X-ray structural analyses clarified that the α-carbon atom of the norvaline scaffold maintained the original chirality and optical purity during both the Suzuki–Miyaura cross-coupling reaction and the sequential deprotection/condensation reactions. This new class of metalated amino acids exhibited physically and chemically interesting properties: the self-assembly behavior of the N- and C-modified norvaline derivatives afforded organogels, thereby indicating that these (ONO pincer)ruthenium-complex-bound norvalines had the potent hydrogen-bonding properties of amino acids, despite the bulky side chains. The (ONO pincer)ruthenium-complex-bound norvalines were found to have higher catalytic oxidizing ability for alcohols compared to the parent (ONO pincer)ruthenium complex. Electrochemical measurements and ICP-OES analysis revealed that the high catalytic activity originated from the formation of phase-transfer micellar aggregates, owing to their self-assembly properties. High catalytic activity was demonstrated by the oxidation of various secondary alcohols and benzyl alcohols. These results clearly demonstrated that the conjugation of Ru complexes to the α-side chain of amino acids provided a promising method for producing useful bioorganometallic molecules,

in which the properties of the metal complex and the biomolecule cooperated to afford new functional materials.

Experimental Section

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 800 and JEOL ECS400NR spectrometers by using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The chemical shifts (δ) were expressed in ppm downfield of tetramethylsilane. IR spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer. Melting points were recorded on a Yanaco MP-500D. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. High-precision isotopic peak-intensity ratios were determined by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) coupled with electrospray ionization on a SolariX FT-ICR-MS spectrometer (Bruker Daltonik GmbH). Elemental analysis was performed by the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. GC analysis was performed on a Shimadzu GC-17A instrument that was equipped with an FID detector and a capillary column (InertCap 1MS, GL Sciences Inc., 30 m×0.25 mm, film thickness: 0.25 μm). Optical purity was determined on a JASCO-PU 2089 plus system with a JASCO CD-2095 plus circular dichroism detector and chiral columns (Daicel CHIRALPAK ID and AY-H, 0.46 cm×25 cm).

Materials

Solvents and reagents were commercially available and used without further purification. [Ru(pydc)(terpy)] (**11a**)[22] and [Ru(pydc)(*t*-Bu-terpy)] (**11b**)[23] were synthesized according to literature procedures. Methyl Boc–L-allylglycinate was synthesized according to a literature procedure from Boc–L-allylglycine dicyclohexylamine salt (Novabiochem).[8] Dimethyl 4-bromopyridine-2,6-dicarboxylate[40] and 2-[2-(2-methoxyethoxy)ethoxy]ethylamine[41] were synthesized according to literature procedures.

X-ray Crystallographic Analysis

Single crystals of complexes L-**1**, D-**1**, and L-**5** suitable for X-ray diffraction analysis were obtained from solutions of EtOH, DMF, and Et_2O and mounted onto MicroMounts (MiTeGen, LLC) with mineral oil. Single-crystal X-ray crystallographic analysis was performed on a Rigaku AFC10 diffractometer with a Saturn 724 CCD detector by using multilayer monochromated $Mo_{K\alpha}$ radiation (λ=0.71075 Å). Synchrotron X-ray diffraction studies were performed on the BL02B1, BL38B1, and BL40XU beamlines at SPring-8.

Electrochemical Measurements

Cyclic voltammetry was performed on an ALS electrochemical analyzer (model 610DH). Glassy carbon, platinum wire, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. Electrochemical measurements were performed in a cell that was charged with a solution of the sample in dry degassed DMF (1.0 mM) with Bu_4NPF_6 (0.1 M) as the supporting electrolyte under an argon atmosphere.

General Procedure for the Oxidation of Cyclohexanol

A solution of complex L-**1** (0.37 mg, 5.0×10^{-4} mmol) in CH_2Cl_2 (0.50 mL) was added to a Schlenk tube (10 mL). The system was evacuated for 30 min by using a vacuum pump to remove the solvent and then charged with argon. Cyclohexanol (501.5 mg, 5.01 mmol) was added to the reaction mixture in the Schlenk tube at RT under vigorous stirring and aqueous H_2O_2 (32% w/w, 0.96 mL, 9.9 mmol) was added. The reaction mixture was stirred vigorously at RT for 4 h. After the reaction had completed, a bilayer mixture was obtained and EtOAc (4.0 mL) and NaCl (5 g) were added. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×4.0 mL). Methyl nonanoate (635.1 mg, 3.69 mmol) was added to the combined organic layer and quantitative gas chromatography (GC) analysis was performed.

(4-Bromo-2,6-pyridinedicarboxylato-κO,κN,κO′)(2,2′:6′,2″-terpyridine-κN,κN′,κN″)ruthenium(II) (10a)

Powders of [{Ru(*p*-cymene)Cl_2}$_2$] (5.25 g, 8.57 mmol) and 2,2′:6′,2″-terpyridine (4.20 g, 18.0 mmol) were dissolved in MeOH (200 mL) at RT to form a dark-violet solution. An aqueous solution of NaOH (0.4 M, 95.7 mL, 38.3 mmol) was added to a solution of dimethyl 4-bromopyridine-2,6-dicarboxylate (4.74 g, 17.3 mmol) in MeOH (200 mL) and the mixture was stirred for 30 min to give a white precipitate. The heterogeneous solution was purged with argon for 15 min and then added dropwise to the Ru solution through a cannula. The reaction mixture was heated at 85 °C for 24 h; during this time, the color of the solution turned deep purple. The dark-violet precipitate was collected by filtration and washed with $CHCl_3$ and water to give compound **10a** (9.53 g, 92% yield). M.p. > 325 °C; ^{1}H NMR ($CDCl_3$, 392 MHz): δ=8.73 (d, J=7.7 Hz, 2H; C_5H_3N), 8.60 (dd, J=7.7, 1.2 Hz, 2H; C_5H_4N), 8.58 (s, 2H; $C_5H_2N_2Br$), 8.05 (t, J=7.7 Hz, 1H; C_5H_3N), 7.97 (ddd, J=8.5, 7.5, 1.3 Hz, 2H; C_5H_4N), 7.81 ppm (dd, J=4.9, 1.4 Hz, 2H; C_5H_4N); IR (neat): $\tilde{\nu}$= 3525, 1630, 1480, 1448, 1381, 1312, 1279, 1177, 1031, 922 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{22}H_{13}BrN_4O_4RuNa$: 600.90563 [*M*+Na]$^+$; found: 600.90733; elemental analysis calcd (%) for $C_{22}H_{13}BrN_4O_4Ru\cdot2.5H_2O$: C 42.39, H 2.91, N 8.99; found: C 42.31, H 3.18, N 9.00.

(4-Bromo-2,6-pyridinedicarboxylato-κO,κN,κO′)(4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine-κN,κN′,κN″)ruthenium(II) (10b)

Powders of [Ru(*p*-cymene)Cl_2]$_2$ (3.80 g, 6.20 mmol) and 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (5.07 g, 12.6 mmol) were dissolved in MeOH (180 mL) at RT to form a dark-violet solution. An aqueous solution of NaOH (0.4 M, 63 mL, 25.2 mmol) was added to a solution of dimethyl 4-bromo-2,6-pyridinedicarboxylate (3.52 g, 12.5 mmol) in MeOH (125 mL) and the mixture was stirred for 30 min to give a white precipitate. The heterogeneous solution was purged with argon for 15 min and then added dropwise to the Ru solution through a cannula. The reaction mixture was heated at 85 °C for 24 h; during this time, the color of the solution turned deep purple. The violet suspension was cooled to RT and diluted with $CHCl_3$ and washed with water. Then, the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by precipitation from $CHCl_3$/*n*-hexane to give compound **10b** (9.24 g, 99% yield). M.p. > 325 °C; ^{1}H NMR ($CDCl_3$, 392 MHz): δ=8.51 (s, 2H; C_5H_2NBr), 8.26 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.12 (s, 2H; $C_5H_3NC(CH_3)_3$), 7.54 (d, J=5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.28 (d, J=5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 1.63 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.40 ppm (s, 18H; $C_5H_3NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ=171.3 (2C; $C_4H_2NBr(COO)_2$), 160.5 (2C; $C_5H_3NC(CH_3)_3$), 159.7 (2C; $C_5H_2NC(CH_3)_3$), 157.1 (2C; $C_4H_2NBr(COO)_2$), 155.4 (1C; $C_5H_2NC(CH_3)_3$), 152.0 (2C; $C_4H_2NBrC(COO)_2$), 151.0 (2C; $C_4H_2NBr(COO)_2$), 130.9 (2C; $C_4H_2NBr(COO)_2$), 128.6 (1C; $C_4H_2NBr(COO)_2$), 123.9 (2C; $C_5H_3NC(CH_3)_3$), 118.7 (2C; $C_5H_3NC(CH_3)_3$), 117.7 (2C; $C_5H_2NC(CH_3)_3$), 35.6 (1C; $C_5H_2NC(CH_3)_3$), 35.1 (3C; $C_5H_2NC(CH_3)_3$), 31.2 (2C;

$C_5H_3NC(CH_3)_3$), 30.6 ppm (6C; $C_5H_3NC(CH_3)_3$); IR (neat): $\tilde{\nu}=2967$, 1633, 1476, 1385, 1294, 1209, 894, 885, 803 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{34}H_{37}BrClN_4O_4Ru$: 781.07266 $[M+Cl]^-$; found: 781.07444; elemental analysis calcd (%) for $C_{34}H_{37}BrN_4O_4Ru$: C 54.69, H 4.99, N 7.50; found: C 54.42, H 5.02, N 7.48.

