N-Heterocyclic Carbenes, Part 33.[1] Combining Stable NHC and Chelating Pyridinyl-Alcoholato Ligands: A Ruthenium Catalyst for Applications at Elevated Temperatures

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Abstract: Ruthenium alkylidene complexes bearing one NHC ligand and one chelating pyridinyl alcoholate ligand **6** are generated by exchange of a phosphine ligand. Two synthetic approaches are presented: reacting the NHC phosphine complex **5** with the chelating ligand or reacting the pyridinyl-alcoholatophosphine complex **3** with a free NHC ligand. To evaluate the properties of **6** as metathesis catalysts, ROMP experiments with the strained olefin norbornene and the less strained cyclooctene were performed at different temperatures.

Keywords: homogeneous catalysis; *N*-heterocyclic carbenes; olefin metathesis; pyridinyl alcoholates; ruthenium

Introduction

During the last few years ruthenium-based alkylidene complexes bearing *N*-heterocyclic carbene (NHC) ligands were established as highly active catalysts for olefin metathesis. A wide range of various systems has been published (Figure 1).[2] One major interest in developing these catalyst systems was achieving higher activities. According to mechanistic and theoretical considerations it is possible to increase reaction rates by orders of magnitude compared to the original bisphosphine system **1**[3] by combining a strongly binding NHC ligand and a rather labile ligand like phosphines,[2d, f,g] pyridine,[4] or easy dissociating metal fragments.[2d]

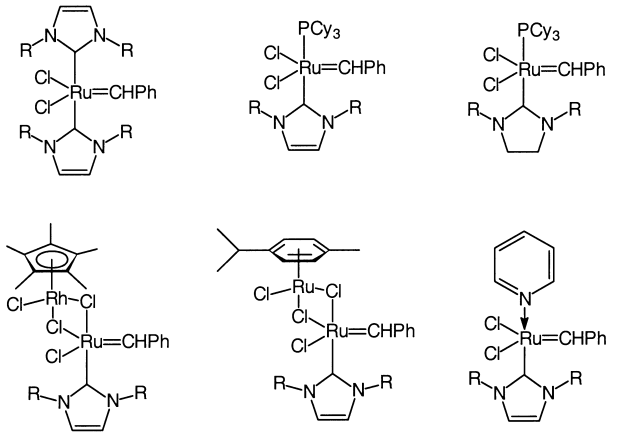

Figure 1. Established highly active NHC ruthenium catalysts for olefin metathesis.[2d,3,4]

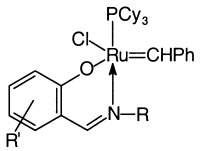

Figure 2. Ruthenium phosphine complex with "dangling" salicylaldimine ligand.[5]

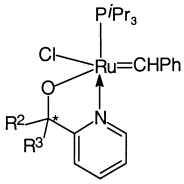

Figure 3. Ruthenium phosphine complex with "dangling" pyridinyl-alcoholato ligand.[6]

Another goal in catalyst design is to generate more stable catalysts, especially for applications at elevated temperatures. A concept that has been pursued in this context is the use of so-called "dangling ligands". These ligands are presumed to act as chelating ligands at room temperature and to open up one coordination site at increased temperature. An example for these systems has been published by Grubbs in 1998, who uses chelating Schiff bases combined with alkylphosphine ligands (Figure 2).[5]

A further example has been patented by Hafner et al. in 1999.[6] Here the ruthenium alkylidene system is

