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Comparative Investigation of Hoveyda–Grubbs Catalysts bearing Modified N-Heterocyclic Carbene Ligands

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Abstract: This paper reports the structural modification of Hoveyda–Grubbs complexes through the introduction of either an *N*-alkyl-*N*′-mesityl heterocyclic carbene, an *N*-alkyl-*N*′-(2,6-diisopropylphenyl) heterocyclic carbene, or an *N*-alkyl-*N*′-alkyl heterocyclic carbene. The effect of the modified N-heterocyclic carbene (NHC) ligand was investigated in representative ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM) and cross metathesis (CM) reactions. A pronounced influence on both catalyst activity and selectivity was found to be exerted by the NHC amino substituents, which emphasizes that a rigorously selected steric environment is critical in olefin metathesis catalyst design.

Keywords: catalyst design; crystal structures; metathesis; N-heterocyclic carbenes; ruthenium

Introduction

Next to the Grubbs 1st generation catalyst **1a**[1] and the Grubbs 2nd generation catalyst **1b**[2], the Hoveyda catalyst **2a**[3] and the Hoveyda–Grubbs catalyst **2b**[4] represent an important class of olefin metathesis initiators (Figure 1). Their remarkable stability and reactivity towards electron-deficient substrates create an interesting application profile.[5] These aryl-ether chelate complexes offer the additional advantage of possible recovery after reaction, which should be assigned to a release/return mechanism. The isopropoxystyrene, which decoordinates during metathesis, can react again with a ruthenium intermediate to regenerate the original catalyst.[6] Steric[7] and electronic[8] effects in the isopropoxystyrene ligand sphere were thoroughly investigated, and were both found to exert a strong influence on catalyst activity.

In this contribution, we describe the preparation, characterization and catalytic behavior of Hoveyda–Grubbs' complexes featuring modified N-heterocyclic carbene (NHC) ligands. The introduction of an ali-

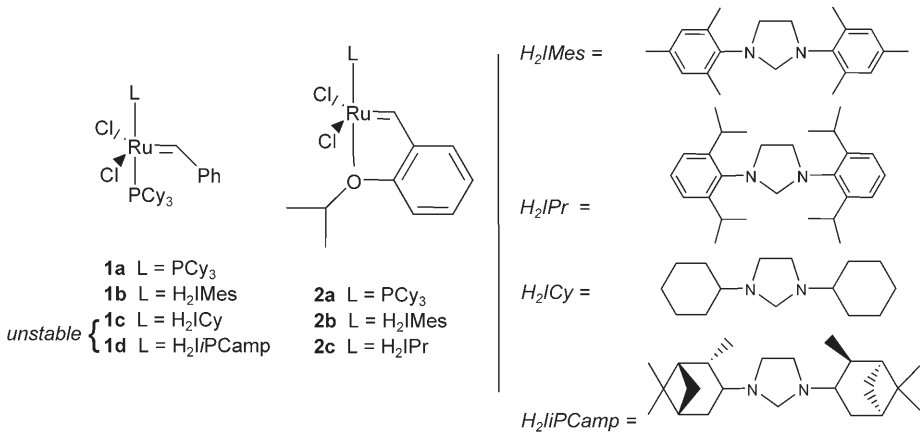


Figure 1.

phatic amino side group into the NHC framework profoundly alters the catalytic activity of the resulting complexes.[9] An intriguing example was given by Blechert et al. who described the *N*-methyl-*N*′-mesityl derived catalyst **3a** which does not improve the catalytic activity but induces higher selectivity in diastereoselective ring-closing metathesis (RCM) and significantly alters *E*/*Z* ratios in cross metathesis (CM).[10] Our recent research on Grubbs' catalysts bearing *N*-alkyl-*N*′-(2,6-diisopropylphenyl) heterocyclic carbenes demonstrated that replacement of the NHC mesityl ring with a 2,6-diisopropylphenyl moiety has a dramatic effect. Facile bis-coordination of the NHC ligands was observed, which was assigned to an enhanced phosphine dissociation rate of the mono(NHC) complexes.[11] These results stimulated us to explore the effects of a similar NHC modification in Hoveyda–Grubbs' catalysts.

Next to these two types of non-symmetrical NHCs, also symmetrical ligands bearing two aliphatic amino side groups were successfully coordinated to the Hoveyda precursor **2a**. We recently reported on the low stability of Grubbs' benzylidene complexes **1c** and **d**, which prevented their isolation. The lack of stability was attributed to steric effects resulting in a weakened NHC to metal bond.[9a] Likely, the sterically less demanding geometry of Hoveyda–Grubbs' complexes explains a herein described more fruitful outcome.

The NHC ligands described in this paper all incorporate a saturated backbone. NHC's with unsaturated backbones have a longer history; ruthenium carbene complexes with NHC's bearing *N*-cyclohexyl groups were even amongst the first 2nd generation catalysts to be described in the literature.[12] In addition, Grubbs-type metathesis catalysts with "unsaturated" NHC's bearing an *N*-alkyl as well as an *N*-aryl group have thoroughly been reported in the literature by Fürstner et al.[13] and Grubbs et al.[14] It was shown that substantial structural variations can be accommodated at the NHC ligand and eventually lead to designer catalysts with tailor-made properties. As "saturated" NHC's generally afford more active metathesis initiators than "unsaturated" ones,[15] we were hoping to successfully contribute to the continuous search for more efficient catalysts.