(4-Butyl-2,6-pyridinedicarboxylato-κO,κN,κO′)(2,2′:6′,2″-terpyridine-κN,κN′,κN″)ruthenium(II) (12)

1-Butene (9.5 g, 0.169 mol) was bubbled through a solution of 9-borabicyclo[3,3,1]nonane (9-BBN; 62.5 mg, 0.51 mmol) in THF (1.8 mL) for 15 min and the mixture was stirred for 4 h. Then, an aqueous solution of K_3PO_4 (3.00 M, 0.180 mL, 0.54 mmol) was added, followed by a mixture solution of compound **10a** (204 mg, 0.353 mmol), $Pd(OAc)_2$ (4.30 mg, 0.0192 mmol), and SPhos (15.2 mg, 0.0370 mmol) in DMF (10.0 mL). The reaction mixture was stirred at RT for 24 h and the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give a violet crude product. The crude product was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$, 5:95 v/v) to afford compound **12** (156 mg, 80% yield). M.p. > 325 °C; ^1H NMR ($CDCl_3/CD_3OD$, 9:1 v/v; 600.2 MHz): $\delta=8.34$ (d, $J=7.9$ Hz, 2H; C_5H_3N), 8.31 (s, 2H; $C_5H_2N(COO)_2$), 8.25 (d, $J=8.1$ Hz, 2H; C_5H_3N), 8.17 (d, $J=8.1$ Hz, 2H; C_5H_4N), 7.78 (dd, $J=7.5$, 1.5 Hz, 2H; C_5H_4N), 7.77 (t, $J=8.1$ Hz, 1H; C_5H_3N), 7.59 (d, $J=5.5$ Hz, 2H; C_5H_4N), 7.32 (ddd, $J=7.0$, 5.5, 1.4 Hz, 2H; C_5H_4N), 3.07 (t, $J=7.7$ Hz, 2H; $CH_2CH_2CH_2CH_3$), 1.94 (m, 2H; $CH_2CH_2CH_2CH_3$), 1.59 (m, 2H; $CH_2CH_2CH_2CH_3$), 1.09 ppm (t, $J=7.3$ Hz, 3H; $CH_2CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3/CD_3OD$, 9:1 v/v; 150.9 MHz): $\delta=173.0$ (2C; $C_5H_2N(COO)_2$), 160.2 (2C; C_5H_4N), 157.7 (2C; C_5H_3N), 152.2 (1C; $C_5H_2N(COO)_2$), 151.4 (2C; C_5H_4N), 150.0 (2C; $C_5H_2N(COO)_2$), 135.8 (2C; C_5H_4N), 130.2 (1C; C_5H_3N), 128.4 (2C; $C_5H_2N(COO)_2$), 126.6 (2C; C_5H_4N), 122.2 (2C; C_5H_4N), 121.1 (2C; C_5H_3N), 35.9 (1C; $CH_2CH_2CH_2CH_3$), 32.7 (1C; $CH_2CH_2CH_2CH_3$), 22.6 (1C; $CH_2CH_2CH_2CH_3$), 14.0 ppm (1C; $CH_2CH_2CH_2CH_3$); IR (neat): $\tilde{\nu}=3406$, 2932, 1616, 1595, 1447, 1424, 1382, 1323, 1278, 1246, 1224, 1158, 1095, 1030, 1009, 921, 804, 767, 745 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{26}H_{22}N_4O_4RuNa$: 579.05837 $[M+Na]^+$; found: 579.05898; elemental analysis calcd (%) for $C_{26}H_{22}N_4O_4Ru\cdot2.5H_2O$: C 52.00, H 4.53, N 9.33; found: C 52.03, H 4.14, N 9.47.

Boc–L-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–OMe (L-1)

A white solid of 9-borabicyclo[3,3,1]nonane (9-BBN; 274 mg, 2.25 mmol) was added to a solution of Boc–L-AllylgGly–OMe (257 mg, 1.12 mmol) in THF (5.5 mL) and the mixture was stirred for 4 h. Then, an aqueous solution of K_3PO_4 (3.00 M, 0.600 mL, 1.80 mmol) was added, followed by a mixture solution of compound **10a** (579 mg, 1.00 mmol), $Pd(OAc)_2$ (11.6 mg, 0.0516 mmol), and SPhos (41.2 mg, 0.100 mmol) in DMF (50.0 mL). The reaction mixture was stirred at RT for 24 h and the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give a violet crude product. The crude product was purified by column chromatography on silica gel ($MeOH/CHCl_3$, 5:95 v/v) to afford complex L-**1** (689 mg, 94% yield). M.p. > 325 °C; ^1H NMR ($CDCl_3$, 800.2 MHz): $\delta=8.27$ (s, 2H; $C_5H_2N(COO)_2$), 8.26 (d, $J=8.1$ Hz, 2H; C_5H_3N), 8.17 (d, $J=7.9$ Hz, 2H; C_5H_4N), 7.72 (dd, $J=7.5$, 1.5 Hz, 2H; C_5H_4N), 7.71 (t, $J=8.1$ Hz, 1H; C_5H_3N), 7.61 (d, $J=5.5$ Hz, 2H; C_5H_4N), 7.28 (ddd, $J=7.0$, 5.5, 1.4 Hz, 2H; C_5H_4N), 5.13 (br s, $J=6.9$ Hz, 1H; CONH), 4.43–4.49 (m, 1H; NHCH), 3.81 (s, 3H; $COOCH_3$), 3.00–3.11 (m, 2H; $CHCH_2CH_2CH_2$), 2.12–1.87 (m, 4H; $CHCH_2CH_2CH_2$), 1.46 ppm (s, 9H; $COOC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 201.2 MHz): $\delta=172.8$ (2C; $C_5H_2N(COO)_2$), 160.7 (2C; C_5H_4N), 158.2 (2C; C_5H_3N), 152.1 (2C; C_5H_4N), 151.0 (2C; $C_5H_2N(COO)_2$), 135.9 (2C; C_5H_4N), 129.7 (1C; C_5H_3N), 128.5 (2C; $C_5H_2N(COO)_2$), 127.0 (2C; C_5H_4N), 122.3 (2C; C_5H_4N), 121.3 (2C; C_5H_3N), 80.8 (1C; $OC(CH_3)_3$), 53.8 (1C; NHCH), 53.2 (1C; $COOCH_3$), 36.4 (1C; $CHCH_2CH_2CH_2$), 33.3 (1C; $CHCH_2CH_2CH_2$), 29.1 (3C; $OC(CH_3)_3$), 27.0 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}=3407$, 2939, 1699, 1618, 1598, 1447, 1333, 1226, 1163, 1030 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{33}H_{33}N_5O_8RuNa$: 752.12740 $[M+Na]^+$; found: 752.12866; elemental analysis calcd (%) for $C_{33}H_{33}N_5O_5Ru\cdot2H_2O$: C 51.83, H 4.71, N 9.18; found: C 51.64, H 4.71, N 9.18.

Boc–D-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–OMe (D-1)

Compound D-**1** was synthesized according to the same procedure as compound L-**1**, by using Boc–D-allylGly–OMe. Yield: 82%; m.p. > 325 °C; ^1H NMR ($CDCl_3$, 800.2 MHz): $\delta=8.27$ (s, 2H; $C_5H_2N(COO)_2$), 8.27 (d, $J=7.9$ Hz, 2H; C_5H_3N), 8.19 (d, $J=7.9$ Hz, 2H; C_5H_4N), 7.74 (dd, $J=6.6$, 1.5 Hz, 2H; C_5H_4N), 7.72 (t, $J=8.1$ Hz, 1H; C_5H_3N), 7.62 (d, $J=5.5$ Hz, 2H; C_5H_4N), 7.28 (ddd, $J=7.0$, 5.5, 1.3 Hz, 2H; C_5H_4N), 5.14 (br s, $J=7.9$ Hz, 1H; CONH), 4.41–4.51 (m, 1H; NHCH), 3.82 (s, 3H; $COOCH_3$), 3.01–3.11 (m, 2H; $CHCH_2CH_2CH_2$), 2.12–1.87 (m, 4H; $CHCH_2CH_2CH_2$), 1.46 ppm (s, 9H; $COOC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 201.2 MHz): $\delta=172.9$ (2C; $C_5H_2N(COO)_2$), 160.7 (2C; C_5H_4N), 158.3 (2C; C_5H_3N), 152.1 (2C; C_5H_4N), 151.0 (2C; $C_5H_2N(COO)_2$), 135.9 (2C; C_5H_4N), 129.8 (1C; C_5H_3N), 128.5 (2C; $C_5H_2N(COO)_2$), 127.0 (2C; C_5H_4N), 122.3 (2C; C_5H_4N), 121.3 (2C; C_5H_3N), 80.8 (1C; $OC(CH_3)_3$), 53.9 (1C; NHCH), 53.2 (1C; $COOCH_3$), 36.4 (1C; $CHCH_2CH_2CH_2$), 33.3 (1C; $CHCH_2CH_2CH_2$), 29.1 (3C; $OC(CH_3)_3$), 27.0 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}=3398$, 2693, 1738, 1705, 1685, 1626, 1511, 1484, 1449, 1423, 1384, 1367, 1338, 1319, 1299, 1281, 1224, 1202, 1161, 1098, 1045, 1030, 1011, 929, 908, 863, 801, 761, 745, 726 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{33}H_{33}N_5O_8RuNa$: 752.12740 $[M+Na]^+$; found: 752.12963; elemental analysis calcd (%) for $C_{33}H_{33}N_5O_5Ru\cdot2H_2O$: C 51.83, H 4.71, N 9.18; found: C 51.16, H 4.56, N 9.61.

