Bis-coordination of *N*-(Alkyl)-*N*′-(2,6-diisopropylphenyl) Heterocyclic Carbenes to Grubbs Catalysts

Nele Ledoux,*,† Bart Allaert,† Anthony Linden,‡ Pascal Van Der Voort,† and Francis Verpoort†

Department of Inorganic and Physical Chemistry, Laboratory of Organometallic Chemistry and Catalysis, Ghent University, Krijgslaan 281 (S-3), 9000 Ghent, Belgium, and Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

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N-(Alkyl)-*N*′-(2,6-diisopropylphenyl) carbenes display an exceptional tendency toward bis(NHC) coordination in their reaction with the Grubbs complex $[RuCl_2(=CHPh)(PCy_3)_2]$. The resulting bis(NHC) complexes show substantial olefin metathesis activity at elevated temperature. One NHC ligand is expected to dissociate from the metal center for the catalyst to be activated. This NHC ligand lability is confirmed by the observation that both NHCs are exchangeable when the complexes are treated with an excess of PCy_3. In addition, the isolation of a new mono(NHC) complex is described, as well as its reactivity in the ring-opening metathesis polymerization (ROMP) of cycloocta-1,5-diene and the ring-closing metathesis (RCM) of diethyl diallylmalonate.

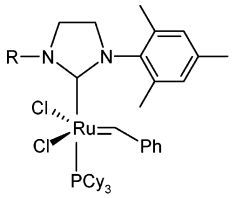
Introduction

Our recent research on *N*-alkyl-*N*′-mesityl-substituted *N*-heterocyclic carbenes (NHCs) as ligands in Grubbs catalysts showed that the modification of the amino side groups induces substantial changes in the reactivity pattern of the corresponding catalysts.[1] Complex **1a**, which bears a small methyl group at one side and an aromatic mesityl group at the other side of the NHC, gave higher ring-closing metathesis activity than the well-known Grubbs second-generation catalyst **2b**.[2] Furthermore, Blechert et al. demonstrated that **1a** provides significantly different *E*/*Z* ratios in cross metathesis and an improved selectivity in diastereoselective ring-closing metathesis reactions.[3] In the present work, we disclose further studies of ruthenium benzylidene complexes bearing asymmetrical NHC ligands.

Complex **4**, described by Mol et al. in 2002, generally displays higher turnover numbers in comparison to complex **2b**.[4] The reason for this enhanced activity is not entirely clear, but likely results from the increased steric bulk of the NHC ligand. We anticipated that replacing the NHC's mesityl group (**1a**,**b**) with a 2,6-diisopropylphenyl group (**3a**,**b**) would analogously have a considerable effect on the catalytic behavior of the corresponding Grubbs complex.

Results and Discussion

Upon treatment of $[RuCl_2(=CHPh)(PCy_3)_2]$ (**2a**) with 1.2 equiv of 1-(2,6-diisopropylphenyl)-3-(methyl)-4,5-dihydroimidazolium chloride, $[H_2IMePr][Cl]$, and 1.2 equiv of a base, the bis(NHC) complex **5a** was formed exclusively, while the expected mono(NHC) complex **3a** was observed only in small traces during the reaction course. In a similar attempt to synthesize the cyclohexyl-bearing analogue **3b**, a mixture of three complexes was obtained. After analysis of the ^1H and ^{31}P NMR spectra, they were identified as the starting complex **2a**, mono(NHC) complex **3b**, and bis(NHC) complex **5b** (Figure



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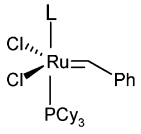
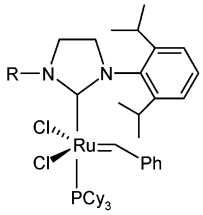
1b R = Cy



2a L = PCy_3
2b L = H_2IMes



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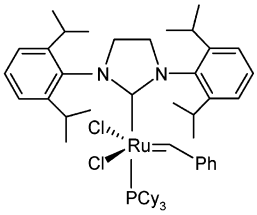

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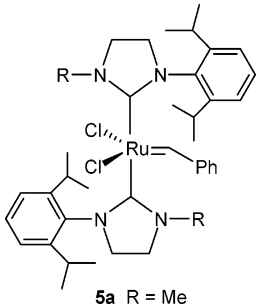

5a R = Me
5b R = Cy

* To whom correspondence should be addressed. Phone: (+32)9-264-4440. Fax: (+32)9-264-4983. E-mail: nele.ledoux@UGent.be.

