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Synthesis and RCM Activity of [(NHC)(NHC_{ewg})$RuCl_2$(3-phenylindenylid-1-ene)] Complexes

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[(NHC)$RuCl_2$(3-phenylindenylid-1-ene)(py)] (**1**) serves as a convenient starting material for the synthesis of [(NHC)(NHC_{ewg})$RuCl_2$(3-phenylindenylid-1-ene)] complexes **3a**−**3g** utilizing [AgI-(NHC_{ewg})] complexes (**2**) as NHC transfer reagents. The respective complexes **3** display excellent activities in RCM reactions leading to tetrasubstituted olefins. The most active precatalyst, **3f**, is characterized by 3,4-dichloro and *N*,*N*′-diethyl substituents and can be obtained in 94% isolated yield. The redox potentials of complexes **3** and the crystal structure of **3g** (3,4-dichloro and *N*,*N*′-diisopropyl substituents) were determined.

Introduction

Active (pre)catalysts of the Grubbs type for olefin metathesis reactions are often characterized by the presence of good leaving groups trans to an N-heterocyclic carbene (NHC) ligand.[1] This is exemplified in Grubbs second-generation (**A** in Scheme 1), Grubbs−Hoveyda (**B**), and Grubbs third-generation complexes (**C**). Consequently, it was not surprising that complexes with a second NHC ligand in this position are not ideal, since such ligands are bonded more tightly than phosphines.[2] Indeed, the [$(NHC)_2RuCl_2$(CHPh)] complexes synthesized by Herrmann et al. (**D**,[3] or Grubbs (**E**)[4] turned out to display only modest activities in olefin metathesis reactions. Until recently bisNHC complexes were considered to be less useful in olefin metathesis reactions, and this is why only few such complexes (**F** and **G** in Scheme 1)[5] have been studied.[6]

In 2007 we realized that the donor ability of NHC ligands substituted with electron-withdrawing substituents (NHC_{ewg}) is significantly reduced[7] and that such ligands display electron donation comparable to PCy_3 or PEt_3.[7a,8] Consequently, the replacement of PCy_3 in Grubbs second-generation complexes by NHC_{ewg} offered the chance to obtain more active [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] species than [$(NHC)_2RuCl_2$(CHPh)]. Indeed such complexes (**H** and **I** in Scheme 1) turned out to be very useful in ring-closing metathesis (RCM) reactions of sterically hindered substrates, leading to tetra-substituted olefins.[9] Complex **H** (Scheme 1) with a tetranitro NHC_{ewg} ligand was the first example of such a [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complex. However, in order to further improve the catalytic performance of such complexes, more easily modifiable NHC_{ewg} ligands were required. 3,4-Substituted *N*,*N*′-dialkyl imidazolinium salts are useful precursors for NHC_{ewg} ligands with variable electron donation (via the 3,4-substituents) as well as steric bulk (via the *N*,*N*′-substituents). Optimization of steric and electronic properties finally led to a modified NHC_{ewg} ligand with 3,4-dichloro-*N*,*N*′-methyl, isopropyl substituents. The respective [AgI(NHC_{ewg})] complex was reacted with **C** to generate the respective bisNHC complex (**I** in Scheme 1) with further improved reactivity for RCM reactions, leading to tetrasubstituted olefins.

Apart from the catalytic properties, the application of complexes in catalysis also depends on the facile synthetic or commercial availability and the stability of the precatalyst. The indenylidene complexes introduced by Nolan et al.[10] and Fürstner et al.[11] combine these properties[12] and show

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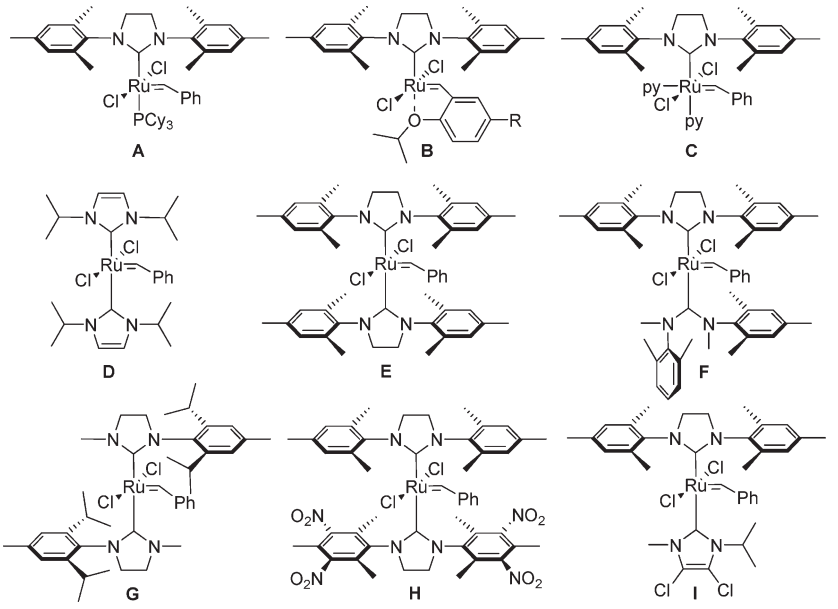
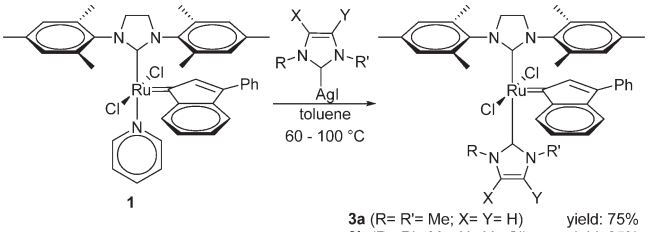
Scheme 1. Grubbs Second- and Third-Generation (A, C), Grubbs−Hoveyda Complex (B), [(NHC)$_2$RuCl$_2$(CHPh)] (D, E, F, G), and [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHPh)] (H, I) Complexes Utilized in Olefin Metathesis