Boc–L-Nva[$C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–OMe (L-5)

A white solid of 9-borabicyclo[3,3,1]nonane (9-BBN; 27.7 mg, 0.227 mmol) was added to a solution of Boc–L-AllylgGly–OMe (25.1 mg, 0.109 mmol) in THF (0.550 mL) and the mixture was stirred for 2 h. An aqueous solution of K_3PO_4 (3.00 M, 87.0 μL, 0.260 mmol) was added, followed by a mixture solution of compound **10b** (88.5 mg, 0.118 mmol), $Pd(OAc)_2$ (1.45 mg, 6.50 μmol), and SPhos (5.40 mg, 0.0130 mmol) in DMF (2.80 mL). The reaction mixture was stirred at RT for 15 h and the solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ and washed with water and brine. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give a violet crude product. The crude product was purified by column chromatography on silica gel ($MeOH/CHCl_3$, 5:95 v/v) to afford complex L-**5** (76 mg, 79% yield). M.p. > 325 °C; ^1H NMR ($CDCl_3$, 800 MHz): $\delta=8.24$ (s, 2H; $C_5H_2NC(CH_3)_3$), 8.22 (s, 2H; $C_5H_2N(COOH)_2$), 8.12 (d, $J=1.7$ Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.51 (d, $J=6.0$ Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.27 (dd, $J=5.9$, 2.1 Hz, 2H; $C_5H_3NC(CH_3)_3$), 5.15 (d, $J=7.0$ Hz, 1H; CONH), 4.45 (br s, 1H; NHCH), 3.82 (s, 3H; $COOCH_3$), 3.06–2.99 (m, 2H; $CHCH_2CH_2CH_2$), 2.09–1.96 (m, 2H; $CHCH_2CH_2CH_2$), 1.96–1.85 (m, 2H; $CHCH_2CH_2CH_2$), 1.63 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.49 (s, 9H; $COOC(CH_3)_3$), 1.39 ppm (s, 18H; $C_5H_3NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 201 MHz): $\delta=173.0$ (1C; $COOCH_3$), 172.5 (2C; $C_4H_2N(COO)_2$), 160.0 (2C; $C_5H_3NC(CH_3)_3$), 159.9 (2C; $C_5H_2NC(CH_3)_3$), 157.4 (2C; $C_5H_3NC(CH_3)_3$), 155.4 (1C; OCONH), 154.4 (1C; $C_5H_2NC(CH_3)_3$), 151.0 (2C; $C_5H_3NC(CH_3)_3$), 150.7 (2C;

$C_5H_2N(COO)_2$), 149.1 (1C; $C_5H_2N(COO)_2$), 127.6 (2C; $C_5H_2N(COO)_2$), 123.7 (2C; $C_5H_2NC(CH_3)_3$), 118.4 (2C; $C_5H_3NC(CH_3)_3$), 117.5 (2C; $C_5H_2NC(CH_3)_3$), 80.1 (1C; $OC(CH_3)_3$), 53.2 (1C; NHCH), 52.5 (1C; $COOCH_3$), 35.6 (3C; $C_5H_2NC(CH_3)_3$), 35.5 (1C; $CHCH_2CH_2CH_2$), 35.0 (3C; $C_5H_2NC(CH_3)_3$), 32.5 (1C; $CHCH_2CH_2CH_2$), 31.2 (3C; $OC(CH_3)_3$), 30.6 (2C; $C_5H_3NC(CH_3)_3$), 28.4 (6C; $C_5H_3NC(CH_3)_3$), 26.3 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}$ = 2940, 2347, 1715, 1630, 1475, 1365, 1320, 1229, 1167, 1033, 806, 743 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{45}H_{58}N_5O_8Ru$: 898.33359 $[M+H]^+$; found: 898.33246; elemental analysis calcd (%) for $C_{45}H_{57}N_5O_8Ru{\cdot}H_2O$: C 59.07, H 6.50, N 7.65; found: C 59.34, H 6.43, N 7.66.

Boc–D-Nva[($C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–OMe (D-5)

Compound D-**5** was synthesized according to the same procedure as compound L-**5**, by using Boc–D-allylGly–OMe. Yield: 91%; m.p. > 325 °C; ^{1}H NMR ($CDCl_3$, 800 MHz): δ = 8.25 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.23 (s, 2H; $C_5H_2N(COOH)_2$), 8.12 (d, *J* = 1.7 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.51 (d, *J* = 5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.27 (dd, *J* = 5.9, 2.0 Hz, 2H; $C_5H_3NC(CH_3)_3$), 5.14 (d, *J* = 6.6 Hz, 1H; CONH), 4.46 (br s, 1H; NHCH), 3.82 (s, 3H; $COOCH_3$), 2.99–3.06 (m, 2H; $CHCH_2CH_2CH_2$), 2.09–1.96 (m, 2H; $CHCH_2CH_2CH_2$), 1.96–1.85 (m, 2H; $CHCH_2CH_2CH_2$), 1.63 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.48 (s, 9H; $COOC(CH_3)_3$), 1.39 ppm (s, 18H; $C_5H_3NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 201 MHz): δ = 172.5 (2C; $C_4H_2N(COO)_2$), 160.0 (2C; $C_5H_3NC(CH_3)_3$), 159.9 (2C; $C_5H_2NC(CH_3)_3$), 157.4 (2C; $C_5H_3NC(CH_3)_3$), 151.0 (2C; $C_5H_3NC(CH_3)_3$), 150.7 (2C; $C_5H_2N(COO)_2$), 127.6 (2C; $C_5H_2N(COO)_2$), 123.7 (2C; $C_5H_2NC(CH_3)_3$), 118.4 (2C; $C_5H_3NC(CH_3)_3$), 117.5 (2C; $C_5H_2NC(CH_3)_3$), 53.3 (1C; NHCH), 52.5 (1C; $COOCH_3$), 35.7 (3C; $C_5H_2NC(CH_3)_3$), 35.5 (1C; $CHCH_2CH_2CH_2$), 35.0 (3C; $C_5H_2NC(CH_3)_3$), 32.6 (1C; $CHCH_2CH_2CH_2$), 31.2 (3C; $OC(CH_3)_3$), 30.6 (2C; $C_5H_3NC(CH_3)_3$), 28.4 (6C; $C_5H_3NC(CH_3)_3$), 26.3 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}$ = 3255, 2953, 1711, 1626, 1542, 1474, 1422, 1363, 1323, 1265, 1223, 1166, 1032, 891, 835, 806, 742 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{45}H_{57}ClN_5O_8Ru$: 932.29420 $[M+Cl]^-$; found: 932.29496; elemental analysis calcd (%) for $C_{45}H_{57}N_5O_8Ru{\cdot}H_2O$: C 59.07, H 6.50, N 7.65; found: C 59.17, H 6.49, N 7.63.

$C_{11}H_{23}NHCO$–L-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–OMe (L-2)