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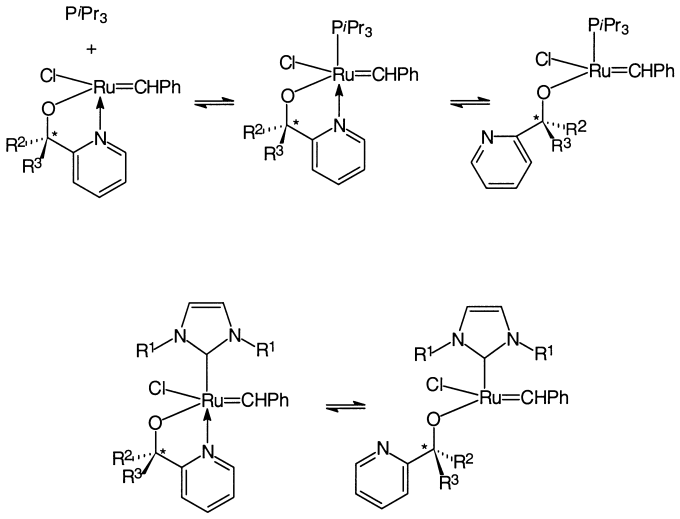
complexed by a combination of an alkylphosphine and a pyridinyl alcoholate (Figure 3).

Results and Discussion

We now report on a ruthenium system that makes use of both the approved NHC ligand and a chelating pyridinyl alcoholate ligand. This class of ligands has quite a long history in our group, especially in molybdenum- and tungsten-catalyzed asymmetric oxidation chemistry.[7,8,9] Pyridinyl alcoholate ligands have numerous advantages: on the one hand they are easily accessible, on the other hand it is possible to transfer chiral information to the metal center by the quaternary carbon atom.[9]



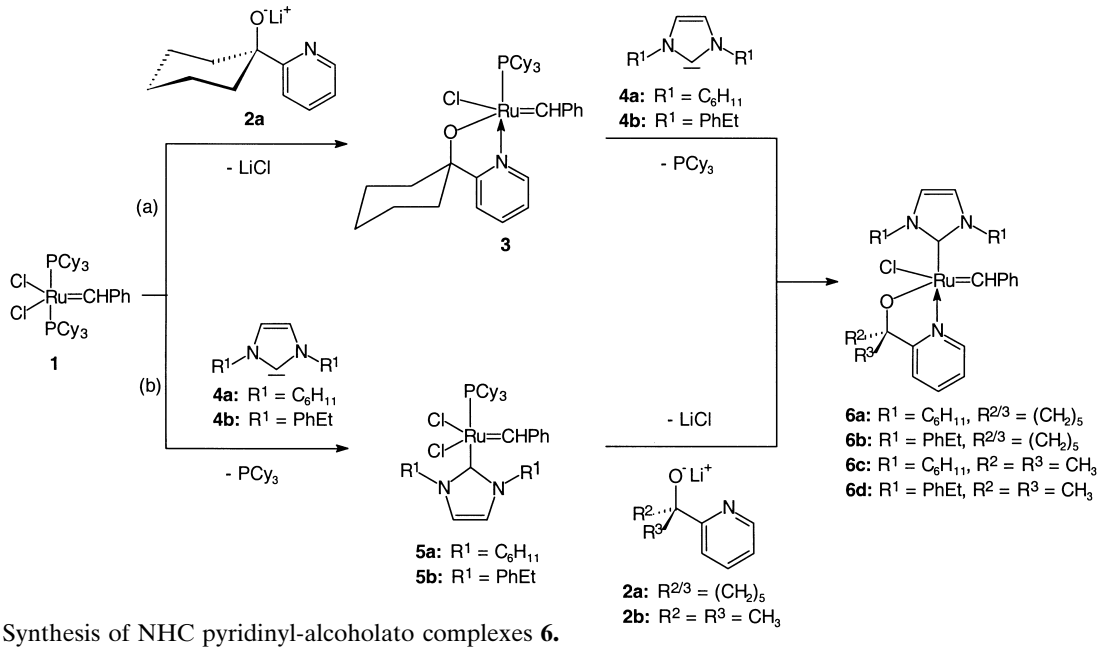
Scheme 1. Ligand dissociation equilibria in phosphine and NHC complexes.

