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Facile synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] complexes

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ABSTRACT

The utility of [(NHC)(PPh$_3$)RuCl$_2$(CHPh)] for the facile and efficient synthesis of ten complexes of the type [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHR)] with saturated and unsaturated NHC ligands in 85–94% isolated yield via a simple one step synthesis utilizing [AgI(NHC$_{ewg}$)] as NHC$_{ewg}$ transfer reagents was demonstrated.

1. Introduction

N-Heterocyclic carbenes substituted with electron withdrawing groups (NHC$_{ewg}$) display donor properties comparable to those of trialkylphosphines [1–7]. Consequently, there was the chance that the substitution of a PCy$_3$ ligand in Grubbs 2nd generation complexes by an NHC$_{ewg}$ ligand would lead to precatalysts of comparable performance in olefin metathesis [8]. This behavior would be in contrast to that of symmetrical [(NHC)$_2$RuCl$_2$(CHR)] type complexes, which were found to display only modest catalytic activity in such reactions [9–11]. Nonetheless, we recently demonstrated the excellent activity of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] complex **1** in RCM reactions leading to tetrasubstituted olefins [12], even though this complex initiates much more slowly than Grubbs 2nd generation complexes. Complex **1**, being the first member of this class, was available only in modest yield (49%) via the reaction of [(NHC)RuCl$_2$(CHPh)(py)$_2$] with an in-situ generated *N*-heterocyclic carbene (Scheme 1) [12].

This motivated us to improve and generalize the synthetic access to such compounds (Scheme 1). It was found that the use of [AgI(NHC$_{ewg}$)] complexes as NHC transfer reagents allows the nearly quantitative conversion of [(NHC)RuCl$_2$(CHPh)(py$_2$)] into the desired complexes **2** (Scheme 1) [13]. This improved synthesis paved the way for the systematic variation of the NHC$_{ewg}$ ligand and the optimization of the catalytic activity, which finally led to a series of new precatalysts with significantly improved activity in RCM reactions [13]. Nonetheless, this approach still relies on the relatively unstable [(NHC)RuCl$_2$(CHPh)(py)$_2$], for whose synthesis a number of additional steps are needed [14]. One approach (of several others) [15–17] leading to such complexes is displayed in Scheme 2 [18].

More recently, the much more stable pyridine complex [(NHC)RuCl$_2$(3-phenylindenylid-1-ene)(py)] [19] was used to prepare a number of new complexes (Scheme 1) [20]. The high stability and the commercial availability of [(NHC)RuCl$_2$(3-phenylindenylid-1-ene)(py)] render this complex useful. Nonetheless, the synthesis of **1**, **2** and **3** from simple ruthenium precursors requires some effort and is not entirely satisfactory with respect to the number of synthetic steps and especially concerning the use of PCy$_3$. This ligand is used to replace PPh$_3$ in [(PPh$_3$)$_2$RuCl$_2$(CHPh)] to obtain the much more stable [(PCy$_3$)$_2$RuCl$_2$(CHPh)]. However, PCy$_3$ does not occur in the final products **1**, **2** or **3**. In the course of the synthesis one PCy$_3$ is replaced by an NHC ligand to furnish [(NHC)(PCy$_3$)RuCl$_2$(CHPh)]. In the next step the second PCy$_3$ is replaced by pyridine to afford [(NHC)RuCl$_2$(CHPh)(py)$_2$] and next this pyridine is replaced by an NHC$_{ewg}$. Obviously, this is not an ideal synthetic strategy.

Consequently, we wish to report here on a new and facilitated synthesis of such complexes, which is shorter and more efficient and does not rely on PCy$_3$ containing intermediates.

2. Results and discussion

2.1. Synthesis of ruthenium complexes

Complexes [(NHC)(PPh$_3$)RuCl$_2$(CHPh)] are known and are directly available from [(PPh$_3$)$_2$RuCl$_2$(CHPh)] and NHC ligands