A powder of complex L-**1** (96.5 mg, 0.132 mmol) was dissolved in HCl (4.0 M in 1,4-dioxane, 5.5 mL, 22 mmol) and the mixture was stirred at RT for 2 h. Et_2O (10 mL) and *n*-hexane (50 mL) were added to the reaction mixture and the slurry was left to stand for 30 min. The solvent was removed by filtration and the residue was dried by using a vacuum pump to give a violet residue. The residue was dissolved in DMF (4.4 mL) and *N*,*N*-diisopropylethylamine (50 μL). Dodecanoic acid (60.0 mg, 0.30 mmol), Et_3N (250 μL), and DMT-MM·PF_6 (110 mg, 0.284 mmol) were added to the solution and the mixture was stirred at 60 °C for 2 h. Et_2O (10 mL) and *n*-hexane (50 mL) were added to the reaction mixture to give a violet crude product. The crude product was collected by filtration and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 5:95 v/v) to afford complex L-**2** (96 mg, 89% yield). M.p. 141.2–142.5 °C; ^{1}H NMR (CD_3OD, 391.8 MHz): δ = 8.60 (d, *J* = 8.1 Hz, 2H; C_5H_3N), 8.50 (d, *J* = 7.8 Hz, 2H; C_5H_4N), 8.33 (s, 2H; $C_5H_2N(COO)_2$), 7.86 (dd, *J* = 7.6, 1.3 Hz, 2H; C_5H_4N), 7.86 (t, *J* = 8.1 Hz, 1H; C_5H_3N), 7.69 (d, *J* = 4.9 Hz, 2H; C_5H_4N), 7.43 (ddd, *J* = 7.2, 5.2, 1.3 Hz, 2H; C_5H_4N), 4.56–4.51 (m, 1H; NHCH), 3.76 (s, 3H; $COOCH_3$), 3.21–3.11 (m, 2H; $CHCH_2CH_2CH_2$), 2.28 (t, *J* = 7.2 Hz, 2H; $C_{10}H_{21}CH_2CONH$), 2.11–1.90 (m, 4H; $CHCH_2CH_2CH_2$), 1.68–1.59 (m, 2H; $C_9H_{19}CH_2CH_2CONH$), 1.41–1.19 (br s, 16H; $CH_3C_8H_{16}$), 0.87 ppm (t, *J* = 6.7 Hz, 3H; $CH_3C_{10}H_{20}$); ^{13}C NMR (CD_3OD, 99.5 MHz): δ = 177.4 (1C; $COOCH_3$), 175.5 (2C; $C_5H_2N(COO)_2$), 175.0 (1C; C=ONH), 162.4 (2C; C_5H_4N), 159.8, (2C; C_5H_3N) 153.5 (2C; C_5H_4N), 152.2 (2C; $C_5H_2N(COO)_2$), 138.5 (2C; C_5H_4N), 133.4 (1C; C_5H_3N), 130.5 (2C; $C_5H_2N(COO)_2$), 129.0 (2C; C_5H_4N), 124.8 (2C; C_5H_4N), 123.8 (2C; C_5H_3N), 54.4 (1C; NHCH), 53.6 (1C; $COOCH_3$), 37.6 (1C; $C_{10}H_{21}CH_2CONH$), 37.1 (1C; $CHCH_2CH_2CH_2$), 33.9 (1C; $C_9H_{19}CH_2CH_2CONH$), 32.8 (1C; $CHCH_2CH_2CH_2$), 31.6 (2C; $C_7H_{15}(CH_2)_2C_2H_4CONH$), 31.5 (1C; $C_6H_{13}CH_2C_3H_6CONH$), 31.3 (2C; $C_4H_9(CH_2)_2C_5H_{10}CONH$), 31.2 (1C; $C_3H_7CH_2C_7H_{14}CONH$), 28.7 (1C; $CHCH_2CH_2CH_2$), 27.9 (1C; $C_2H_5CH_2C_8H_{16}CONH$), 24.6 (1C; $CH_3CH_2C_9H_{18}CONH$), 15.3 ppm (1C; $CH_3C_{10}H_{20}CONH$); IR (neat): $\tilde{\nu}$ = 3851, 3747, 3672, 3650, 3280, 2920, 2851, 1612, 1598, 1542, 1448, 1422, 1381, 1324, 1279, 1226, 1030, 1010, 928, 764, 726, 725 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{40}H_{47}ClN_5O_7Ru$: 846.22091 $[M+Cl]^-$; found: 846.21778; elemental analysis calcd (%) for $C_{40}H_{47}N_5O_7Ru{\cdot}H_2O$: C 57.96, H 5.96, N 8.45; found: C 57.76, H 6.05, N 8.38.

$C_{11}H_{23}NHCO$–D-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–OMe (D-2)

Compound D-**2** was synthesized according to the same procedure as compound L-**2**, by using complex D-**1**. Yield: 66%; m.p. 174.6–176.0 °C; ^{1}H NMR (CD_3OD, 391.8 MHz): δ = 8.52 (d, *J* = 8.1 Hz, 2H; C_5H_3N), 8.44 (d, *J* = 7.8 Hz, 2H; C_5H_4N)), 8.34 (s, 2H; $C_5H_2N(COO)_2$), 7.82 (dd, *J* = 7.6, 1.3 Hz, 2H; C_5H_4N), 7.78 (t, *J* = 8.1 Hz, 1H; C_5H_3N), 7.69 (d, *J* = 4.9 Hz, 2H; C_5H_4N), 7.41 (ddd, *J* = 7.2, 5.2, 0.9 Hz, 2H; C_5H_4N), 4.56–4.51 (m, 1H; NHCH), 3.76 (s, 3H; $COOCH_3$), 3.21–3.11 (m, 2H; $CHCH_2CH_2CH_2$), 2.28 (t, *J* = 7.2 Hz, 2H; $C_{10}H_{21}CH_2CONH$), 2.11–1.90 (m, 4H; $CHCH_2CH_2CH_2$), 1.68–1.59 (m, 2H; $C_9H_{19}CH_2CH_2CONH$), 1.41–1.19 (br s, 16H; $CH_3C_8H_{16}$), 0.87 ppm (t, *J* = 6.7 Hz, 3H; $CH_3C_{10}H_{20}$); ^{13}C NMR (CD_3OD, 99.5 MHz): δ = 177.4 (1C; $COOCH_3$), 175.6 (2C; $C_5H_2N(COO)_2$), 175.0 (1C; C=ONH), 162.3 (2C; C_5H_4N), 159.8 (2C; C_5H_3N), 153.5 (2C; C_5H_4N), 152.3 (2C; $C_5H_2N(COO)_2$), 138.5 (2C; C_5H_4N), 133.3 (1C; C_5H_3N), 130.5 (2C; $C_5H_2N(COO)_2$), 129.0 (2C; C_5H_4N), 124.8 (2C; C_5H_4N), 123.8 (2C; C_5H_3N), 54.4 (1C; NHCH), 53.7 (1C; $COOCH_3$), 37.6 (1C; $C_{10}H_{21}CH_2CONH$), 37.1 (1C; $CHCH_2CH_2CH_2$), 33.9 (1C; $C_9H_{19}CH_2CH_2CONH$), 32.8 (1C; $CHCH_2CH_2CH_2$), 31.6 (2C; $C_7H_{15}(CH_2)_2C_2H_4CONH$), 31.5, (1C; $C_6H_{13}CH_2C_3H_6CONH$), 31.4 (2C; $C_4H_9(CH_2)_2C_5H_{10}CONH$), 31.2 (1C; $C_3H_7CH_2C_7H_{14}CONH$), 28.7 (1C; $CHCH_2CH_2CH_2$), 27.9 (1C; $C_2H_5CH_2C_8H_{16}CONH$), 24.6 (1C; $CH_3CH_2C_9H_{18}CONH$), 15.3 ppm (1C; $CH_3C_{10}H_{20}CONH$); IR (neat): $\tilde{\nu}$ = 3447, 3072, 2925, 2851, 2385, 1727, 1626, 1450, 1435, 1385, 1324, 1276, 1247, 1230, 1159, 1096, 1029, 1009, 928, 903, 827, 803, 762, 745, 725 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{40}H_{47}ClN_5O_7RuNa$: 846.22091 $[M+Cl]^-$; found: 846.21925; elemental analysis calcd (%) for $C_{40}H_{47}N_5O_7Ru{\cdot}H_2O$: C 57.96, H 5.96, N 8.45; found: C 57.55, H 5.85, N 8.29.

Boc–L-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–$NHC_{11}H_{23}$ (L-3)

An aqueous solution of LiOH (0.27 M, 400 μL, 0.11 mmol) was added to a suspension of complex L-**1** (39.6 mg, 0.054 mmol) and THF (1.62 mL) and the mixture was stirred at RT for 2 h. An aqueous solution of HCl (0.50 M, 200 μL, 0.10 mmol) was added and the system was evacuated for 30 min by using a vacuum pump to remove the solvent. The violet residue was charged with argon and dissolved in DMF (2.0 mL) and Et_3N (110 μL). Undecyl amine (28 μL, 20.4 mg, 0.12 mmol) and DMT-MM·PF_6 (63.2 mg, 0.16 mmol) were added and the mixture was stirred at 60 °C for 2 h. Et_2O (10 mL) and *n*-hexane (50 mL) were added to the mixture to give a violet crude product. The crude product was collected by filtra-