Scheme 2. Synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(3-phenylindenylid-1-ene)] Complexes 3a−3g via Reactions of Complex 1 with the Various [AgI(NHC$_{ewg}$)] Complexes 2a−2g



3a (R= R'= Me; X= Y= H) yield: 75%
3b (R= R'= Me; X= Y= Cl) yield: 95%
3c (R= R'= Me; X= H, Y= NO_2) yield: 90%
3d (R= R'= Me, X= Y= CN) yield: 70%
3e (R= Me, R'= *i*Pr; X= Y= Cl) yield: 93%
3f (R= R'= Et; X= Y= Cl) yield: 94%
3g (R= R'= *i*Pr; X= Y= H) yield: 90%

excellent performance in various olefin metathesis reactions.[13] This is why we initiated a study aimed at preparing and testing the respective (NHC)(NHC$_{ewg}$)Ru complexes in RCM reactions.

Synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(3-phenylindenylid-1-ene)] Complexes 3a −3g. Compared to our previous work,[9] we have now considerably simplified the synthesis of [(NHC)(NHC$_{ewg}$)RuCl$_2$(CHR)] complexes. A one-step reaction from the commercially available complex[14] **1** with a [AgI(NHC$_{ewg}$)] complex (**2a**−**2g**) yields the respective complexes **3a**−**3g**, five of them (**3b**,**c** **e**,**f**,**g**) in excellent yields (Scheme 2). Notably, the catalytically most active complex, **3f** (Table 2), was obtained in 94% yield at 60 °C. The lower yield (75%) for the cyano-substituted complex **3d** is probably due to the significantly higher reaction temperatures (100 °C) required for the pyridine versus NHC$_{ewg}$ substitution. In the case of complex **3a** with hydrogen atoms in the 3,4-position, the lower stability may have led to the loss of this complex in the course of the chromatographic purification. However, complexes **3b**−**3g** are highly stable for extended periods of time in the solid state and in solution, even when exposed to air and moisture.

Crystal Structure of 3g. We determined the crystal structure[15] of a single member in the series of complexes **3a**−**3g** to learn whether there are unusual structural features. The diisopropyl-substituted complex **3g** was chosen, since it contains the most bulky NHC$_{ewg}$ ligand. Single crystals were obtained by slow evaporation of a CH_2Cl_2/*i*PrOH solution of **3g** under ambient atmosphere over the course of several days. The practicability of such an approach provides evidence for the high stability of complex **3g**. The structure of **3g**, featuring trans NHC groups and trans chloro substituents, is as expected (Figure 1). Moderate distortions from an ideal trigonal-planar geometry appear to be due to the bulky isopropyl groups. Despite the very different electronic and steric properties of the two NHC ligands, the two Ru−C(NHC) bond lengths in **3g** are virtually identical (205.2(9) and 205.7(9) pm). The similarity of the two Ru−C(NHC) bonds in other Ru complexes with different NHC ligands was observed previously. However, despite the considerable steric bulk in the present complex, the respective Ru−C(NHC) bonds in **3g** are significantly shorter than in related (NHC)(NHC′)Ru complexes [(207.2 and 207.8 pm)[9b] or (211.2 and 213.2 pm)[5a] or (207.3 and 208.6 pm; 212.1 and 212.2 pm)][5b] or in symmetrical bisNHC complexes, which range from 210.3 to 211.7 pm.[3,6b,16]

Electrochemistry of [(NHC)(NHC$_{ewg}$)RuCl$_2$(3-phenylindenylid-1-ene)] Complexes. The redox potentials of complexes **3a**−**3g** were determined by cyclic voltammetry in CH_2Cl_2

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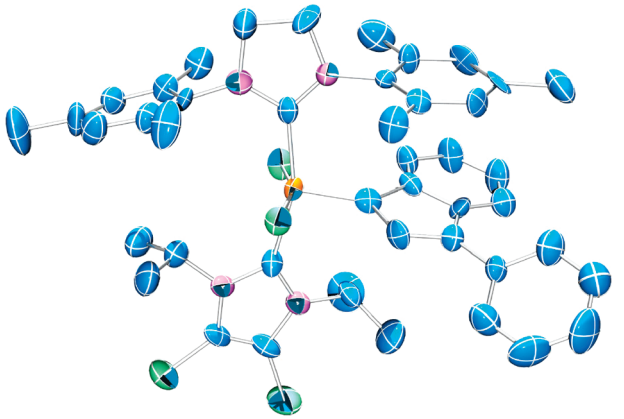

Figure 1. Crystal structure of **3g** (CCDC 770090). Important bond lengths (pm) and angles (deg): Ru−C(NHC) 205.2(9), Ru−C(NHC_{ewg}) 205.7(9), Ru−C(indenylidene) 186.3(9), Ru−Cl (239.3(3), 239.6(3), (NHC)C−Ru−C(NHC_{ewg}) 160.4(4), Cl−Ru−Cl 162.6(1).