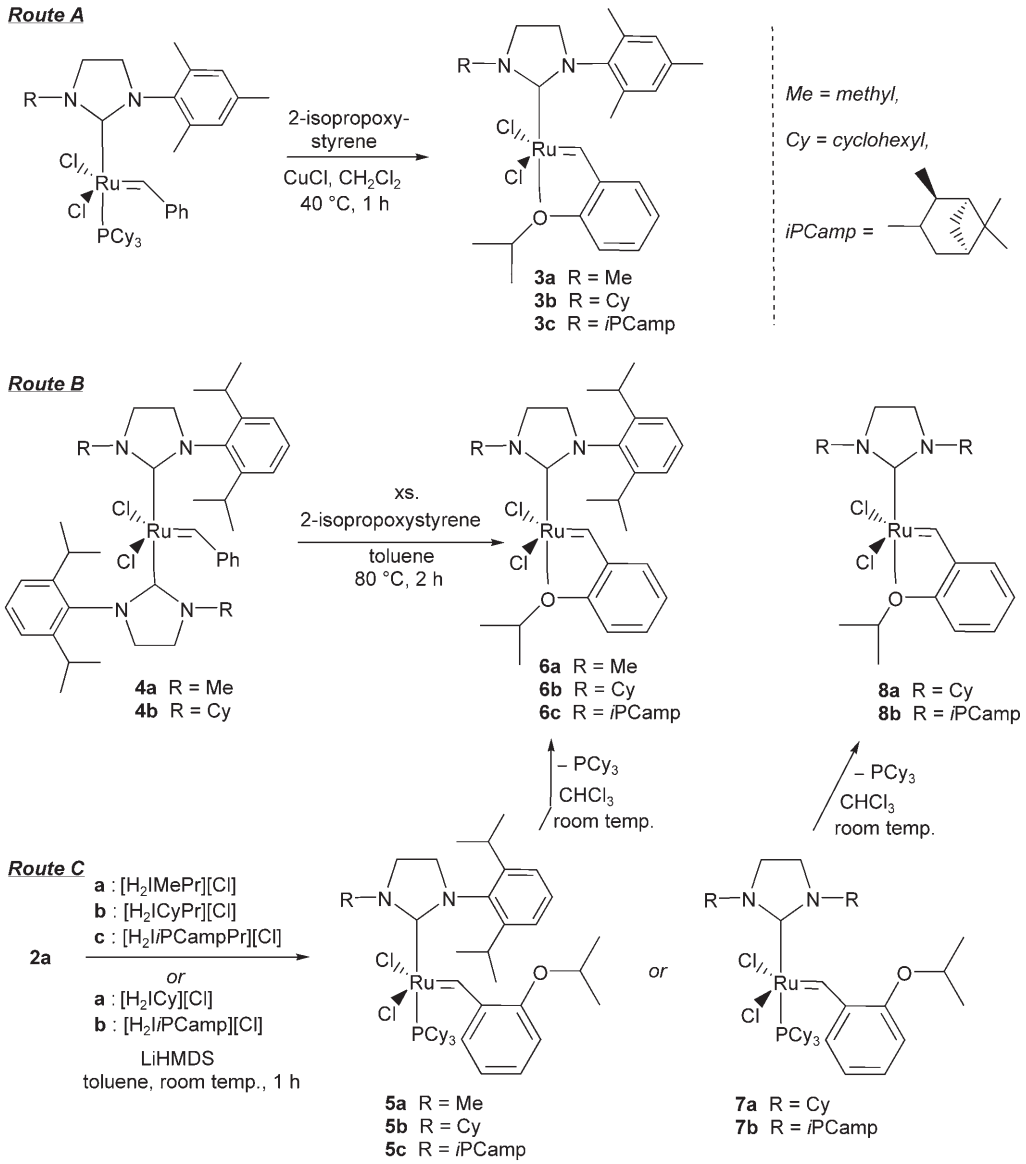
Results and Discussion

In contrast to complexes **2b** and **c** and **3a–c**, which were prepared through an established route involving their Grubbs' 2nd generation analogue and CuCl as a phosphine scavenger (Scheme 1, route A),[4a,7,8] complexes **6a** and **b** required an alternative protocol. Since the *N*-(alkyl)-*N*′-(2,6-diisopropylphenyl) heterocyclic carbenes induce preferential bis-coordination in their reaction with **1a**, we disclose an unconventional synthetic strategy which uses the bis(NHC) complexes **4a** and **b** as starting materials. Reaction with an excess of 2-isopropoxystyrene at elevated temperature allows for the decoordination of one NHC ligand with formation of the desired complexes in good yield (Scheme 1, route B). In addition, a synthetic approach inspired by a procedure described by Blechert et al. proved successful.[4b] Treatment of Hoveyda catalyst **2a** with the appropriate NHC chloride salt and LiHMDS (lithium hexamethyldisilazane) as a base afforded the intermediates **5a–c**, which were stirred in chloroform to liberate their phosphine ligand (Scheme 1, route C). Here, it is notheworthy that no bis(NHC) substitution was observed during the course of the reaction. This strategy, which circumvents the need for Grubbs' precursors **1c** and **d**, was also applied to synthesize complexes **8a** and **b** bearing symmetrical aliphatic NHC ligands.

Single crystals suitable for X-ray crystal-structure analysis were obtained for **3b** and **c**, **6a** and **b**, and **8a**. The resulting structures shown in Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6 confirm the formation of a single isomer. Selected bond lengths and angles are provided in Table 1. All complexes display a typical distorted square pyramidal coordination with the Cl atoms *trans* to one another and the apical position occupied by the Ru=C bond. Compared with the standard Hoveyda–Grubbs' catalyst **2b**, all complexes bearing an aliphatic NHC amino side group are characterized by a slightly decreased Ru–*C*NN bond length. This indicates a stronger σ-donation of the NHC ligand caused by the aliphatic amino groups. While for complexes **3a–c**, the Ru–O bond remains within the same range as for **2b**, a slightly longer bond length is observed for complexes **6a** and **6b**. This is probably due to steric requirements demanded by the presence of a bulkier diisopropylphenyl group.

Remarkably, complexes **3a–c** and **6a** and **b** all have their aromatic amino side group oriented towards the benzylidene unit. This formation of only one isomer is well precedented in the literature for Grubbs-type complexes, and was assigned to a π–π interaction between the two nearly coplanar aromatic groups.[10,11,13a,c] In the here described Hoveyda–Grubbs-type complexes the two aromatic groups are arranged almost perpendicularly and the observed molecular feature can thus not be ascribed to an intramolecular π–π stacking as stated formerly for Grubbs' complexes.