tion and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 5:95 v/v) to afford complex L-**3** (38 mg, 81% yield). M.p. 150.9–152.0 °C; ^{1}H NMR (CD_3OD, 391.8 MHz): δ = 8.59 (d, J = 8.1 Hz, 2H; C_5H_3N), 8.50 (d, J = 8.1 Hz, 2H; C_5H_4N), 8.34 (s, 2H; $C_5H_2N(COO)_2$), 7.86 (dd, J = 8.2, 1.3 Hz, 2H; C_5H_4N), 7.85 (t, J = 7.9 Hz, 1H; C_5H_3N), 7.69 (d, J = 4.9 Hz, 2H; C_5H_4N), 7.45 (ddd, J = 7.0, 5.3, 1.4 Hz, 2H; C_5H_4N), 4.17–4.12 (m, 1H; NHC*H*), 3.29–3.18 (m, 2H; NHC$H_2C_{10}H_{21}$), 3.18–3.13 (m, 2H; CHCH_2CH_2CH_2), 2.11–1.79 (m, 4H; CHCH_2CH_2CH_2), 1.59–1.51 (m, 2H; NHCH_2C$H_2C_9H_{19}$), 1.48 (s, 9H; COOC(CH_3)$_3$), 1.40–1.25 (br s, 16H; $C_8H_{16}CH_3$), 0.89 ppm (t, J = 6.7 Hz, 3H; $C_{10}H_{20}CH_3$); ^{13}C NMR (CD_3OD, 99.5 MHz): δ = 175.8 (1C; *C*ONC$_4H_9$), 175.6 (2C; $C_5H_2N(COO)_2$), 162.4 (2C; C_5H_4N), 159.9 (2C; C_5H_3N), 158.8 (1C; O*C*ONH), 153.8 (1C; $C_5H_2N(COO)_2$), 153.5 (2C; C_5H_4N), 152.2 (2C; $C_5H_2N(COO)_2$), 138.5 (2C; C_5H_4N), 133.4 (1C; C_5H_3N), 130.5 (2C; $C_5H_2N(COO)_2$), 129.0 (2C; C_5H_4N), 124.8 (2C; C_5H_4N), 123.7 (2C; C_5H_3N), 81.5 (1C; *C*O(CH$_3$)$_3$), 56.8 (1C; NH*C*H), 41.3 (1C; NH*C*H$_2$), 37.2 (1C; CHCH$_2$CH$_2$*C*H$_2$), 33.9 (2C; NHCH$_2$*C*H$_2$C$_9$H$_{19}$, CH*C*H$_2$CH$_2$CH$_2$), 31.6 (3C; NHC$_2$H$_4$(*C*H$_2$)$_3$C$_6$H$_{13}$), 31.4 (3C; NHC$_5$H$_{10}$(*C*H$_2$)$_3$C$_3$H$_7$), 29.6 (3C; 3C, OC(*C*H$_3$)$_3$), 29.0 (1C; NHC$_8$H$_{16}$*C*H$_2$C$_2$H$_5$), 28.8 (1C; CHCH$_2$*C*H$_2$CH$_2$), 24.6 (1C; NHC$_9$H$_{18}$*C*H$_2$CH$_3$), 15.3 ppm (1C; NHC$_{10}$H$_{20}$*C*H$_3$); IR (neat): $\tilde{\nu}$ = 3286, 3068, 2924, 2854, 1615, 1598, 1485, 1449, 1384, 1365, 1324, 1380, 1247, 1229, 1163, 1049, 1030, 1011, 928, 763, 745, 726 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{43}H_{54}ClN_6O_7Ru$: 903.27891 $[M+Cl]^-$; found: 903.27310; elemental analysis calcd (%) for $C_{43}H_{54}N_6O_7Ru{\cdot}2H_2O$: C 57.13, H 6.47, N 9.30; found: C 56.82, H 6.57, N 9.04.

Boc–D-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–NHC$_{11}$H$_{23}$ (D-3)

Compound D-**3** was synthesized according to the same procedure as compound L-**3**, by using complex D-**1**. Yield: 81%; m.p. 150.3–151.2 °C; ^{1}H NMR (CD_3OD, 391.8 MHz): δ = 8.62 (d, J = 8.1 Hz, 2H; C_5H_3N), 8.52 (d, J = 8.1 Hz, 2H; C_5H_4N), 8.34 (s, 2H; $C_5H_2N(COO)_2$), 7.82 (dd, J = 8.2, 1.3 Hz, 2H; C_5H_4N), 7.89 (t, J = 7.9 Hz, 1H; C_5H_3N), 7.71 (d, J = 4.9 Hz, 2H; C_5H_4N), 7.45 (ddd, J = 7.0, 5.3, 1.4 Hz, 2H; C_5H_4N), 4.17–4.12 (m, 1H; NHC*H*), 3.29–3.18 (m, 2H; NHC$H_2C_{10}H_{21}$), 3.18–3.13 (m, 2H; CHCH$_2$CH$_2$CH_2), 2.11–1.79 (m, 4H; CHCH_2CH_2CH$_2$), 1.59–1.51 (m, 2H; NHCH$_2$C$H_2C_9H_{19}$), 1.48 (s, 9H; COOC(CH_3)$_3$), 1.40–1.25 (br s, 16H; $C_8H_{16}CH_3$), 0.89 ppm (t, J = 6.7 Hz, 3H; $C_{10}H_{20}CH_3$); ^{13}C NMR (CD_3OD, 99.5 MHz): δ = 175.8 (1C; *C*ONC$_4H_9$), 175.6 (2C; $C_5H_2N(COO)_2$), 162.4 (2C; C_5H_4N), 159.9 (2C; C_5H_3N), 158.8 (1C; $C_5H_2N(COO)_2$), 153.7 (1C; O*C*ONH), 153.5 (2C; C_5H_4N), 152.2 (2C; $C_5H_2N(COO)_2$), 138.5 (2C; C_5H_4N), 133.4 (1C; C_5H_3N), 130.5 (2C; $C_5H_2N(COO)_2$), 129.0 (2C; C_5H_4N), 124.8 (2C; C_5H_4N), 123.7 (2C; C_5H_3N), 81.5 (1C; *C*O(CH$_3$)$_3$), 56.9 (1C; NH*C*H), 41.3 (1C; NH*C*H$_2$), 37.2 (1C; CHCH$_2$CH$_2$*C*H$_2$), 33.9 (2C; NHCH$_2$*C*H$_2$C$_9$H$_{19}$, CH*C*H$_2$CH$_2$CH$_2$), 31.6 (3C; NHC$_2$H$_4$(*C*H$_2$)$_3$C$_6$H$_{13}$), 31.4 (3C; NHC$_5$H$_{10}$(*C*H$_2$)$_3$C$_3$H$_7$), 29.6 (3C; 3C, OC(*C*H$_3$)$_3$), 28.9 (1C; NHC$_8$H$_{16}$*C*H$_2$C$_2$H$_5$), 28.8 (1C; CHCH$_2$*C*H$_2$CH$_2$), 24.6 (1C; NHC$_9$H$_{18}$*C*H$_2$CH$_3$), 15.3 ppm (1C; NHC$_{10}$H$_{20}$*C*H$_3$); IR (neat): $\tilde{\nu}$ = 3421, 2926, 2854, 1615, 1598, 1449, 1383, 1365, 1324, 1380, 1247, 1230, 1247, 1229, 1164, 1050, 1011, 1030, 929, 865, 804, 763, 46, 726 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{43}H_{54}ClN_6O_7Ru$: 903.27882 $[M+Cl]^-$; found: 903.27581; elemental analysis calcd (%) for $C_{43}H_{54}N_6O_7Ru{\cdot}H_2O$: C 58.29, H 6.37, N 9.49; found: C 58.01, H 6.59, N 9.54.

C$_{11}$H$_{23}$NHCO–L-Nva[($C_5H_2N(CO_2)_2$)Ru($C_5H_3N(C_5H_4N)_2$)]–NHC$_{11}$H$_{23}$ (L-4)