(Table 1) in order to learn about the influence of NHC_{ewg} ligands on the Ru(II/III) redox potentials. In general, the complexes studied here are characterized by a reversible electrochemistry. The redox potentials range from $E = +0.458$ V (**3a**) to $E = +0.669$ V for the cyano-substituted complex **3d**. The redox potentials in the series of complexes **3a**−**3d** accurately reflect the electron-donating ability of the various X, Y substituents attached to the NHC_{ewg}[17] and are consistently (by ca. 30−50 mV) more cathodic than those of the related benzylidene complexes.[9b] This points to a slightly stronger electron-donating effect of the indenylidene group compared to benzylidene. In the steric series **3b**, **3e**, **3f**, and **3g** even subtle effects, such as the improved donation of $-CH(CH_3)_2 > -C_2H_5 > -CH_3$ groups, are evident in the ordering of the redox potentials. There is, however, no correlation of the redox potentials and the catalytic activity of complexes **3**.

Catalytic Activity of Complexes 3a−3g in RCM Reactions. Various [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes were shown to be excellent catalysts for RCM reactions involving sterically demanding substrates. Until recently such substrates were considered to be difficult.[18] We first screened all of the precatalysts **3a**−**3g** in two different olefin metathesis reactions (Scheme 3).

The screening results for substrates **S1** and **S2** are summarized in Table 2. Indenylidene complexes normally require higher reaction temperatures than the corresponding benzylidene complexes. For the complexes **3b**−**3g** studied here, 100 °C is necessary for efficient transformations. The only exception is the less stable complex **3a**, which gives better results at 80 °C, but at the same time is the least efficient one of the complexes studied here. For **S1** at 0.5 mol % loading (Table 1, entry 1) little discrimination between **3a**−**3g** was observed; nonetheless **3f** is the top performer, with 77% conversion. At 0.2 mol % loading (Table 1, entry 2) the superiority of **3f** is more obvious. At this loading a number of RCM reactions were carried out at 80 °C reaction

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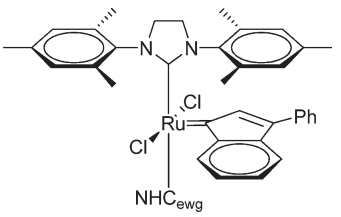
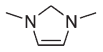
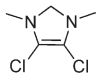
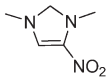
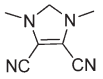
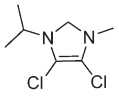
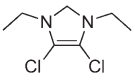
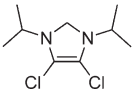
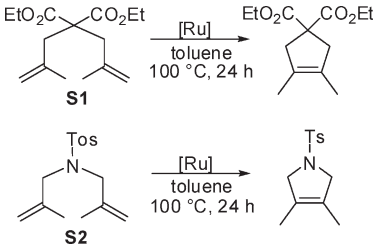
Table 1. Ru(II/III) Redox Potentials *E* of [(NHC)(NHC_{ewg})$RuCl_2$(3-phenylindenylid-1-ene)] Complexes 3a−3g[a]



complex	NHC_{ewg}	E/V (ΔE/mV)
3a		0.458 (64)
3b		0.540 (72)
3c		0.589 (77)
3d		0.669 (65)
3e		0.525 (75)
3f		0.515 (68)
3g		0.493 (65)

[a] Conditions: solvent CH_2Cl_2 (0.1 M NBu_4PF_6) at 293 K; referenced vs $FcMe_8$ ($E = -0.010$ V); scan rate 100 mV s^{-1}. ΔE is the difference of the respective anodic and cathodic peak potentials.

Scheme 3. Test Reactions for Catalyst Evaluation



temperature, but significantly lower yields were observed. With **S2** all of the complexes tested gave nearly quantitative yields of the RCM product at 0.5 mol % loading (Table 2, entry 3). At 0.2 mol % loading (Table 2, entry 4) this still holds true for **3b** and **3f**; at 0.1 mol % (Table 2, entry 5) the 80% conversion with **3f** and 77% with **3b** are impressive. The effect of high substrate concentration on the RCM performance was tested; however, neither 1 mol/L nor neat substrate led to improvements.

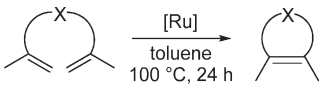
The combination of facile, efficient synthesis and superior RCM performance of **3f** motivated us to study this complex for a number of additional transformations (Table 3). At 0.5 mol % loading most substrates are converted in >90%

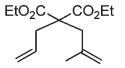
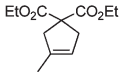
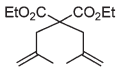
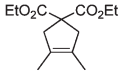
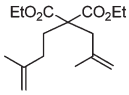
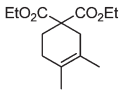
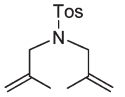
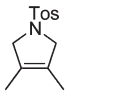
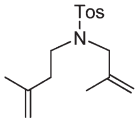
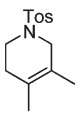
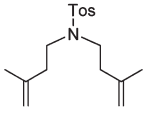
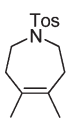
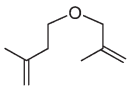
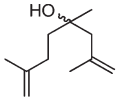
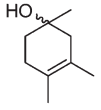
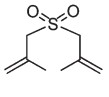
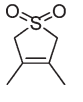
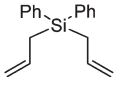
Table 2. Catalyst Comparison: RCM Reactions Using Model Substrates S1 and S2[a]

entry	substrate	loading/ mol %	3a	3b	3c	3d	3e	3f	3g
1	**S1**	0.5	50[b]	71	58	67	69	77	63
2	**S1**	0.2	22/36[b]	37/5[b]	28/22[b]	42/3[b] 22[c]/18[d]	24/3[b]	58/37[b]	45/23[b]
3	**S2**	0.5	92[b]	98	97	98	96	98	99
4	**S2**	0.2	75[b]	97	93	81, 32[d]	91	98	85
5	**S2**	0.1	58[b]	77	60	45	72	80	66