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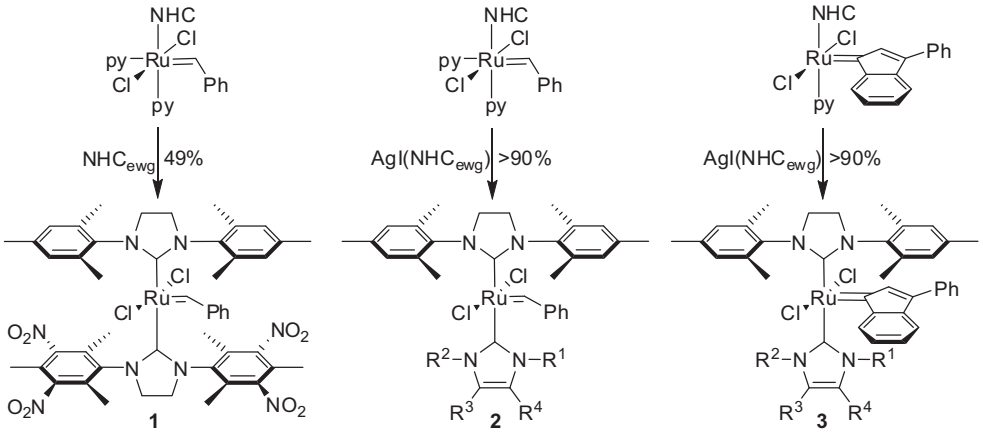


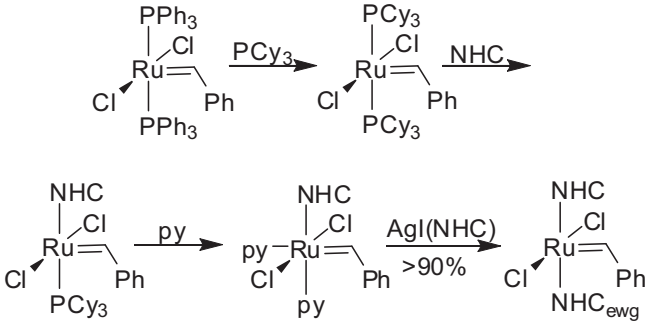
Scheme 1. Synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHR)] complexes, see Scheme 3 for the nature of R groups.

(Scheme 3). Complex **4** was first reported by Grubbs et al. and prepared in the reaction of [(NHC)RuCl$_2$(CHPh)(py)$_2$]with PPh$_3$ [14]. Later the synthesis of this complex was facilitated, when Ren He et al. described its preparation from [(PPh$_3$)$_2$RuCl$_2$(CHPh)] and NHC [21,22]. Nolan first reported the closely related complex **5** [23], the unsaturated relative of **4**. We tested the reactions of **4** and **5** with [AgI(NHC$_{ewg}$)] which led to the clean and quantitative conversion into the respective new [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHR)] complexes **6** and the previously reported complexes **2**. The products were obtained in 89–94% isolated yield for **2** and in 85–94% isolated yield for **6**. With the exception of the complex **6e** with R^3, R^4 = H all compounds are very stable and the microcrystalline material can be stored under ambient atmosphere. In solution the complexes are stable for a short time, but some decomposition can be observed after a few hours of exposure to air. Nonetheless, the synthesis reported here provides facile access to the previously reported complexes **2a**–**d** and the new complexes **6a**–**f** in excellent yields without the need for PCy$_3$ or PCy$_3$ containing intermediates.

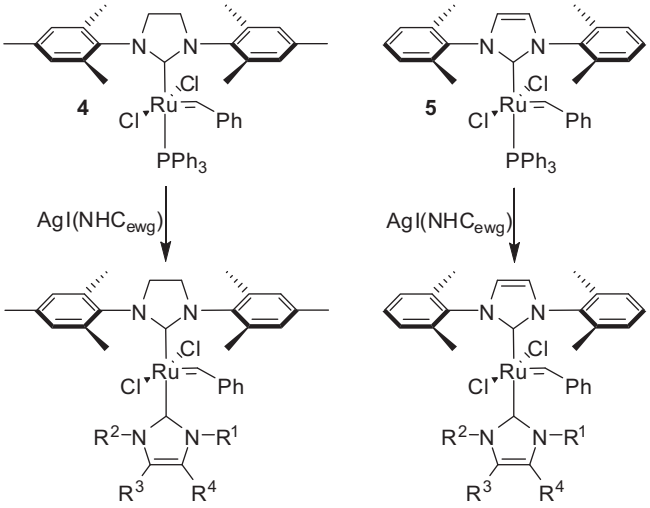
The complexes with two different alkyl groups at the nitrogen of the NHC$_{ewg}$ (**6b**, **d**, **f**) occur as two different rotamers in a ratio of ca. 2: 1. Considering the significantly different bulk of the methyl and the isopropyl group this was unexpected, but was observed before for related complexes **2**.