An aqueous solution of LiOH (0.27 M, 660 μL, 0.175 mmol) was added to a suspension of complex L-**2** (71.7 mg, 0.088 mmol) and THF (2,65 mL) and the mixture was stirred at RT for 2 h. An aqueous solution of HCl (0.50 M, 350 μL, 0.175 mmol) was added and the system was evacuated for 30 min by using a vacuum pump to remove the solvent. The violet residue was charged with argon and the residue was dissolved in DMF (3.0 mL) and Et_3N (185 μL). Undecyl amine (54 μL, 39.23 mg, 0.23 mmol) and DMT-MM·PF_6 (67.8 mg, 0.098 mmol) were added and the mixture was stirred at 60 °C for 2 h. Et_2O (10 mL) and *n*-hexane (50 mL) were added to the mixture to give a violet crude product. The crude product was collected by filtration and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 5:95 v/v) to afford complex L-**4** (61 mg, 73% yield). M.p. 95.8–96.4 °C; ^{1}H NMR ($CDCl_3$, 391.8 MHz): δ = 8.28 (d, J = 8.1 Hz, 2H; C_5H_3N), 8.27 (s, 2H; $C_5H_2N(COO)_2$), 8.19 (d, J = 7.9 Hz, 2H; C_5H_4N), 7.74 (dd, J = 7.5, 1.5 Hz, 2H; C_5H_4N), 7.73 (t, J = 8.1 Hz, 1H; C_5H_3N), 7.64 (d, J = 5.5 Hz, 2H; C_5H_4N), 7.31 (ddd, J = 7.0, 5.5, 1.4 Hz, 2H; C_5H_4N), 6.16–6.23 (m, 2H; CON*H*C$_{11}$H$_{23}$, C$_{11}$H$_{23}$CON*H*), 4.45–4.56 (m, 1H; NHC*H*), 3.00–3.11 (m, 2H; CHCH$_2$CH$_2$CH_2), 3.16 (td, J = 13.4, 7.2 Hz, 2H; NHCOCH_2C$_{10}$H$_{21}$), 2.22 (t, J = 7.6 Hz, 2H; CONHCH_2C$_{10}$H$_{21}$), 2.12–1.79 (m, 4H; CHCH_2CH_2CH$_2$), 1.58–1.49 (m, 2H; CONHCH$_2$CH_2C$_9$H$_{19}$), 1.35–1.20 (m, 34H; CONHCH$_2$CH$_2$C$_8$H$_{16}$CH$_3$, NHCOCH$_2$C$_9$H$_{18}$CH$_3$), 0.90–0.80 ppm (m, 6H; NHCOC$_{10}$H$_{20}$CH_3, CONHC$_{10}$H$_{20}$CH_3); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ = 173.0 (1C; *C*ONHC$_{11}$H$_{23}$), 172.8 (2C; $C_5H_2N(COO)_2$), 171.7 (1C; NH*C*OC$_{11}$H$_{23}$), 160.6 (2C; C_5H_4N), 158.2 (2C; C_5H_3N), 152.2 (2C; C_5H_4N), 151.1 (1C; $C_5H_2N(COO)_2$), 150.1 (2C; $C_5H_2N(COO)_2$), 135.9 (2C; C_5H_4N), 129.8 (1C; C_5H_3N), 128.5 (2C; $C_5H_2N(COO)_2$), 127.0 (2C; C_5H_4N), 122.4 (2C; C_5H_4N), 121.3 (2C; C_5H_3N), 53.8 (1C; NH*C*H), 40.4 (1C; NHCOCH_2C$_{10}$H$_{21}$), 37.4(1C; CONHCH_2C$_{10}$H$_{21}$), 36.5 (1C; CHCH$_2$CH$_2$*C*H$_2$), 32.8 (1C; CH$_2$*C*H$_2$CH$_2$CH$_3$), 32.6 (2C; CONHCH$_2$*C*H$_2$C$_9$H$_{19}$, NHCOCH$_2$*C*H$_2$C$_9$H$_{19}$), 30.2–30.4 (6C; CONHC$_2$H$_4$C$_6$H$_{12}$C$_3$H$_7$), 29.9–30.1 (6C; NHCOC$_2$H$_4$C$_6$H$_{12}$C$_3$H$_7$), 27.6 (1C; CONHC$_8$H$_{16}$*C*H$_2$C$_2$H$_5$), 27.0 (1C; CHCH$_2$*C*H$_2$CH$_2$), 26.9 (1C; CONHC$_8$H$_{16}$*C*H$_2$C$_2$H$_5$), 26.3 (1C; NHCOC$_8$H$_{16}$*C*H$_2$C$_2$H$_5$), 23.4 (2C; CONHC$_9$H$_{18}$*C*H$_2$CH$_3$, NHCOC$_9$H$_{18}$*C*H$_2$CH$_3$), 14.8 ppm (2C; CONHC$_{10}$H$_{20}$*C*H$_3$, NHCOC$_{10}$H$_{20}$*C*H$_3$); IR (neat): $\tilde{\nu}$ = 3286, 3068, 2924, 2854, 1615, 1598, 1485, 1449, 1384, 1365, 1324, 1380, 1247, 1229, 1163, 1049, 1030, 1011, 928, 763, 745, 726 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{50}H_{69}N_6O_6Ru$: 951.43304 $[M+H]^+$; found: 951.43372; elemental analysis calcd (%) for $C_{50}H_{68}N_6O_6Ru{\cdot}4H_2O$: C 58.75, H 7.49, N 8.22; found: C 58.86, H 7.11, N 8.08.

C$_{12}$H$_{25}$NHCO–L-Nva[($C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–OMe (L-6)

A mixture of complex L-**5** (26.01 mg, 0.029 mmol) and a solution of HCl (4.0 M in 1,4-dioxane, 1.01 mL, 4.04 mmol) was stirred at RT for 1 h. Et_2O (1 mL) and *n*-hexane (5 mL) were added to the reaction mixture and the slurry was left to stand for 30 min. The solvent was removed by filtration and the system was evacuated for 30 min by using a vacuum pump to give a violet residue. The residue was charged with argon and dissolved in CH_2Cl_2. *N*,*N*-Diisopropylethylamine (16 μL, 0.093 mmol) and dodecyl isocyanate (13 μL, 11.4 mg, 0.054 mmol) were added to the solution and the mixture was stirred at RT for 4 h. Et_2O (1 mL) and *n*-hexane (5 mL) were added to give a violet crude product. The crude product was collected by filtration and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 3:97 v/v) to afford complex L-**6** (25.4 mg, 87% yield). M.p. 97.5–98.8 °C; ^{1}H NMR ($CDCl_3$, 392 MHz): δ = 8.25 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.24 (s, 2H; $C_5H_2N(COOH)_2$), 8.11 (d, J = 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.51 (d, J = 5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.27 (dd, J = 5.9, 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 5.20 (d, J = 8.1 Hz, 1H; CONHCH), 4.79 (br s, 1H; N*H*CONH), 4.60 (br s, 1H; NHC*H*), 3.78 (s, 3H; COOCH_3), 3.13–3.00 (m, 2H; CHCH$_2$CH$_2$CH_2), 2.98 (br s, 2H; CH_2NHCO), 2.05–1.78 (m, 2H; CHCH$_2$CH_2CH$_2$), 2.05–1.78 (m, 2H; CHCH_2CH$_2$CH$_2$), 1.61 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.38 (s, 18H;

$C_5H_3NC(CH_3)_3$), 1.23 (s, 20H; $CH_3(CH_2)_{10}CH_2NH$), 0.87 ppm (t, 3H; J= 6.4 Hz, $CH_3(CH_2)_{10}CH_2NH$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ = 174.0 (1C; $COOCH_3$), 172.7 (2C; $C_4H_2N(COO)_2$) 156.0 (2C; $C_5H_3NC(CH_3)_3$), 159.8 (2C; $C_5H_2NC(CH_3)_3$), 157.6 (1C; NHCONH), 157.4 (2C; $C_5H_3NC(CH_3)_3$), 154.5 (1C; $C_5H_2NC(CH_3)_3$), 151.0 (2C; $C_5H_3NC(CH_3)_3$), 150.4 (2C; $C_5H_2N(COO)_2$), 149.3 (1C; $C_5H_2N(COO)_2$), 127.7 (2C; $C_5H_2N(COO)_2$), 123.8 (2C; $C_5H_3NC(CH_3)_3$), 118.5 (2C; $C_5H_3NC(CH_3)_3$), 117.6 (2C; $C_5H_2NC(CH_3)_3$), 52.8 (1C; NHCH), 52.7 (1C; $COOCH_3$), 40.6 (1C; CH_2NHCO), 35.6 (1C; $C_5H_2NC(CH_3)_3$), 35.5 (1C; $CHCH_2CH_2CH_2$), 35.0 (3C; $C_5H_2NC(CH_3)_3$), 32.6, (1C; $CHCH_2CH_2CH_2$), 32.5 (1C; $CH_3(CH_2)_{10}CH_2NH$), 31.9(2C; $C_5H_3NC(CH_3)_3$), 30.6 (6C; $C_5H_3NC(CH_3)_3$), 30.2 (1C; $CH_3(CH_2)_{10}CH_2NH$), 29.7 (3C; $CH_3(CH_2)_{10}CH_2NH$), 29.6 (3C; $CH_3(CH_2)_{10}CH_2NH$), 26.9 (1C; $CH_3(CH_2)_{10}CH_2NH$), 26.2 (1C; $CHCH_2CH_2CH_2$), 22.7 (1C; $CH_3(CH_2)_{10}CH_2NH$), 14.2 ppm (1C; $CH_3(CH_2)_{10}CH_2NH$); IR (neat): $\tilde{\nu}$ = 2924, 1743, 1633, 1568, 1476, 1264, 1034, 835, 805 cm^{-1}; HRMS (ESI-FT-ICR): m/z calcd for $C_{53}H_{74}ClN_6O_7Ru$: 1043.43624 $[M+Cl]^-$; found: 1043.43587; elemental analysis calcd (%) for $C_{53}H_{74}N_6O_7Ru{\cdot}2H_2O$: C 60.96, H 7.53, N 8.05; found: C 61.20, H 7.47, N 7.98.