According to DFT calculations and experimental observations, the metal-carbon bond in NHC complexes is usually much stronger than a metal-phosphorus bond in analogous phosphine complexes.[1,2d,10] Due to this fact NHC complexes with dangling ligands should show only one ligand dissociation equilibrium, different to the analogous phosphine complexes, where two different dissociation reactions may occur (Scheme 1).

Accordingly, the NHC ligand should stay coordinated to the metal center through the whole catalytic cycle thus stabilizing the undercoordinated, catalytically active ruthenium fragment. The dangling pyridine moiety, on the one hand, should be able to open up a coordination site at elevated temperatures and, on the other hand, should stabilize the resting state of the catalyst at room temperature.

We have established two synthetic routes leading to NHC pyridinyl-alcoholato complexes **6**, which differ in the order of ligand coordination (Scheme 2).

Starting from the original Grubbs' catalyst **1**, one possibility is to introduce the chelating ligand first (route a): by reaction with the lithium salt **2** of the corresponding pyridinyl alcohol, which is easily obtained by the reaction of the alcohol with butyllithium,[7] one phosphine ligand and one chloro ligand are replaced under the elimination of LiCl. The remaining phosphine ligand is now substituted by a free NHC ligand **4**.[11] A solution of **4** in cold THF is slowly added to a solution of the phosphine pyridinyl-alcoholato complex **3**. After two hours a clear emerald green solution of the desired NHC pyridinyl-alcoholato complex **6** is obtained, from which the free phosphine can be removed following



Scheme 2. Synthesis of NHC pyridinyl-alcoholato complexes **6.**

Table 1. ROMP of norbornene and cyclooctene at room temperature.

Catalyst	ROMP of norbornene [%][a]	ROMP of cyclooctene [%][b]
6a	60	oligomers
6b	57	18
6c	65	14
6d	64	oligomers

[a] Room temperature, monomer/catalyst = 100/1, CH_2Cl_2, reaction time 30 min, isolated yields, not optimized.
[b] Room temperature, monomer/catalyst = 500/1, CH_2Cl_2, reaction time 1 h, isolated yields, not optimized.

Table 2. ROMP of norbornene and cyclooctene at 60 °C.

Catalyst	ROMP of norbornene [%][a]	ROMP of cyclooctene [%][b]
6a	100	75
6b	98	78
6c	99	72
6d	100	80
5[2k]	100	88

[a] 60 °C, monomer/catalyst = 100/1, toluene, reaction time 15 min, isolated yields, not optimized.
[b] 60 °C, monomer/catalyst = 500/1, toluene, reaction time 25 min, isolated yields, not optimized.

common procedures.[2d] According to this procedure the two complexes **6a** and **6b** were obtained.

Following route b) the first step is the substitution of one phosphine ligand by a free NHC ligand, resulting in a mixed NHC phosphine complex **5**.[2d] The second step comprises the coordination of the "dangling" ligand system by substituting the remaining phosphine ligand and one of the two chloro ligands. Using the cyclohexyl-substituted pyridinyl alcoholate, a solution of lithium salt **2a** in THF is added to a solution of **5**. After one hour the reaction mixture turns to clear emerald green. By extraction of the raw product with toluene the formed LiCl can be removed, followed by the usual separation from the free phosphine. According to this procedure complexes **6a** and **6b** were also obtained.

The lithium salt of the dimethyl-substituted pyridinyl alcohol **2b** is only very poorly soluble in THF, so we slightly modified the experimental procedure. The solved ruthenium species **5** is added to a vigorously stirred suspension of **2b** in THF (Scheme 2). Isolation and purification of the product follow the standard procedures resulting in **6c** and **6d**.

It is a known fact that the analogous phosphine systems with chelating nitrogen donor atoms are not very active metathesis catalysts at room temperature.[5,6] As expected our new NHC pyridinyl-alcoholato systems **6** showed rather low activity in ROMP of norbornene and cyclooctene at room temperature (Table 1).