In complexes **3a–c** and **6a** and **b**, the α-benzylidene proton is located directly underneath the *N*-aryl group of the NHC, however, in complex **8a** the *N*-alkyl group is distorted away from the benzylidene unit. This different arrangement reduces the NHC–benzylidene steric interactions and explains the smaller N_2C–Ru=C angle found for complex **8a**.



Scheme 1.

To explore the catalytic potential of the new complexes, they were compared with the benchmark catalysts **2a–c** in a few model olefin metathesis reactions. (Scheme 2) Figure 7 and Figure 8 illustrate how the catalysts perform in the ROMP of the low strain *cis*,*cis*-cycloocta-1,5-diene (COD) under standard conditions. Using a COD/catalyst ratio of 300, the Hoveyda–Grubbs' complexes bearing symmetrical NHC ligands (**2b**, **c**, and **8a**, **b**) reach full conversion within the first measurement. When a COD/catalyst ratio of 3000 is applied, complexes **8a**, **b** show an increased activity relative to the classic Hoveyda–Grubbs' complexes **2b**, **c**.

The Hoveyda–Grubbs' complexes coordinated with an *N*-alkyl-*N*′-mesityl carbene (**3a–c**) display a higher ROMP activity than the ones substituted with *N*-alkyl-*N*′-(2,6-diisopropylphenyl) carbenes (**6a–c**). Furthermore, complexes **6b** and **6c** fail to reach the reactivity of their phosphine precursor **2a**.

The activity trends observed in the RCM of diethyl diallylmalonate (Figure 9) are somewhat different from those observed in the ROMP of COD. Originally, we anticipated that changing the electronic nature of the NHC through the introduction of aliphatic groups might positively affect the catalytic activity of the corresponding complexes. However, we came to conclude that the influence of the steric bulk plays a much more compelling role in determining the RCM activity. As the steric bulk of the NHC ligand increases, a decrease in catalyst activity is found. In all three

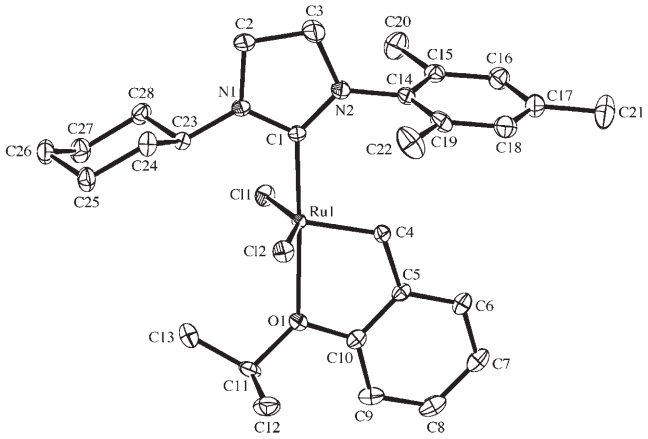


Figure 2. The molecular structure of **3b**, showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Crystals were grown from toluene.

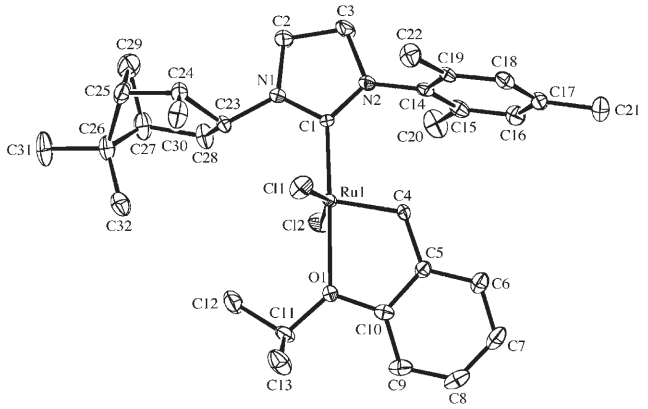


Figure 3. The molecular structure of **3c**, showing 50% probability ellipsoids. Crystals were grown from CH_2Cl_2/acetone.

series of catalysts we observe a distinct negative steric bulk-catalytic activity relationship: **3a** > **3b** > **3c**, **6a** > **6b** > **6c**, **8a** > **8b**.

It is also noteworthy that the highly ROMP-active complexes **8a** and **b** display rather modest RCM activity. This substrate specificity likely results from a large steric bulk around the ruthenium center, which hampers coordination of the bulky RCM substrate. A more demanding steric environment stems from the three-dimensional bulk of the aliphatic amino side groups compared with the only two-dimensional bulk of the flat aromatic side groups. This extra bulkiness is expected to cause a greater shielding of the metal center and explains the lower RCM activity of all new complexes compared with the benchmark catalysts **2a–c**. These data are in agreement with earlier findings, which indicated that future NHC ligand design should focus on a rigorously selected steric environment, rather than on a tuning of electronic effects.[16]

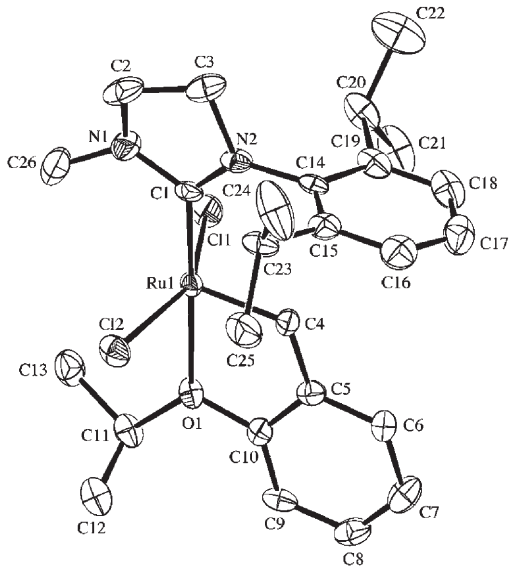


Figure 4. The molecular structure of **6a**, showing 50% probability ellipsoids. Crystals were grown from benzene.