[a] 0.2 mmol of olefinic substrate in 10 mL of toluene (0.02 M), T = 100 °C, 24 h; Ru complexes were added as a stock solution (3 mmol/L in toluene). Substrate conversion determined by GC (conversions given in %). [b] Reactions carried out at 80 °C. [c] Substrate conc 1 mol/L. [d] Neat substrate.

Table 3. RCM Reactions Leading to Tetrasubstituted Olefins Using Complex 3f[a]



Entry	Substrate	Product	[Ru] mol%	Yield / %
1			0.05	96
2			0.5	77
3			0.2	91
4			0.2	98
5			0.5 0.2	99 87
6			0.5	73
7			0.5	86
8			0.5	99
9			0.5	99
10			0.1 0.05	99 79

[a] General conditions see Table 1.

yield into the respective RCM products. The comparison with previously published complexes reveals that complexes **3a**−**3g** are more efficient than the tetranitro-NHC complex **H** and comparable to the corresponding benzylidene complexes related to **I**.[9b] For the RCM of diallyldiphenylsilane, complex **3f** shows unprecedented RCM activity (entry 10).[9b]

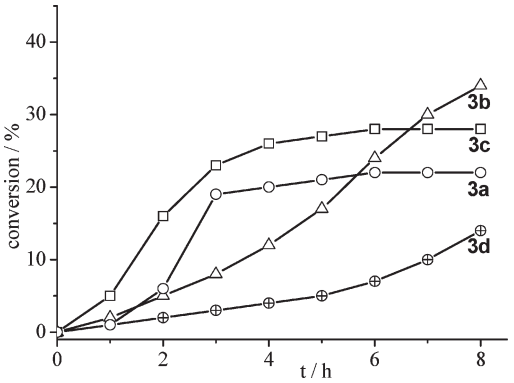


Figure 2. RCM of substrate **S1** in the electronic series of complexes **3a**−**3d** (T = 100 °C, 0.2 mol % cat., conversion after 24 h: **3a** (22%), **3b** (37%), **3c** (28%), **3d** (42%)).

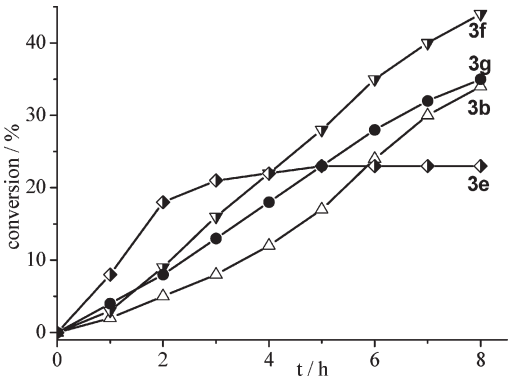


Figure 3. RCM of substrate **S1** in the electronic series of complexes **3b**,**e**,**f**,**g** (T = 100 °C, 0.2 mol % cat., conversion after 24 h: **3b** (37%), **3e** (24%), **3f** (58%), **3g** (45%)).

The conversion−time plots (Figures 2, 3) for the RCM of diethyl dimethallyl malonate (**S1**) lend additional support to the high stability of complexes **3** and the activation behavior, which depends on the electronic and steric nature of the imidazolium substituents. Complexes **3a** and **3c** initiate relatively fast, but appear to have decomposed after ca. 4 h since at around this time product formation comes to an end. **3b** and **3d** are much slower, and after 8 h only 15% conversion was observed, compared to 42% after 24 h reaction time.

Within the steric series (Figure 3), the fastest initiating catalyst provides the lowest substrate conversion after 24 h. Notably, this complex carries the NHC_{ewg} substituents (*N*,*N*′-Me, *i*Pr, and 3,4-Cl,Cl) that were considered as the "best" substituents in the previously reported benzylidene

precatalysts.[9b] However, in the indenylidene series of complexes **3** the same substituents result in a less efficient precatalyst. The "best" precatalyst in the present study is characterized by *N*,*N*′-Et, Et, and 3,4-Cl,Cl substituents, while this pattern had been one of the poorest performers in the previous benzylidene study.[9b]

But why are the (NHC)(NHC_{ewg})Ru complexes more efficient than Grubbs second-generation or Grubbs−Hoveyda complexes? We have shown before that the initiation reaction of the [(NHC)(NHC_{ewg})$RuCl_2$(CHPh)] complexes involves the dissociation of the NHC_{ewg} ligand.[9b] Consequently, all of the complexes utilized here should finally generate the same active species, which in turn should be the same as the one generated from Grubbs−Hoveyda and Grubbs second-generation complexes. Nonetheless, complexes **3** are much more efficient for RCM reactions of sterically demanding substrates. We therefore believe that the stability of the precatalyst and the rate at which the active species is generated from this precatalyst make the difference. When this rate corresponds to the rate at which a certain substrate is converted into the respective product (here tetrasubstituted olefins) with the aid of the active catalyst, efficient substrate conversion is observed.[19]

Summary and Conclusions

We have synthesized a series of easily available [(NHC)(NHC_{ewg})$RuCl_2$(CHR)] complexes in excellent yields from easily available precursors. The activity of such precatalysts in various RCM reactions leading to tetrasubstituted olefins was studied and found to be superior to that of the previously reported [(NHC)(NHC-tetranitro)$RuCl_2$(CHPh)] complex **H**. One of the main lessons learned from this study is that the nature of the substituents at the NHC_{ewg} enables the fine-tuning of the initiation rate and its adaption to the needs of certain substrates.