As mentioned above the strong point of chelate complexes is a different field of application: due to the additional stabilization by the chelating ligand they are too unreactive for catalytic applications at room temperature. But the combination of a strongly binding NHC ligand and a "dangling" pyridinyl-alcoholato ligand should induce better activities for catalytic reactions at higher temperatures. For this purpose, ROMP of norbornene and cyclooctene were carried out at 60 °C in toluene with the same catalyst loadings as mentioned above (Table 2).

As norbornene is a very strained system and therefore very easy to be opened metathetically, the conversions of the less strained olefin cyclooctene are much more meaningful in terms of catalytical performance. The yields obtained at 60 °C by our new NHC pyridinyl-alcoholato complexes **6** are comparable to those achieved by the very reactive mixed-substituted NHC phosphine systems **5**.[2k]

Conclusion

In conclusion, we describe the synthesis of NHC ruthenium complexes bearing a chelating pyridinyl-alcoholato ligand, that can act as a so called "dangling" ligand during the catalytic cycle. These complexes are easily accessible from common starting materials, e.g., the original Grubbs' catalyst, NHCs and their imidazolium precursors and pyridinyl alcoholates. As expected these catalyst systems show rather low activity at room temperature due to their resting state stabilization. But at elevated temperatures their performance can definitely be compared to those of the very reactive mixed-substituted NHC phosphine systems. Further catalytic applications, e.g., RCM and asymmetric synthesis, are under investigation.

Experimental Section

General Remarks

All reactions were performed by standard Schlenk techniques in an oxygen-free argon or nitrogen atmosphere. Solvents were dried by standard methods and distilled under nitrogen. ^1H, ^{31}P, and ^{13}C NMR spectra were measured at 400, 161.6, and 100.54 MHz, respectively, on a FT Jeol GX 400 instrument. Elemental analyses were performed in the microanalytical laboratory of the TU München.

Benzylidenedichloro(tricyclohexylphosphane)-[1-(2′-pyridinyl)cyclohexan-1-olato]ruthenium (3)

A solution of lithium alcoholate **2a**[7] (0.18 mmol, 33.0 mg) in THF (10 mL) was added dropwise to a solution of $RuCl_2(PCy_3)_2(=CHPh)$ (**1**; 0.15 mmol, 123.4 mg) in THF (20 mL). After stirring for

2 hours all volatiles were removed under vacuum. The raw product was extracted with toluene (5 mL), to separate from the formed lithium chloride. This solution was concentrated to a volume of 1 mL and the product was precipitated by adding *ca.* 30 mL of pentane. The product was washed twice with 3 mL of cold pentane, then dried for several hours under vacuum; yield: 91.6 mg (0.134 mmol, 89%). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ = 17.80 (1H, d, $^3J_{PH}$ = 17.2 Hz, RuC*H*Ph), 9.14 (2H, app. s, *o*-H of C_6H_5), 8.49 (1H, app. s, H1), 7.71 (1H, app. s, *p*-H of C_6H_5), 7.52 (1H, app. s, H3), 7.25 (2H, app. s, *m*-H of C_6H_5), 7.08 (1H, app. s, H4), 6.95 (1H, app. s, H2), 2.44 (3H, m, CH of PCy_3), 2.44 – 0.85 (43H, m, CH_2 of PCy_3 and C_6H_{10}); ^{13}C NMR (CD_2Cl_2, 25 °C, 100.54 MHz): δ = 298.3 (Ru=*C*HPh), 166.9 (C5), 153.4 (*ipso*-C of C_6H_5), 148.1 (C1), 137.8 (C3), 134.2 – 128.7 (*o*-H, *m*-H and *p*-H of C_6H_5), 123.4 (C4), 119.8 (C2), 76.8 (*ipso*-C of C_6H_{10}), 41.7, 40.8 (CH_2 of C_6H_{10}), 33.4 (*ipso*-C of C_6H_{11}), 30.7 (*m*-C of C_6H_{11}), 30.5 (*m*-C of C_6H_{11}), 28.2 (*o*-C of C_6H_{11}), 26.7 (*p*-C of C_6H_{11}), 22.9, 22.4, 21.8 (CH_2 of C_6H_{10}); ^{31}P NMR (CD_2Cl_2, 25 °C, 161.6 MHz): δ = 49.8; anal. calcd. for $C_{36}H_{53}ClNOPRu$ (683.76 g/mol): C 63.24, H 7.81, N 2.05; found: C 63.18, H 7.85, N 2.17.