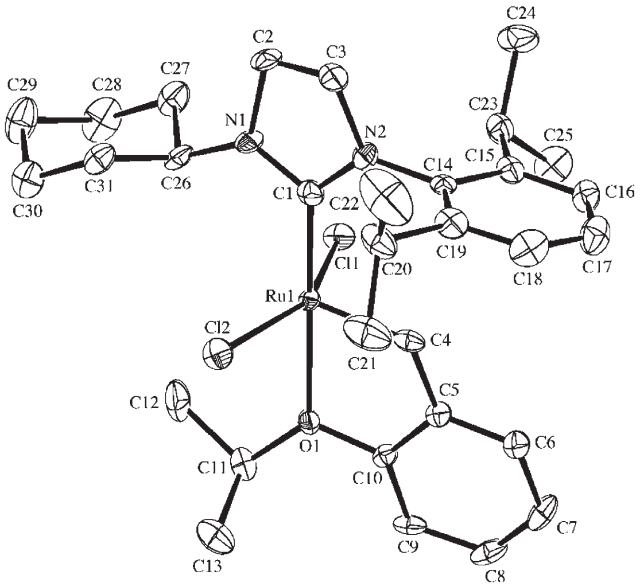
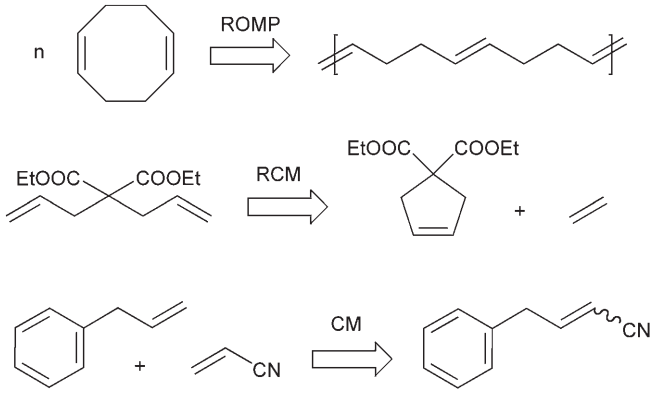


Figure 5. The molecular structure of **6b**, showing 50% probability ellipsoids. Crystals were grown from CH_2Cl_2/MeOH.

The applicability in CM was examined for the challenging substrate acrylonitrile (Table 2).[5,8a–b,17] The catalytic activity was measured using two catalyst loadings (2.5 and 5 mol%) and compared with the results obtained for the conventional complexes **2a–c**. Phosphine complex **2a** demonstrates very poor activity; the NHC-bearing complexes show better results. Our modified complexes **3a–c**, **6a–c**, and **8a**, **b** display lower activity than the classic Hoveyda–Grubbs' complexes **2b** and **c**, and induce different *E*/*Z* selectivities. The complexes bearing symmetrical NHC ligands (**2b**,

Table 1. Selected bond lengths [Å] and angles [°] with standard uncertainties in parentheses.

	2b[4]	**3a**[10]	**3b**	**3c**	**6a**	**6b**	**8a**
Bond Lengths							
Ru=C	1.828(5)	1.821(3)	1.836(2)	1.832(3)	1.839(5)	1.834(6)	1.824(3)
Ru−*C*NN	1.981(5)	1.978(3)	1.964(2)	1.973(3)	1.968(6)	1.980(6)	1.972(3)
Ru−O	2.261(3)	2.270(2)	2.266(2)	2.260(2)	2.281(4)	2.297(4)	2.274(2)
N(1)−C(1)	1.351(6)	1.341(4)	1.344(3)	1.360(4)	1.353(8)	1.327(8)	1.346(4)
N(2)−C(2)	1.350(6)	1.345(4)	1.353(3)	1.349(4)	1.456(9)	1.343(8)	1.348(4)
Bond Angles							
Cl−Ru−Cl	156.5(5)	153.53(4)	153.19(2)	157.41(3)	151.47(6)	152.08(6)	154.36(3)
N_2C−Ru=C	101.5(14)	102.68(13)	102.9(10)	102.52(11)	101.5(2)	101.20(18)	96.68(13)
N_2C−Ru−O	176.2(14)	178.16(10)	178.04(8)	174.21(11)	178.5(2)	177.8(2)	175.66(10)



Scheme 2.

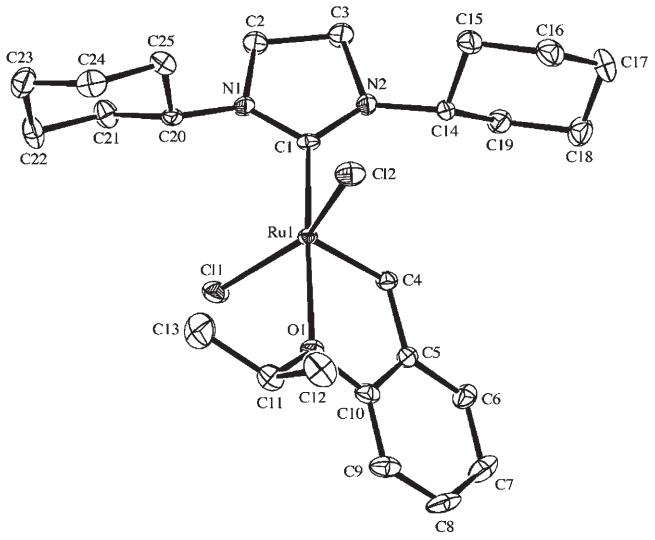


Figure 6. The molecular structure of **8a**, showing 50% probability ellipsoids. Crystals were grown from CH_2Cl_2/hexane.

c and **8a**, **b**) show higher *Z* selectivity. For all but one (**3c**) of the complexes coordinated with an asymmetrical NHC, a remarkable *E*/*Z* selectivity reversal is observed.