2.2. Catalytic activity in ring closing metathesis reactions

Complexes **1** and **2a** (and other related complexes) were shown to display excellent activities in RCM reactions leading to tri- and tetrasubstituted olefins [13], which were previously considered to be difficult RCM reactions [24–26]. We were therefore interested in testing the performance of the newly synthesized complexes **6a**–**f** with an unsaturated NHC backbone in six different RCM reactions (Table 1). There is no clear "best" precatalyst, but the performance of **6e** is better than that of the other complexes, while the cyano substituted **6c** clearly is the least efficient in this series. The modest performance of **6c** is in line with our previous results. Despite the fact that the cyano substituted NHC$_{ewg}$ ligand is the least efficient donor (see Table 2), it also tends to be a poor leaving group compared to other NHC$_{ewg}$ ligands. It seems that the cyano substituted NHC$_{ewg}$ is more strongly bound to ruthenium than other NHC$_{ewg}$ ligands – possibly the weaker σ-donor capacity of this NHC$_{ewg}$ is overcompensated by its strong π-accepting ability [27]. For a better evaluation of the screening data, the yields from the best performers from two previous studies are also listed in Table 1. For the reactions tested here, complex **2a** with a saturated NHC backbone is slightly better than **6e**, which has an unsaturated NHC ligand. However, the performance of **1** and **6e** are comparable.

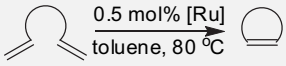


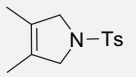
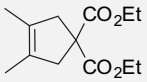
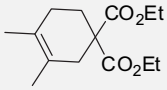
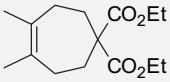
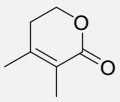
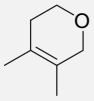
Scheme 2. Synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] complexes.



Scheme 3. Facile synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] complexes.

Table 1
Yields (%) for RCM reactions leading to the depicted products using [Ru] complexes **6a–f** and comparative data using complexes **2a** and **1**.



Product	6a	6b	6c	6d	6e	6f	2a	1
	88	97	–	62	93	77	99	98
	30	35	2	44	47	37	84	48
	86	99	–	83	99	–	99	99
	74	92	93	–	90	–	95	60
	17	–	1	17	23	<1	–	26
	88	52	51	70	91	58	95	98

Screening conditions: reaction time: 24 h, substrate conversion determined by GC, other reaction conditions as reported in ref. [20].

2.3. Cyclic voltammetry

All of the newly synthesized complexes are characterized by a reversible electrochemistry and consequently the redox potentials for the new complexes **6a–f** were determined (Table 2). Those redox potentials reflect the different electron donation of the substituents at the NHC_{ewg} ligands [28,29]. The cyano substituted complex **6c** has by far the most anodic redox potential ($E = 0.727$ V), while the redox potential of **6f** with two *N*-isopropyl groups and hydrogen substituents ($E = 0.474$ V) the least anodic.

Complexes **6a–f** are characterized by the absence of two methyl groups *para* to the nitrogen atoms and consequently their redox potentials are slightly different from that of complexes **2**[13]. Therefore the comparison of the redox potentials is less straightforward. We observed before that the redox potentials with unsaturated heterocycles are only slightly (20–30 mV) more anodic than those with saturated NHC [1], and that the effect of two methyl groups (compared to two hydrogen substituents) amounts to a ca. 30 mV cathodic shift [30]. It is therefore not surprising that the redox potentials of complexes **6** and **2** are very similar (Table 2).

Table 2
Redox potentials of complexes **6a–f** and the closely related (i.e. same substituent at the NHC_{ewg} ligand) complexes **2** (taken from Ref. [5]) with saturated NHC ligand.