Benzylidenedichloro(1,3-dicyclohexylimidazolin-2-ylidene)[1-(2′-pyridinyl)cyclohexan-1-olato]ruthenium (6a)

A solution of lithium alcoholate **2a**[7] (0.13 mmol, 23.8 mg) in THF (5 mL) was added dropwise to a solution of Ru NHC phosphine complex **5a**[2d] (0.1 mmol, 78.8 mg) in THF (20 mL). The reaction mixture was stirred for 2 hours at room temperature, during which time the color changed from green brown to clear emerald green. After removing the solvent in vacuum the residue was extracted with 10 mL of toluene to separate the formed lithium chloride. This solution was concentrated to a volume of 1 mL and the product was precipitated by adding *ca.* 35 mL of pentane at –78 °C. The product was washed twice with 3 mL of cold pentane, then dried for several hours under vacuum; yield: 45.5 mg (0.073 mmol, 73%). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ = 18.82 (1H, s, RuC*H*Ph), 8.37, (1H, app. s, *o*-H of C_6H_5), 8.87, (1H, app. s, H1), 7.65 (1H, app. s, *p*-H of C_6H_5), 7.58 (1H, app. s, H3), 7.48 (1H, app. s, H4), 7.40 (2H, app. s, *m*-H of C_6H_5), 7.22 (1H, s, NC*H*), 7.01 (1H, app. s, H2), 6.55 (1H, s, NC*H*), 6.45 (1H, m, CH of C_6H_{11}), 3.68 (1H, m, CH of C_6H_{11}), 2.00 – 0.73 (30H, m, CH_2 of NC_6H_{11} and C_6H_{10}); ^{13}C NMR (CD_2Cl_2, 25 °C, 100.54 MHz): δ = 299.40 (Ru=CH), 182.9 (NCN), 166.7 (C5), 152.1 (*ipso*-C of C_6H_5), 147,8 (C1), 137.3 (C3), 129.3, 129.1 and 126.1 (*o*-C, *m*-C and *p*-C of C_6H_5), 122.3 (C4), 120.0 (C2), 119.4 and 118.3 (NCH), 59.6 (CH of NC_6H_{11}), 76.3 (*ipso*-C of C_6H_{10}), 41.9, 41.0 (CH_2 of C_6H_{10}), 34.9, 33.3, 33.1, 28.2, 28.1 and 25.7 (CH_2 of NC_6H_{11}), 23.0, 22.4, 21.8 (CH_2 of C_6H_{10}); anal. calcd. for $C_{32}H_{44}ClN_3ORu$ (623.86 g/mol): C 61.61, H 7.11, N 6.73; found: C 61.66, H 7.14, N 6.69.

Benzylidenedichloro[1,3-di-(*R*)-1′-phenylethylimidazolin-2-ylidene][1-(2′-pyridinyl)cyclohexan-1-olato]ruthenium (6b)

Route a: A cold solution of NHC **4b**[11] (0.25 mmol, 58.1 mg) in THF (10 mL) was added dropwise to a solution of Ru complex **3** (0.20 mmol, 136.8 mg) in THF (30 mL). The reaction mixture was stirred for 30 min at room temperature. After removing the solvent in vacuum the residue was extracted with 4 mL of toluene. This solution was concentrated to a volume of about 2 mL. Upon adding 35 mL of pentane the product precipitated. After washing twice with 5 mL of cold pentane the product was dried under vacuum for several hours.