Conclusions

In summary, a comparison between the classical Hoveyda–Grubbs' complexes **2b**, **c** and complexes **3a**, **b** and **6a**, **b** demonstrates that the introduction of one aliphatic group into the NHC framework does not improve the catalytic activity in any of the tested metathesis reactions. The introduction of two aliphatic amino side groups (complexes **8a** and **b**) enhances the reactivity in the ROMP reaction while the increase of steric interactions lowers the RCM and CM activity. The lower activity of the *N*-alkyl-*N*′-(2,6-diisopropylphenyl) heterocyclic carbene complexes **6a** and **b** compared with the *N*-alkyl-*N*′-mesityl heterocyclic carbene complexes **3a** and **b**, may analogously be attributed to a more demanding steric environment. These results confirm that the NHC's amino side groups play a pivotal role in determining the reactivity and selectivity of the corresponding catalysts. While small differences in donor capacities might cause a significantly different catalytic behavior, it is plausible that subtle steric differences exert a more determining influence on the activity of the catalysts.

Experimental Section

All reactions and manipulations involving organometallic compounds were conducted in oven-dried glassware under an argon atmosphere using standard Schlenk techniques. Solvents were dried with appropriate drying agents and distilled prior to use. COD and allylbenzene were dried over CaH_2. Acrylonitrile, stabilized with 35–45 ppm hydroquinone monomethyl ether, was distilled prior to use. ^1H and ^{13}C NMR measurements were performed with a Varian Unity-300 spectrometer. Complexes **2b**,[4a] **2c**[18] and **3a**[10] were prepared according to literature procedures.

$(H_2ICyMes)Cl_2Ru$=CH-*o*-O-*i*-PrC_6H_4 (3b)

$(H_2ICyMes)(PCy_3)Cl_2Ru$=CHPh (0.114 g, 0.14 mmol) and CuCl (0.014 g, 0.14 mmol) were weighed into a dry Schlenk flask. 2-Isopropoxystyrene (0.023 g, 0.14 mmol) in CH_2Cl_2

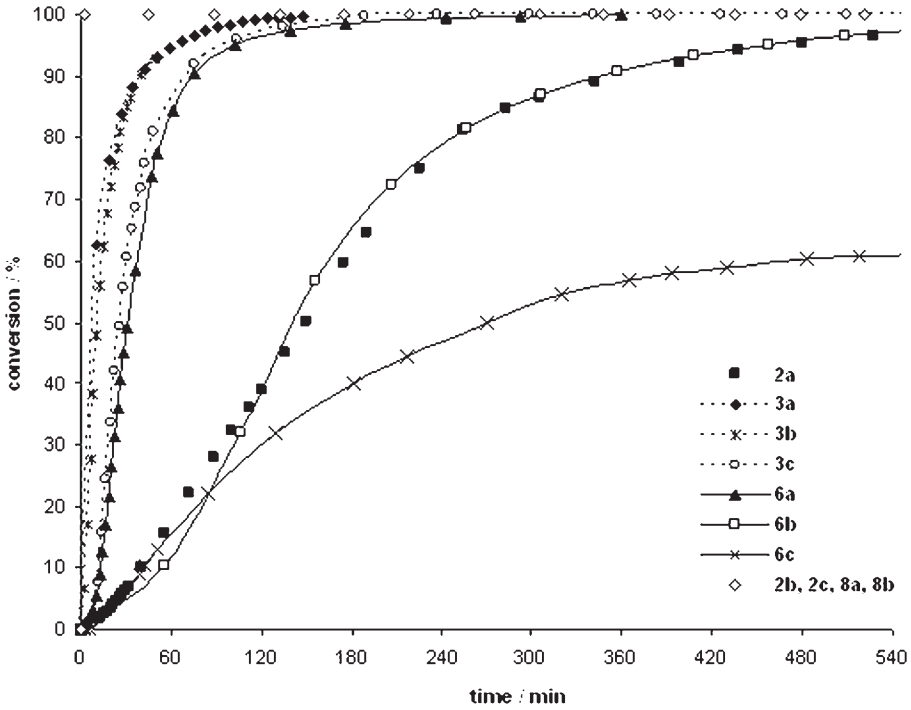


Figure 7. Monitoring ROMP of COD *via* ^{1}H NMR spectroscopy (20 °C), COD/catalyst = 300, catalyst concentration = 4.52 mM, solvent = $CDCl_3$

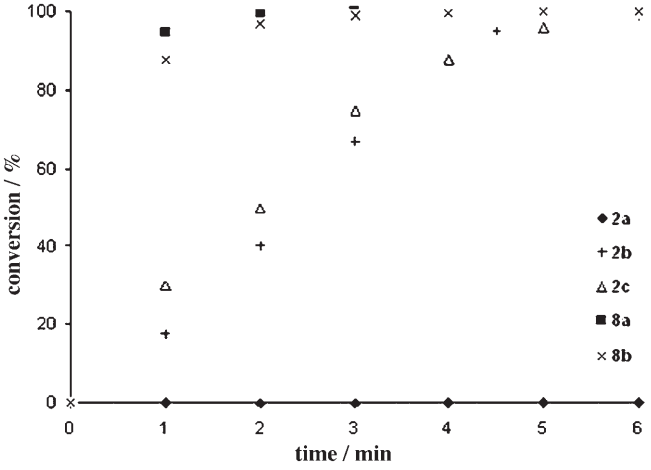


Figure 8. Monitoring ROMP of COD *via* ^{1}H NMR spectroscopy (20 °C), COD/catalyst = 3000, catalyst concentration = 0.452 mM, solvent = $CDCl_3$

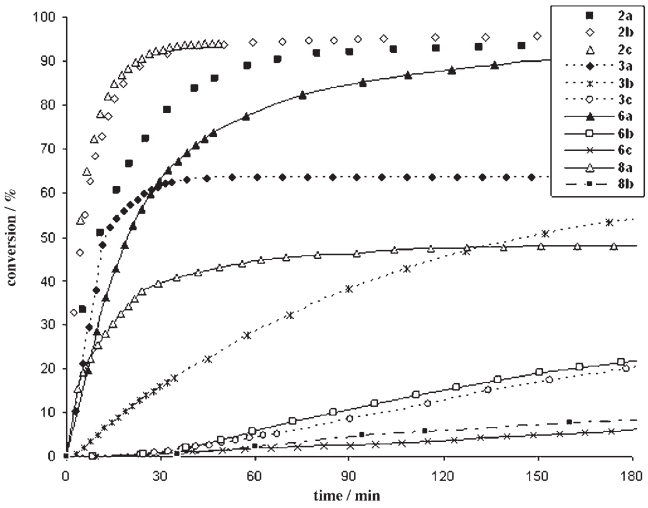


Figure 9. Monitoring RCM of diethyl diallylmalonate *via* ^{1}H NMR spectroscopy (20 °C), diethyl diallylmalonate/catalyst = 200, catalyst concentration = 4.52 mM, solvent = CD_2Cl_2.