$C_{12}H_{25}NHCO$–D-Nva[($C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–OMe (D-6)

Compound D-**6** was synthesized according to the same procedure as L-**6**, by using complex D-**5**. Yield: 87%; m.p. 98.1–99.1 °C; ^1H NMR ($CDCl_3$, 391.8 MHz): δ = 8.26 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.26 (s, 2H; $C_5H_2N(COOH)_2$), 8.13 (d, J = 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.53 (d, J = 5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.29 (dd, J = 5.9, 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 5.41 (d, J = 8.1 Hz, 1H; CONHCH), 4.98 (brs, 1H; NHCONH), 4.60 (brs, 1H; NHCH), 3.78 (s, 3H; $COOCH_3$), 3.14–3.04 (m, 2H; $CHCH_2CH_2CH_2$), 2.98 (brs, 2H; CH_2NHCO), 2.05–1.78 (m, 2H; $CHCH_2CH_2CH_2$), 2.05–1.78 (m, 2H; $CHCH_2CH_2CH_2$), 1.71 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.39 (s, 18H; $C_5H_3NC(CH_3)_3$), 1.23 (s, 20H; $CH_3(CH_2)_{10}CH_2NH$), 0.87 ppm (t, J = 6.4 Hz, 3H; $CH_3(CH_2)_{10}CH_2NH$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ = 174.9 (1C; $COOCH_3$), 173.4 (2C; $C_4H_2N(COO)_2$) 160.7 (2C; $C_5H_3NC(CH_3)_3$), 160.5 (2C; $C_5H_2NC(CH_3)_3$), 158.5 (1C; NHCONH), 158.1 (2C; $C_5H_3NC(CH_3)_3$), 155,2 (1C; $C_5H_2NC(CH_3)_3$), 151.8 (2C; $C_5H_3NC(CH_3)_3$), 151.1 (2C; $C_5H_2N(COO)_2$), 150.0 (1C; $C_5H_2N(COO)_2$), 128.4 (2C; $C_5H_2N(COO)_2$), 124.5 (2C; $C_5H_3NC(CH_3)_3$), 119.2 (2C; $C_5H_3NC(CH_3)_3$), 118.3 (2C; $C_5H_2NC(CH_3)_3$), 53.4 (1C; NHCH), 53.0 (1C; $COOCH_3$), 41.1 (1C; CH_2NHCO), 36.3 (1C; $C_5H_2NC(CH_3)_3$), 36.2 (1C; $CHCH_2CH_2CH_2$), 35.7 (3C; $C_5H_2NC(CH_3)_3$), 33.1 (1C; $CHCH_2CH_2CH_2$), 32.6 (1C; $CH_3(CH_2)_{10}CH_2NH$), 31.9 (2C; $C_5H_3NC(CH_3)_3$), 31.3 (6C; $C_5H_3NC(CH_3)_3$), 30.9 (1C; $CH_3(CH_2)_{10}CH_2NH$), 30.3 (6C; $CH_3(CH_2)_{10}CH_2NH$), 30.1 (1C; $CH_3(CH_2)_{10}CH_2NH$), 30.0 (1C; $CH_3(CH_2)_{10}CH_2NH$), 27.6 (1C; $CH_3(CH_2)_{10}CH_2NH$), 26.8 (1C; $CHCH_2CH_2CH_2$), 23.4 (1C; $CH_3(CH_2)_{10}CH_2NH$), 14.8 ppm (1C; $CH_3(CH_2)_{10}CH_2NH$); IR (neat): $\tilde{\nu}$ = 3317, 2924, 2853, 1728, 1627, 1559, 1463, 1899, 1367, 1321, 1265, 1226, 1128, 1034, 921, 833, 805, 742 cm^{-1}; HRMS (ESI-FT-ICR): m/z calcd for $C_{53}H_{74}ClN_6O_7Ru$: 1043.43624 $[M+Cl]^-$; found: 1043.43465; elemental analysis calcd (%) for $C_{54}H_{74}N_6O_8Ru{\cdot}H_2O$: C 62.03, H 7.46, N 8.19; found: C 61.55, H 7.57, N 7.85.

Boc–L-Nva[($C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–NHTEG (L-7; TEG = triethyleneglycol)

An aqueous solution of LiOH (0.27 M, 1.7 mL, 0.45 mmol) was added to a suspension of complex L-**5** (210 mg, 0.233 mmol) in THF (6.8 mL) and the mixture was stirred at RT for 2 h. The solution was diluted with $CHCl_3$ and washed with 0.1 M HCl and brine. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give a violet residue. The residue was dissolved in DMF (6.0 mL) and triethylamine (0.6 mL). 2-[2-(2-Methoxyethoxy)ethoxy]ethylamine (176 mg, 1.08 mmol) and DMT-MM·PF_6 (262 mg, 0.68 mmol) were added to the solution and the mixture was stirred at RT for 24 h. Et_2O (20 mL) and n-hexane (100 mL) were added to give a violet crude residue. The residue was collected by filtration and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 3:97 v/v) to afford complex L-**7** (208 mg, 88% yield). M.p. 89.5–90.8 °C; ^1H NMR ($CDCl_3$, 392 MHz): δ = 8.24 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.23 (s, 2H; $C_5H_2N(COOH)_2$), 8.11 (d, J = 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.52 (d, J = 5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.28 (dd, J = 5.9, 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 6.70 (brs, 1H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 5.34 (d, J = 7.6 Hz, 1H; CONH), 4.25 (brs, 1H; NHCH), 3.72–3.61 (m, 10H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 3.42 (s, 3H; $COOCH_3$), 3.13–3.00 (m, 2H; $CHCH_2CH_2CH_2$), 2.11–1.94 (m, 2H; $CHCH_2CH_2CH_2$), 2.01–1.80 (m, 2H; $CHCH_2CH_2CH_2$), 1.55 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.48 (s, 9H; $COOC(CH_3)_3$), 1.39 ppm (s, 18H; $C_5H_3NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ = 172.6 (1C; $COOCH_3$), 171.8 (2C; $C_4H_2N(COO)_2$), 160.1 (2C; $C_5H_3NC(CH_3)_3$), 160.0 (2C; $C_5H_2NC(CH_3)_3$), 157.5 (2C; $C_5H_3NC(CH_3)_3$), 155.7 (1C; OCONH), 154.4 (1C; $C_5H_2NC(CH_3)_3$), 151.2 (2C; $C_5H_3NC(CH_3)_3$), 150.6 (2C; $C_5H_2N(COO)_2$), 149.5 (1C; $C_5H_2N(COO)_2$), 127.8 (2C; $C_5H_2N(COO)_2$), 123.9 (2C; $C_5H_3NC(CH_3)_3$), 118.6 (2C; $C_5H_3NC(CH_3)_3$), 117.6 (2C; $C_5H_2NC(CH_3)_3$), 80.1 (1C; $OC(CH_3)_3$), 72.1 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.6 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.5 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.3 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 69.7 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 59.1 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 54.4 (1C; NHCH), 39.4 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 36.0 (1C; $CHCH_2CH_2CH_2$), 35.6 (1C; $C_5H_2NC(CH_3)_3$), 35.1 (3C; $C_5H_2NC(CH_3)_3$), 32.9 (1C; $CHCH_2CH_2CH_2$), 31.1 (2C; $C_5H_3NC(CH_3)_3$), 30.5 (6C; $C_5H_3NC(CH_3)_3$), 28.3 (3C; $OC(CH_3)_3$), 26.3 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}$ = 3263, 2956, 1710, 1630, 1475, 1365, 1320, 1260, 1166, 1104, 1033, 920, 836, 805 cm^{-1}; HRMS (ESI-FT-ICR): m/z calcd for $C_{51}H_{70}ClN_6O_{10}Ru$: 1063.38909 $[M+Cl]^-$; found: 1063.39084; elemental analysis calcd (%) for $C_{51}H_{70}N_6O_{10}Ru{\cdot}2H_2O$: C 57.56, H 6.99, N 7.90; found: C 57.51, H 6.86, N 7.90.

Boc–D-Nva[($C_5H_2N(CO_2)_2$)Ru(C_4H_9–$C_5H_3N(C_4H_9$–$C_5H_4N)_2$)]–NHTEG (D-7)

Compound D-**7** was synthesized according to the same procedure as compound L-**7**, by using complex D-**5**. Yield: 62%; m.p. 89.5–90.8 °C; ^1H NMR ($CDCl_3$, 391.8 MHz): δ = 8.25 (s, 2H; $C_5H_2NC(CH_3)_3$), 8.24 (s, 2H; $C_5H_2N(COOH)_2$), 8.12 (d, J = 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.54 (d, J = 5.9 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.30 (dd, J = 5.9, 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.0 (brs, 1H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 5.42 (d, J = 7.6 Hz, 1H; CONH), 4.28 (brs, 1H; NHCH), 3.72–3.46 (m, 10H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 3.43 (s, 3H; $COOCH_3$), 3.12–2.98 (m, 2H; $CHCH_2CH_2CH_2$), 2.11–1.94 (m, 2H; $CHCH_2CH_2CH_2$), 2.01–1.80 (m, 2H; $CHCH_2CH_2CH_2$), 1.64 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.49 (s, 9H; $COOC(CH_3)_3$), 1.40 ppm (s, 18H; $C_5H_3NC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 98.5 MHz): δ = 173.3 (1C; $COOCH_3$), 172.5 (2C; $C_4H_2N(COO)_2$), 160.7 (2C; $C_5H_3NC(CH_3)_3$), 160.5 (2C; $C_5H_2NC(CH_3)_3$), 158.1 (2C; $C_5H_3NC(CH_3)_3$), 156.2 (1C; OCONH), 155.1 (1C; $C_5H_2NC(CH_3)_3$), 151.8 (2C; $C_5H_3NC(CH_3)_3$), 151.2 (2C; $C_5H_2N(COO)_2$), 150.1 (1C; $C_5H_2N(COO)_2$), 128.4 (2C; $C_5H_2N(COO)_2$), 124.5 (2C; $C_5H_3NC(CH_3)_3$), 119.1 (2C; $C_5H_3NC(CH_3)_3$), 118.2 (2C; $C_5H_2NC(CH_3)_3$), 80.6 (1C; $OC(CH_3)_3$), 72.7 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 71.2 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 71.1 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.9 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.4 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 59.7 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 54.9 (1C; NHCH), 40.0 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 36.4 (1C; $CHCH_2CH_2CH_2$), 36.2 (1C; $C_5H_2NC(CH_3)_3$), 35.9 (3C; $C_5H_2NC(CH_3)_3$), 33.5 (1C; $CHCH_2CH_2CH_2$), 31.9 (2C; $C_5H_3NC(CH_3)_3$), 31.5 (6C; $C_5H_3NC(CH_3)_3$), 29.0 (3C; $OC(CH_3)_3$), 27.1 ppm (1C; $CHCH_2CH_2CH_2$); IR (neat): $\tilde{\nu}$ = 3321, 2925, 2854, 1626, 1555, 1463, 1422, 1399, 1367,

1322, 1291, 1261, 1228, 1103, 1032, 925, 901, 834, 806, 742 cm^{-1}; HRMS (ESI-FT-ICR): *m/z* calcd for $C_{51}H_{70}ClN_6O_{10}Ru$: 1063.38909 $[M+Cl]^-$; found: 1063.38793; elemental analysis calcd (%) for $C_{51}H_{70}N_6O_{10}Ru{\cdot}2.5\,H_2O$: C 57.07, H 7.04, N 7.83; found: C 57.28, H 7.11, N 7.35.