† Ghent University.

‡ University of Zürich.

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10.1021/om060937u CCC: $37.00
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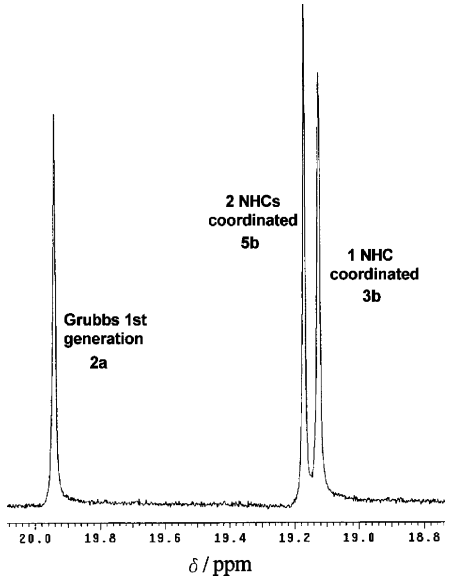

Figure 1. ^{1}H NMR spectrum after reaction at room temperature of **2a** with 1.2 equiv of [H_2ICyPr][Cl] and 1.2 equiv of base. (Only part of the spectrum is shown.)

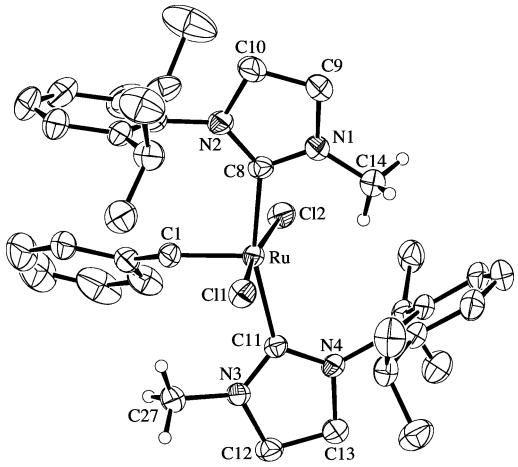

Figure 2. Molecular structure of **5a**, showing 30% probability ellipsoids. Most hydrogen atoms have been omitted for clarity. Crystals were grown from Et_2O.

1). Reaction of **2a** with 2.2 equiv of the appropriate NHC ligand allowed full conversion into complexes **5a**,**b**.

The molecular structure of both bis(NHC) complexes was confirmed by single-crystal X-ray analysis (Figures 2 and 3). In both complexes, the Ru atom has a distorted square pyramidal coordination with the Cl atoms *trans* to one another and the apical position occupied by the Ru=C bond (Table 1). To minimize steric congestion around the metal center, the NHC ligands are arranged in such a way that only one NHC has the diisopropylphenyl group orientated toward the benzylidene side of the ruthenium center. Dihedral angles of 17.0(3)° (complex **5a**) and 29.8(2)° (complex **5b**) show that the two NHC rings are somewhat staggered as a result of their high steric demand. The benzylidene and diisopropylphenyl aromatic rings are not coplanar. This contrasts with our expectation of a $\pi-\pi$ interaction between the two aromatic units.[1] The short distances between the metal center and a H atom at C(14) (H(14)−Ru: 2.53 Å) for complex **5a** and between the metal atom and the H atom at C(14) (H(14)−Ru: 2.64 Å) for complex **5b** suggest the existence of agostic interactions. These agostic interactions were also reflected in the ^{1}H spectra of **5a** (δ 0.07 ppm) and **5b** (δ −0.43 ppm). Interestingly, the

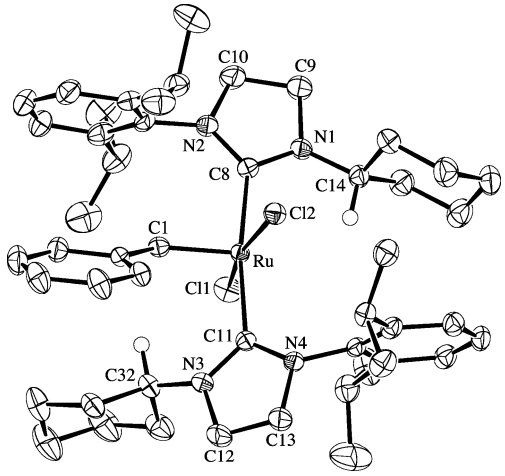

Figure 3. Molecular structure of **5b**, showing 50% probability ellipsoids. Most hydrogen atoms have been omitted for clarity. Crystals were grown from CH_2Cl_2/THF.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 5a, 5b, and 2b with Standard Uncertainties in Parentheses