Route b: A solution of lithium alcoholate **2a**[7] (0.13 mmol, 23.8 mg) in THF (5 mL) was added dropwise to a solution of Ru complex **5b**[2d] (0.1 mmol, 163.8 mg) in THF (20 mL). The solution was stirred for 2 hours at room temperature. During this time the color changed from red brown to emerald green. After removing the solvent in vacuum the residue was extracted with 10 mL of toluene to separate the formed lithium chloride. This solution was concentrated to a volume of 1 mL and the product precipitated upon addition of 35 mL of pentane. The product was washed twice with 5 mL of cold pentane and then dried under vacuum for several hours; yield: 43.4 mg (0.064 mmol). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ = 17.78 (1H, s, RuC*H*Ph), 8.52 (1H, s, H1), 8.42 (2H, br, *o*-H of C_6H_5), 8.02 – 6.72 (19H, m, including 2 *m*-H and 1 *p*-H of C_6H_5, 10H of NCHMe*Ph*, 1H of NC*H*MePh, 2H of N*H*C, H3, H4 and H2), 5.42 (1H, s, N*H*CMe), 2.8 – 1.1 (16H, including 3H of NCH*Me*Ph, 10H of C_6H_{10}); ^{13}C NMR (CD_2Cl_2, 25 °C, 100.54 MHz): δ = 292.8 (Ru*C*HPh), 182.3 (NCN), 166.7 (C5), 155.2 (*ipso*-C of C_6H_5), 147.8 (C1), 143.8, 142.3 (*ipso*-C of NCHMe*Ph*), 140.5 (C3), 137.8 – 125.7 (*o*-C, *m*-C, *p*-C of C_6H_5 and NCHMe*Ph*), 123.4 (C4), 122.1 (C2), 119.4 (N*C*H), 78.5 (*ipso*-C of C_6H_{10}), 68.1, 58.2 (N*C*HMePh), 39.0, 34.5, 28.7 – 26.5 (CH_2 of C_6H_{10}), 22.6, 21.2 (NCH*Me*Ph); anal. calcd. for (677.86 g/mol): C 65.56, H 5.65, N 6.20; found: C 65.48, H 5.69, N 6.14.

Benzylidenedichloro(1,3-dicyclohexylimidazolin-2-ylidene)[2-(2′-pyridinyl)propan-2-olato]ruthenium (6c)

A solution of Ru complex **5a**[2d] (0.1 mmol, 78.8 mg) in THF (20 mL) was added dropwise to a vigorously stirred suspension of lithium alcoholate **2b**[7] (0.12 mmol, 17.2 mg) in THF (20 mL). The reaction mixture was stirred for 2 hours at room temperature. A clear brownish green solution was obtained. After removing the solvent in vacuum the residue was extracted with 10 mL of toluene to separate the formed lithium chloride. This solution was concentrated to a volume of 1 mL and the product precipitated by addition of 35 mL of pentane at –78 °C. After washing twice with 5 mL of cold pentane the product was dried under vacuum for several hours; yield: 43.49 mg (0.073 mmol, 73%). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ = 18.76 (1H, s, Ru=CH), 8.48 (1H, d, $^3J_{HH}$ = 5 Hz, H1), 8.36 (2H, br, *o*-H of C_6H_5), 7.62 (1H, m, H3), 7.56 (1H, app.s, *p*-H of C_6H_5), 7.21 (1H, app. s, H4), 7.15 (2H, br, *m*-H of C_6H_5), 7.04 (1H, app. s, H2), 6.98 (1H, br, NCH), 6.80 (1H, br, NCH), 5.90 (1H, br, CH of C_6H_{11}), 3.67 (1H, br, CH of C_6H_{11}), 1.82 – 0.95 (26 H, m, including 20H of C_6H_{11}, 6H of CH_3); ^{13}C NMR (CD_2Cl_2, 25 °C, 100.54 MHz): δ = 299.50 (Ru=CH), 183.9 (NCN), 167.4 (C5), 155.1 (*ipso*-C of C_6H_5), 147.5 (C1), 136.3 (C3), 129.2, 128.9 and 127.2 (*o*-C, *m*-C and *p*-C of C_6H_5), 122.5 (C4), 119.8 (C2), 118.9 and 118.5 (NCH), 55.2 (CH of NC_6H_{11}), 35.1, 34.3, 33.7 (CH_2 of NC_6H_{11}), 31.42, 28.2 (CH_3), 27.9, 27.1 and 25.5 (CH_2 of NC_6H_{11}); anal. calcd. for