Experimental Section

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. All reactions involving ruthenium complexes were performed under an atmosphere of argon. Toluene, CH_2Cl_2, and pentane were dried by using a column purification system.[20] ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 at 500 MHz (^1H) and 126 MHz (^{13}C), respectively. The chemical shifts are given in ppm on the delta scale (δ) and are referenced to tetramethylsilane (^1H, ^{13}C NMR 0 ppm) or the residual peak of $CHCl_3$ (^1H NMR 7.26 ppm) or $CDCl_3$ (^{13}C NMR 77.16 ppm).[21] Abbreviations for NMR data: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; bs = broad signal; Ar = aromatic protons. Cyclic voltammograms were recorded in dry CH_2Cl_2 under an argon atmosphere at ambient temperature using an EG&G 263A-2 potentiostat. 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 (−10 mV (CH_2Cl_2) vs Ag/AgCl). NBu_4PF_6 (0.1 mol/L) was used as supporting electrolyte. Thin-layer chromatography (TLC) was performed using silica gel 60 F 254 (0.2 mm) on aluminum plates. Preparative chromatography was performed using E. Merck silica 60 (0.063−0.02 mesh). GC experiments were run on a Clarus 500 GC with autosampler and FID detector. Column: Varian CP-Sil 8 CB (l = 15 m, d_i = 0.25 mm, d_F = 1.0 μm), N_2 (flow: 17 cm s^{-1}; split 1:50); injector temperature: 270 °C, detector temperature: 350 °C. The following compounds were prepared according to literature procedures: AgI(NHC) complexes,[9b] diethyl 2,2-bis-(2-methylallyl)malonate,[22] *N*,*N*-dimethallylsulfonamide.[9b] (NHC)-(py)$RuCl_2$(3-phenylindenylid-1-ene) (**1**) was provided by Umicore.

General Procedure for the Synthesis of [(NHC)(NHC_{ewg})-$RuCl_2$(3-phenylindenylid-1-ene)] Complexes 3a−3g. [(NHC)(py)-$RuCl_2$(3-phenylindenylid-1-ene)] (100 mg, 0.14 mmol) and the appropriate silver complex (0.20 mmol) were dissolved in 10 mL of toluene. The reaction mixture was heated to 60−100 °C (chosen temperature depending on the silver complex). The reaction was monitored via TLC. After 30 min, the solvent was evaporated in vacuo and the crude product purified by column chromatography (silica, cyclohexane/ethyl acetate, 2:1, v/v). The obtained product was washed with cold pentane (−10 °C) to provide complexes **3a**−**3g** as microcrystalline red solids (yields: 75−95%).

Complex 3a: reaction temperature 60 °C; dark red crystals, yield 78 mg (75%). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.60 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.75 (2H, m, Ph*H*), 7.49 (1H, tt, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.37 (2H, m, Ph*H*), 7.25 (1H, td, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.21 (1H, s, indenylidene-*H*), 7.15 (1H, td, J = 7.5, 1.0 Hz, Ph*H*), 7.12 (1H, d, J = 7.4 Hz, indenylidene), 7.06 (2H, s, mesityl-*H*), 6.56 (1H, d, J = 1.8 Hz), 6.50 (1H, d, J = 1.8 Hz, HC = C*H*), 6.44 (1H, s, mesityl-*H*), 6.14 (1H, s, mesityl-*H*), 4.09 (2H, m, $NCH_2CH_AH_BN$), 3.94 (1H, m, $NCH_2CH_AH_BN$), 3.84 (1H, m, $NCH_2CH_AH_BN$), 3.27 (3H, s NCH_3), 2.77 (3H, s, $ArCH_3$), 2.70 (3H, s NCH_3), 2.68 (3H, s, $ArCH_3$), 2.36 (3H, s, $ArCH_3$), 2.32 (3H, s, $ArCH_3$), 1.99 (3H, s, $ArCH_3$), 1.79 (3H, s, $ArCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 291.5, 221.7, 181.8, 143.6, 140.6, 140.4 (2 signals), 139.0, 137.3, 137.2, 137.1 (2 signals), 136.8 (2 signals), 136.7, 135.5, 129.7 (2 signals), 129.2, 129.0, 128.5, 128.4, 127.6, 127.3, 126.6, 123.3, 121.9, 116.4, 52.5, 51.8, 36.7, 36.2, 21.2, 21.1, 20.5, 18.8, 18.5. HRMS (EI): m/z calcd for $C_{41}H_{44}N_4Cl_2Ru$ 764.1978, found 764.2003.