		5a	5b	2b[5,6]
	Bond Lengths			
Ru=C		1.818(4)	1.828(3)	1.835(2)
Ru−*C*NN	Ru−C(8)	2.073(4)	2.086(3)	2.085(2)
	Ru−C(11)	2.121(4)	2.122(3)	
Ru−P				2.4245(5)
	Bond Angles			
Cl−Ru−Cl		170.66(4)	167.08(3)	167.71(2)
Ru=C−Ph		134.4(3)	133.7(3)	136.98(16)
N_2C−Ru−CN_2		162.0(2)	171.2(1)	
N_2C−Ru−P				163.73(6)
N_2C−Ru=C	C(8)−Ru=C(1)	95.9(2)	94.6(1)	100.24(8)
	C(11)−Ru=C(1)	102.0(2)	94.2(1)	
P−Ru=C				95.98(6)

Ru−*C*NN bond length for the ligand potentially involved in the agostic interaction is slightly shorter than the other Ru−*C*NN bond.

To gain some insight into their catalytic performance, complexes **5a** and **5b** were tested in the ROMP of *cis*,*cis*-cycloocta-1,5-diene (COD) (Table 2). Both complexes display poor activity at room temperature (entries 1 and 6), while the use of an elevated temperature (80 °C) substantially improves conversions (entries 2−5 and 7−10). The NHC decoordination, which is expected to induce catalyst initiation,[5−7] thus proceeds more smoothly when the temperature is raised. A dissociative mechanistic model is generally accepted for Grubbs catalysts **2a**,**b** and finds strong support by computational[8−13] and experimental[14−17] studies. However, since the lability of NHC

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Table 2. ROMP of COD

entry	catalyst	temperature (°C)	COD/cat.	time (h)	conversion (%)[a]	*cis* (%)[b]	M_n[c]	PDI[c]
1	**5a**	20	100	20	2			
2	**5a**	80	100	1	100	43	31 200	1.4
3	**5a**	80	300	1	96	73	33 200	1.6
4	**5a**	80	3000	20	100	60	42 800	1.7
5	**5a**	80	30 000	20	4			
6	**5b**	20	100	20	24	91		
				40	63	80	48 100	1.5
7	**5b**	80	100	0.5	100	21	33 500	1.3
8	**5b**	80	300	0.5	100	31	39 000	1.6
9	**5b**	80	3000	1	98	46	44 300	1.8
10	**5b**	80	30 000	20	60	81	80 000	2.5
11	**3b**	20	300	1	94	76		
				1.5	100	74	49 000	1.6
12	**3b**	20	3000	1	79	76		
				1.5	85	72		
				20	100	64	69 000	1.8
13	**3b**	20	30 000	20	13	85	77 000	2.0

[a] Determined by ^{1}H NMR spectroscopy. [b] Percent olefin with *cis*-configuration in the polymer backbone; ratio based on ^{13}C NMR spectra (δ 32.9: allylic carbon *trans*, 27.6: allylic carbon *cis*). [c] Determined by GPC ($CHCl_3$) analysis. Results are relative to polystyrene standards.