	E/V ($E_a - E_c$)/(mv)		E/V
6a	0.538 (74)	**2a**	0.528
6b	0.573 (78)	**2b**	0.556
6c	0.727 (75)	**2c**	0.711
6d	0.627 (68)		–
6e	0.492 (64)	**2e**	0.482
6f	0.474 (88)		–

3. Summary and conclusions

The simple, efficient and high-yielding synthesis of [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes with saturated and unsaturated NHC ligands via [(NHC)(PPh_3)$RuCl_2$(CHPh)] and [AgI(NHC_{ewg})] was reported. The new synthetic route to such complexes requires fewer synthetic steps than before, avoids the use of PCy_3 and affords excellent yields of the respective [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes. The new [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes containing ligands with unsaturated backbones were obtained and tested in demanding RCM reactions and found to be only slightly less efficient in such transformations than optimized complexes with saturated NHC ligands.

4. Experimental section

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification unless otherwise noted. Solvents were dried by passing over Al_2O_3 and/or by storing over molecular sieves unless otherwise noted. Pyridine was degassed by freeze-pump-thaw cycles technique. Flash column and preparative thin layer chromatography were performed using silica gel 60 (0.063–0.20 mesh ASTM). TLC was performed by using Fluka silica gel 60 F254 (0.2 mm) on alumina plates. NMR spectra were recorded on Bruker DRX500 at 500 MHz (^{1}H) and 126 MHz (^{13}C), respectively or on Bruker DRX300 at 300 MHz (^{1}H), 75 MHz (^{13}C), 121 MHz (^{31}P). The chemical shifts (δ) are given in ppm relative to TMS. MS spectra were recorded on a Finnigan MAT95 spectrometer. GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB (l = 15 m, diam. = 0.25 mm, d_F = 1.0 μm), N_2 (flow: 17 cm/s; split 1:50); Injector-temperature: 200 °C, detector temperature: 270 °C. Temperature program: isotherm 60 °C for 5 min, heating to 300 °C with 25 °C/min, isotherm for 5 min. The identity of all GC product peaks was established by GC/MS on Finnigan MAT GC–MS. The spectroscopic data (^{1}H NMR) of the isolated products are identical to those reported in the literature. Cyclic voltammetry: EG&G 263A-2 potentiostat. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene (−0.010 mV (CH_2Cl_2) vs. Ag/AgCl). NBu_4PF_6 (0.1 mol/L) was used as supporting electrolyte.

[(NHC)(PPh_3)$RuCl_2$(CHPh)] **5**: A dry Schlenk flask was charged with imidazolium chloride (200 mg, 0.637 mmol), potassium *t*-amylate (toluene 1.7 M, 375 ml, 0.637 mmol) and toluene (50 mL) under an Ar atmosphere. The solution was stirred at room temperature for 15 min. To this mixture was added [(PPh_3)$_2RuCl_2$(CHPh)] (500 mg, 0.637 mmol). The reaction mixture was stirred for 1 h at room temperature, then the solvent was completely removed under vacuum. The residue was washed with pentane (3 × 25 ml) and filtered, and the resulting orange-brown solid was dried under vacuum. Yield: 410 mg, 80%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 19.43 (s, 1H), 7.35 (d, 2H), 7.21 (d, 2H), 7.17 (bs, 1H), 7.16 (t, 3H), 7.05 (bs, 1H), 7.01 (t, 6H), 6.96 (bs, 1H), 6.91 (t, 6H), 6.72 (bs, 1H), 6.68 (t, 3H), 6.57 (d, 2H), 2.43 (s, 6H), 2.04 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 306.6 (t), 187.8, 187.0, 151.1, 151.1, 139.1, 138.6, 138.0, 137.4, 137.3, 136.7,

134.3, 134.2, 134.0, 133.8, 130.8, 130.5, 130.4, 129.8, 129.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.8, 127.7, 124.5, 124.0, 20.0, 18.6. ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.4. MS (ESI): *m*/*z*: 795.3 (M − Cl), 307.3 ($C_{21}H_{27}N_2$).

4.1. General procedure for the synthesis of complexes **2a–d** and **6a–f**

A dry Schlenk flask containing the respective [(NHC)(PPh_3)$RuCl_2$(CHPh)] complex **4** or **5** (0.086 mmol) and [AgI(NHC_{ewg})] (0.094 mmol, 1.1 equiv) was evacuated and flushed with argon two times. Toluene (5 mL) was added via a syringe and the reaction mixture was stirred at 60 °C for 30 min. The volatiles were evaporated and the residue purified by column chromatography. The crude product was dissolved in minimal amount of CH_2Cl_2 and this solution added to pentane (40 mL) to slowly precipitate green microcrystalline material, which was collected by decantation of the mother liquor.