Complex 3b: reaction temperature 60 °C; red crystals, yield 108 mg (95%). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.56 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.74 (2H, m, Ph*H*), 7.50 (1H, tt, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.38 (2H, t, J = 7.6 Hz, Ph*H*), 7.26 (1H, td, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.11−7.07 (2H, overlapped signals, Ph*H* + indenylidene-*H*), 7.11 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.08 (2H, s, mesityl-*H*), 6.44 (1H, s, mesityl-*H*), 6.17 (1H, s, mesityl-*H*), 4.10 (2H, m, $NCH_2CH_AH_BN$), 3.94 (1H, m, $NCH_2CH_AH_BN$), 3.84 (1H, m, $NCH_2CH_AH_BN$), 3.25 (3H, s, NCH_3), 2.76 (3H, s, $ArCH_3$), 2.71 (3H, s, NCH_3), 2.67 (3H, s, $ArCH_3$), 2.38 (3H, s, $ArCH_3$), 2.32 (3H, s, $ArCH_3$), 1.98 (3H, s, $ArCH_3$), 1.79 (3H, s, $ArCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 295.2, 220.0, 183.6, 143.5, 140.5, 140.4 (2 signals), 139.2, 138.1, 137.5, 137.0, 136.8, 136.7 (2 signals), 135.2, 129.8, 129.7, 129.2, 129.1 (2 signals), 128.8, 128.4, 127.9, 127.8, 126.6, 117.5, 116.5, 52.5, 51.7, 34.8, 33.7, 21.2, 21.0, 20.5, 18.7, 18.4. HRMS (EI): m/z calcd for $C_{41}H_{42}N_4Cl_4Ru$ 832.1190, found 832.1187.

Complex 3c: reaction temperature 80 °C; dark red crystals, yield 99 mg (90%). Two isomers (ratio 1:0.45). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.57 (isomer 1, 1H, dd, J = 0.83, 7.5 Hz, indenylidene-*H*), 8.48 (isomer 2, 1H, d, J = 7.4 Hz, 1H, indenylidene-*H*), 7.75−7.70 (overlapped signals, isomer 1, 2H, Ph*H*; isomer 2, 2H, Ph*H*), 7.60 (isomer 2, 1H, s, indenylidene-*H*), 7.55−7.48 (o s, isomer 1, 2H, indenylidene-*H*; isomer 2, 1H, indenylidene-*H*), 7.41−7.36 (o s, isomer 1, 2H, Ph*H*; isomer 2, 2H, Ph*H*), 7.29−7.23 (o s, isomer 1, 1H, Ph*H*; isomer 2, 1H,

(19) We are currently studying this problem in detail; our results will be reported in due course.

(20) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(21) Gottlieb, H. E.; Kotlyar, V.; Nudelmann, A. *J. Org. Chem.* **1997**, *62*, 7512.

(22) Stewart, I. C.; Ung, T.; Pletnev, A. A.; Berlin, J. M.; Grubbs, R. H.; Schrodi, Y. *Org. Lett.* **2007**, *9*, 1589.

Ph*H*), 7.20−7.04 (o s, isomer 1, 2H, mesityl-H + 2H indenylidene-*H* + 1H, NC*HC*(NO_2)N; isomer 2, 2H, mesityl-H + 2H indenylidene-*H* + 1H, NC*HC*(NO_2)N), 6.45 (isomer 2, s, 1H, mesityl-H), 6.44 (isomer 1, s, 1H, mesityl-H), 6.18 (isomer 2, s, 1H, mesityl-H), 6.16 (isomer 1, s, 1H, mesityl-H), 4.14−4.03 (o s, isomer 1, 2H, N$CH_2$$CH_2$N; isomer 2, 2H, N$CH_2$$CH_2$N), 3.96−3.80 (o s, isomer 1, 2H, NCH_2CH_2N; isomer 2, 2H, NCH_2CH_2N), 3.63 (isomer 1, 3H, s, NCH_3), 3.36 (isomer 2, 3H, s, NCH_3), 3.06 (isomer 2, 3H, s, NCH_3), 2.79 (isomer 1, 3H, s, NCH_3), 2.76 (isomer 2, 3H, s, ArCH_3), 2.75 (isomer 1, 3H, s, ArCH_3), 2.65 (os, isomer 1, 3H, s, ArCH_3, isomer 2, 3H, s, ArCH_3), 2.39 (isomer 1, 3H, s, ArCH_3), 2.36 (isomer 2, 3H, s, ArCH_3), 2.33 (isomer 2, 3H, s, ArCH_3), 2.31 (isomer 1, 3H, s, ArCH_3), 1.97 (isomer 1, 3H, s, ArCH_3), 1.96 (isomer 2, 3H, s, ArCH_3), 1.80−1.77 (o s, isomer 1, 3H, s, ArCH_3, isomer 2, 3H, s, ArCH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 298.1, 297.1, 218.9, 218.8, 194.0, 192.7, 143.5, 143.2, 140.5 (2 signals), 140.4, 140.3, 139.5, 139.2, 139.0, 138.4, 137.7, 137.6, 136.9, 136.8, 136.7, 136.4, 136.3, 135.2, 135.0, 129.8 (2 signals), 129.7, 129.2 (2 signals), 129.1, 129.0, 128.4, 128.3, 128.1 (2 signals), 126.7, 126.6, 125.5, 116.8, 116.7, 52.5, 51.7, 38.1, 37.4, 37.2, 35.3, 21.2, 21.1, 21.0, 20.4 (2 signals), 18.6, 18.4 (2 signals). HRMS (EI): *m*/*z* calcd for $C_{41}H_{42}N_5O_2Cl_2Ru$ $[M - H]^+$ 808.1751, found 808.1776.