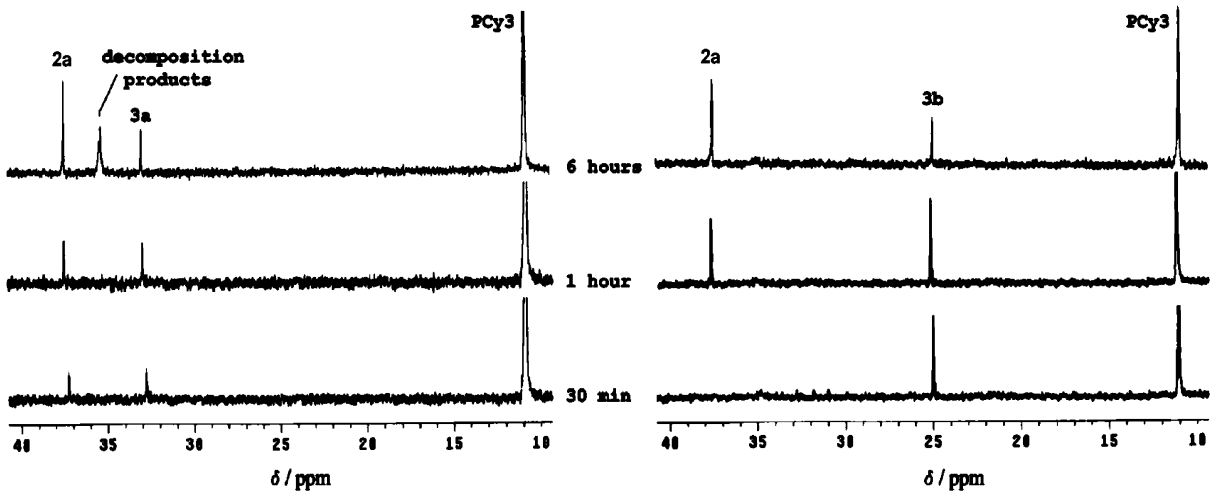

Figure 4. ^{31}P NMR spectra showing the reaction of **5a** (left) and **5b** (right) with 10 equiv of PCy_3, C_6D_6, 80 °C.

ligands in organometallic complexes is typically quite low,[18,19] particularly in comparison to phosphine ligands, further investigation was needed to obtain more support for the hypothesized NHC dissociation pathway. This was achieved through NMR monitoring of the reaction between complex **5a** or **5b** and a 10-fold excess of PCy_3 at 80 °C. For **5a**, the formation of the mono(NHC) analogue **3a** and the bis(phosphine) complex **2a** was observed after 30 min (Figure 4, left). A time span of 6 h allowed full reaction of the starting complex, but at this point decomposition products were also observed. Likewise, the reaction of complex **5b** with an excess of PCy_3 resulted in NHC decoordination (Figure 4 right). A precise selection of the reaction conditions even allowed us to trap and isolate the mono-(NHC) complex **3b** (see Experimental Section).

The here observed NHC lability strengthens our idea that complexes **5a** and **5b** are metathesis active because NHC dissociation at elevated temperature provides the necessary initiation step.

In contrast to the bis(NHC) complexes **5a**,**b**, complex **3b** displays substantial ROMP activity at room temperature (Table 2, entries 11−13). Figure 5 illustrates a somewhat higher initiation rate for **3b** than for **1b** and **2b**; however propagation appears to be slower. Also in the RCM of diethyl diallylmalonate, complex **3b** displays faster initial reaction than complexes **1b** and **2b** (Figure 6). Even though we are not able to provide full evidence, one could presume that the higher initiation rate of **3b** goes together with a higher lability of its phosphine ligand. A dissociative mechanism in which catalyst initiation depends upon phosphine dissociation is then taken for granted. As mentioned above, such a dissociative model has emerged as the most reliable mechanism for the olefin metathesis reaction catalyzed by Grubbs complexes **2a** and **2b**, and more than likely also holds for complexes with modified NHC ligands (**1a**,**b**, **3a**,**b**).

As phosphine dissociation promotes catalyst decomposition,[15,20] it is then not surprising that complex **3b** was found to decompose faster than its mesityl analogue **1b**. It is plausible that an even higher initiation rate is responsible for the low stability of complex **3a**. The exclusive formation of bis(NHC) complex **5a** when an approximately equimolar quantity of H_2-IMePr is reacted with **2a** suggests that the presumed intermediate