$C_{30}H_{40}ClN_3ORu$ (595.80 g/mol): C 60.47, H 6.77, N 7.05; found: C 60.50, H 6.75, N 7.01.

Benzylidenedichloro-[1,3-di-(*R*)-1′-phenylethyl-imidazolin-2-ylidene][1-(2′-pyridinyl)propan-2-olato]ruthenium (6d)

A solution of **5b**[2d] (0.3 mmol, 491.4 mg) in THF (30 mL) was added dropwise to a vigorously stirred suspension of lithium alcoholate **2b**[7] (0.39 mmol, 55.8 mg) in THF (40 mL). After 2 hours of stirring at room temperature a clear emerald green solution is obtained. All volatiles were removed in vacuum. The residue was extracted with 1 mL of toluene to separate the formed lithium chloride. This solution was concentrated to a volume of 1 mL and the product precipitated by addition of 35 mL of pentane. After washing twice with 5 mL of cold pentane the product was dried under vacuum for several hours; yield: 88.6 mg (0.138 mmol, 46%). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz): δ = 18.92 (1H, s, Ru=CH), 8.45 (1H, br, H1), 8.23 (2H, br, *o*-H of C_6H_5), 8.00 – 6.25 (20H, m, including 2 *m*-H and 1 *p*-H of C_6H_5, 10H of NCHMe*Ph*, 2H of NC*H*MePh, 2H of N*H*C, H3, H4 and H2), 1.84 (3H, br, NCH*Me*Ph), 1.74 (3H, s, Me), 1.65 (3H, s, Me), 1.30 (3H, br, NCH*Me*Ph); ^{13}C NMR (CD_2Cl_2, 25 °C, 100.54 MHz): δ = 298.8 (Ru*C*HPh), 186.3 (NCN), 167.7 (C5), 154.2 (*ipso*-C of C_6H_5), 147.5 (C1), 141,5, 141.3 (*ipso*-C of NCHMe*Ph*), 141.0 (C3), 137.6 – 124.7 (*o*-C, *m*-C, *p*-C of C_6H_5 and NCHMe*Ph*), 123.6 (C4), 122.3 (C2), 118.7 (N*C*H), 69.3, 56.4 (N*C*HMePh), 32.7, 25.8 (CH_3), 21.3, 19.7 (NCH*Me*Ph); anal. calcd. for $C_{34}H_{38}ClN_3ORu$ (641.82 g/mol): C 63.63, H 5.97, N 6.54; found: C 63.69, H 5.91, N 6.50.

ROMP Experiments

A typical ROMP experiment was performed by adding the monomer (100 or 500 equivalents, dissolved in 0.3 mL of methylene chloride) to a solution of 6.3 μmol of catalyst in 0.2 mL of methylene chloride. After 30 minutes, 5 mL of methylene chloride containing small amounts of *tert*-butyl ether and 2,6-di-*tert*-butyl-4-methylphenol, are added. Ten minutes later this solution is slowly added to a large excess of methanol, filtered, and the reside dried under vacuum. The yield is determined gravimetically. The experiments at 60 °C are performed in toluene and quenched after 15 minutes.

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