Complex 3d: reaction temperature 100 °C; red crystals, yield 78 mg (70%). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.44 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.71 (2H, d, J = 7.8 Hz, Ph*H*), 7.53 (1H, t, J = 7.4 Hz, indenylidene-*H*), 7.40 (2H, t, J = 7.8 Hz, Ph*H*), 7,28 (1H, t, J = 7.4 Hz, indenylidene-*H*), 7.17 (1H, t, J = 7.8 Hz, Ph*H*), 7.11 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.09 (2H, s, mesityl-*H*), 7.06 (1H, s, indenylidene-*H*), 6.44 (1H, s, mesityl-*H*), 6.19 (1H, s, mesityl-*H*), 4.08 (2H, m, $NCH_2CH_AH_BN$), 3.94 (1H, m, $NCH_2CH_AH_BN$), 3.84 (1H, m, $NCH_2CH_AH_BN$), 3.46 (3H, s, NCH_3), 2.93 (3H, s, NCH_3), 2.75 (3H, s, ArCH_3), 2.64 (3H, s, ArCH_3), 2.39 (3H, s, ArCH_3), 2.32 (3H, s, ArCH_3), 1.94 (3H, s, ArCH_3), 1.78 (3H, s, ArCH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 299.6, 217.8, 197.0, 143.2, 140.6, 140.5, 140.3, 139.6 (2 signals), 137.9, 137.0, 136.7 (2 signals), 136.6, 136.0, 134.9, 129.9, 129.8, 129.3, 129.2 (2 signals), 128.7, 128.4 (2 signals), 126.7, 117.1, 116.2, 115.2, 106.9, 106.8, 52.6, 51.7, 36.9, 35.9, 21.2, 21.0, 20.5, 20.4, 18.6, 18.3. HRMS (EI): *m*/*z* calcd for $C_{43}H_{41}N_6Cl_2Ru$ $[M - H]^+$ 813.1805, found 813.1809.

Complex 3e: reaction temperature 60 °C; red crystals, yield 109 mg (93%). Two isomers (ratio 1:0.45). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.61 (isomer 1, 1H, dd, J = 0.83, 7.5 Hz, indenylidene-*H*), 8.57 (isomer 2, 1H, d, J = 7.4 Hz, 1H, indenylidene-*H*), 7.76 (isomer 2, m, 2H, Ph*H*), 7.71 (isomer 1, m, 2H, Ph*H*), 7.53−7.48 (overlapped signals, isomer 1, 1H, indenylidene-*H*; isomer 2, 1H, indenylidene-*H*), 7.41−7.36 (o s, isomer 1, 2H, Ph*H*; isomer 2, 2H, Ph*H*), 7.30−7.22 (o s, isomer 1, 2H, indenylidene-*H*, isomer 2, 2H, indenylidene-*H*), 7.22−7.15 (o s, isomer 1, 1H, Ph*H*; isomer 2, 1H, Ph*H*), 7.13−7.05 (overlapped signals, isomer 1, 1H, indenylidene-*H* + 2H, mesityl-*H*; isomer 2, 1H, indenylidene-*H* + 2H, mesityl-*H*), 6.44 (o s, isomer 1, 1H, mesityl-H, isomer 2, 1H, mesityl-H), 6.14 (isomer 1, s, 1H, mesityl-H), 6.08 (isomer 2, s, 1H, mesityl-H), 4.72 (isomer 2, 1H, sept, NC*H*(CH_3)$_2$, J = 6.9 Hz), 4.12−3.71 (o s, isomer 1, 1H, NC*H*(CH_3)$_2$, 4H, N$CH_2$$CH_2$N, isomer 2, 4H, N$CH_2$$CH_2$N), 3.26 (isomer 1, s, 3H, NCH_3), 2.75 (isomer 2, s, 3H, ArCH_3), 2.73 (isomer 1, s, 3H, ArCH_3), 2.71 (isomer 2, s, 3H, NCH_3), 2.70 (isomer 2, s, 3H, ArCH_3), 2.68 (isomer 1, s, 3H, ArCH_3), 2.40 (isomer 2, s, 3H, ArCH_3), 2.37 (isomer 1, s, 3H, ArCH_3), 2.26 (o s, isomer 1, s, 3H, ArCH_3, isomer 2, s, 3H, ArCH_3), 2.03 (isomer 1, s, 3H, ArCH_3), 1.99 (isomer 2, s, 3H, ArCH_3), 1.85 (isomer 1, s, 3H, ArCH_3), 1.84 (isomer 2, s, 3H, ArCH_3), 1.34 (isomer 2, 3H, d, J = 7.0 Hz, NCH(CH_3)$_2$), 1.32 (isomer 2, 3H, d, J = 7.0 Hz, NCH(CH_3)$_2$), 0.88 (isomer 1, 3H, d, J = 7.0 Hz, NCH(CH_3)$_2$, 0.62 (isomer 1, 3H, d, J = 7.0 Hz, NCH(CH_3)$_2$. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 296.2, 293.8, 220.2, 219.1, 184.3, 183.6, 144.0, 143.6, 140.6, 140.5, 140.4 (2 signals), 139.5, 139.3, 138.8, 138.0, 137.6, 137.4, 137.3, 137.1 (2 signals), 137.0, 136.9, 136.0, 135.4, 130.2, 129.8 (2 signals), 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 127.9 (2 signals), 127.8, 127.7, 126.6, 126.5, 119.4, 118.3, 116.4, 116.2, 115.4, 114.0, 57.0, 52.4, 52.3, 52.2, 51.8, 34.8, 33.7, 21.4, 21.3 (2 signals), 21.2 (2 signals), 21.1, 20.5, 20.3, 18.8, 18.7, 18.6, 18.5. HRMS (EI): *m*/*z* calcd for $C_{43}H_{46}N_4Cl_4Ru$ 860.1503, found 860.1533.