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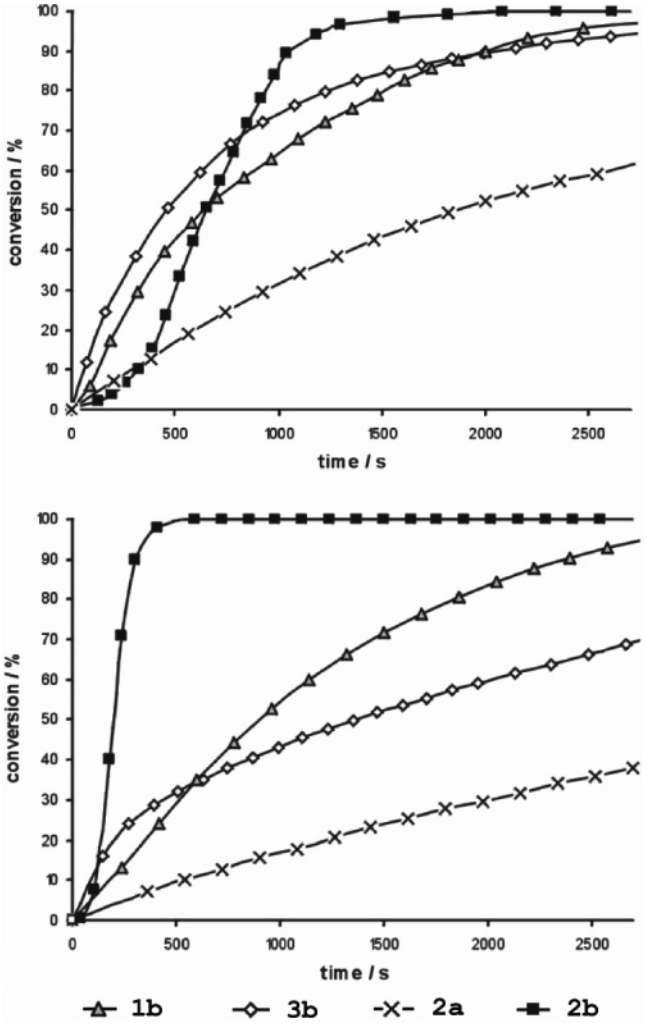

Figure 5. Monitoring ROMP of COD via ^{1}H NMR spectroscopy (20 °C). Conditions: monomer/catalyst = 300, catalyst concentration = 4.52 mM, solvent = $CDCl_3$ (top), C_6D_6 (bottom).

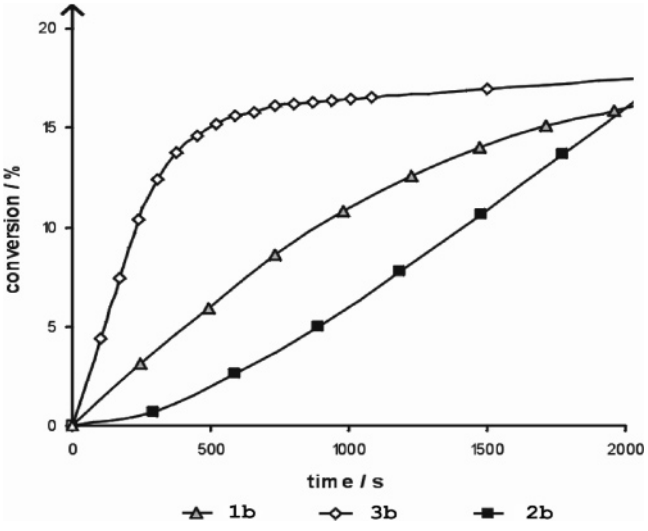

Figure 6. Monitoring RCM of diethyl diallylmalonate via ^{1}H NMR spectroscopy (20 °C). Conditions: diethyl diallylmalonate/catalyst = 200, catalyst concentration = 4.52 mM, solvent = CD_2Cl_2.

3a is much more likely to react with remaining NHC than its precursor **2a**. We assign this to a high phosphine exchange rate, which accompanies fast NHC coordination in a dissociative ligand substitution pathway.

The heating of complex **1a**, **1b**, or **2b** in the presence of an excess of PCy_3 does not cause any NHC decoordination at all. On the other hand, the NHCs in complexes **3a**,**b** are capable of decoordination, and therefore their NHC−metal bond is expected to be weaker. This demonstrates that the strength of the NHC−metal bond, which is believed to depend mainly[21]—though not exclusively[22−28]—on the σ-donating ability of the NHC, does not correlate directly with the dissociation rate of the phosphine ligand. Our observations confirm that other, more subtle effects than a *trans* effect determine the reactivity of Grubbs type complexes.[29−32] The *trans* effect, which explains the dissociation energies of nonsteric ligands in Grubbs complexes,[10,12] should be compensated by additional effects when sterically demanding ligands are used.[9,33]

Conclusion

In summary, two new *N*-(alkyl)-*N*′-(2,6-diisopropylphenyl) heterocyclic carbenes were synthesized. These NHC ligands revealed a different reactivity toward Grubbs complexes than the hitherto reported imidazolinylidenes: (i) facile bis(NHC) coordination was found; (ii) both NHCs on the bis(NHC) complexes can be exchanged with a phosphine, thereupon regenerating the Grubbs first-generation complex. The exchange of one NHC in **5b** for PCy_3 allowed the isolation of a new mono(NHC) complex, **3b**, which displays fair olefin metathesis activity with a higher initiation rate than the benchmark catalyst **2b**. On the other hand, the rather low stability of mono(NHC) complex **3a**, together with the low ratio present in the reaction mixture, prevented its isolation.