(10 mL) was added and the resulting solution was stirred at 40 °C for 1 h. The reaction mixture was filtered and concentrated under vacuum. The resulting crude product was purified by column chromatography using hexane/CH_2Cl_2 (1/1) as an eluent. After concentration of the solvent, the desired complex precipitated as a bright green solid which was filtered and vacuum dried; yield: 80 %. ^{1}H NMR ($CDCl_3$): δ = 16.32 (s, 1H, Ru=C*H*), 7.51 (t, 1H, Ar-*H*), 7.05 (s, 2H, Ar-*H*), 6.92 (m, 3H, Ar-*H*), 5.17 [sept, 1H, OC*H*(CH_3)$_2$], 5.06 [m, 1H, N-C*H*(Cy)], 3.94 (app. s. 4H, NCH_2CH_2N), 2.45 (s, 3H, *p*-CH_3), 2.23 (s, 6H, *o*-CH_3), 1.99 (m, 2H), 1.81 (s, 6H, CH_3), 1.56 (m, 6H), 1.26 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 293.3 (Ru=*C*H), 206.8 (CyN*C*NAr), 152.6 (Ar-*C*), 144.5 (Ar-*C*), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.0 (Ar-*C*), 129.7 (Ar-*C*), 122.9 (Ar-*C*), 122.7 (Ar-*C*), 113.1 (Ar-*C*), 74.9 [O*C*H-(CH_3)$_2$], 61.3 (N*C*H), 51.6 (N*C*H), 43.7 (N*C*H), 31.1 (C-2 Cy), 26.1 (C-3 Cy), 25.8 (C-4 Cy), 22.3 [CH(*C*H$_3$)$_2$], 21.4 (*p*-*C*H$_3$), 18.4 (*o*-*C*H$_3$); anal. calcd. (%) for $C_{28}H_{38}N_2Cl_2ORu$

Table 2. CM of allylbenzene and acrylonitrile. 40 °C, 3 h, solvent = CH_2Cl_2. Conversion and *E*/*Z* ratios determined by ^{1}H NMR (ArCH_2R protons allylbenzene: $\delta = 3.36$, *Z*-isomer: $\delta = 3.73$, *E*-isomer: $\delta = 3.51$).

Catalyst	Loading [mol %]	Conversion [%]	*E*/*Z* ratio
2a	5	<2	-
2b	2.5	91	0.7/1
2c	2.5	93	0.5/1
3a	2.5	20	1.9/1
3a	5	34	1.8/1
3b	2.5	33	1.5/1
3b	5	39	1/1
3c	2.5	43	0.6/1
3c	5	44	0.6/1
6a	2.5	15	2.5/1
6a	5	31	2.8/1
6b	2.5	12	3.2/1
6b	5	26	2.9/1
6c	2.5	21	2.2/1
6c	5	31	2.4/1
8a	2.5	5	0.8/1
8a	5	26	0.6/1
8b	2.5	7	0.5/1
8b	5	30	0.4/1

(590.6): C 56.94, H 6.49, N 4.74; found: C 56.68 H 6.65 N 4.79.

(H_2I*i*PCampMes)Cl_2Ru=CH-*o*-O-*i*-PrC_6H_4 (3c)

Analogously (H_2I*i*PCampMes)(PCy_3)Cl_2Ru=CHPh (0.122 g, 0.14 mmol), CuCl (0.014 g, 0.14 mmol) and 2-isopropoxystyrene (0.023 g, 0.14 mmol) afforded complex **3c**, which was purified by column chromatography using hexane/CH_2Cl_2 (1/1) as an eluent; yield: 84 %. ^{1}H NMR ($CDCl_3$): $\delta = 16.39$ (s, 1 H, Ru=C*H*), 7.52 (t, 1 H, Ar-*H*), 7.06 (s, 1 H, Ar-*H*), 7.05 (s, 1 H, Ar-*H*), 6.91 (m, 3 H, Ar-*H*), 5.52 (m, 1 H, N-C_a*H*), 5.12 [sept, 1 H, OC*H*(CH_3)$_2$], 4.04–3.95 (m, 4 H, NCH_2CH_2N), 3.16 (m, 1 H), 2.50 (m, 2 H), 2.45 (s, 3 H), 2.23 (d, 6 H), 2.10 (s, 1 H), 1.98 (m, 2 H), 1.74 (m, 6 H), 1.54 (m, 3 H), 1.29 (s, 3 H), 1.22 (s, 3 H), 0.94 (d, 1 H); ^{13}C NMR ($CDCl_3$): $\delta = 294.5$ (Ru=*C*H), 209.3 (N*C*N), 152.3, 144.9, 138.8, 138.6, 138.5, 138.3, 129.8, 129.7, 123.0, 122.7, 113.2, 74.9 [O*C*H(CH_3)$_2$], 59.9 (N*C*H), 51.7 (N*C*H), 48.5 (N*C*H), 43.6, 42.0, 41.1, 38.8, 34.4, 34.1, 28.0, 23.8, 22.3, 21.8, 21.4, 18.4; anal. calcd. (%) for $C_{32}H_{44}N_2Cl_2ORu$ (644.7): C 59.62, H 6.88, N 4.35; found: C 58.13, H 6.65 N 4.27.