Complex 3f: reaction temperature 60 °C; red crystals, yield 110 mg (94%). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.67 (1H, d, J = 7.4 Hz, indenylidene-*H*), 7.75 (2H, m, Ph*H*), 7.50 (1H, tt, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.38 (3H, overlapped signals, Ph*H* + indenylidene-*H*), 7.26 (1H, td, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.19 (1H, td, J = 7.6, 1.2 Hz, Ph*H*), 7.11−7.08 (3H, overlapped signals, indenylidene-*H* + mesityl-*H*), 6.46 (1H, s, mesityl-*H*), 6.08 (1H, s, mesityl-*H*), 4.06 (2H, t, J = 10.3 Hz, $NCH_2CH_AH_BN$), 3.91 (1H, J = 10.3 Hz, $NCH_2CH_AH_BN$), 3.82 (1H, q, J = 10.3 Hz, $NCH_2CH_AH_BN$), 3.58 (2H, m, N$CH_2$$CH_3$), 3.22 (2H, m, N$CH_2$$CH_3$), 2.71 (3H, s, Ar$CH_3$), 2.68 (3H, s, N$CH_3$), 2.39 (3H, s, Ar$CH_3$), 2.27 (3H, s, Ar$CH_3$), 2.04 (3H, s, Ar$CH_3$), 1.84 (3H, s, Ar$CH_3$), 1.31 (3H, t, J = 7.0 Hz, NCH_2CH_3), 0.54 (3H, t, J = 7.1 Hz, NCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 293.4, 219.8, 183.4, 143.9, 140.6, 140.0, 138.9, 137.5, 137.3, 137.2, 137.0, 136.9 (2 signals), 136.8, 135.5, 130.0, 129.2, 129.1, 129.0, 128.9, 128.6, 127.8, 127.6, 126.6, 117.6, 116.3, 116.2, 52.5, 52.0, 44.8, 43.6, 21.3, 21.1, 20.20.4, 18.7 (2 signals), 16.5, 15.6. HRMS (EI): *m*/*z* calcd for $C_{43}H_{46}N_4Cl_4Ru$ 860.1503, found 860.1530.

Complex 3g: reaction temperature 60 °C; red crystals, yield 109 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.60 (1H, dd, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.74 (2H, m, Ph*H*), 7.50 (1H, tt, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.39 (2H, m, Ph*H*), 7.33 (1H, s, indenylidene-*H*), 7.26 (1H, td, J = 7.4, 1.2 Hz, indenylidene-*H*), 7.21 (1H, td, J = 7.5, 1.2 Hz, Ph*H*), 7.12−7.08 (3H, overlapped signals, indenylidene-*H* + mesityl-*H*), 6.46 (1H, s, mesityl-*H*), 6.07 (1H, s, mesityl-*H*), 4.89 (1H, sep, J = 6.8 Hz, NC*H*(CH_3)$_2$), 4.01−3.70 (5 H, overlapped multiplets, NC*H*-(CH_3)$_2$ + N$CH_2$$CH_2$N), 2.73 (3H, s, Ar$CH_3$), 2.70 (3H, s, N$CH_3$), 2.39 (3H, s, Ar$CH_3$), 2.24 (3H, s, Ar$CH_3$), 2.02 (3H, s, Ar$CH_3$), 1.87 (3H, s, Ar$CH_3$), 1.35 (3H, d, J = 6.8 Hz, NCH(CH_3)$_2$), 1.29 (3H, d, J = 6.8 Hz, NCH(CH_3)$_2$), 0.86 (3H, d, J = 6.8 Hz, NCH(CH_3)$_2$), 0.56 (3H, d, J = 6.8 Hz, NCH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 294.8, 219.2, 184.2, 143.9, 140.6, 139.5, 138.8, 137.6, 137.4, 137.3 (2 signals), 137.2, 137.1, 136.8, 136.2, 130.3 (2 signals), 129.2, 129.1, 129.0, 128.6 (2 signals), 127.8, 127.6, 126.5, 117.1, 116.0, 115.8, 56.9, 53.4, 52.4, 52.3, 21.3, 21.2 (2 signals), 21.1, 20.4, 20.2, 18.8 (2 signals). MS (EI): *m*/*z* calcd for $C_{45}H_{50}N_4Cl_4Ru$ 888.2, found 888.5.

General Protocol for Catalyst Screening. All reactions were carried out in closed 25 mL Schlenk tubes under an atmosphere of argon at 80 or 100 °C. To a 25 mL Schlenk tube was added substrate (0.2 mmol) dissolved in dry toluene (10 mL, substrate conc 0.02 M) under an atmosphere of argon. This solution was heated to 80 or 100 °C, and catalyst (0.05−0.5 mol %) from a stock solution (3 mmol/L) in toluene was added. For the determination of substrate conversion, samples were taken every hour under a stream of argon and were injected into GC vials containing 150 μL of 25% ethyl vinyl ether solution in toluene. A final sample was taken after 24 h.

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Supporting Information Available: Copies of ^{1}H, ^{13}C NMR spectra of complexes **3a**−**3g**, cyclic voltammograms, and a CIF file providing information on the crystal structure of complex **3g** are available free of charge via the Internet at http://pubs.acs.org.