4.1.1. Complex **6a**

Chromatography (cyclohexane/EtOAc = 5:1), green microcrystalline, yield 61 mg (91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 19.68 (s, 1H), 8.98 (bs, 1H), 7.45 (t, 2H), 7.38 (t, 4H), 7.34 (s, 1H), 7.33 (s, 1H), 7.30 (s, 2H), 7.29 (s, 1H), 6.39 (bs, 1H), 4.66 (septet, 1H), 3.65 (septet, 1H), 2.68 (bs, 3H), 2.50 (bs, 3H), 2.34 (bs, 3H), 1.62 (bs, 3H), 1.46 (d, 3H), 1.25 (d, 3H), 1.19 (d, 3H), 0.95 (d, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 301.1, 190.5, 189.1, 151.9, 151.7, 139.5, 138.8, 138.5, 137.3, 136.8, 131.9, 129.9, 129.4, 129.2, 128.8, 128.4, 128.1, 127.7, 124.6, 124.5, 124.3, 116.5, 115.8, 56.8, 54.2, 53.8, 29.8, 22.2, 22.1, 21.7, 19.8, 19.3, 18.8, 18.0. HR-MS (EI) calcd for $C_{35}H_{38}N_6Cl_2Ru$ (M+•) 714.1566, found 714.1571.

4.1.2. Complex **6b**

Chromatography (cyclohexane/EtOAc = 5:1), green microcrystalline, yield 60 mg (93%).

Two rotamers 0.7:1, ^{1}H NMR (500 MHz, $CDCl_3$) δ 19.59 (s, 0.7H), 19.50 (s, 1H), 7.75 (bs, 1.4H), 7.49–7.00 (overlapping triplets, 19.3H), 6.49 (bs, 1H), 4.60 (septet, 0.7H), 3.66 (septet, 1H), 3.25 (s, 3H), 2.69–2.32 (m, 18H), 1.61 (bs, 3.5H), 1.43 (s, 1H), 1.36–1.26 (m, 5H), 0.98–0.86 (m, 5H), 0.45 (bs, 2.8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 304.8, 301.2, 191.1, 190.8, 188.5, 151.7, 139.4, 137.8, 137.1, 130.6 (br s), 130.3, 129.9, 129.8, 129.4, 129.4, 129.2, 128.8, 128.4, 128.3, 124.3, 118.5, 118.4, 114.8, 114.2, 56.8, 54.2, 35.5, 35.0, 32.1, 29.8, 29.8, 29.5, 22.8, 22.2, 20.0, 19.8, 14.2. HR-MS (EI) calcd for $C_{33}H_{36}N_4Cl_4Ru$ (M+•) 730.072, found 730.07287.

4.1.3. Complex **6c**

Chromatography (cyclohexane/EtOAc = 4:1), green microcrystalline, yield 57 mg (94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 19.34 (s, 1H), 7.68 (bs, 2H), 7.54 (t, 1H), 7.40 (bs, 2H), 7.29–7.20 (m, 4H), 7.17 (t, 2H), 7.08 (bs, 1H), 6.99 (bs, 1H), 3.52 (s, 3H), 2.74 (s, 3H), 2.47 (bs, 6H), 2.06 (bs, 3H), 2.04 (s, 1H), 1.54 (s, 1H), 1.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 309.3, 200.7, 189.1, 151.4, 139.5, 139.1, 137.4, 137.0, 130.7, 130.2, 130.1, 129.5, 128.8, 128.7, 124.3, 115.6, 115.5, 107.0, 106.9, 60.5, 37.3, 37.1, 27.1, 20.0, 18.2. HR-MS (EI) calcd for $C_{33}H_{32}N_6Cl_2Ru$ (M+•) 684.1101, found 684.10952.