$C_{12}H_{25}NHCO$–L-Nva[$(C_5H_2N(CO_2)_2)Ru(C_4H_9$–$C_5H_3N(C_4H_9$–$C_5H_4N)_2)$]–NHTEG (L-8)

A mixture of compound L-**7** (40.0 mg, 0.039 mmol) and a solution of HCl (4.0 M in 1,4-dioxane, 1.46 mL, 5.83 mmol) was stirred at RT for 2 h. The solvent was removed in vacuo to give a violet residue and the residue was dissolved in CH_2Cl_2. *N,N*-Diisopropylethylamine (15 μL, 0.087 mmol) and dodecyl isocyanate (20 μL,16.39 mg, 0.077 mmol) were added to the solution and the mixture was stirred at RT for 24 h. Et_2O (10 mL) and *n*-hexane (50 mL) were added to give a violet crude residue. The residue was collected by filtration and purified by column chromatography on silica gel (MeOH/$CHCl_3$, 3:97 v/v) to afford complex L-**8** (38.5 mg, 87% yield). M.p. 55.8–56.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.25$ (s, 2H; $C_5H_2NC(CH_3)_3$), 8.21 (s, 2H; $C_5H_2N(COOH)_2$), 8.12 (d, $J = 1.8$ Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.53 (d, $J = 6.0$ Hz, 2H; $C_5H_3NC(CH_3)_3$), 7.29 (dd, $J = 6.0$, 1.8 Hz, 2H; $C_5H_3NC(CH_3)_3$), 6.93 (br s, 1H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 5.60 (d, $J = 8.2$ Hz, 1H; CONH), 5.17 (br s, 1H; NHCONH), 4.40 (m, 1H; NHCH), 3.68–3.58 (m, 10H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 3.54 (m, 2H; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 3.42 (s, 3H; $COOCH_3$), 3.05 (m, 2H; $CHCH_2CH_2CH_2$), 2.95 (m, 2H; CH_2NHCO), 2.04–1.72 (m, 2H; $CHCH_2CH_2CH_2$), 1.62 (s, 9H; $C_5H_2NC(CH_3)_3$), 1.38 (s, 18H; $C_5H_3NC(CH_3)_3$), 1.23 (s, 20H; $CH_3(CH_2)_{10}CH_2NH$), 0.86 ppm (t, 3H; $J = 6.9$ Hz, $CH_3(CH_2)_{10}CH_2NH$); ^{13}C NMR ($CDCl_3$, 99.5 MHz): $\delta = 172.9$ (1C; $CHCONHCH_2$), 172.6 (2C; $C_4H_2N(COO)_2$), 160.0 (2C; $C_5H_3NC(CH_3)_3$), 159.8 (2C; $C_5H_2NC(CH_3)_3$), 158.1 (1C; NHCONH), 157.4 (2C; $C_5H_3NC(CH_3)_3$), 154.4 (1C; $C_5H_2NC(CH_3)_3$), 151.0 (2C; $C_5H_3NC(CH_3)_3$), 150.3 (2C; $C_5H_2N(COO)_2$), 149.6 (1C; $C_5H_2N(COO)_2$), 127.7 (2C; $C_5H_2N(COO)_2$), 123.9 (2C; $C_5H_3NC(CH_3)_3$), 118.5 (2C; $C_5H_3NC(CH_3)_3$), 117.6 (2C; $C_5H_2NC(CH_3)_3$), 72.0 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.6 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.3 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 70.3 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 69.6 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 59.0 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 53.6 (1C; NHCH), 40.5 (1C; $NHCH_2CH_2O(CH_2CH_2O)_2CH_3$), 39.2 (1C; CH_2NHCO), 35.7 (1C; $CHCH_2CH_2CH_2$), 35.5 (1C; $C_5H_2NC(CH_3)_3$), 35.0 (3C; $C_5H_2NC(CH_3)_3$), 32.5, (1C; $CHCH_2CH_2CH_2$), 31.9 (1C; $CH_3(CH_2)_{10}CH_2NH$), 31.2 (2C; $C_5H_3NC(CH_3)_3$), 30.6 (6C; $C_5H_3NC(CH_3)_3$), 30.2 (1C; $CH_3(CH_2)_{10}CH_2NH$), 29.7 (3C; $CH_3(CH_2)_{10}CH_2NH$), 29.4 (3C; $CH_3(CH_2)_{10}CH_2NH$), 27.0 (1C; $CH_3(CH_2)_{10}CH_2NH$), 26.4 (1C; $CHCH_2CH_2CH_2$), 22.7 (1C; $CH_3(CH_2)_{10}CH_2NH$), 14.2 ppm (1C; $CH_3(CH_2)_{10}CH_2NH$); HRMS (ESI-FT-ICR): *m/z* calcd for $C_{59}H_{87}ClN_7O_9Ru$: 1174.53048 $[M+Cl]^-$; found: 1174.52799; elemental analysis calcd (%) for $C_{59}H_{87}N_7O_9Ru{\cdot}2\,H_2O$: C 60.29, H 7.80, N 8.34; found: C 60.53, H 7.90, N 8.33.

1-Indanone (14e)

535 mg (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$–7.74 (d, $J = 8.0$ Hz, 1H), 7.62–7.55 (t, $J = 7.6$ Hz, 1H), 7.50–7.45 (d, $J = 8.0$ Hz, 1H), 7.40–7.33 (t, $J = 7.6$ Hz, 1H), 3.20–3.10 (d, $J = 5.7$ Hz, 2H), 2.72–2.66 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 207.2$, 155.3, 137.2, 134.7, 127.4, 126.8, 123.8, 36.3, 25.9 ppm.

4-Chlorobenzaldehyde (16c)

488 mg (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 9.99$ (s, 1H; CHO), 7.83 (d, $J = 8.2$ Hz, 2H; ArH), 7.52 ppm (d, $J = 8.2$ Hz, 2H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 190.9$, 141.0, 134.7, 130.9, 129.5 ppm.

4-Chlorobenzoic Acid (17c)

169 mg (22% yield); ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 8.04$ (d, $J = 8.6$ Hz, 2H; ArH), 7.56 ppm (d, $J = 8.6$ Hz, 2H; ArH); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) $\delta = 166.7$, 139.5, 132.2, 130.3, 129.6 ppm.

4-Nitrobenzaldehyde (16d)

488 mg (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.17$ (s, 1H; CHO), 8.41 (d, $J = 8.6$ Hz, 2H; ArH), 8.09 ppm (d, $J = 8.6$ Hz, 2H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 190.3$, 151.1, 140.0, 130.5, 124.3 ppm.

4-Nitrobenzoic Acid (17d)

169 mg (22% yield); ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 8.38$ (d, $J = 8.6$ Hz, 2H; ArH), 8.29 ppm (d, $J = 8.6$ Hz, 2H; ArH); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): $\delta = 166.1$, 151.5, 137.0, 131.8, 124.4 ppm.

6-Hydroxy-2,3-dihydro-6H-pyrano-3-one (18)

328 mg (57% yield); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.99$–6.94 (dd, $J = 10.4$ Hz, 3.0 Hz, 1H), 6.20–6.14 (d, $J = 10.4$ Hz, 1H), 5.66–5.61 (d, $J = 3.2$ Hz, 1H), 4.62–4.55 (d, $J = 16.8$ Hz, 1H), 4.18–4.11 (d, $J = 16.4$ Hz, 1H), 3.56–3.23 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.6$, 145.8, 128.0, 88.3, 66.7 ppm.

Bis-(1,3-dihydro-isobenzofuran-1-yl)-peroxide (20)

401 mg (59% yield); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$–7.21 (m, 8H), 6.74–6.71 (d, $J = 2.1$ Hz, 2H), 5.22–5.14 (d, $J = 13.0$ Hz, 2H), 5.07–5.00 ppm (d, $J = 12.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 141.0, 134.2, 129.8, 127.6, 123.8, 121.0, 109.8, 72.8 ppm.

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