These observations confirm that small changes in the *N*,*N*′-substitution pattern of NHC ligands significantly alter the catalytic activity of the corresponding olefin metathesis 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. ^{1}H, ^{13}C, and ^{31}P NMR measurements were performed with a Varian Unity-300 spectrometer.

[$RuCl_2$(=CHPh)(IMePrH$_2$)$_2$], 5a. A 0.5 M solution of KHMDS in toluene (2.06 mL, 1.03 mmol) was added to [H_2IMePr][Cl] (0.290 g, 1.03 mmol) in 5 mL of dry toluene. The mixture was stirred for 10 min. Complex **2a** (0.37 g, 0.450 mmol) was added, and the reaction mixture was stirred for 2 h. The solvent was evaporated, followed by addition of 50 mL of diethyl ether. The resulting

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suspension was filtered to remove salts. The volume of the green filtrate was reduced to ~10 mL and stored in the refrigerator overnight. The bis(NHC) complex precipitated as green crystals, which were filtered and washed with hexane (5 mL). Yield: 0.23 g, 69%. ^{1}H NMR ($CDCl_3$): δ 19.01 (s, 1H, Ru=C*H*Ph), 7.45 (m, 2H, aryl-*H*), 7.34 (m, 2H, aryl-*H*), 7.24 (m, 4H, aryl-*H*), 7.13 (m, 3H, aryl-*H*), 3.95 (m, 4H, C*H*(CH_3)$_2$), 3.66 (m, 4H, NC*H*$_2$C*H*$_2$N), 3.47 (m, 4H, NC*H*$_2$C*H*$_2$N), 3.11 (br s, 3H, NC*H*$_3$), 2.12 (br s, 2H, NC*H*$_3$), 1.60 (m, 6H, CH(C*H*$_3$)$_2$), 1.25−1.15 (several peaks, 18H, CH(C*H*$_3$)$_2$), 0.07 (app s, 1H, $H_{agostic}$). ^{13}C NMR ($CDCl_3$): δ 309.5 (Ru=CHPh), 218.9 (s, MeN*C*NAr), 216.3 (s, MeN*C*NAr), 151.4 (*i*-C_6H_5), 148.5 (Ar-*C*), 148.4 (Ar-*C*), 138.2 (Ar-*C*), 137.3 (Ar-*C*), 129.7 (Ar-*C*), 129.2 (Ar-*C*), 128.9 (Ar-*C*), 128.0 (Ar-*C*), 124.6 (Ar-*C*), 123.6 (Ar-*C*), 54.7 (MeNCH$_2$*C*H$_2$NAr), 53.9 (MeNCH$_2$*C*H$_2$-NAr), 51.9 (MeN*C*H$_2$CH$_2$NAr), 51.4 (MeN*C*H$_2$CH$_2$NAr), 37.6 (*C*H$_3$N), 29.3, 27.9, 27.6, 26.6, 23.1. Anal. Calcd (%) for $C_{39}H_{54}N_4$-Cl_2Ru (750.87): C 62.39, H 7.25, N 7.46. Found: C 62.03, H 7.77, N 7.05.