4.1.4. Complex **6d**

Chromatography (cyclohexane/EtOAc = 4:1), red–brown microcrystalline, yield 56 mg (90%). Two rotamers 0.35:1, ^{1}H NMR (500 MHz, $CDCl_3$) δ 19.48 and 19.47 (overlapping singlets, 1H), 7.82 (s, 0.3H), 7.64 (s, 0.7H), 7.52–6.97 (m, 12.3H), 6.49 (bs, 0.7H), 4.53 (septet, 0.3H), 3.63 (s, 2.1H), 3.48 (septet, 0.8H), 2.83 (s, 0.9H), 2.67–2.31 (m, 8.6H), 1.68–1.13 (m, 7.8H), 0.36 (bs, 1.6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 303.1, 303.1, 197.9, 196.5, 190.4, 190.0, 151.6, 151.5, 139.3, 137.6, 134.1, 134.0, 132.3, 132.2, 132.1, 130.3, 130.2, 130.0, 129.8, 129.4, 128.8, 128.8, 128.7, 128.4, 124.4, 122.2, 121.8, 121.2, 120.3, 120.2, 54.6, 52.3, 37.3, 37.1, 31.1, 30.5, 29.6, 29.4, 29.0, 28.9, 27.1, 26.6, 25.1, 23.3, 23.0, 21.7, 19.9, 18.2. HR-MS (EI) calcd for $C_{33}H_{37}N_5O_2Cl_2Ru$ (M+•) 707.1359, found 707.13875.

4.1.5. Complex **6e**

Chromatography (cyclohexane/EtOAc = 2:1), it is necessary to use a short column and degassed eluent to obtain the green microcrystalline product, yield 48 mg (85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 19.46 (s, 1H), 7.74 (d, 2H), 7.44 (t, 1H), 7.33 (t, 1 H), 7.25 (s, 2H), 7.16 (s, 3H), 7.09 (t, 3H), 7.05 (bs, 1H), 6.64 (d, 1H), 6.52 (d, 1H), 3.33 (s, 3H), 2.62 (s, 3H) 2.51 (bs, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 301.2, 192.9, 186.1, 151.6, 139.6, 139.5, 137.9, 137.0, 129.9, 129.6, 129.0, 128.8, 128.1, 124.1, 122.6, 122.2, 60.5, 37.3, 37.0, 29.8, 19.9, 18.4. HR-MS (EI) calcd for $C_{31}H_{34}N_4Cl_2Ru$ (M+•) 634.1196, found 634.12134.

4.1.6. Complex **6f**

Chromatography (cyclohexane/EtOAc = 2:1), it is necessary to use a short column and degassed eluent to obtain the green microcrystalline product, yield 88%. Two rotamers 0.8:1, ^{1}H NMR (500 MHz, $CDCl_3$) δ 19.60 (s, 0.8H), 19.50 (s, 1H), 7.77 (bs, 1.8 H), 7.45–7.01 (m, 19.7H), 6.78 (s, 1.2 H), 6.67 (s, 1.2 H), 6.63 (s, 1.2H), 6.54 (s, 1H), 6.50 (bs, 0.8H), 4.42 (septet, 0.79H), 3.40 (septet, 1H), 3.30 (s, 3H), 2.69 (bs, 3H), 2.55 (s, 3H), 2.53 and 2.34 (overlapping bs, 10.2H), 1.62 (bs, 4H), 1.43 (s, 1.4H), 1.26 (s, 1.4H), 1.21 (bs, 4.4H), 0.85 (bs, 4.4H), 0.34 (bs, 2.8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 301.4, 298.1, 192.9, 192.6, 185.5, 185.4, 151.7, 151.6, 139.7, 139.5, 139.3, 138.8, 138.2, 138.0, 137.1, 136.8, 130.5, 130.1, 129.6, 129.0, 128.7, 128.2, 128.1, 124.1, 123.3, 122.9, 117.1, 116.4, 52.5, 50.2, 37.3, 36.7, 29.8, 27.0, 25.0 (br s), 20.0, 19.9, 18.8, 18.4, 18.0. HR-MS (EI) calcd for $C_{33}H_{38}N_4Cl_2Ru$ (M+•) 662.1509, found 662.15734.

4.1.7. Complex **2a**

Chromatography (cyclohexane/EtOAc = 4:1), green microcrystalline, yield 94%.

4.1.8. Complex **2b**

Chromatography (cyclohexane/EtOAc = 4:1), green microcrystalline, yield 92%.

4.1.9. Complex **2c**

Chromatography (cyclohexane/EtOAc = 2:1), it is necessary to use short column and degassed eluent to obtain the green microcrystalline product, yield 81%.

4.1.10. Complex **2d**

Chromatography (cyclohexane/EtOAc = 4:1), red–brown microcrystalline, yield 89%.

Spectroscopic data for complexes **2a–f** are in accord with literature data [13].

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