(H_2IMePr)Cl_2Ru=CH-*o*-O-*i*-PrC_6H_4 (6a), *Route B*

Bis(NHC) complex **4a** (0.152 g, 0.20 mmol) and 2-isopropoxystyrene (0.170 g, 1.05 mmol, 5.25 equivs.) were weighed into a dry Schlenk flask and dissolved in toluene (5 mL). The solution was heated at 80 °C for 2 h. After evaporation of the solvent, the crude product was purified by column chromatography (hexane/CH_2Cl_2 = 2/3). After evaporation of the chromatography solvent, the product was obtained as a light green solid, and washed with hexane; yield: 75 %. ^{1}H NMR ($CDCl_3$): $\delta = 16.22$ (s, 1 H, Ru=C*H*), 7.60 (t, 1 H, Ar-*H*), 7.48 (m, 1 H, Ar-*H*), 7.38 (m, 2 H, Ar-*H*), 6.94 (d, 1 H, Ar-*H*), 6.85 (m, 2 H, Ar-*H*), 5.17 [sept, 1 H, OC*H*(CH_3)$_2$], 4.02–3.98 (m, 7 H, CH_3N and NCH_2CH_2N), 3.14 [m, 2 H, C*H*(CH_3)$_2$], 1.80 [d, 6 H, OCH(CH_3)$_2$], 1.21 [d, 6 H, CH(CH_3)$_2$], 0.86 [d, 6 H, CH(CH_3)$_2$]; ^{13}C NMR ($CDCl_3$): $\delta = 290.3$ (Ru=*C*H), 210.2 (MeN*C*NAr), 152.9, 148.8, 143.5, 137.5, 129.8, 129.6, 125.1, 122.5, 122.3, 113.1, 75.4 [O*C*H(CH_3)$_2$], 55.3 (N*C*H), 51.7 (N*C*H), 38.7 (N*C*H), 28.1 [*C*H(CH_3)$_2$], 25.8 [CH-(*C*H$_3$)$_2$], 24.0 [CH(*C*H$_3$)$_2$], 22.4 [CH(*C*H$_3$)$_2$]; anal. calcd. (%) for $C_{26}H_{36}N_2Cl_2ORu$ (564.57): C 55.32, H 6.43, N 4.96; found: C 55.32, H 6.43, N 4.94.

(H_2ICyPr)Cl_2Ru=CH-*o*-O-*i*-PrC_6H_4 (6b), *Route B*

Analogously, bis(NHC) complex **4b** (0.207 g, 0.23 mmol) and 2-isopropoxystyrene (0.187 g, 1.15 mmol, 5 equivs.) were weighed into a dry Schlenk flask and dissolved in toluene (10 mL). The solution was stirred at 80 °C during 2 h. The reaction mixture was concentrated under vacuum. The dark green residue was purified by column chromatography using hexane/CH_2Cl_2 (1/1) as an eluent. The desired complex was obtained as a bright green solid, which was washed with hexane; yield: 84 %. ^{1}H NMR ($CDCl_3$): $\delta = 16.30$ (s, 1 H, Ru=C*H*), 7.58 (t, 1 H, Ar-*H*), 7.48 (m, 1 H, Ar-*H*), 7.37 (d, 2 H, Ar-*H*), 6.92 (d, 1 H, Ar-*H*), 6.86 (m, 2 H, Ar-*H*), 5.13 [m, 2 H, OC*H*(CH_3)$_2$ and N-C*H*], 3.92 (app. s. 4 H, NCH_2CH_2N), 3.11 [m, 2 H, C*H*(CH_3)$_2$], 2.51 (m, 2 H), 2.00 (m, 2 H), 1.81 [d, 6 H, OCH(CH_3)$_2$], 1.61 (m, 2 H), 1.55 (m, 4 H), 1.20 [d, 6 H, CH(CH_3)$_2$], 0.87 [d, 6 H, CH(CH_3)$_2$]; ^{13}C NMR ($CDCl_3$): $\delta = 290.5$ (Ru=*C*H), 207.3 (CyN*C*NAr), 152.9, 149.0, 143.9, 137.7, 129.6, 129.4, 125.0, 122.6, 122.4, 113.2, 75.0 [O*C*H(CH_3)$_2$], 61.4 (N*C*H), 54.9 (N*C*H), 43.5 (N*C*H), 31.2, 29.9, 28.1, 26.2, 25.9, 25.8, 24.0, 22.5; anal. calcd. (%) for $C_{31}H_{44}N_2Cl_2ORu$ (632.69): C 58.85, H 7.01, N 4.43; found: C 58.62, H 7.00, N 4.40.

Complexes 6a–c, *Route C:* General Procedure

Complex **2a** (1 equiv.) and 1.4 equivs. of the appropriate NHC chloride salt were weighed into a dry Schlenk flask, and toluene was added. The resulting suspension was treated with LiHMDS (lithium hexamethyldisilazane, 1.0 M solution in toluene, 1.4 equivs.) and stirred at room temperature for 1 h. The mixture was then filtered to remove residual salts and concentrated under vacuum. The dark green residue was analyzed as a mixture of the phosphine-bearing complex **5a/b/c** and the desired complex **6a/b/c**. To achieve full formation of the desired complex, the crude product was dissolved in chloroform and stirred during 1 h. The solution was then evaporated and the remainder was subjected to column chromatography (hexane/CH_2Cl_2 1/1) to obtain pure complexes **6a** (yield: 76 %), **6b** (yield: 72 %), or **6c** (yield: 73 %).