[RuCl$_2$(=CHPh)(H$_2$ICyPr)$_2$], 5b. Analogously, [H_2ICyPr][Cl] (0.345 g, 0.989 mmol) was reacted during 10 min with a 0.5 M solution of KHMDS in toluene (1.98 mL, 0.989 mmol) in 5 mL of dry toluene. After addition of the Ru precursor **2a** (0.35 g, 0.426 mmol), the reaction mixture was stirred for an additional 2 h. The solution was filtered to remove residual salts and evaporated to dryness. Acetone was added, and the resulting suspension was stirred until a finely ground green precipitate had formed, which was filtered and dried thoroughly. Yield: 0.32 g, 84%. ^{1}H NMR ($CDCl_3$): δ 19.22 (s, 1H, Ru=C*H*Ph), 8.64 (br s, 1H, *o*-C_6H_5), 7.45 (t, 2H, aryl-*H*), 7.38 (m, 2H, aryl-*H*), 6.99 (s, 2H, aryl-*H*), 6.82 (s, 2H, aryl-*H*), 6.32 (br s, 2H, aryl-*H*), 4.03 (m, 2H), 3.89 (m, 2H), 3.76 (m, 1H), 3.47 (m, 4H), 3.14 (m, 1H), 2.84 (m, 2H), 2.32 (m, 1H), 1.62−0.57 (several peaks, 44H), −0.43 (br m, 1H, $H_{agostic}$). ^{13}C NMR ($CDCl_3$): δ 307.5 (Ru=CHPh), 216.1 (CyN*C*-NAr), 215.6 (CyN*C*NAr), 149.8 (*i*-C_6H_5), 148.7 (Ar-*C*), 147.4 (Ar-*C*), 146.7 (Ar-*C*), 146.0 (Ar-*C*), 139.4 (Ar-*C*), 137.4 (Ar-*C*), 131.1 (Ar-*C*), 130.0 (Ar-*C*), 128.0 (Ar-*C*), 127.4 (Ar-*C*), 126.9 (Ar-*C*), 125.9 (Ar-*C*), 123.9 (Ar-*C*), 123.4 (Ar-*C*), 57.5 (N*C*H), 56.4 (N*C*H), 53.2 (N*C*H), 53.0 (N*C*H), 43.2 (N*C*H), 42.1 (N*C*H), 32.1, 30.3, 29.6, 28.6, 27.9, 27.4, 27.0, 26.1, 25.8, 25.0, 24.5, 24.0, 23.5, 23.3, 22.7, 21.0. Anal. Calcd (%) for $C_{49}H_{70}N_4Cl_2Ru$ (887.11): C 66.34, H 7.95, N 6.32. Found: C 66.16, H 7.96, N 6.26.

[RuCl$_2$(=CHPh)(H$_2$ICyPr)(PCy$_3$)], 3b. A solution of bis(NHC) complex **5b** (0.250 g, 0.282 mmol) and tricyclohexylphosphine (0.80 g, 2.853 mmol, 10 equiv) in toluene (10 mL) was stirred at 70 °C for 1 h, during which time it turned red-brown from green. Toluene was removed by evaporation in vacuo, and MeOH (15 mL) was added under vigorous stirring. The resulting suspension was filtered, washed with more MeOH (3 × 5 mL), and dried to give complex **3b** as a light pink powder. Yield: 0.14 g, 59%. (The yield decreased considerably due to repeated washing with MeOH, which was necessary to remove all PCy_3.) ^{1}H NMR ($CDCl_3$): δ 19.18 (s, 1H, Ru=C*H*Ph), 7.84 (br s, 1H, *o*-C_6H_5), 7.36 (t, 1H, *p*-C_6H_5), 7.04 (m, 2H), 6.94 (br s, 1H), 6.82 (m, 1H), 6.74 (m, 2H), 4.58 (m, 1H, N-C*H*), 3.85 (app s, 4H, NC*H*$_2$C*H*$_2$N), 3.27 (m, 2H, C*H*(CH_3)$_2$), 2.45 (d, 2H), 2.09 (m, 2H), 1.88 (m, 2H), 1.75, 1.55, 1.43, 1.23, 1.02 (remaining 49 protons). ^{31}P NMR ($CDCl_3$): δ 25.43. ^{13}C NMR ($CDCl_3$): δ 296.2 (broad signal, Ru=*C*HPh), 213.8 (d, $J_{P,C}$ = 76.0 Hz, CyN*C*NAr), 149.3, 146.5, 135.7, 130.4, 129.0, 128.0, 127.8, 127.6, 126.9, 126.6, 123.4, 122.6, 56.8 (N*C*H), 52.4 (N*C*H), 42.3 (N*C*H), 34.7, 33.9, 31.4, 31.2, 29.3, 28.1, 26.5, 26.4, 26.0−25.1 (several peaks), 24.3, 23.7, 22.2. Anal. Calcd (%) for $C_{46}H_{71}N_2Cl_2PRu$ (855.04): C 64.62, H 8.37, N 3.28. Found: C 64.05, H 8.36, N 3.22.

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Supporting Information Available: Synthetic details for [H_2-IMePr][Cl] and [H_2ICyPr][Cl]; cif files for crystal structure determinations of **5a** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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