(H_2I*i*PCampPr)Cl_2Ru=CH-*o*-O-*i*-PrC_6H_4 (6c): ^{1}H NMR ($CDCl_3$): $\delta = 16.36$ (s, 1 H, Ru=C*H*), 7.59 (t, 1 H, Ar-*H*), 7.48 (m, 1 H, Ar-*H*), 7.38 (d, 2 H, Ar-*H*), 6.91 (d, 1 H, Ar-*H*), 6.85 (m, 2 H, Ar-*H*), 5.57 (m, 1 H, N-C_a*H*), 5.11 [sept, 1 H, OC*H*-(CH_3)$_2$], 4.02–3.92 (m, 4 H, NCH_2CH_2N), 3.14 (m, 3 H), 2.50 (m, 2 H), 2.11 (s, 1 H), 1.98 (m, 2 H), 1.77 (d, 6 H), 1.57 (m, 3 H), 1.30 (s, 3 H), 1.22 (m, 9 H), 1.05 (m, 1 H), 0.89 (d, 6 H); ^{13}C NMR ($CDCl_3$): $\delta = 291.2$ (Ru=*C*H), 209.8 (N*C*N), 152.7, 148.9, 148.6, 144.2, 138.4, 129.6, 125.0, 122.5, 113.3, 75.1 [O*C*H(CH_3)$_2$], 60.0 (N*C*H), 54.9 (N*C*H), 48.6 (N*C*H), 43.3, 42.0, 41.1, 38.8, 34.5, 34.1, 28.1, 26.0, 25.8, 24.0, 23.8, 22.5,

21.9; anal. calcd. (%) for $C_{35}H_{50}N_2Cl_2ORu$ (686.78): C 61.21, H 7.34, N 4.08; found: C 61.28 H 7.39 N 4.05.

$(H_2ICy)Cl_2Ru{=}CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4$ (8a)

$[H_2ICy][BF_4]$ (0.201 g, 0.624 mmol, 1.4 equivs.), complex **2a** (0.268 g, 0.446 mmol, 1 equiv.) and toluene (5 mL) were placed in a Schlenk flask. LiHMDS (0.624 mL, 0.624 mmol, 1.4 equivs.) was added and the resulting suspension was stirred at room temperature for 1 h. The mixture was then filtered and the filtrate was concentrated under vacuum to afford a brownish residue, which was analyzed as the phosphine-bearing complex **7a** (benzylidene α-proton: $\delta = 20.82$).

Full formation of complex **8a** required stirring in chloroform (20 mL) for 8 h. Purification was achieved by column chromatography with gradient elution (CH_2Cl_2/hexane 3/1 to 100% CH_2Cl_2). The desired complex was obtained as an olive green solid; yield: 58%. ^{1}H NMR ($CDCl_3$): $\delta = 18.27$ (s, 1H, Ru=C*H*), 7.67 (m, 2H, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 5.24 [sept, 1H, OC*H*$(CH_3)_2$], 4.96 (m, 1H, N-C*H*), 4.72 (m, 1H, N-C*H*), 3.68 (m, 4H, NCH_2CH_2N), 2.20 (broad signal, 4H), 1.89 (m, 4H), 1.83 (d, 6H), 1.72 (m, 2H), 1.56 (m, 8H), 1.15 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 287.9 (Ru=*C*H), 203.0 (N*C*N), 153.3, 145.1, 129.8, 123.1, 122.9, 113.6, 75.2 [O*C*H$(CH_3)_2$], 60.0 (broad signal, N*C*H), 57.7 (broad signal, N*C*H), 44.4 (N*C*H), 43.5 (N*C*H), 31.8, 26.0, 25.8, 22.4; anal. calcd (%) for $C_{25}H_{38}N_2Cl_2ORu$ (554.57): C 54.15, H 6.91, N 5.05; found: C 53.67 H 6.91 N 4.99.

$(H_2I\mathit{i}PCamp)Cl_2Ru{=}CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4$ (8b)

$[H_2I\mathit{i}PCamp][Cl]$ (0.173 g, 0.456 mmol, 1.4 equivs.) and **2a** (0.196 g, 0.326 mmol) were weighed into a dry Schlenk flask and dry toluene (5 mL) was added. The resulting suspension was treated with LiHMDS (0.456 mL of a 1.0 M solution in toluene, 1.4 equivs.) and stirred at room temperature for 1 h. The reaction mixture was filtered to remove residual salts and evaporated. The brownish residue was analyzed as the phosphine-bearing complex **7b** (benzylidene α-proton: $\delta =$ 18.74). Chloroform (25 mL) was added and the solution was stirred for 1 h at room temperature. The so-formed complex was purified by column chromatography using hexane/CH_2Cl_2 (2/3) as the eluent. After evaporation of the chromatography solvent, the product was obtained as a bright green solid, which was washed with hexane; yield: 81%. ^{1}H NMR ($CDCl_3$): $\delta = 18.74$ (s, 1H, Ru=C*H*), 7.67 (m, 2H, Ar-*H*), 7.05 (m, 2H, Ar-*H*), 5.42 (br s, 2H, NC_aH), 5.20 [sept, 1H, OC*H*$(CH_3)_2$], 3.84 (m, 4H, NCH_2CH_2N), 2.65 (broad signal, 2H), 2.36 (m, 2H), 2.31 (t, 2H), 1.99 (m, 2H), 1.91 (m, 2H), 1.83–1.78 (m, 12H), 1.47 (d, 6H), 1.23 (s, 6H), 1.02 (m, 2H), 0.94 (d, 2H); ^{13}C NMR ($CDCl_3$): δ 289.9 (Ru=*C*H), 206.3 (N*C*N), 153.3, 145.1, 129.8, 122.9, 121.8, 113.8, 75.4 [O*C*H$(CH_3)_2$], 59.7 (broad signal, N*C*H), 58.1 (broad signal, N*C*H), 48.5 (N*C*H), 43.3, 42.2, 40.4, 38.9, 34.6, 28.3, 23.5, 22.5, 22.2, 21.9; anal. calcd (%) for $C_{33}H_{49}N_2Cl_2ORu$ (661.75): C 59.90, H 7.46, N 4.23; found: C 59.01 H 7.27 N 4.23.

Typical Procedure for the CM Reaction (Catalyst Loading = 2.5 mol %)

A dry Schlenk flask equipped with a reflux condenser was charged with 0.0495 mmol of catalyst in 25 mL of dry CH_2Cl_2. Acrylonitrile (0.14 mL, 2.13 mmol, 43 equivs.) and allylbenzene (0.26 mL, 1.96 mmol, 40 equivs.) were added and the resulting reaction mixture was stirred at 40 °C during 3 h. The reaction mixture was then analyzed by ^{1}H NMR spectroscopy.

Crystal Structures

CCDC-634495–CCDC-634499 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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